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ELECTROCHEMICAL REMOVAL OF HEAVY METALS FROM ACID MINE DRAINAGE

By

Nicholas B. Franco
Robert A. Balouskus
ECOTROL, Inc.
Columbia, Maryland 21044

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Project Officer

Ronald D. Hill
Mining Pollution Control Branch
Industrial Waste Treatment Research Laboratory
National Environmental Research Center
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

NATIONAL ENVIRONMENTAL RESEARCH CENTER
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CINCINNATI, OHIO 45268

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A 18.9 liter/min (5 gal./min) pilot plant was operated at an actual mine site to evaluate treatment of 40 and 250 ppm ferrous iron AMD at pH levels of 2 and 5. A conventional aeration system was also included to generate comparative data. Approximately 86 percent of the ferrous iron was oxidized during electrolysis of the low pH water. The conversion rate was less in the pH 5 AMD due to coating of electrode sites with ferric hydroxide. A 4 to 10% decrease from 4 ppm occurred in manganese concentration, while aluminum feed values of approximately 1 ppm were reduced by 40 to 60% especially in the pH 2 water.

Estimates for a 473 liter/min (125 gal./min) plant based on the pilot data for oxidation only indicate that capital and operating costs for electrochemical treatment would be higher than those for aeration by factors of 5 and 1.7 respectively.

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This project focused on the development of a new method for treating acid mine drainage from coal mines. An electrochemical technique was developed and field tested for converting ferrous iron to ferric iron to enhance rapid removal of the iron pollutant from mine drainage.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

ABSTRACT

Laboratory and field studies were conducted to determine the economics of ferrous iron oxidation in a cell containing a bed of conductive particles in the space between the cathode and the anode. The effects of the process on other heavy metals present in acid mine drainage (AMD) and on the character of solids precipitated during treatment of low acidity water were also observed.

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Estimates for a 473 liter/min (125 gal./min) plant based on the pilot data for oxidation only indicate that capital and operating costs for electrochemical treatment would be higher than those for aeration by factors of 5 and 1.7 respectively.

This report was submitted in fulfillment of Project Number 14010 GAO, under the partial sponsorship of the Office of Research and Monitoring, Environmental Protection Agency and Pennsylvania Department of Environmental Resources (Project CR-110) by Ecotrol, Inc., 7379 Route 32, Columbia, Maryland, 21044.

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Dr. R. B. Rozelle of Wilkes College provided much information on the nature of AMD in the Wilkes-Barre area.

Witco Chemical Corporation, West Virginia Pulp and Paper, Pittsburgh Activated Carbon, Union Carbide Corporation, Berol Corporation, Blue Coal Corporation, and the Pittsburgh Bureau of Mines are acknowledged for providing samples of carbon, graphite and coal used in the evaluation of electrode bed materials.

Other personnel who contributed in part to the project are Mr. J. Shockcor, Mr. W. E. Litz, Mr. D. B. Smith, Mr. R. Hess, Mr. F. Ferraro, and Mr. E. T. Woodruff.

SECTION I

CONCLUSIONS

The technology of electrochemical oxidation in particulate electrode cells to reduce ferrous iron concentrations in AMD to low levels has been demonstrated. However, based on the data obtained and the scale-up factors applied, the electrochemical approach was found to be more expensive in capital and operating costs than conventional aeration.

An important factor affecting the performance of the cells during treatment of low pH AMD is the occurrence of back reduction of ferric ion by electrolytic reaction at the cell cathode and by chemical reaction with hydrogen, which is also generated in the high acidity water. The steps taken during this study to minimize these reactions apparently were not adequate. More effective cell membranes and more efficient means for gas venting should be incorporated in future systems.

The back reduction effect should be minimized during oxidation of AMD at pH 3 or higher since the acidity is lower in these cases and ferric ion is precipitated from solution. However, deposits of the usual gelatinous ferric hydroxide in the cell reduce its efficiency by coating electrode sites. This has a more deleterious effect than the back reduction problem as indicated by the lower ferrous conversion in high pH waters. During the pilot study, attempts were made to remove solids from the cells by applying high feed velocities to expand the beds. However, the maximum velocity that could be used was limited by the retention time requirement for ferrous oxidation. Periodic maintenance procedures involving vigorous purging of the bed with an inert gas or flushing of the cells with dilute sulfuric acid to dissolve the precipitate should be tried.

Throughout the course of the laboratory work, it was repeatedly observed that during electrolysis of synthetic AMD at a pH of 3 or greater, a small fraction of the total solids formed consisted of a dark reddish-brown material with rather desirable properties. It appeared to be crystalline and definitely settled at a rapid rate compared to the usual ferric hydroxide sludge. All attempts in the lab and in the field to generate the solid in large quantities and to identify it were unsuccessful. It is concluded that the formation of this solid in significant quantity probably requires close control of cell operating conditions.

Electrochemical treatment of AMD has essentially no effect on calcium and magnesium concentrations. Additional studies with high manganese AMD are required to confirm current observations of low percentage removal for this metal. Indications are that reductions of about 50% in aluminum concentration may be effected under conditions which also cause 86% conversion of the iron. Aluminum removal therefore should also be investigated further.

SECTION II

RECOMMENDATIONS

In order to improve the economics of electrochemical treatment:

1. Re-evaluate procedure for scale-up from laboratory data.
2. Modify cells and operational conditions for more efficient gas and solids expulsion.
3. Evaluate different cell membrane materials.
4. Employ multi-outlet rectifiers to sectionalize power to the cells system for more efficient power utilization.
5. Establish periodic bed cleaning procedures.

Pilot studies should be conducted with 378 liter/min (100 gal./min) plant to provide more reliable scale-up data for commercial-size systems.

Investigate further the effects of electrochemical treatment on manganese and aluminum removal.

Determine operating conditions for maximum generation of the rapid settling solid described in this report.

Investigate the economics of electrochemical conversion followed by limestone neutralization.

SECTION III

INTRODUCTION

This is the final report on the Pennsylvania Department of Environmental Resources Project CR-110. The project was initiated on September 1, 1971 with financial support from Resource Control, Inc., the Pennsylvania Department of Environmental Resources, (D.E.R.) and the U. S. Environmental Protection Agency (E.P.A.) Office of Research & Development through Grant 14010 GAO to the Commonwealth of Pennsylvania.

Objectives and Phasing

The primary objective of the overall project was to demonstrate the economic advantage of using the Ecotrol, Inc. Electrochemical Process (formerly called the Resource Control, Inc. Process) to oxidize ferrous iron to ferric iron in acid mine drainage (AMD). Subordinate objectives include:

1. Process parameter definition for future application;
2. Determination of effect of the process on ionic species, other than iron, that can normally be expected in the waste water; and
3. Determination of effect of the process on removal of suspended solids in the discharge from the electrolytic cell by settling and filtration.

The overall project was divided into two main parts:

1. Phase I - Laboratory Studies
2. Phase II - Field Studies

Phase I activities, which were geared toward developing laboratory data for the design of a 18.9 liter/min (5 gal./min) pilot plant, were completed by mid-April of 1972, when authorization was given by the E.P.A. and D.E.R. to proceed with Phase II.

The pilot plant was installed at the Delaware Pumps Station in Wilkes Barre, Pennsylvania during the last week of June, 1972. However, due to various operational restrictions and problems resulting from the disastrous June flood, initial systems testing could not be started until mid-August and the project was not completed by November as originally planned. In view of the potential for damage to equipment from freezing temperatures at the station, it was decided on November 10, 1972, that activity be halted and essential equipment be removed from the site until April, 1973, when the project would be resumed. The field work was completed on July 30, 1973.

On August 6, 1973, the D.E.R. service contract with Resource Control, Inc. was assigned to Ecotrol, Inc., a wholly owned subsidiary of W. R. Grace & Co., which on July 10, 1973, acquired substantially all of the assets and technology of Resource Control, Inc.

Background

The nature, extent and impact of the acid mine drainage (AMD) problem are amply documented in numerous articles and reports[1]. Basically, the problem occurs when, in the process of mining coal, the surrounding rock strata is exposed to air and water. This rock strata contains metal sulfides, the most common of which is iron pyrite (FeS_2). The sulfides of aluminum (Al_2S_3) and manganese (MnS) are also found to a lesser extent. When in contact with air and moisture, these sulfides are oxidized to sulfates via a reaction that also generates acid. The basic reaction involving iron pyrite can be expressed as follows:

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

The drainage from coal mines will vary in degree of contamination from area to area. A typical AMD will have approximately the following composition:

Fe^{+2}	100 - 500 ppm
Fe^{+3}	90 - 300 ppm
$SO_4^{=}$	1,000 - 4,000 ppm
Mn^{+2}	15 ppm
Al^{+3}	50 ppm
pH	2.9 - 4.0

Untreated AMD leads to stream pollution in many ways. The acid is not only harmful to the ecological balance in the receiving stream, but is also corrosive to man-made structures, such as bridge abutments and concrete dams. The ferrous iron is gradually oxidized to the ferric state with a simultaneous reduction of dissolved oxygen in the stream. Both the ferrous and ferric iron, while soluble in acidic water, will precipitate out of solution as the pH is increased through dilution. The precipitated yellow-brown hydrous oxides gradually settle out and cause enough silting to cover the vegetation in the stream bed. Although precipitated, the ferrous species will continue to be oxidized to the ferric state by the dissolved oxygen. Aluminum and manganese in the AMD will also precipitate out as the pH is increased.

Various physical-chemical processes for the removal of contaminants from AMD have been evaluated. Purification by crystallization, distillation, ion-exchange and reverse osmosis produce high-quality water[2-8]. However, it must be recognized that each of these techniques is not a complete treatment. In addition to pure water there is also produced a concentrate of the contaminating salts and acid which subsequently must be treated by chemical means before disposal. Studies on the treatment of AMD by sulfide or carbonate precipitation, adsorption on mill tailings and by foam separation of contaminants have revealed problems in the control of process parameters and have shown unfavorable cost figures[9-12].

By far the most common method for pollution control of AMD is treatment with alkaline reagents to neutralize the acid and precipitate metal oxides or hydroxides. While lime neutralization has been used in most cases, studies with limestone show the latter to be more desirable on the basis of cost, availability, hazards of handling and quality of the precipitated sludge [13-17]. Not all types of limestone work equally well. In general, the more effective materials are those with a high calcium content, low magnesium content, small particle size and large surface area[14,16].

The major disadvantage to the alkaline neutralization approach has always been the production of waste sludges. These sludges are generally quite voluminous and require relatively long retention times to permit settling out prior to discharge from the treatment facility. Conventional filtration has not been too successful, since the form in which the metal precipitates from solution readily clogs the pores in the filters. The use of various flocculating agents, coagulant aids and inert waste materials as additives to increase the density and enhance the filterability of the sludges has been studied[14,18,19]. One report on the treatment of AMD sludges includes a procedure for converting sludges with high ferrous contents (mainly $Fe(OH)_2$) to a ferro-magnetic form which is denser and faster settling than the material normally encountered[19]. All of the aforementioned approaches for sludge handling exhibit some potential for success, but the problem is still far from being solved economically. The most promising sludge dewatering techniques appear to be centrifugation, conventional rotary vacuum filtration, and rotary precoat vacuum filtration[20,21].

In the neutralization of AMD from various locations there is an appreciable difference in the ease of treatment depending mainly upon the ratio of ferrous iron to ferric iron in the raw waste water[14-17]. With high ferric iron AMD, free acid and the combined acid resulting from hydrolysis of ferric iron are neutralized, and a maximum degree of iron precipitation is achieved as the pH is increased to three[22]. The pH is subsequently adjusted to a vlaue in the range of 5-7 where precipitate quality and rate of coagulation are best. Mine drainage with a high ferrous iron concentration is the most difficult to treat by neutralization. Although ferric iron is removed from the solution ideally at a pH of about 6.5, ferrous iron requires a pH of 10 for maximum precipitation. This necessitates the use of large amounts of lime and introduces appreciable alkalinity to the treated water. In addition, the $Fe(OH)_2$ precipitate is light, more voluminus and, therefore, more difficult to handle than the sludge with predominately ferric iron.

Attempts have been made to oxidize and hydrolyze the ferrous iron by aeration after neutralization to pH 6.5. However, a decrease in pH occurs due to the protons liberated. Thus, an excess of alkali is still required with this technique.

Finally, investigators have concentrated on the oxidation of ferrous iron before neutralization as another possible solution to the problem. Although aeration is probably the easiest and least expensive method, the conversion of Fe(II) to Fe(III) by air oxidation is known to be extremely slow in solutions with a pH less than six[22,23,24]. Various transition metal ions catalyze the reaction, but still not to an effective degree. Laboratory tests with various solid substances have revealed high rates of Fe(II) oxidation when aerated synthetic and actual AMD at a pH of about 3 were passed through beds of coal-base activated carbons [14,25,26]. Adsorption, as well as oxidation, is the mechanism involved. The major disadvantage of the process is the cost of the activated carbons which apparently became inactive after relatively short periods of use.

Favorable results have been obtained from a bench-scale examination of AMD treatment by ozone oxidation before neutralization[22]. An engineering design and economic study to evaluate this system concludes that an ozone process is feasible and compares economically with existing processes[27]. Field tests with on-site generation of ozone by electrical discharge are recommended.

Laboratory studies have indicated that acidophilic iron bacteria can effectively accelerate the oxidation of Fe(II) in AMD, but the bacteria metabolism is temperature dependent, being greatly reduced at low temperatures[28]. The biochemical iron-oxidation limestone process has been successfully demonstrated during the treatment of AMD streams containing up to 450 ppm Fe(II)[29]. Presumably consideration is being given to the design of treatment plants based on this process.

Electrolysis has been considered as a technique for oxidizing ferrous iron in AMD and for removing total iron by plating and precipitation[22]. However, standard electrolytic methods have never been practical when applied to the removal of trace contaminants from water (less than 1000 ppm). The long retention time required for the ions to migrate to the electrode surface, together with the high power consumption necessary for treating the increasingly purer water, have seriously restricted the use of electrochemical technology. To date, conventional electrolysis has been used only in waste treatment cases where high concentrations are reduced to lower concentrations prior to chemical treatment.

The present report covers the use of electrolytic cells containing a semiconductive bed of particles between the electrodes. The bed particles, while not reacting chemically with the contaminants in solution, behave as small intermediate electrodes in the electric field between the major electrodes. That is, ends of the particles facing the major cathode exhibit anodic characteristics, and ends facing the major anode exhibit cathodic characteristics. The particles themselves become bipolar. The result is a cell with a multiplicity of anodic and cathodic sites. The cell can also be modified to provide a bed with predominantly anodic or cathodic character. When the solution to be treated is passed through this medium, the distance contaminant ions have to migrate to any one of the numerous electrode sites is drastically reduced. This feature overcomes the excessive residence time required by conventional cells in the treatment of dilute waste water. Since the particles are conductive, and because of their proximity in the cell, abnormally high voltages are not needed to oxidize or reduce trace quantities of dissolved impurities.

While initial development of the Ecotrol cell was directed towards applications in the metal finishing industry, exploratory tests with synthetic AMD containing up to 500 ppm ferrous iron showed that the iron could be oxidized at an acceptable rate in the cell. In addition, it was found that in AMD with a pH of 3 or higher, the ferrous iron was converted to a relatively dense red solid that appeared to be readily filterable.

In February 1972, Tyco Laboratories, Inc. completed a laboratory study on the electrochemical oxidation of ferrous AMD in a packed bed electrode cell similar to the Ecotrol Cell[30]. Solutions with pH 2 or less were used. Calculations from the laboratory data indicate favorable economics for the operation of commercial scale systems.

For the present project, the laboratory work was followed by a field study on the treatment of pH 2 and pH 5 AMD.

SECTION IV

PHASE I - LABORATORY STUDIES

The purpose of this part of the overall project was to examine the effects of cell configuration, electrode bed material, power, AMD composition, and temperature on the degree of treatment in bench-scale cells in order to gain some idea of the range of operational capabilities which had to be incorporated in the design of the Phase II system. While consideration was given to wide variations in AMD composition, some emphasis was placed on those conditions which were to be encountered at the mine site chosen for the field demonstration.

Experimental Details

Laboratory Cells and Associated Equipment

Cells were designed in two different configurations. The Ecotrol Electrochemical System in its basic form, used, for example, in treating waste waters from the metal finishing industry, consists of a series of cells having rectangular plane-parallel anodes and cathodes with the semi-conductive bed of particles dispersed in between. The basic rectangular configuration was, therefore, considered first for evaluation of AMD treatment. From other studies in this laboratory, cylindrical cells with concentric anodes and cathodes were found to give more favorable results than the rectangular type in certain applications. Thus, the cylindrical configuration was also chosen for AMD study.

A typical rectangular cell is illustrated in Figure 1a. It consists of a stainless steel cathode (#304) and graphite anode (Union Carbide Electrolytic Graphite) supported and spaced from each other at a desired distance with polyvinyl chloride (PVC) or clear Lucite side walls. This assembly is mounted on a PVC bottom plate, which is equipped with a solution inlet tube and a PVC screen (18 x 36 mesh). The latter acts as a support and permits even distribution of solution flow through the bed of small particulate electrodes dispersed between the graphite and steel electrode plates. A sidearm is provided on the solution inlet tube or a separate tube is attached to the bottom section of the cell in order to introduce gases such as nitrogen or air. These can be used

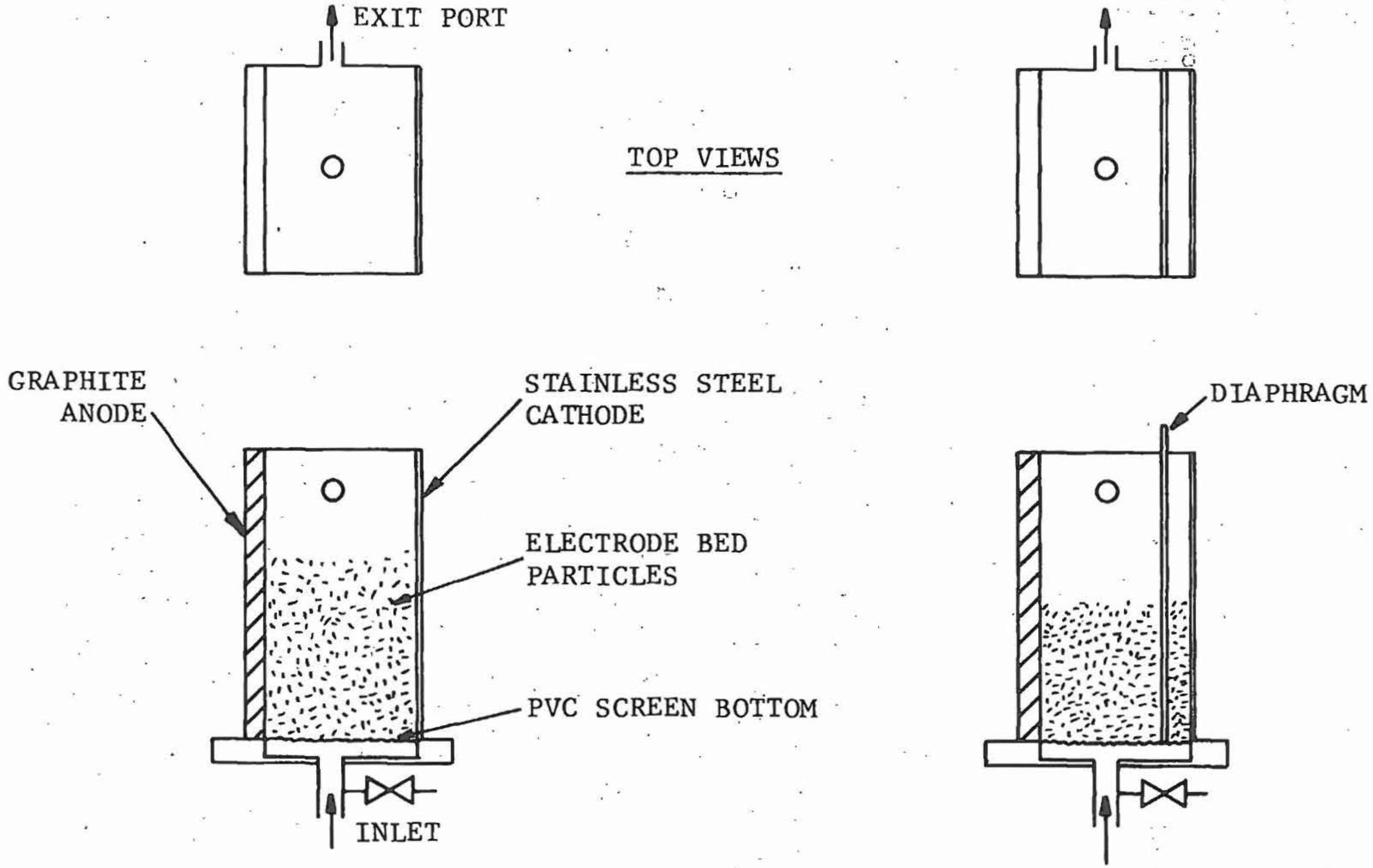

FIGURE 1. Rectangular Cells

periodically to sparge the bed so as to remove any accumulated solids which could clog the bed or insulate it electrically. The cell is assembled by bolting various components together, cementing with epoxy, or welding with a hot air gun (plastic to plastic bonds).

Figure 1b shows the same cell equipped with a diaphragm. The material used in this study is PVC coated fiberglass insect screen (18 x 36 mesh) welded to a rigid PVC frame. The diaphragm can be placed directly against one of the major electrodes, or can be positioned at some desired distance between the two. These features permit one to operate the cell with the electrode bed particles completely isolated from the graphite anode or the steel cathode. Also, the bed can be sectionalized into anodic and cathodic compartments.

A typical cylindrical cell with concentric major electrodes is shown in Figure 2a. The bottom plenum chamber, made from PVC or clear Lucite, is equipped with a solution and gas inlet tube. The chamber is bolted to a top section which holds a PVC flow distributor and the inner cylindrical electrode. The top section, with built-in solution exit port, may be metallic and thus act as the outer major electrode, or may be constructed from plastic material. In the latter case, the outer electrode would consist of a thin-wall metallic cylinder which is slid into the top section and fits snugly against the inner plastic wall. The bed of small particulate electrodes is dispersed in the annular space between the inner and outer major electrodes. The bottom of the inner electrode is sealed to insure that all the solution flowing through the cell is in contact with the bed in the electric field between the major electrodes. Because of the difference in surface areas of the concentric major electrodes, one possible modification in the operation of the circular cell involves the polarity impressed on these electrodes. The inner electrode could be the anode and the outer the cathode as in Figure 2b, or vice versa (Figure 2c). For this study stainless steel (#304) was employed as the cathode material. The anodes were constructed from graphite and titanium coated with ruthenium dioxide (Electrode Corporation). The latter material is more chemically inert than graphite, and the oxide coating is known to catalyze oxidation reactions. As is true for the rectangular cells, the circular cells can be equipped with PVC screen diaphragms, which in this case would be cylindrical and concentric with the major electrodes.

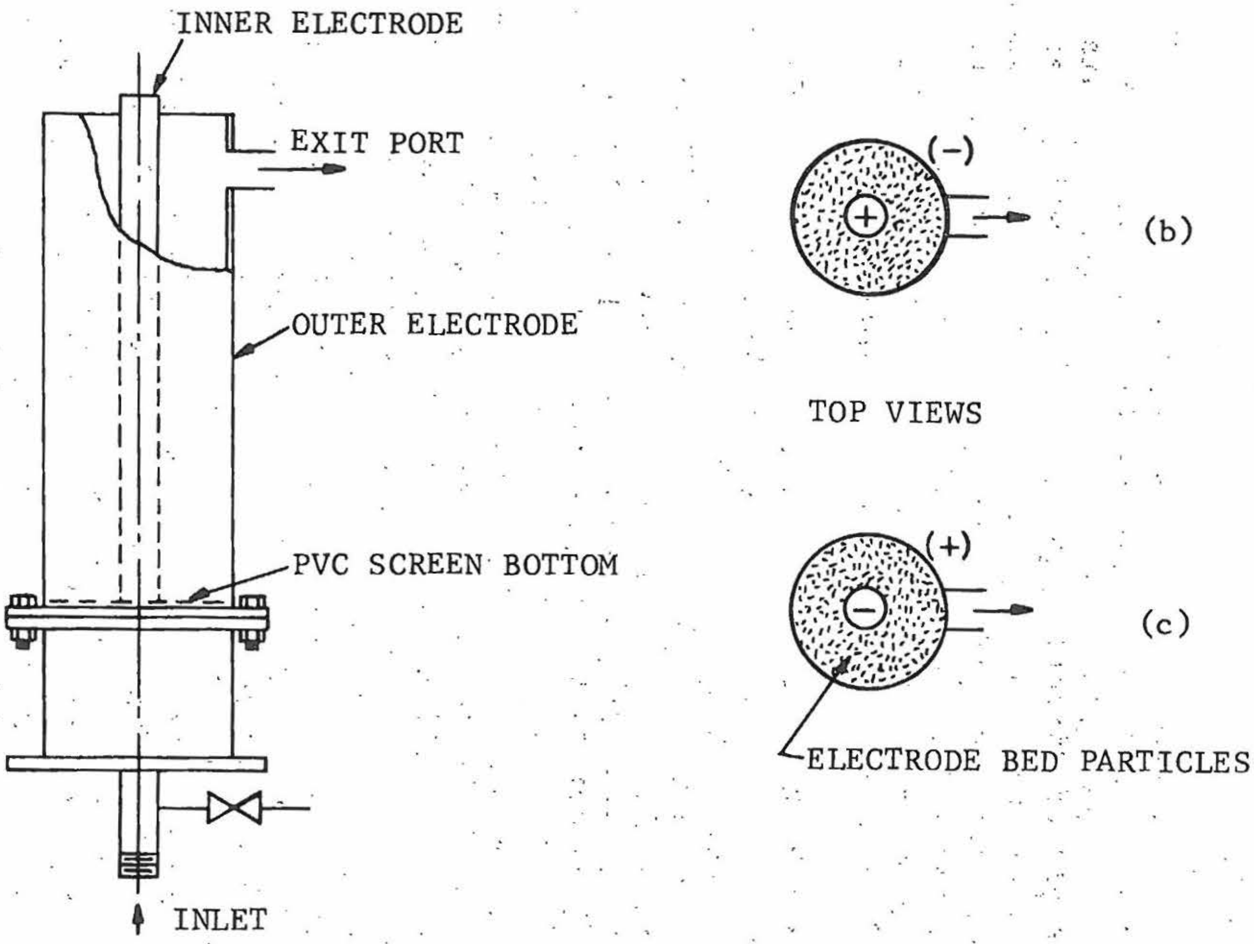

FIGURE 2. Circular Cells

Ten different materials were evaluated as particulate electrode bed media for AMD treatment in the Ecotrol cells. The candidates are listed in Table 1. In this laboratory Norit RB-II carbon had been used in cells for treating various metal finishing waste waters. The Nuchar and Pittsburg carbons have been studied as catalysts for the oxidation of Fe(II) in AMD by aeration[14,25,26]. Witco carbons were chosen because of their relatively high surface area (1200 m^2/g), low ash content (1%), and low acid soluble iron content (0.1%). Their uniform spherical shape was also a property of interest. In this regard, Columbia LCK carbon was tested because of the platelet geometry of the particles. The economic advantage of using ground-up bituminous and anthracite coals prompted examination of these materials. Finally, samples of graphite were tested. These have the same rod-like shape of the Norit RB-II particles, but are not activated or porous like the carbon. In addition, it was thought that the graphite would exhibit greater abrasion resistance upon continued use.

The cells described above were designed for continuous flow-thru treatment of AMD with the liquid flowing from the bottom to the top of the cell. Under this general mode of operation, two variations are possible in regard to the physical disposition of the bed during fluid flow. In one case, the bed is held in a static compact state, either by mounting a constraining PVC screen on the top of the bed or simply by pumping at relatively low volume flow rates so that the apparent liquid velocity is less than required to expand the bed over its normal backwash and drain condition. In the second case, the bed is allowed to expand or become fluidized by virtue of the high liquid velocities employed. Preliminary work with waste water similar to AMD had demonstrated a need for some form of bed agitation to free the precipitate that may form on the particles and major electrodes. Beyond this, the benefits of reduced chemical polarization, enhanced mass transfer and gas bubble expulsion caused by agitation and separation of the particulate electrodes warranted further investigation in the area of AMD treatment.

For runs at low flow rates (less than 0.4 liter/min or 0.1 gal./min) batches of synthetic AMD were made up and stored in 114 to 189 liter (35 to 50 gallon) plastic tanks from which the liquid was fed to the cells by means of bench-top peristaltic pumps (Masterflex Pump, Cole Palmer Co.). For studies

TABLE 1. ELECTRODE BED MATERIALS

Material	Description	Source
Norit RB-II	Activated carbon from peat; rod-shape (2x7 millimeters)	American Norit
Nuchar WV-W	Coal base activated carbon; granules (8x30 mesh)	West Virginia Pulp & Paper
Witco 337	Petroleum base activated carbon; spherical granules (6x16 mesh)	Witco Chemical
Witco 256	Spherical granules (4x10 mesh)	Witco Chemical
Pittsburgh BPL	Bituminous base activated carbon; granules (6x16 mesh)	Pittsburgh Activated Carbon
Columbia LCK	Coke base activated carbon; platelets (4x10 mesh)	Union Carbide
Bituminous Coal	Jagged granules (6x16 mesh)	Pittsburgh Bureau of Mines
Anthracite Coal	Jagged granules (6x16 mesh)	Blue Coal Corp.
Graphite 9H	Hard pencil lead; rod-shape (2x10 millimeters)	Berol Corp.
Graphite 6B	Soft pencil lead; rod-shape (2x7 millimeters)	Berol Corp.

at high flow rates (up to 11 liter/min or 3 gal./min) a more complex system was used. This is illustrated by the flow diagram in Figure 3. The symbols refer to the following components:

FV-10	Flow Control Valve (PVC)
V-20,30,40	Quick-close Ball Valves (PVC)
FM-10	Rotameter (No.FP-1-35-G-10-83), Fisher-Porter
FM-20	Orifice Flowmeter with Mercury Manometer
P-10	Jabsco Centrifugal Pump (39 liter/min or 10 gal./min)
P-20	BIF Metering Pump (1 liter/min or 0.3 gal./min)
T-10	Plastic-Lined Fiberpak Drum (208 liter or 55 gal.)
CM/R-10	Recording Conductivity Meter, Balsbaugh 910
VC-10	D.C. Power Supply (15V - 6/30A), R. O. Hull

Plumbing between components consisted of 3.8 cm (1.5 in.) rigid and flexible PVC tubing and fittings. In order to accommodate the need for high feed flow rates while avoiding the inconvenience of storing large volumes of premixed feed, synthetic AMD with the desired composition was continually generated during a given run by in-line mixing of metered tap water and concentrated acidic ferrous sulphate solution.

For all of the Phase I electrochemical runs, D. C. power was applied to the cells with rectifiers manufactured by the R. O. Hull Co. (0-15 Volts, 0-6/0-30 Amps). When applied voltages greater than 15 were required, the rectifiers were ganged in series.

Synthetic AMD

Simulated AMD was used for the laboratory studies. Solutions with the desired pH and metal composition were prepared by dissolving appropriate amounts of reagent grade sulfuric acid, sodium hydroxide, and the common hydrated sulfates of Fe(II), Fe(III), Mn(II), Ca(II), Mg(II), and Al(III) in tap water. During runs with AMD at pH 5, the surface of the feed solution was blanketed with nitrogen to prevent oxidation of Fe(II) by aeration.

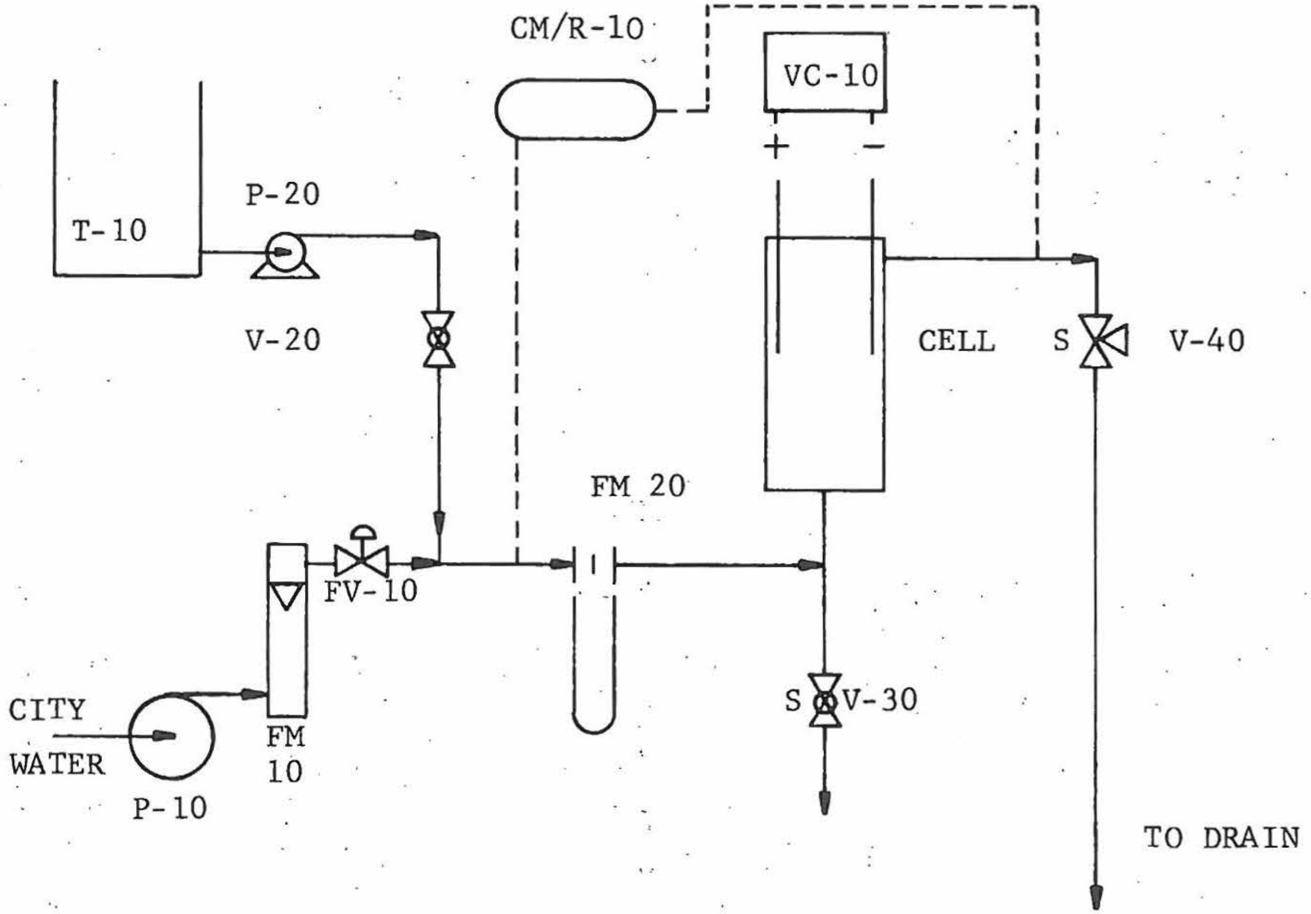

FIGURE 3. Flow System for Evaluation of AMD Treatment at High Flow Rates

Operating Procedures

In preparation for a run with AMD of a given composition, an ample supply of electrode bed material was pretreated by first soaking the particles in 10 percent H_2SO_4 for three days to dissolve any acid soluble matter. The bed was then rinsed continuously with tap water until the supernatant wash liquid exhibited a pH approximately equal to that of the AMD to be studied. After this rinse, the particles were soaked for several days in the AMD solution. During this period, the supernatant liquid was removed and fresh AMD added several times in order to saturate the bed with the test solution. This procedure was followed to minimize carbon absorption and pH aging effects, which would otherwise have been encountered during electrolysis of the AMD.

The pretreated bed was slurried into the cell with the aid of the AMD feed solution. For the runs at low flow rates with static beds, the bed was tamped slightly with a PVC screen assembly. The latter was left resting on the top of the bed for the duration of the experiment in an attempt to insure a constant degree of compaction from run to run. Voltage was applied to the cell soon after the flow of AMD was adjusted to the desired rate.

For the runs at high flow rates, concentrated acidic ferrous sulphate solution 8,000 ppm Fe(II), stored in a plastic drum, T-10 (Figure 3), was metered to the tap water line to provide the required AMD feed. To insure constancy of AMD composition the feed was monitored periodically by withdrawing samples for analysis from the exit of the valve, V-30. Also, on-the-spot checks for any drastic changes were made by reading the recorded output from a conductivity cell placed in the feed line. Once the appropriate valve and pump settings were made, the concentration of Fe(II) in the feed usually remained within a few percent of the desired value for the duration of the run.

Feed solution was continually pumped through the cells for periods of a few to sixteen hours depending on the amount of data required from the run. Samples of feed and effluent were taken periodically for analysis to evaluate the degree of treatment under a given set of operating conditions.

Analytical Methods

The approved methods listed in Table 2 were used during the Phase I study. Initial attempts to analyse for Fe(II) in solutions with high Fe(III)/Fe(II) ratios by the bypyridine method indicated that high concentrations of Fe(III) interfered with this test. In order to obtain an accurate analysis, therefore, Fe(II) was determined by titration with standard dichromate solution. Total iron was measured in the usual manner with bypyridine following the reduction of Fe(III) with hydroxylamine.

Analyses were generally done within one hour after the samples were taken. Aliquots of high pH solution were fixed with acid to preserve Fe(II) values. All samples were filtered before analysis to remove suspended solids.

TABLE 2. ANALYTICAL METHODS

Parameter	Method
Aluminum	Colorimetric-Phenanthroline
Calcium and Magnesium	EDTA Titration for Total Hardness
Iron, Total	Colorimetric-Bipyridine
Ferrous	Colorimetric-Bipyridine for Low Fe(III) Samples
	Dichromate Titration for High Fe(III) Samples
Manganese	Colorimetric-Persulfate

Results and Discussion

It should be noted at this point that no attempt was made to effect 100 percent conversion of Fe(II) or reduction in total iron (Fe_T) concentration during the Phase I studies, as the cells used were too small to provide the required residence time. The main objective was to cause enough change in the concentration of these species by various cell and operating adjustments so that the effects of these adjustments could be clearly distinguished and the data applied to the design of the Phase II system.

Screening Runs with Rectangular Cell

Initial experiments consisted of evaluating the effects of power and the addition of a PVC screen diaphragm to the cell. High ferrous AMD with pH 3 and Fe(II) concentration of about 500 ppm was processed at the rate of 83 ml/min (0.022 gal./min). Data obtained with a static Norit bed in a cell containing major electrodes (15.2 cm wide by 17.8 cm high) spaced 5 cm (2 in.) apart are listed in Table 3. The first column on the left shows the cumulative running time and the hour at which a sample of the effluent from the cell was taken for analysis. The remaining columns list the applied potential, current drawn, exact composition of the feed and effluent, and the percent conversion of Fe(II) relative to the feed value. All iron concentrations are expressed in parts per million (mg/liter).

Since it is known that the oxidation of Fe(II) by oxygen is catalyzed by activated carbon, AMD was initially pumped through the cell while the major electrodes were disconnected from the rectifier, in order to determine the degree of Fe(II) oxidation by any oxygen dissolved in the feed or absorbed on the Norit bed. After five hours of such operation, analysis of the effluent indicated only 2% conversion of Fe(II). A small amount of ferric hydroxide precipitate was formed. Shortly after the fifth hour sample was collected, a potential of 10 volts was applied to the cell and maintained for an additional nine hours. During this period solids were continually precipitated throughout the bed while a steady-state Fe(II) conversion of about 23% was recorded.

A second run was conducted using the same cell fitted with a PVC diaphragm against the major cathode. In this condition the unit drew about one-third the current observed without the diaphragm at the same applied potential. However, the average percent conversion of Fe(II) was almost twice the value measured during the previous run. After the fifth hour effluent was sampled, ferric hydroxide precipitate was

TABLE 3. DATA FOR AMD TREATMENT IN TWO INCH RECTANGULAR CELL WITH STATIC NORIT BED

TIME (hr)	Volts	Amps	AMD FEED[a]				EFFLUENT[a]				% CONV Fe(II)
			pH	Fe_T	Fe(II)	Fe(III)	pH	Fe_T	Fe(II)	Fe(III)	
(No Diaphragm)											
5.0	0	0	3.0	495	487	8	2.8	475	475	0	2
6.5	10.0	6.0	3.0	495	487	8	2.7	412	350	62	28
12.0	10.0	7.8	3.0	495	487	8	2.7	410	368	42	24
12.5	10.0	7.9	3.0	495	487	8	2.7	432	388	45	20
14.0	10.0	8.3	3.0	495	487	8	2.7	410	368	42	24
(Diaphragm Against Cathode)											
1.0	10.0	2.2	3.1	475	462	13	2.9	322	272	50	41
5.0	10.0	2.4	3.1	475	462	13	2.8	388	325	63	30
6.0	10.0	2.6	3.1	475	462	13	2.8	322	265	57	43
10.0	10.0	2.6	3.1	475	462	13	2.8	345	288	57	38

[a] Iron concentrations measured as ppm or mg/liter.

removed from the bed by a combination of nitrogen purge and fast flow of feed solution applied for several minutes. As a result, the current immediately increased to 2.8 amps. An hour later, when there was a small amount of fresh solids generated on the bed, the effluent showed an improvement in Fe(II) conversion. However, the improvement decreased as the run was continued into the tenth hour and more solids were deposited on the bed.

The results of these initial runs indicated that for efficient Fe(II) conversion the Ecotrol cell should be modified with the inclusion of a diaphragm against the major cathode to increase the anodic character of the bed and that means must be provided for periodic purging of the bed to remove non-conductive solids precipitated during the treatment of AMD at pH 3 or higher.

Evaluation of Electrode Bed Media

The materials described in Table 1 were evaluated as static beds in a rectangular cell with major electrodes (15.2 cm wide by 17.8 cm high) spaced 10.2 cm (4 in.) apart and PVC screen placed against the cathode. Electrolysis was conducted for seven hours while AMD (pH 3, 500 ppm Fe(II)) was continuously pumped through the bed at a rate of 0.16 liter/min (0.043 gal./min). Except for the runs with the coal samples, the cell current was maintained at 3 amps in each case.

The results of the evaluation are shown in Table 4. The applied potential, current and percentage figures are averages of values measured on an hourly basis after the cell attained equilibrium in regard to Fe(II) and Fe_T removal. The pH values of the effluents were generally the same as the feed (3.0) or slightly less (2.8). Solids were generated in every run, the most voluminous being observed when anthracite and bituminous coals were used.

The bed materials are listed in Table 4 in the order of decreasing effectiveness for AMD treatment. The percent reduction in Fe(II) concentration observed with Graphite 9H was almost as high as that for the Norit bed with similar shaped particles; however, the graphite required a much higher applied voltage. Apparently the high surface area and porous structure of activated carbon are not essential properties for an effective electrode bed material in view

TABLE 4. EVALUATION OF ELECTRODE BED MATERIALS

BED	Volts	Amps	PERCENT REDUCTION IN CONCENTRATION OF Fe(II)	Fe_T
Norit RB-II	6.4	3.0	32	18
Graphite 9H	16.0	3.0	23	11
Pittsburgh BPL	8.8	3.0	18	12
Witco 337	10.9	3.0	17	12
Graphite 6B	8.0	3.0	17	8
Nuchar WV-W	9.7	3.0	15	10
Columbia LCK	11.4	3.0	13	9
Anthracite	25.0	0.25	10	10
Witco 256	8.4	3.0	10	6
Bituminous	25.0	0.20	6	5

of the results with the smooth, non-porous particles of Graphite 9H.

It was impossible to pass a current greater than 0.25 amps through the anthracite and bituminous beds even at an applied potential of 25 volts. Consequently, the degree of Fe(II) oxidation was poor for these systems. The high resistance of the coal-filled cells is probably due to the high resistivity of the particles, 10^5 to 10^{14} ohm-cm. Another factor is the jagged shape of the ground coal which would influence electrical contact between the particles and solution flow patterns.

From a consideration of the data in Table 4 and costs of the materials, it was concluded that, of the solids tested, Norit RB-II would be the best electrode media for demonstration of the treatment of AMD. Further work may identify other bed materials which could be considered from a cost standpoint for commercial units. However, to meet the objectives of this project, Norit was used in all subsequent tests.

Effects of AMD pH

The data in Table 5 illustrate the effects of varying the pH of AMD solutions containing Fe(II) in essentially two different initial concentrations. Runs 13 to 16 were conducted with 500 ppm Fe(II) solutions, while 50-60 ppm Fe(II) AMD was used for Runs 17 and 18. A rectangular cell with 10.2 cm (4 in.) spacing of the major electrodes (12.7 cm wide by 17.8 cm high) and static anode bed was used. The flow rate was 0.15 liter/min (0.040 gal./min) and running time generally about 12 hours during which samples were taken from the cell exit port and analyzed on an hourly basis. All of the data in Table 5 are average values of measurements made after the cell exhibited a steady-state level of treatment.

Consider first the runs with high ferrous AMD. A comparison of the values for applied voltage necessary to maintain a current of approximately 3 amps indicates a solution conductivity effect. As the sulfuric acid concentration was decreased in going from a pH 2 to a pH 3 solution, the applied voltage had to be increased by a factor of almost 2. Further increase in pH to 4 and higher by the addition of sodium hydroxide resulted in a decrease of the applied voltage

TABLE 5. DATA ON EFFECTS OF AMD pH

	AMD FEED[a]							PERCENT REDUCTION IN CONCENTRATION OF	
RUN	pH	Fe_T	Fe(II)	Fe(III)	Volts	Amps	DECREASE IN Fe(II)	Fe(II)	Fe_T
13	2.0	500	495	5	7.3	3.1	195	39	2
14	3.0	490	485	5	17.2	3.1	115	24	5
15	4.0	515	503	12	13.5	3.0	120	24	15
16	5.3	488	480	8	13.5	3.0	114	24	15
17	2.0	51	48	3	8.0	3.0	40	83	6
18	5.3	64	61	3	14.6	3.1	44	72	52

[a] All iron concentrations measured as ppm or mg/liter.

relative to the value for the pH 3 run.

The effect of pH on the degree of AMD treatment is indicated by the Fe(II) data (Decrease in Fe(II)) and the values of percent reduction in Fe(II) and Fe_T concentrations. The last two variables are plotted in Figure 4. The degree of Fe(II) conversion drops from its value of 39 percent for the pH 2 solution to a plateau value of 24 percent for the AMD with pH 3 to 5. At pH 2 some elemental iron was plated on the cathode, and only a small amount of hydrous oxides was produced. An increase in solids production at the high pH levels is reflected by curve in Figure 4 for percent reduction in total dissolved iron. This value increases and levels off with increasing pH of AMD feed.

The influence of pH variation on the applied potential for the two runs with 50-60 ppm AMD is the same as observed with 500 ppm Fe(II). Considering the Fe(II) values, however, there appears to be little change in the degree of Fe(II) oxidation with pH in the low ferrous solutions. The percent reduction in Fe_T increased significantly with pH, as would be expected on the basis of the results with the 500 ppm Fe(II) solutions.

It was concluded that the effect of pH on the Fe(II) conversion lies mainly in the extent of ferric hydroxide formation. Conductivity differences can be compensated for by appropriate adjustment of the applied potential. While a decrease in oxidation effeciency with increased pH was observed with the high ferrous AMD, the pH effect was negligible for the 50-60 ppm solutions since much less solid was deposited during the pH 5 run by virtue of the low iron concentration.

Variation of Fe(II) and Fe(III) Concentrations

The same cell and operating conditions as used for the work on pH effects were applied in a study of Fe(III)/Fe(II) variations. The results are shown in Table 6. For the first three runs, the concentration of Fe(II) was varied in pH 2 water containing very little Fe(III). To examine the effect of the Fe(III)/Fe(II) ratio, the same pH and Fe(II) concentrations were used for the next three runs. However, Fe_T was kept as close as possible to 500 ppm by the addition of Fe(III) in $Fe_2(SO_4)_3.xH_2O$.

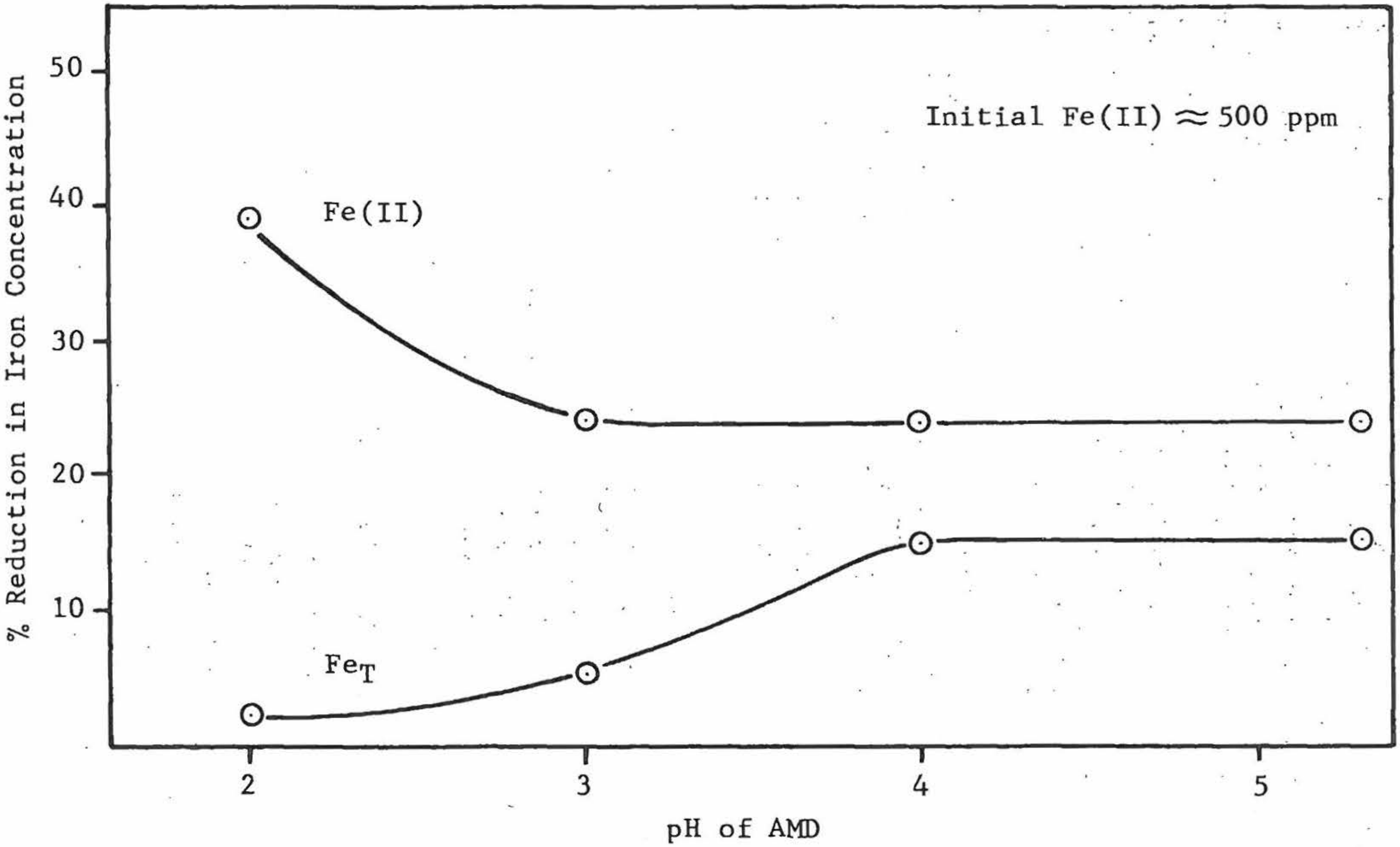

FIGURE 4. Effect of pH on Percent Reduction in Iron Concentration

TABLE 6. DATA ON EFFECTS OF Fe(II) AND Fe(III) CONCENTRATIONS

AMD FEED[a]						Effluent[a]
pH	Fe_T	Fe(II)	Fe(III)	Volts	Amps	Fe(II)
2.0	500	495	5	7.3	3.1	300
2.1	266	260	6	7.6	3.1	125
2.0	51	48	3	8.0	3.0	8
2.0	500	495	5	7.3	3.1	300
2.0	495	285	210	8.2	3.1	130
2.0	448	55	393	7.9	3.1	30
5.3	488	480	8	13.5	3.0	366
5.3	250	250	0	14.5	3.1	150
5.3	64	61	3	14.6	3.1	17

[a] All iron concentrations measured as ppm or mg/liter.

The last three runs were performed to observe the effect of Fe(II) concentration in AMD with pH 5. Attempts were not made to maintain a Fe_T value of 500 ppm in this series, as the excess Fe(III) would merely have precipitated when added to the pH 5 feeds.

Figure 5 contains plots of effluent Fe(II) concentrations versus the corresponding feed values. A comparison of the curves for the pH 2 solutions with and without initial Fe(III) addition indicates some degree of back reduction of Fe(III) to Fe(II) in the AMD with high Fe(III)/Fe(II) ratio. Although the electrode bed was made predominately anodic, the probability for Fe(III) reduction at the surface of the major cathode would be higher in solutions with a high Fe(III)/Fe(II) ratio than in the high Fe(II) water. Some chemical reduction of Fe(III) by hydrogen generated at the cathode could also occur.

Although a lower conversion of Fe(II) takes place in the high ferrous AMD at pH 5 than at pH 2, the precipitation of Fe(III) from the high pH solution would result in less back reduction to Fe(II). Also, a lower concentration of hydrogen would be produced in the pH 5 water. The difference in results between the high and low pH AMD therefore, approaches zero at low Fe(II) feed concentrations.

Attempts to fit the data to simple first and second order rate equations were unsuccessful. However, the plots in Figure 5 can be used as working curves to determine the minimum length of cell needed to effect a desired degree of Fe(II) oxidation. Consider, for example, the pH 2 solution with 500 ppm Fe(II) and no Fe(III). According to the corresponding curve in Figure 5, as this solution is passed through the unit cell used in this case, the effluent will have a Fe(II) concentration of 305 ppm. The concentration of the effluent that would be obtained by flowing the 305 ppm solution through another unit length of cell can then be approximated by reading from the curve the effluent value corresponding to a 305 ppm feed. This procedure is continued until the required cell length is determined.

Treatment of AMD Containing Other Metals Besides Iron

A series of runs were conducted with synthetic AMD containing aluminum, calcium, magnesium and manganese. It was of interest

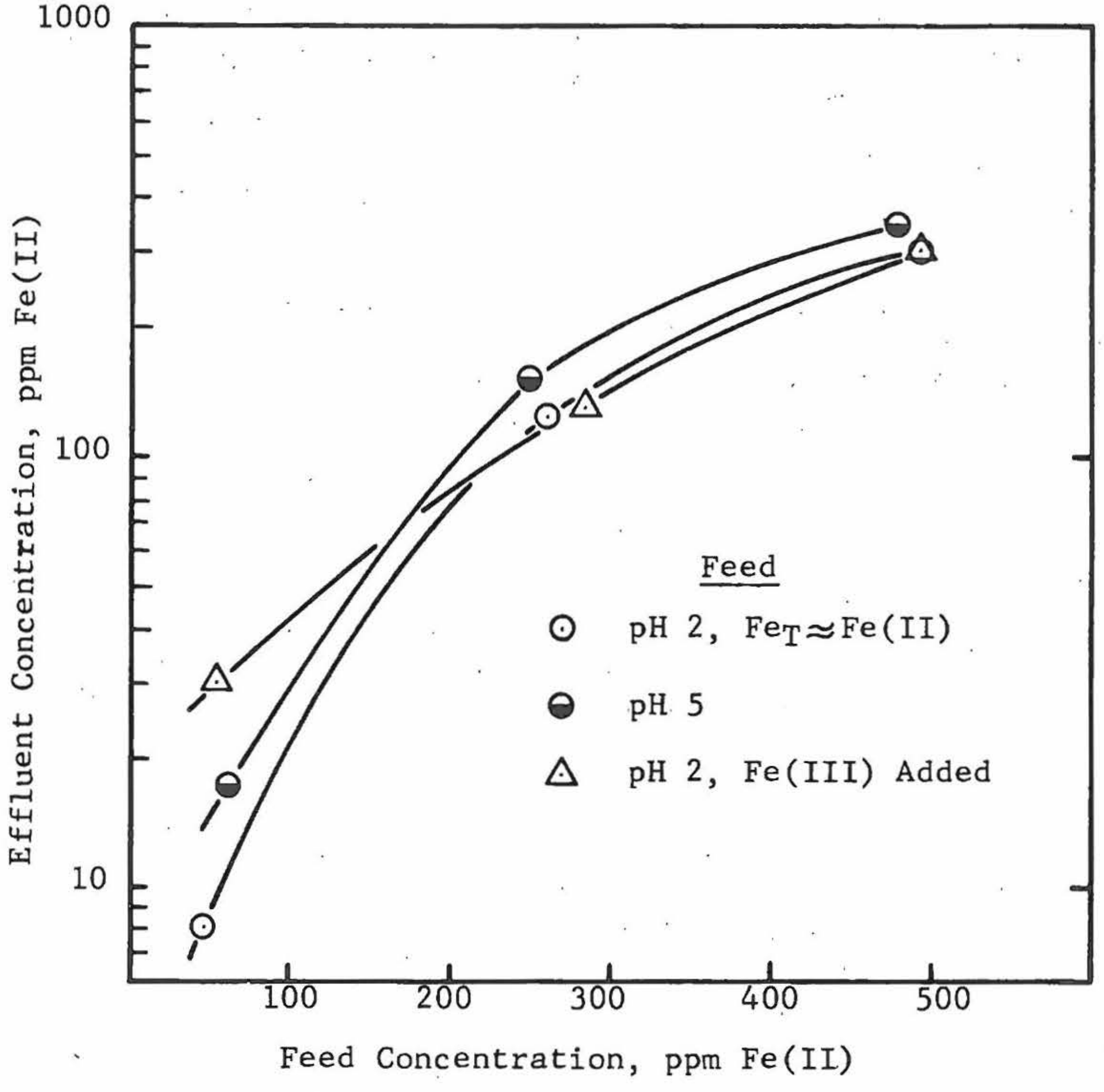

FIGURE 5. Effluent Concentration versus feed Concentration of Fe(II) for Treatment in Small Rectangular Cell

to determine the effect of electrolysis on these metals and the effect of these metals on the degree of Fe(II) oxidation. Cells and operating conditions were the same as used for the pH and iron concentration studies. The results are shown in Table 7, wherein Me is a general symbol for the metal present besides iron. For the run with calcium and magnesium, these were added in a weight ratio of 1.4 Ca/Mg. The magnesium concentration was converted to a calcium equivalent and the feed value of Me expressed as total calcium.

As for the effect of electrolytic treatment on Mn(II) in the electrode bed cell, only a small percent reduction in this metal's concentration was observed. The analytical procedure used for determining manganese in solution does not differentiate oxidation states, but converts all lower valence ions to the permanganate form (MnO_4^-) by oxidation with persulfate. The presence of MnO_4^- in the effluent samples before the addition of persulfate was precluded by the absence of the familiar pink color characteristics of MnO_4^- which is detectable even in 1 ppm Mn solutions containing excess Fe(II). The small reduction in Mn(II) concentration could have resulted from oxidation to insoluble MnO_2; however, it was impossible to detect a small amount of this solid in the mixture with excess iron oxides, which were also formed.

In regard to an effect of Mn(II) on the conversion of Fe(II), the data show a reduction of about 25% in the fraction of initial Fe(II) oxidized in the presence of 50 or 90 ppm Mn(II). The same data were obtained from replicate runs. These results present an anomaly as one might expect the opposite effect when known redox potentials are considered; i.e., oxidation of Mn(II) to MnO_4^- which in turn would oxidize Fe(II). No explanation can be offered at this time.

It was concluded from this series of runs that, in view of the small deleterious effect of manganese on the Fe(II) conversion, the treatment of actual AMD containing 50 ppm or more of this metal would require a somewhat longer residence time than drainage waters having little or no manganese. It was hoped that more definitive data would be obtained during the field study. The results of the runs with calcium, magnesium and aluminum indicate essentially no effect on the degree of Fe(II) oxidation and a small percentage removal of these metal ions in the high pH AMD.

TABLE 7. DATA ON TREATMENT OF AMD CONTAINING OTHER METALS BESIDES IRON

FEED[a]						Decrease in	Percent Reduction in	
pH	Fe(II)	Fe(III)	Me	Volts	Amps	Fe(II)	Fe(II)	Me
5.1	413	0	0	13.4	3.1	113	27	-
				[MANGANESE]				
5.1	395	0	48	15.6	3.1	80	20	4
4.9	352	5	87	12.3	3.1	74	21	10
				[CALCIUM/MAGNESIUM (1.4)]				
4.8	395	0	326[b]	10.6	3.1	114	29	3
				[ALUMINUM]				
4.5	390	4	61	12.0	3.1	105	27	3

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[a] All metal concentrations measured as ppm or mg/liter.

[b] Total calcium (actual plus magnesium equivalent).

Effect of AMD Temperature

All of the tests previously described were conducted with the feed solution at room temperature. In anticipation of the lower temperatures which would be encountered at the field site, runs were carried out with feeds kept at 1.1°C (34°F) and 8.8°C (48°F) (deep well temperature). Synthetic AMD with a pH of 5 and Fe(II) concentration of approximately 400 ppm was treated in the same cell as used for pH and iron concentration studies. Table 8 lists the average voltage, current and percent reduction in Fe(II) and Fe_T concentrations observed after steady-state treatment was attained during the 7-hour runs. At a constant cell current, the degree of AMD treatment was approximately the same in each case. The only difference among the three runs is the voltage which had to be applied to maintain a current of 3 amps. As was expected, the necessary applied voltage increased with decreasing temperature. Figure 6 is a plot of the cell voltage versus temperature of the feed. The best straight line drawn through the points yields an average temperature coefficient of -0.12 volts/degree, which indicated that temperature variations to be encountered in the field could be compensated for by small adjustments in applied voltage.

Solids Generated by Electrolysis

Throughout the course of the laboratory work, it was repeatedly observed that during electrolysis of synthetic AMD at a pH of 3 or greater, a small fraction of the total solids generated in the cell consisted of what appeared to be a dark reddish-brown crystalline material that settled at a rapid rate compared to the usual gelatinous $Fe(OH)_3$ precipitate. Some effort was directed in Phase I to a closer examination of the properties of this solid and of the sludge formed after lime neutralization of the electrolyzed mine water. Characteristics of the electrolysis solids were compared with those observed for AMD treated by aeration.

Synthetic AMD with a pH of 4.7 and Fe(II) concentration of 283 ppm was pumped through a small rectangular cell with 2-inch electrode spacing. The effluent generated during this treatment had a pH of 3.1 and contained some of the desired reddish-brown crystalline flakes mixed with hydrous ferric oxide. Analysis of a portion of the effluent after

TABLE 8. EFFECT OF TEMPERATURE ON AMD TREATMENT

Feed: pH=5.0

Fe_T=Fe(II)=400 ppm

TEMPERATURE				PERCENT REDUCTION IN CONCENTRATION OF	
(°F)	(°C)	Volts	Amps	Fe(II)	Fe_T
34	1.1	18.0	3.1	29	15
48	8.8	16.9	3.0	23	16
72	22.2	13.4	3.1	27	20

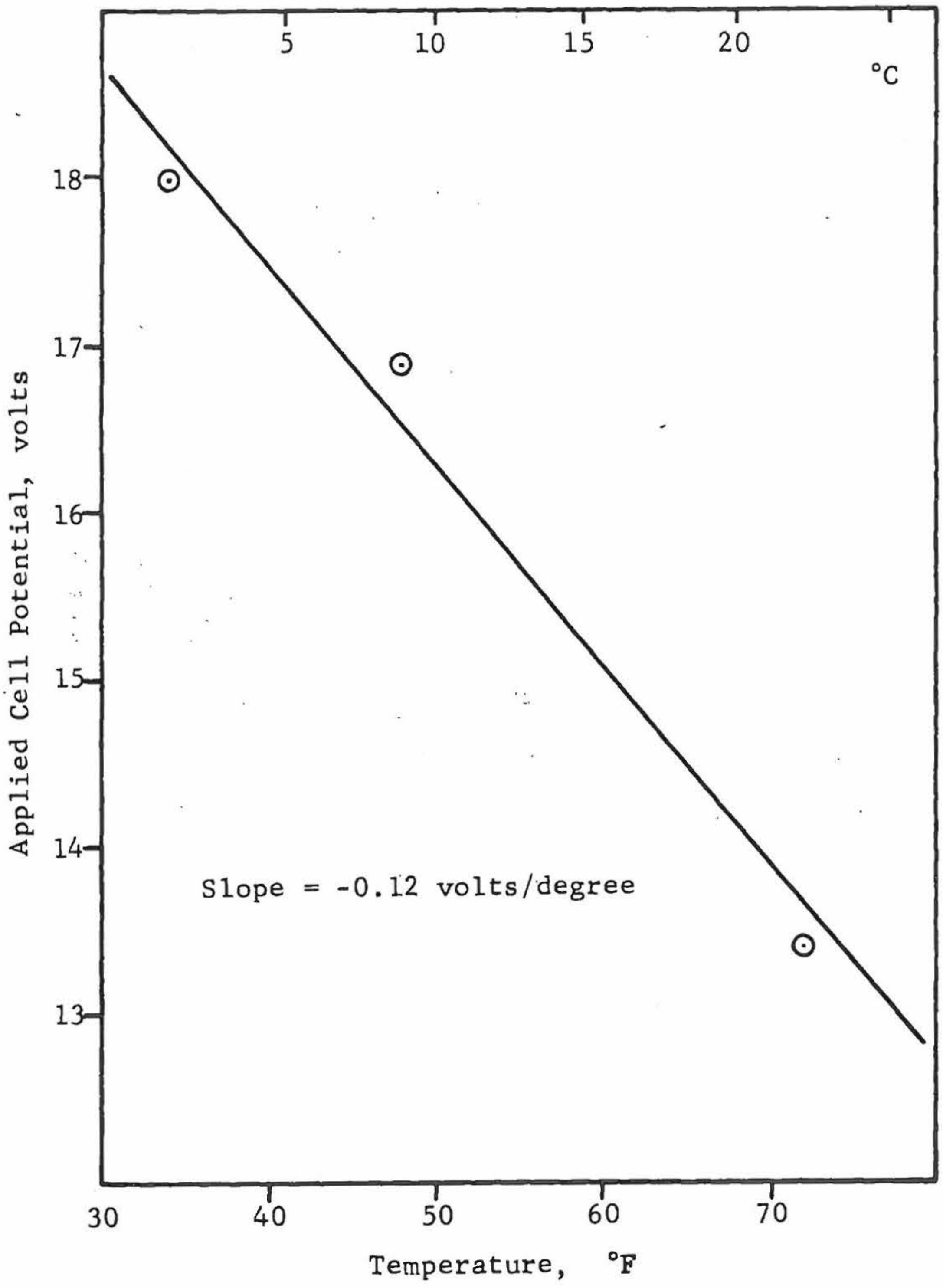

FIGURE 6. Applied Cell Potential vs Temperature of AMD

filtration showed 170 ppm Fe_T and 145 ppm Fe(II). While the bulk of the collected effluent was stirred to distribute the solid uniformly throughout the solution, a sample of the mixture was taken for the usual measurements of settling rate and sludge volume in a one-liter graduate cylinder. Sludge density (weight of solids per final volume of sludge) was determined by weighing the solid after drying at 110°C. A second sample of the effluent was neutralized with lime and the aforementioned sludge characteristics were measured.

In order to compare these results with the properties of the solids generated by air oxidation, AMD with the same Fe(II) concentration and pH as used for the electrolytic treatment was aerated for approximately 30 hours until the composition of the effluent approximated that from the Ecotrol cell -- pH 3.1, 156 ppm Fe_T and 125 ppm Fe(II). No crystalline solid, characteristic of the electrolyzed effluent, was observed in the aerated solution. Samples of the latter were taken for measurement of sludge properties before and after lime addition.

Because of the small scale of the laboratory runs, the amount of total suspended solids per volume of effluent was quite small. Consequently, in determining settling rates it was not possible to time the drop in sludge volume starting from the top of the graduate cylinder, since no discernible sludge boundary was formed at this height after stirring was stopped. What could be followed, however, was the change in volume of a distinct sludge blanket formed at the bottom of the cylinder. The level of this blanket rose at first then fell in the normal manner. Sludge volume versus time curves measured in this way for the electrolyzed and aerated effluents before lime addition are shown in Figure 7. Figure 8 contains similar curves for the lime-treated effluents.

It is quite evident from Figure 7 that the solids generated in the cell settled more rapidly than those formed during aeration of the AMD. Although the difference is not as great in Figure 8 for the lime-treated waters, the settling rate of the solid in the electrolyzed effluent still appears to be higher than that for the aerated AMD.

Table 9 contains values of the final sludge volumes (24 hours) and sludge densities measured for the above systems.

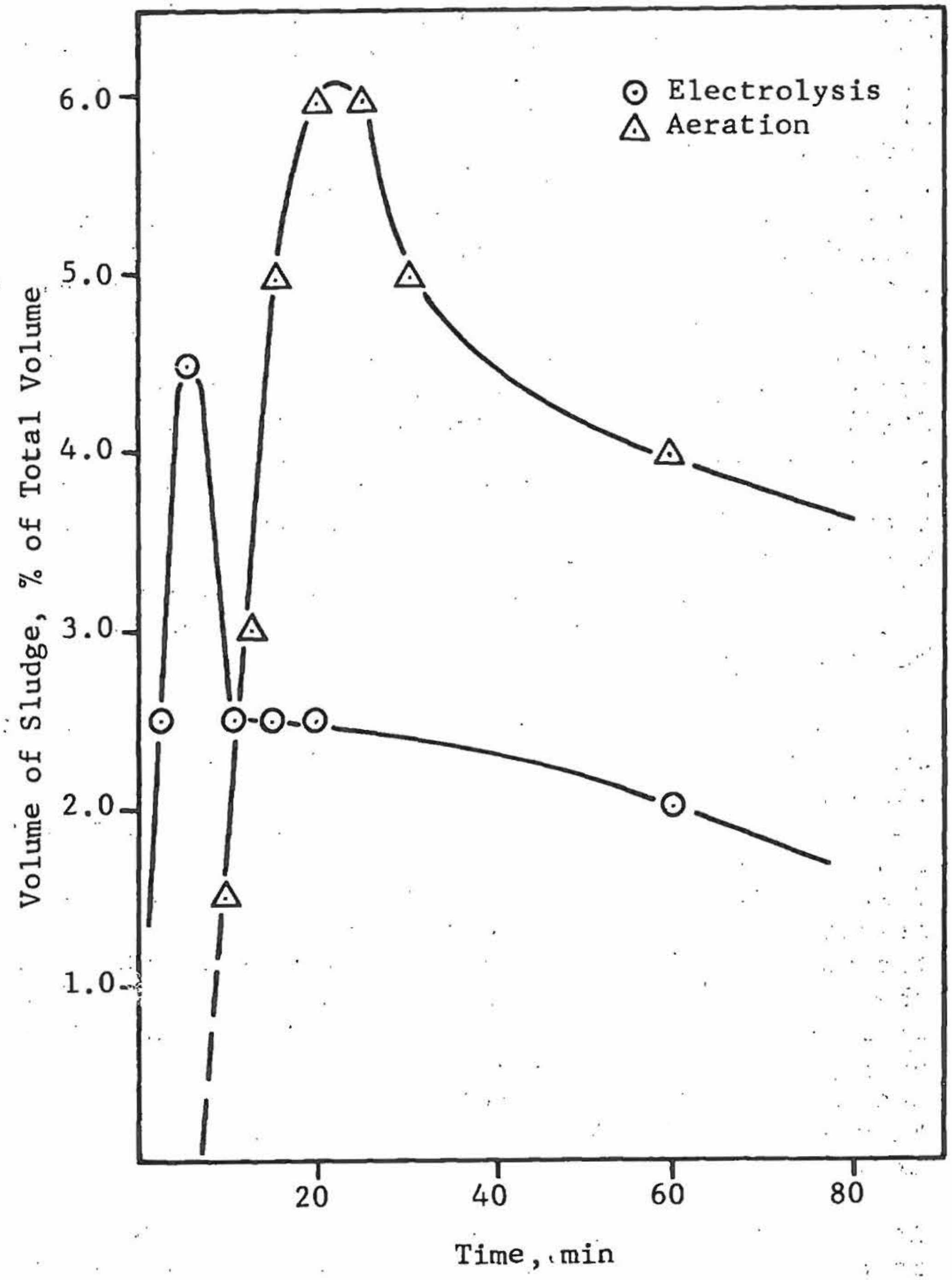

FIGURE 7. Comparison of Sludge Settling Rates for Electrolyzed and Aerated AMD Before Lime Addition

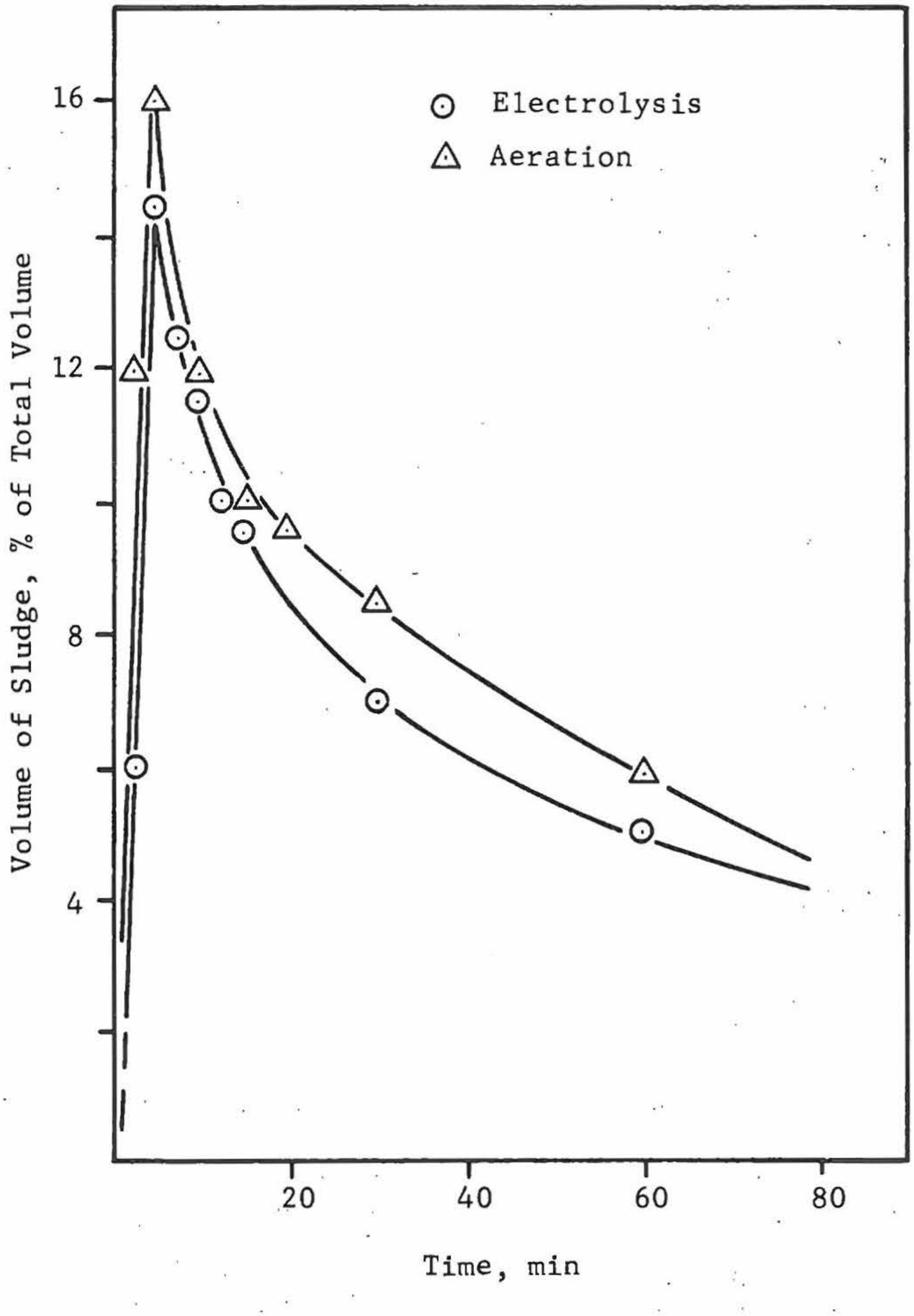

FIGURE 8. Comparison of Sludge Settling Rates for Electrolyzed and Aerated AMD After Lime Addition

The data for the sludges present before lime addition concur with the difference in settling rates illustrated by the curves in Figure 7. The opposite is true for the solids after lime addition. However, the beneficial effect of the small amount of crystalline solid in the effluent right after electrolysis might have been diminished by dilution with excess $Fe(OH)_3$ formed during the neutralization. Also, it is possible that upon standing over a long period in neutral or high pH water, the crystalline solid formed by electrolysis undergoes transition to an amorphous state.

TABLE 9. SLUDGE CHARACTERISTICS

METHOD OF GENERATION	FINAL VOLUME (ml)	DENSITY (mg/ml)
	(Before Lime Addition)	
Electrolysis	8	16
Aeration	12	12
	(After Lime Addition)	
Electrolysis	35	20
Aeration	30	24

An air-dried sample of the mixture of solids from the electrolyzed water was examined by x-ray analysis. The powder photograph showed that the material was essentially amorphous. Some scattering occurred, but the lines could not be clearly identified. In view of the large excess of $Fe(OH)_3$ in the mixture, the volume fraction of the crystalline solid might have been below the detectable limit of the instrument (minimum sensitivity, 2 to 3%).

Further work in this area was scheduled for the Phase II study in anticipation of essentially complete conversions of Fe(II) and generation of large concentrations of the desired solids.

Cell Evaluation and Sizing

Rectangular Cells

A series of runs were conducted to evaluate the degree of Fe(II) conversion at various flow rates in a cell with constrained bed and with the bed free to expand at relatively high feed velocities. For this series the rectangular cell with 15.2 cm (6 in.) wide major electrodes spaced 10.2 cm (4 in.) apart and PVC screen against the cathode was connected into the flow system illustrated in Figure 3.

First, measurements of bed expansion versus fluid velocity were taken with no DC potential applied to the cell. The height of the bed after backwash and drain was taken as the reference point, $h°_B$. After recording the bed height at flow rates in the range of 3.8 to 11.3 liter/min (1 to 3 gal./min), a plot of percent bed expansion ($100\Delta h_B/h_B°$) versus apparent velocity was made. The curve is shown in Figure 9. It was impossible to obtain precise readings of bed height, since expansion was not uniform throughout the bed. This is most likely due to the shape and variation in size of the Norit particles. Detectable expansion occurred at a velocity of approximately 42.7 cm/min (1.4 ft/min) As the velocity was increased above 76.2 cm/min (2.5 ft/min), the bottom corners of the bed started to compact while the center started a vortex motion, rising to the top center of the column, falling along the middle of the walls, and flowing back into the center in the bottom half of the column. After extended application of high feed velocities, a slight degree particle attrition and fines production was noticeable. Percent expansion was independent of $h_B°$ for values of the latter in the range of 17.8 cm (7 in.) to 45.7 cm (18 in.). No hysteresis effect was detectable.

Table 10 contains the data obtained during steady-state treatment of high ferrous AMD at pH 5. The feed velocities applied in the first three runs were below the threshold value for bed expansion, and the bed was held in a fairly compact state by means of a retaining screen as described earlier. Under these conditions, the percent conversion of Fe(II) at constant current decreased as the flow rate was increased from 0.15 to 0.45 liter/min (0.04 to 0.12 gal./min).

The second set of data in Table 10 was obtained by allowing

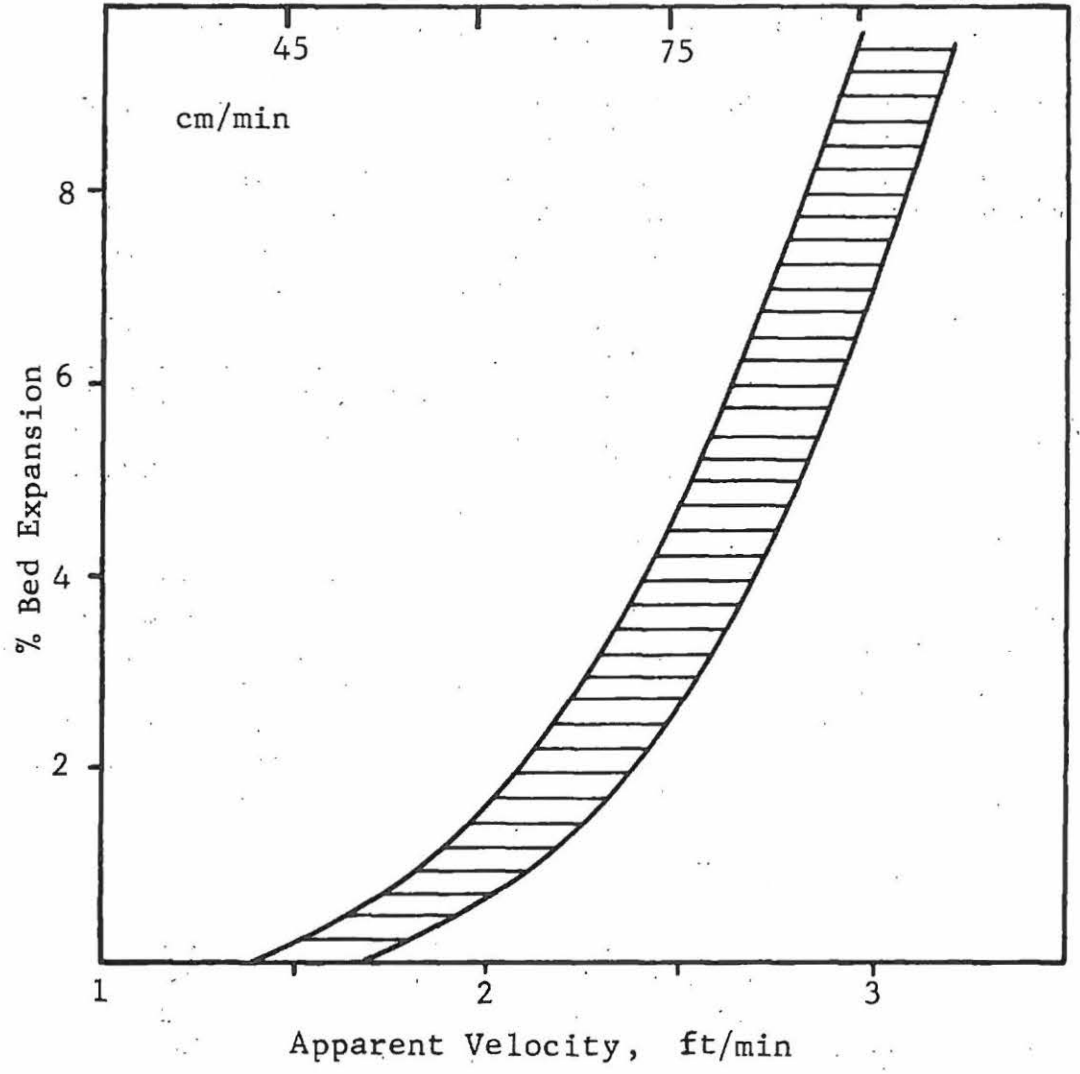

FIGURE 9. Percent Expansion of Norit Bed in Rectangular Column

TABLE 10. DATA ON AMD TREATMENT AT HIGH FLOW RATES IN RECTANGULAR CELL

SYNTHETIC AMD FEED [a]							
pH	Fe_T	Fe(II)	Fe(III)	Flow Rate (liter/min)	Volts	Amps	% CONV Fe(II)
			(Compact Bed $h_B^\circ = 17.8$ cm)				
5.3	488	480	8	0.15	13.5	3.0	24
5.0	505	500	5	0.23	10.4	3.1	17
5.2	515	503	12	0.45	10.6	3.1	8
			(Free Bed $h_B^\circ = 45.7$ cm)				
5.6	438	438	0	6.6	25.0	2.7	3
5.4	470	455	15	7.6	25.0	3.0	7
4.2	-	319	-	8.5	25.0	1.0	23
5.5	458	453	5	8.7	25.0	1.7	21
5.3	438	438	0	10.6	25.0	1.5	5

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[a] All iron concentrations measured as ppm or mg/liter.

the bed to expand by about one percent while the feed flow rate was increased with each run up to 10.6 liter/min (2.8 gal./min). Separation of the electrode particles by flows greater than 7.6 liter/min (2.0 gal./min) is reflected by the drop in current drawn by the cell at a constant potential of 25 volts. In Figure 10, the values of percent Fe(II) conversion are plotted versus flow rate. The bell-shaped curve shows an optimum flow rate of about 8.7 liter/min (velocity of 51.8 cm/min) for Fe(II) oxidation. The appearance of the maximum in the curve is probably due to a combination of factors, such as efficient solids removal, optimum separation of bed particles and optimum residence time. At feed velocities corresponding to flow rates greater than 8.7 liter/min (2.3 gal./min), either the residence time is not sufficient and/or the separation of the particles, though visibly small, is great enough so that the behavior of the system approaches that of a conventional cell without the electrode bed.

The increase in efficiency derived from the operation with the slightly expanded bed is exemplified by comparing results from this system in Table 10 with the data obtained using the compact bed. Although a larger bed volume and higher potential were applied in the former case, approximately the same percent conversion of Fe(II) was attained at one-third the current drawn by the compact bed and at about 60 times the mass loading (8.5 liter/min or 2.25 gal./min for expanded bed versus 0.15 liter/min or 0.04 gal./min for compact bed).

Circular Cells

For the evaluation of the cylindrical configuration, measurements were made first with a small cell containing a static packed bed of Norit carbon. The height of the bed was 10.2 cm (4 in.). The diameter of the inner electrode was 1.9 cm (0.75 in.), while that of the outer electrode was 8.6 cm (3.4 in.) I.D. Stainless steel was used as the cathode material and titanium coated with ruthenium dioxide as the anode. Test solution with pH 3 and 500 ppm Fe(II) was pumped through the cell at the rate of 57 ml./min (0.015 gal./min).

Because of the difference in surface areas of the concentric major electrodes, the main purpose of the runs with the small cell was to determine any difference in power characteristics and degree of AMD treatment between the configuration having inner cathode -- outer anode and vice-versa. Runs were also

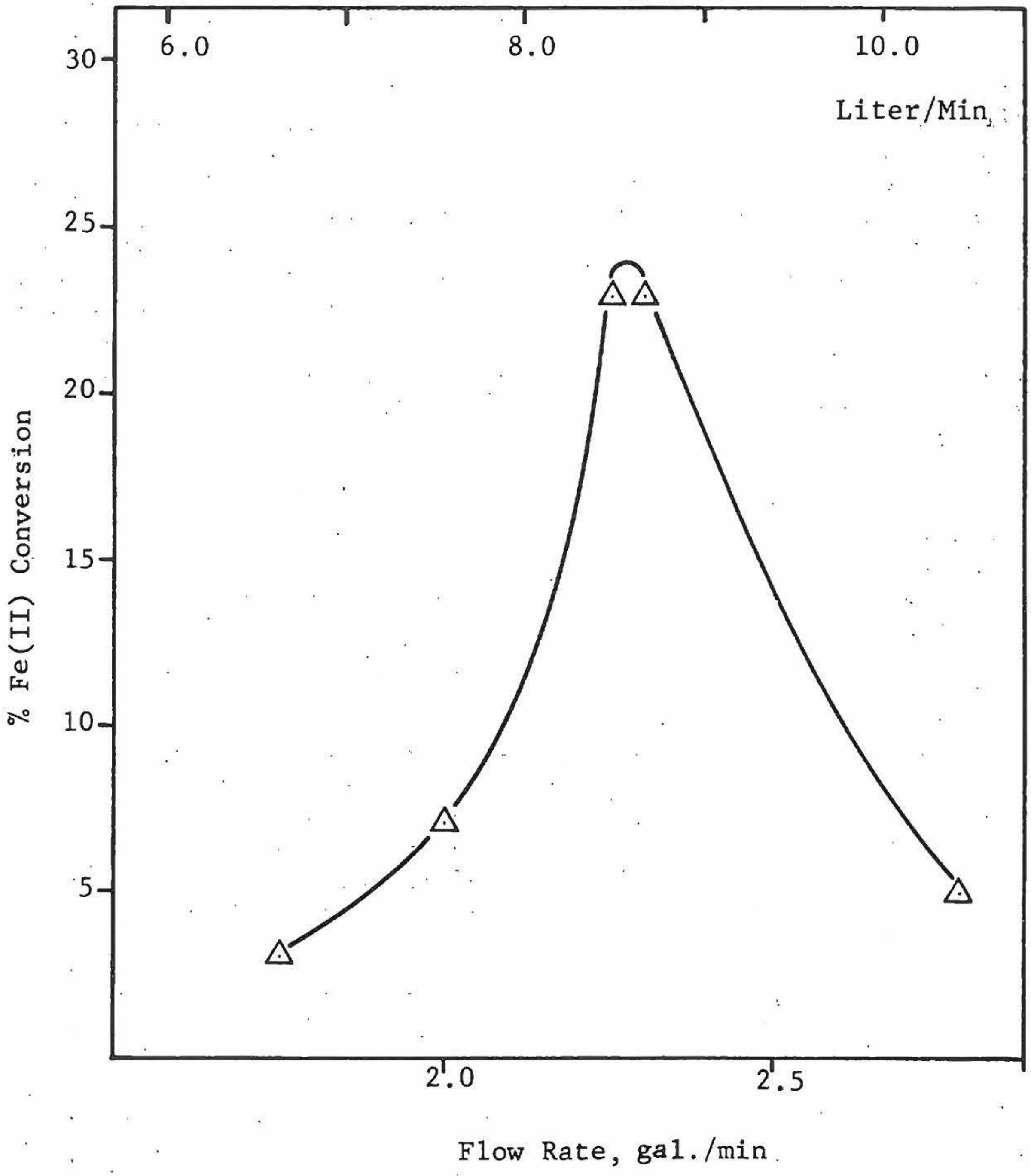


FIGURE 10. Percent Fe(II) Conversion vs Flow Rate in Rectangular Cell

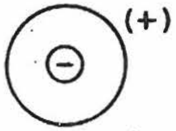
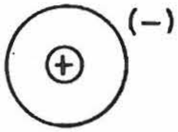
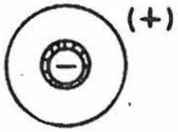
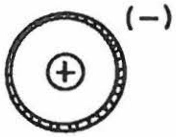
carried out with a PVC diaphragm placed against the cathode wall.

Table 11 contains data taken during electrolysis in the small circular cells. Consider first the cells without diaphragm. A comparison of the current-voltage values indicates that the cell behaves to some degree like a diode due to the difference in surface areas of the inner and outer electrodes, i.e., the configuration with the small anode conducts better than that with the small cathode. At the same cell current, the degree of Fe(II) oxidation was less in the cell with the inner anode. In addition, a pronounced odor of hydrogen sulfide was generated from this cell which was not noticed during electrolysis with the small cathode configuration nor during treatment in any of the rectangular cells.

With the screens placed against the cathodes, the same diode effect as described above was observed. The potential drop across the cells with diaphragm is higher than that without diaphragm, since the screen prevents the semi-conductive bed from coming in direct contact with the cathode. Thus the current is lower in the diaphragm cell at a given applied voltage. Introduction of the diaphragm to the small cathode cell caused only a slight increase in Fe(II) removal. With the small anode cell, however, the presence of the screen doubled the percent reduction in Fe(II) concentration. In addition, no sulfide odor was detectable, as was the case without the screen. On the basis of these results, further laboratory studies with circular cells were performed using the inner anode-outer cathode configuration with diaphragm against the cathode.

As was done with the rectangular cells, a series of runs were conducted to evaluate the degree of Fe(II) conversion at relatively high flow rates in large cylindrical cells containing beds without constraints. In order to determine the percent bed expansion with feed velocity, measurements were taken using simulated cells made from clear Lucite tubes. The curve for bed expansion in an annular volume bounded by an inner tube with 5.1 cm (2 in.) diameter and outer tube with 20.3 cm (8 in.) I.D. is plotted in Figure 11. Points for a system with 25.4 cm (10 in.) outer and 10.2 cm (4 in.) inner tubes fell within the same region as shown in this figure. Bed expansion was more uniform than in the rectangular cells. A change from uniform expansion to

TABLE 11. DATA ON AMD TREATMENT IN SMALL CIRCULAR CELLS

			AMD FEED^a				
ELECTRODE CONFIGURATION	Volts	Amps	pH	Fe_T	Fe(II)	Fe(III)	% CONV Fe(II)
			(NO DIAPHRAGM)				
	8.0	0.8	2.8	500	495	8	24
	6.6	0.8	2.8	503	495	8	16
			(WITH DIAPHRAGM - PVC SCREEN)				
	13.0	0.64	3.0	500	488	12	28
	9.1	0.64	3.0	500	498	2	32

[a] All iron concentrations measured in ppm or mg/liter.

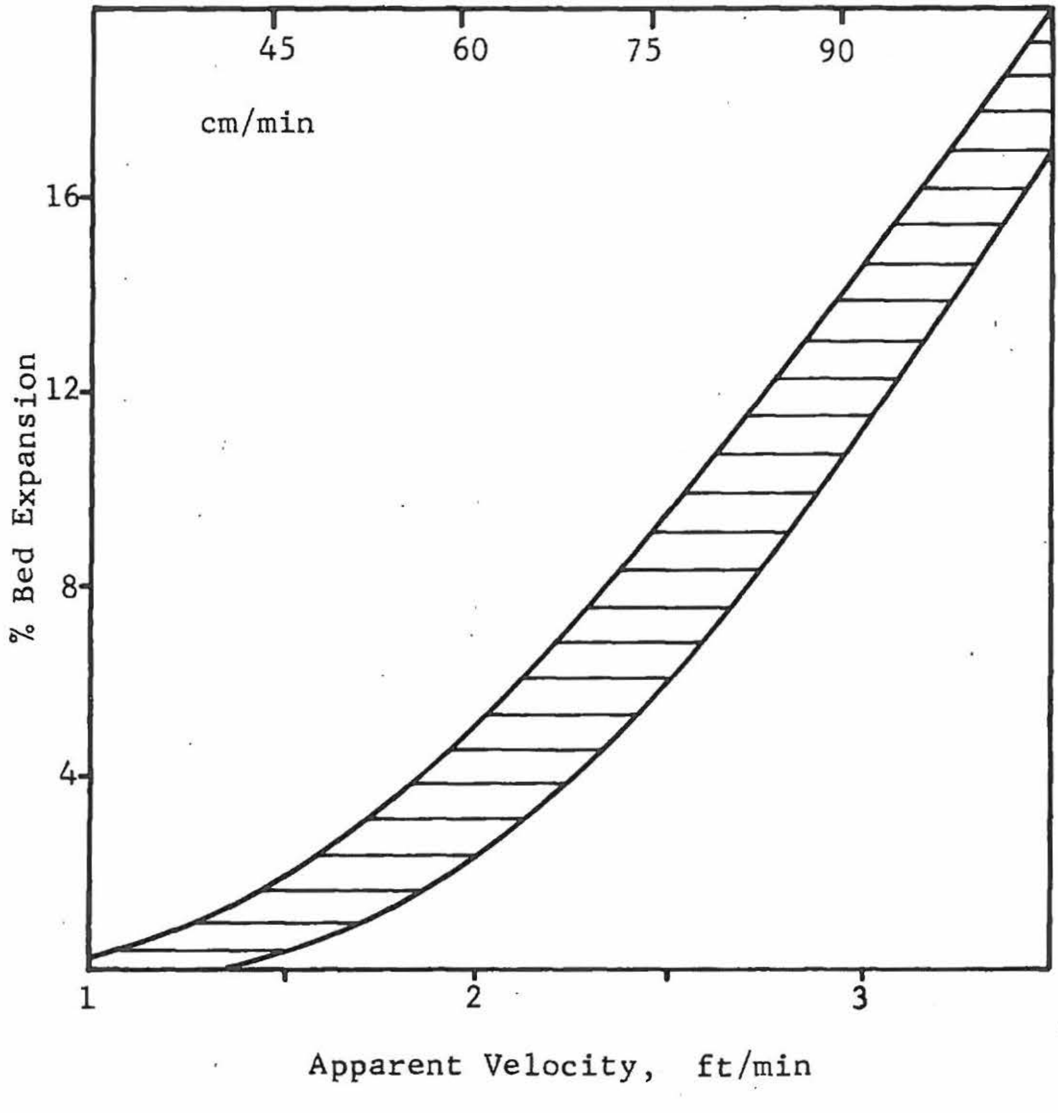


FIGURE 11. Percent Expansion of Norit Bed in Cylindrical Columns

turbulent wave motion occurred at a velocity of approximately 83.8 cm/min (2.75 ft./min).

Electrochemical measurements were made with one cell consisting of an outer stainless steel cathode (20.3 cm or 8 in. I.D.) and inner coated titanium anode (5.1 cm or 2 in. O.D.). A graphite rod was also substituted for the titanium to compare results. A second cell with outer steel cathode (25.4 cm or 10 in. I.D.) and inner graphite anode (10.2 cm or 4 in. D.) was also used. The results with AMD at pH 2 and 5 are given in Table 12.

All runs except the first one with pH 2 AMD were conducted with beds free to expand. Percent Fe(II) conversion on the free beds (h_B°=20.3 cm) is plotted versus flow rate in Figure 12. In view of the results obtained for the rectangular configuration, a bell-shaped curve was drawn through the three points. From this curve it appeared that maximum oxidation occurred at a feed flow rate of about 7.2 liter/min or 1.9 gal./min (velocity of 24.4 cm/min or 0.8 ft./min). At this velocity, the bed was barely expanded. A comparison of these results with the data for the first run in Table 12 indicates that conversion was higher in the compact bed. However, it should be noted that 2.5 times the current was drawn in the latter case. The expanded bed with h_B° equal to 50.8 cm (20 in.) yielded a conversion equal to that on the compact 20.3 cm (8 in.) bed for the same current draw. There was no difference in the results with graphite and coated titanium anodes.

The first three runs with pH 5 water showed essentially no change in the amount of Fe(II) oxidized as the flow was increased from 6.8 to 9.5 liter/min (1.8 to 2.5 gal./min). The last three runs with the high pH AMD were conducted with different initial Fe(II) concentrations to generate a working curve for scale-up.

Choice of Configuration, Sizing & Materials for Phase II Pilot Cells

It was difficult to make a choice of configurations based solely on the raw data obtained during the Phase I study. For example, consider the numbers in Table 13. For the treatment of pH 5 AMD at approximately the same flow rate

TABLE 12. DATA ON AMD TREATMENT AT HIGH FLOW RATES IN CIRCULAR CELLS[a]

AMD FEED[b]								
pH	Fe_T	Fe(II)	Fe(III)	Flow Rate (liter/min)	H_B° (cm)	Volts	Amps	% CONV Fe(II)
				(CELL WITH 20.3 cm. I.D. CATHODE)				
2.3	450	450	0	6.8	20.3	14.0	10.0	30
2.3	455	455	0	6.8	20.3	16.0	4.0	17
2.3	525	525	0	7.6	20.3	15.5	4.0	18
2.2	388	383	5	9.5	20.3	12.5	4.0	4
1.9	493	488	5	6.8	50.8	13.0	10.0	26
				(CELL WITH 25.4 cm. I.D. CATHODE)				
5.3	463	455	8	6.8	45.7	32.0	10.5	11
5.3	480	475	5	8.5	45.7	33.0	8.0	11
5.7	475	475	0	9.5	45.7	32.0	8.5	10
5.3	480	475	5	8.5	45.7	33.0	8.0	11
5.4	265	265	0	8.5	45.7	28.0	6.5	27
5.8	61	59	2	8.5	45.7	44.0	4.0	32

[a] All runs except the first were conducted with free beds.

[b] All iron concentrations measured as ppm or mg /liter.

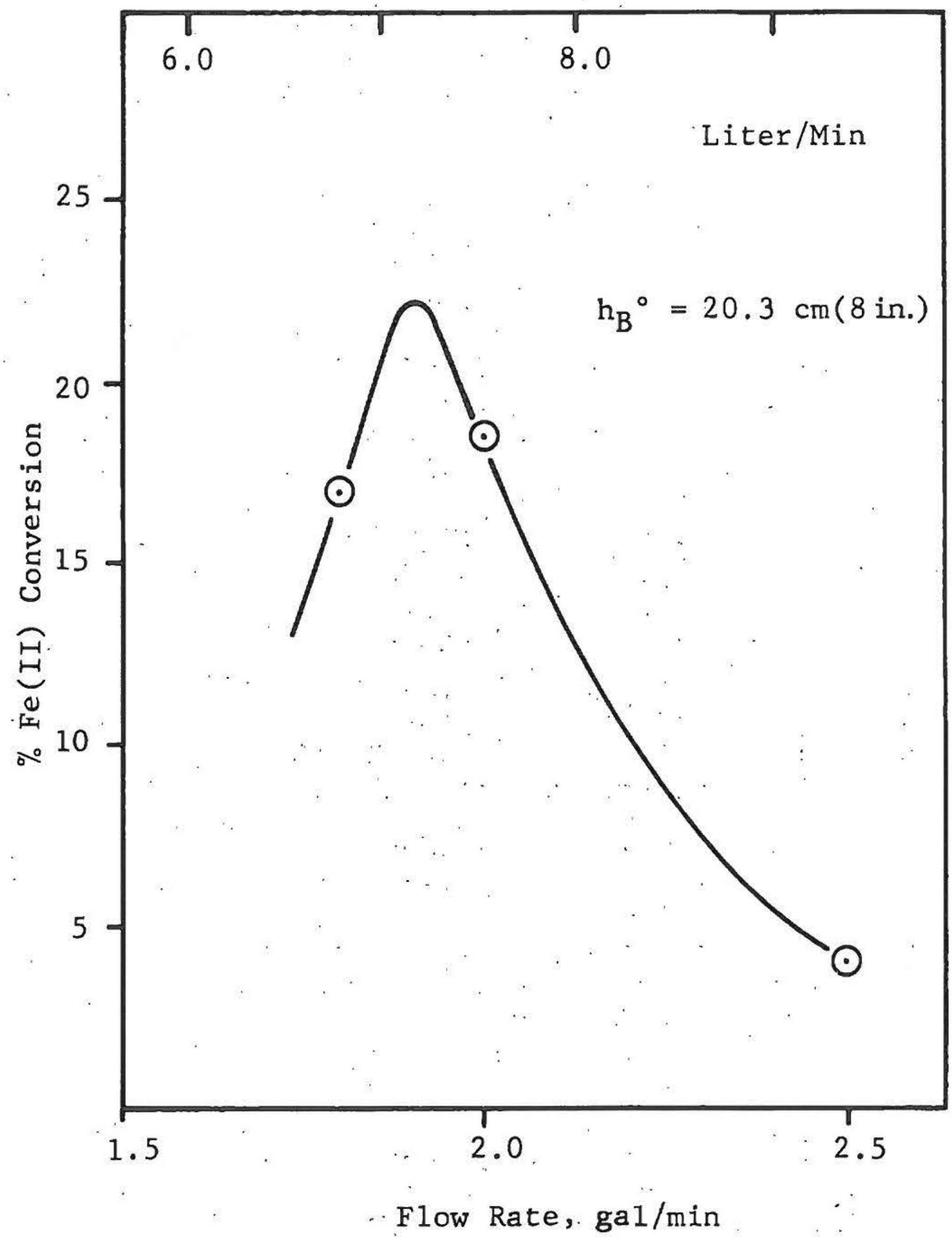


FIGURE 12. Percent Fe(II) Conversion vs Flow Rate in Large Circular Cell

TABLE 13. COMPARISON OF RECTANGULAR AND CIRCULAR CELL PERFORMANCE

CELL	LENGTH OF CELL (cm)	FLOW RATE (liter/min)	RESIDENCE TIME (min)	APPARENT VOLUME (liter)	AMPS	% CONV Fe(II)
		(AMD - pH 5, 500 ppm Fe(II)	Bed-Expanded)			
Rec.	45.7	8.7	0.867	7.53	1.7	23
Cir.	45.7	8.5	2.54	21.7	8.0	11
Rec.	45.7	6.8	1.11	7.53	2.7	3
Cir.	45.7	6.8	3.18	21.7	10.5	11
		(AMD - pH 2, 500 ppm Fe(II)	Bed-Compact)			
Rec.	17.8	0.45	5.05	2.29	3.1	24
Cir.	20.3	6.8	0.845	5.77	10.0	30

(8.7 liter/min or 2.3 gal./min) in rectangular and circular cells of equal length and with approximately the same major electrode spacing, the percent reduction in Fe(II) concentration in the rectangular cell was twice that observed for the circular cell despite the higher current drawn by the latter and longer residence time in this higher volume cell. When the same AMD was pumped through the same two cells at a flow rate of 6.8 liter/min (1.8 gal./min), the difference in performance was not as great as in the first case. The percent reduction in Fe(II) concentration by the circular cell was 3.7 times that in the rectangular system. However, the circular cell drew 3.9 times the current. A consideration of residence time would still let the rectangular cell appear to be somewhat better, but the exact degree of improvement cannot be estimated. For runs with the pH 2 AMD, the reverse was found to be true. The degree of Fe(II) oxidation was slightly higher in the circular cell. However, although this cell drew 3.2 times the current in the rectangular cell, a consideration of the higher mass loading in the circular system and the higher residence time in the rectangular cell would make the circular configuration with compact bed appear to be superior for treating low pH AMD.

After examining the raw data, calculations were made for scale-up to pilot size (18.9 liter/min or 5 gal./min average, 500 ppm initial iron, 10 ppm or lower final iron) to compare dimensions and gain some idea of the design of the Phase II system depending on cell configuration. The total residence time or length of cell required for the desired treatment was determined from working curves such as those in Figure 5. Figure 13 shows a comparable working curve plotted from the data in Table 12 on treatment of pH 5 AMD with different initial iron concentrations in the large circular cell. In those cases where the data was not sufficient to permit plotting of actual working curves, an average percent removal of Fe(II) per unit length cell based on available numbers was taken as a guiding factor. After the required total length of cell was determined for each configuration and flow rate employed in the laboratory studies, the dimensions required for a 18.9 liter/min (5 gal./min) loading were calculated.

Based on the results of such calculations and a consideration of factors such as availability of components with the desired size, ease of construction, and timing, the circular

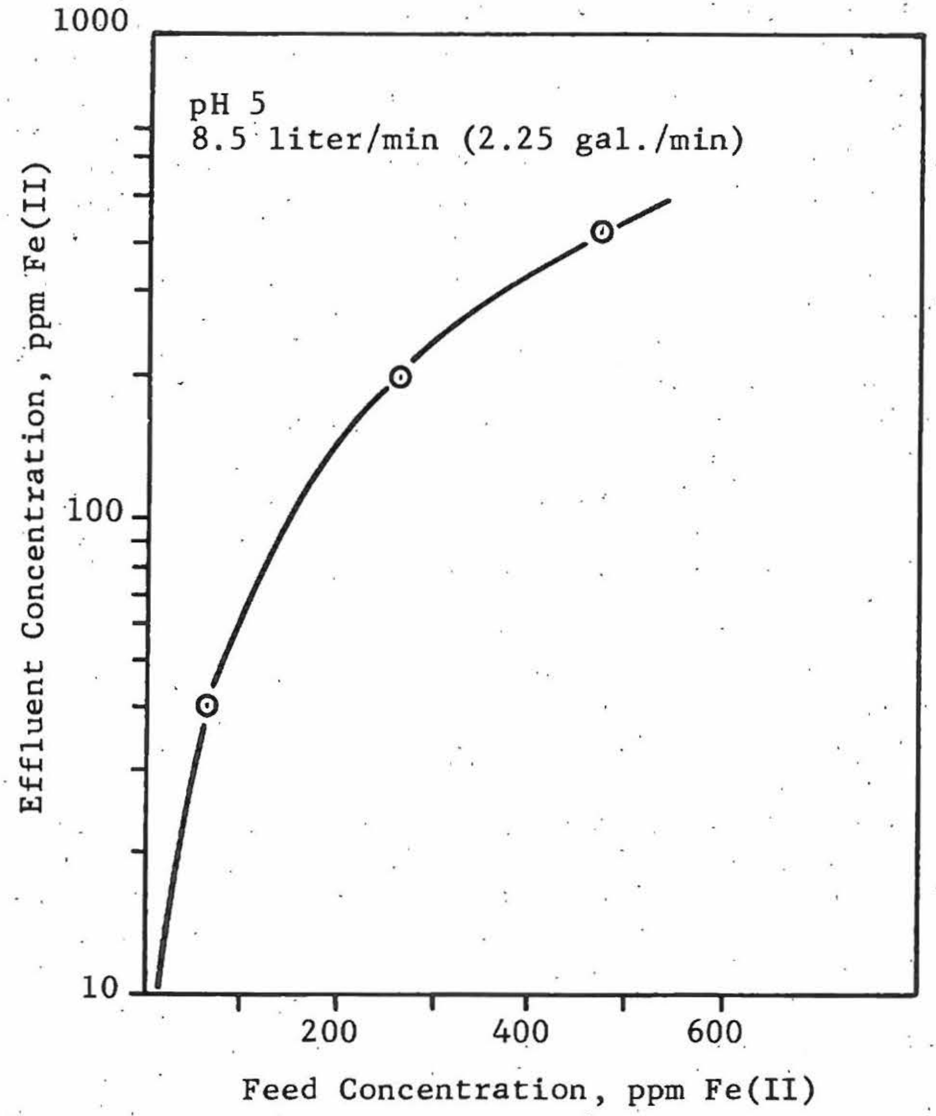


FIGURE 13. Effluent Concentration versus Feed Concentration of Fe(II) for Treatment in Large Circular Cell

cell was found to be the preferred configuration.

For sizing purposes, the laboratory data on treatment of pH 5 AMD was used, since the rate of Fe(II) oxidation was lower in this solution than in the pH 2 water. From calculations based on the working curve in Figure 13 and information on the diameter of commercially available major electrode materials, a basic unit cell was designed which is 45.7 cm (18 in.) long and has a 10.2 cm (4 in.) diameter inner anode enclosed by an outer cathode cylinder with 25.4 cm (10 in.) I.D. (7.6 cm or 3 in. spacing of major electrodes). Initial plans called for six of these unit cells to be used for preliminary testing in the field. Then, 12 additional units were to be added to provide the calculated total contact time required for the desired degree of treatment.

The total required length of cell was broken down into 45.7 cm (18 in.) segments to provide flexibility in testing and operation. Also, it was thought that advantage could be taken of a known multiple entry effect, whereby a greater net conversion of Fe(II) could occur if the AMD is passed through a number of unit cells than if the solution were passed through a single cell with a length equal to the total of the unit cells. The unit cells were provided with the means for treating the AMD on a compact and expanded bed and for adding the PVC-screen diaphragm described throughout this report.

As for the choice of material for the major electrodes, it was decided that graphite would be used for both cathode and anode. Since no data was obtained which suggested that coated titanium would yield superior results, graphite was the immediate anode candidate in view of the lower cost of this material. All of the laboratory data were measured with cells having stainless steel cathodes. However, plans were made to elaborate on the previously discussed polarity reversal tests during initial systems testing in the field. Use of the all graphite cell would enable this to be accomplished without having to dismantle the cells to exchange an outer steel electrode, for example, with an outer graphite electrode. The latter procedure would be a required operation in a mixed electrode cell in order to eliminate anodic dissolution of iron from the steel surface. On the basis of the laboratory evaluation, Norit RB-II pellets were chosen as the electrode bed media in the pilot cells.

From a comparison of the size of the Phase II cells and the voltage-current values applied to the large circular cell during the laboratory work, a D.C. power supply providing a maximum of 50 volts and 500 amps was considered to be ample for the field study.

SECTION V

PHASE II - FIELD STUDIES

The Delaware Pumping Station located in Wilkes-Barre, Pennsylvania was selected by the D.E.R. as the field site for pilot plant operation. Prior to the June 1972 flood generally four 9462 liter/min (2500 gal./min) pumps had been continuously operated to prevent surface subsidence and basin flooding. Three of the pumps were used to draw water from a depth of about 152 m (500 ft). The fourth was operated from a 76.2 m (250 ft) depth in order to discharge AMD with a lower iron content. Table 14 lists the composition of deep and shallow well samples taken in January 1972.

As indicated by this data, the Delaware Pumping Station had provided the opportunity for evaluating treatment of high and low ferrous AMD. Since the pH values of the waters were relatively high and did not differ greatly between the two levels, provision was also made during the planning stage of Phase II for incorporating an acid feed - pH control unit into the pilot plant to permit observation of the treatment of pH 2 AMD.

As soon as the restriction on operating the pumps was lifted by the D.E.R. in August after the flood, samples of the deep well water were analyzed for Fe(II) and Fe_T. The total iron concentration was a few parts per million higher than the ferrous content which averaged about 52 ppm. This value is approximately an order of magnitude lower than the usual numbers observed before the flood occurred. It was thought that if the deep pump were kept running over a sufficient period, the Fe(II) content would increase to the normal value. However, as seen in Figure 14, the Fe(II) content of the raw AMD in shaft #2 did not recover to pre-flood values over the period of the Phase II work. In fact, during project down time (November to May) when the pumps were not operated, the Fe(II) concentration fell below 50 ppm.

In order to evaluate treatment of high ferrous AMD, therefore, the initial plant was modified by adding a system for metering concentrated ferrous sulfate into the raw AMD, similar to what was done during the laboratory studies.

TABLE 14. ANALYSIS[a] OF AMD FROM DELAWARE PUMPING STATION

	PUMP NOS. 1, 2 & 3	P P NO. 1 DH RAISED
pH	4.9	5.9
Alkalinity	11	101
Acidity, pH_4	0	0
pH_8	765	40
Fe_T	355	60
Fe(II)	360	60
Mn	49	14
Ca	259	109
Mg	68	18
Al	3.5	0.1
Na	115	32
SO_4	2700	1200
Turbidity	50	30
Total Solids	5085	1990
Suspended Solids	120	30
Settleable Solids	0.025	0.025
Specific Conductance (micromhos/cm)	3750	2150

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[a] Samples taken January 25, 1972, and analyzed by Department of Health - Division of Sanitary Engineering, Commonwealth of Pennsylvania; values in units of ppm or mg/liter unless specified otherwise.

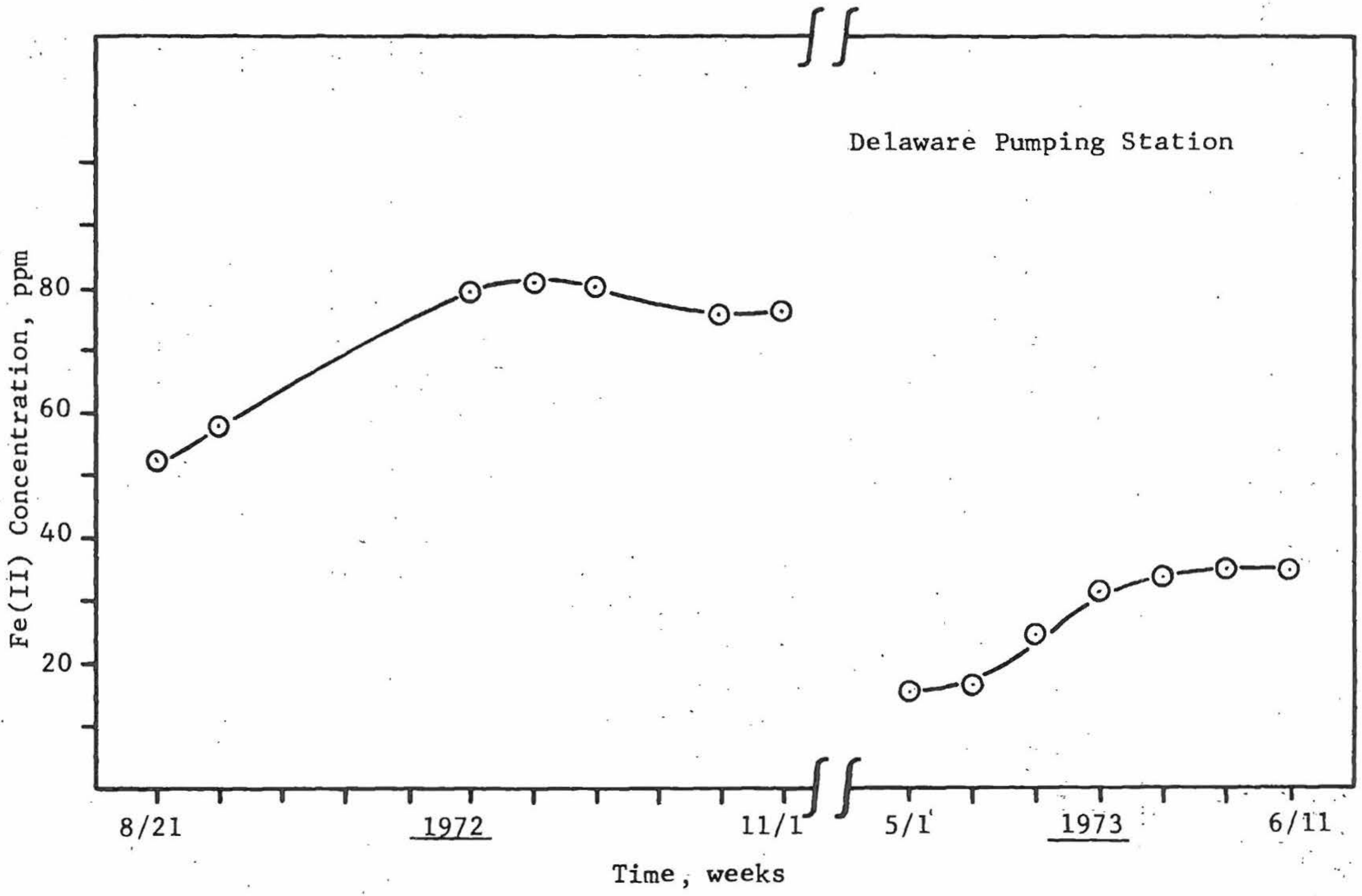

FIGURE 14. Variation in Deep Well AMD Composition with Time

In addition to electrochemical processing, the AMD was treated by aeration in order to develop comparative economics. Aeration runs were carried out in the Operation Yellowboy Van, a mobile pilot plant built for this purpose by Dorr-Oliver under a grant from the Commonwealth of Pennsylvania[31].

Description of Pilot Plant

Figure 15 shows a schematic diagram of the Phase II system. Raw AMD was pumped into a 568 liter (150 gallon) stainless steel tank for mixing either with 10% sulfuric acid and/or 1.5% ferrous sulphate solution if a change in pH or composition were required. The pH was controlled by means of a Universal Interloc, Inc. Controller (Model 1000) in conjunction with a Precision Products metering pump, (Model 9701-21). The concentrated ferrous sulphate solution was added with an identical metering pump adjusted as required.

For evaluation of electrolytic treatment the AMD was fed to the bank of cells and the effluent subsequently treated with lime in a flash mixer housed in the Yellowboy Van. During the aeration runs, AMD feed was pumped directly to the flash mixer for pH adjustment with lime prior to treatment in the aeration tank also housed in the van. Samples for analysis were taken from the overflow of the feed pH adjust tank, the cells effluent sump, and from the overflow of the aeration tank.

The raw AMD was delivered to the system by means of a 37.8 liter/min (10 gal./min) Jabsco Positive Displacement Pump. The cells feed and effluent pumps were of the centrifugal type, 37.8 liter/min (10 gal./min), A.O. Smith Corporation. Plumbing consisted mainly of one inch PVC pipe, fittings and ball valves. Calibrated Fischer & Porter Rotameters were used for monitoring the flow.

Figure 16 shows a cutaway view of a unit cell. The outer electrode consists of electrolytic graphite pipe (Union Carbide, 45.7 cm or 18 in. high, 25.4 cm or 10 in. I.D., 2.54 cm or 1 in. wall) coated on the outside surface with phenolic resin to prevent seepage. A four inch diameter graphite rod served as the central electrode. To provide electrical contact, a copper strap was bolted to the outer shell, and a copper rod was threaded into the central electrode. Not shown in Figure 16 are the PVC screen diaphragm which was

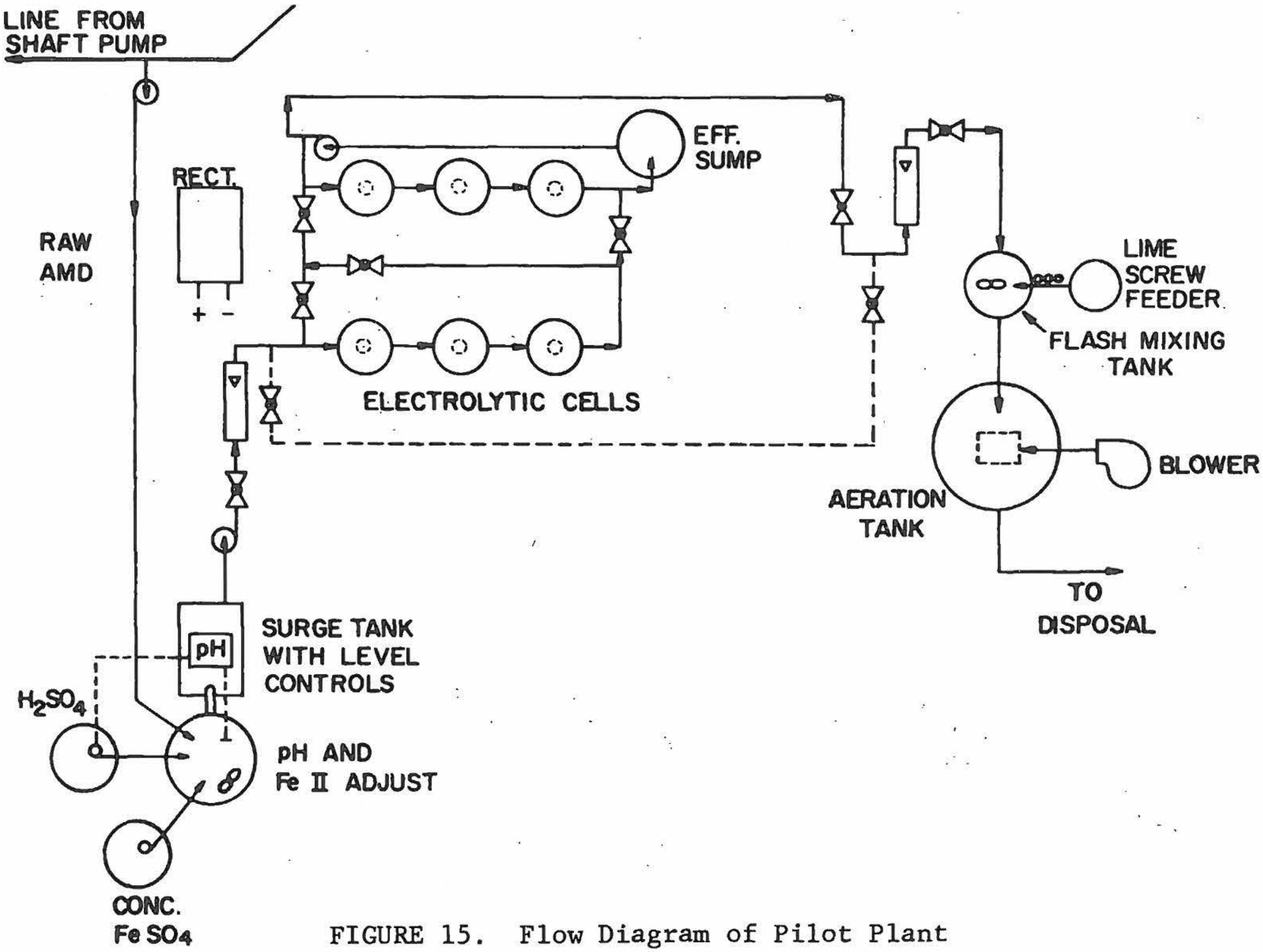

FIGURE 15. Flow Diagram of Pilot Plant

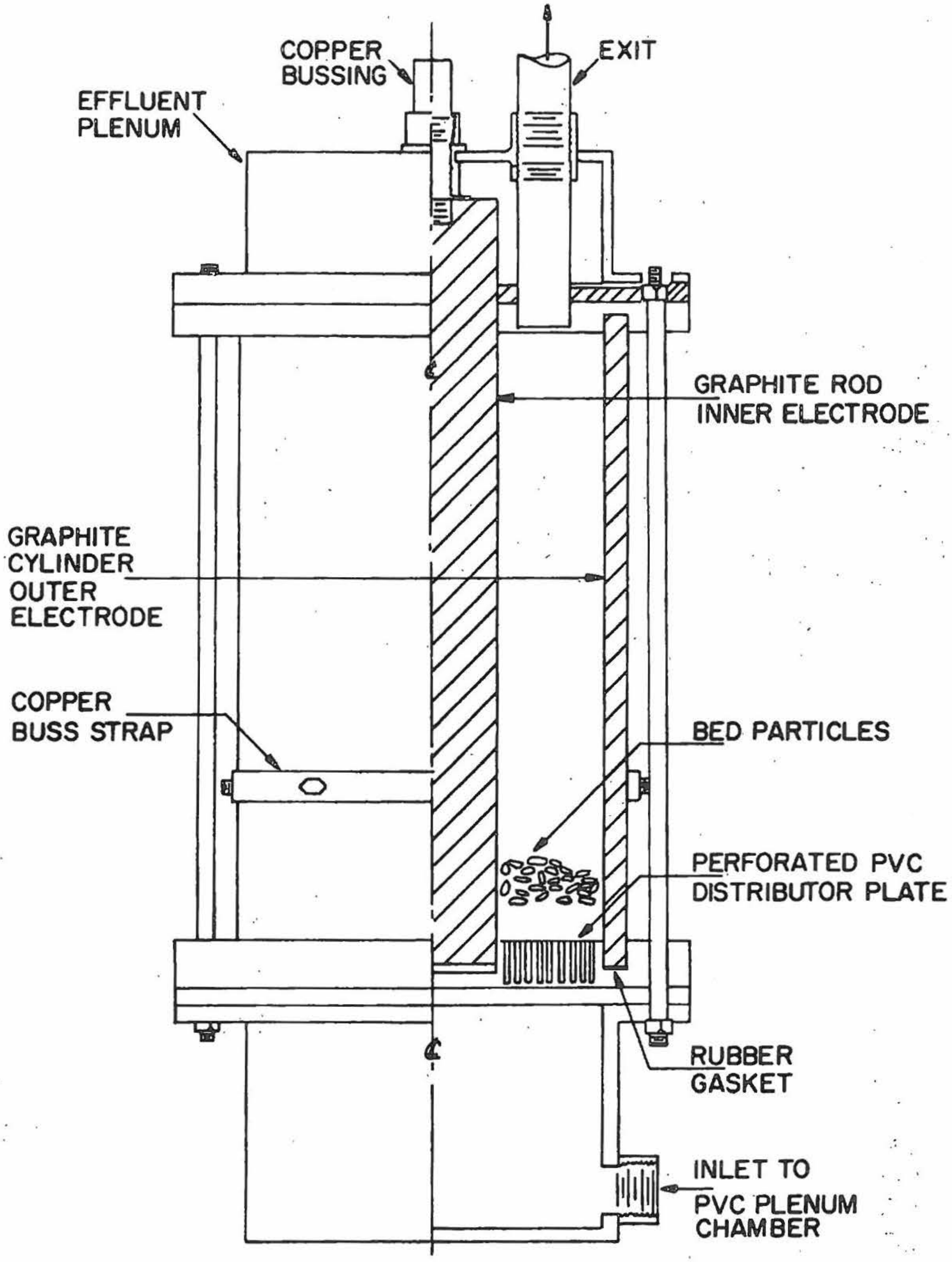

FIGURE 16. Unit Cell Used in Pilot Plant

fitted against the cathode and a top restraining screen which was used when runs with a compact bed were conducted. For convenience in initial systems testing, six of the unit cells were connected for series hydraulic operation with the flow upward in each cell. This system is shown in Figure 17.

For final systems operation six three-stage units were used in series (Figure 18). Staging was accomplished by replacing the top plenum assembly shown in Figure 16 with PVC flanges and using one central graphite rod common to all three sections. The intervening flanges could be fitted with distributor plates for bed support in each section in order to attain the multiple entry effect, or the effect of one long compact bed could be studied by removing these distributors.

For all runs the cells were connected electrically in parallel. Power was supplied by means of a Rapid Electric Rectifier, 0-48DCV/500 A. The rectifier and central control panel are shown in Figure 19.

Operational Data

Problems were encountered when attempts were made to dissolve technical grade ferrous sulphate in water for making up the concentrated Fe(II) solution to be metered into the raw AMD. Vigorous mixing, addition of acid, and heating would not provide the required Fe(II) concentrate for high ppm feed. It was decided to use the more costly reagent grade material which dissolved readily. Because of the prohibitive expense involved in the addition of large quantities of this salt, the decision was made to conduct all Phase II runs using the AMD at its natural composition and with Fe(II) concentration adjusted to 250 ppm instead of 500 ppm as originally planned.

Initial Systems Testing

Initial runs were conducted using the 50 ppm Fe(II) mine water with pH adjusted to 2. Feed was pumped through individual cells shown in Figure 16 while observations of percent Fe(II) conversion versus cell current were made. With this system a reevaluation of the effect of major electrode polarity was conducted. The resulting data plotted in Figure 20 confirmed observations made during Phase I that conversion is higher when the central graphite electrode is anodic and the PVC screen is placed against the cathode wall.

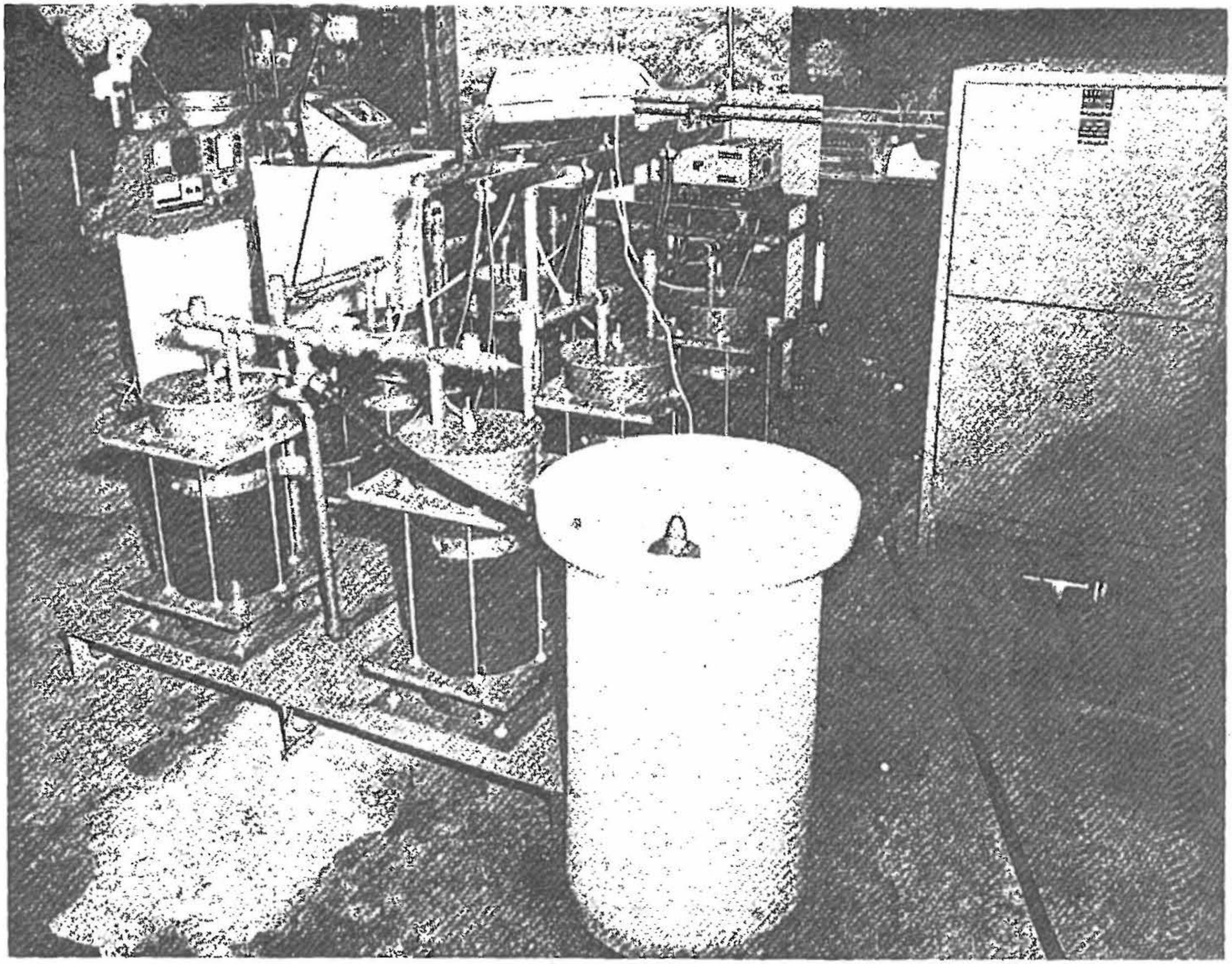

FIGURE 17. Operation with Six Unit Cells

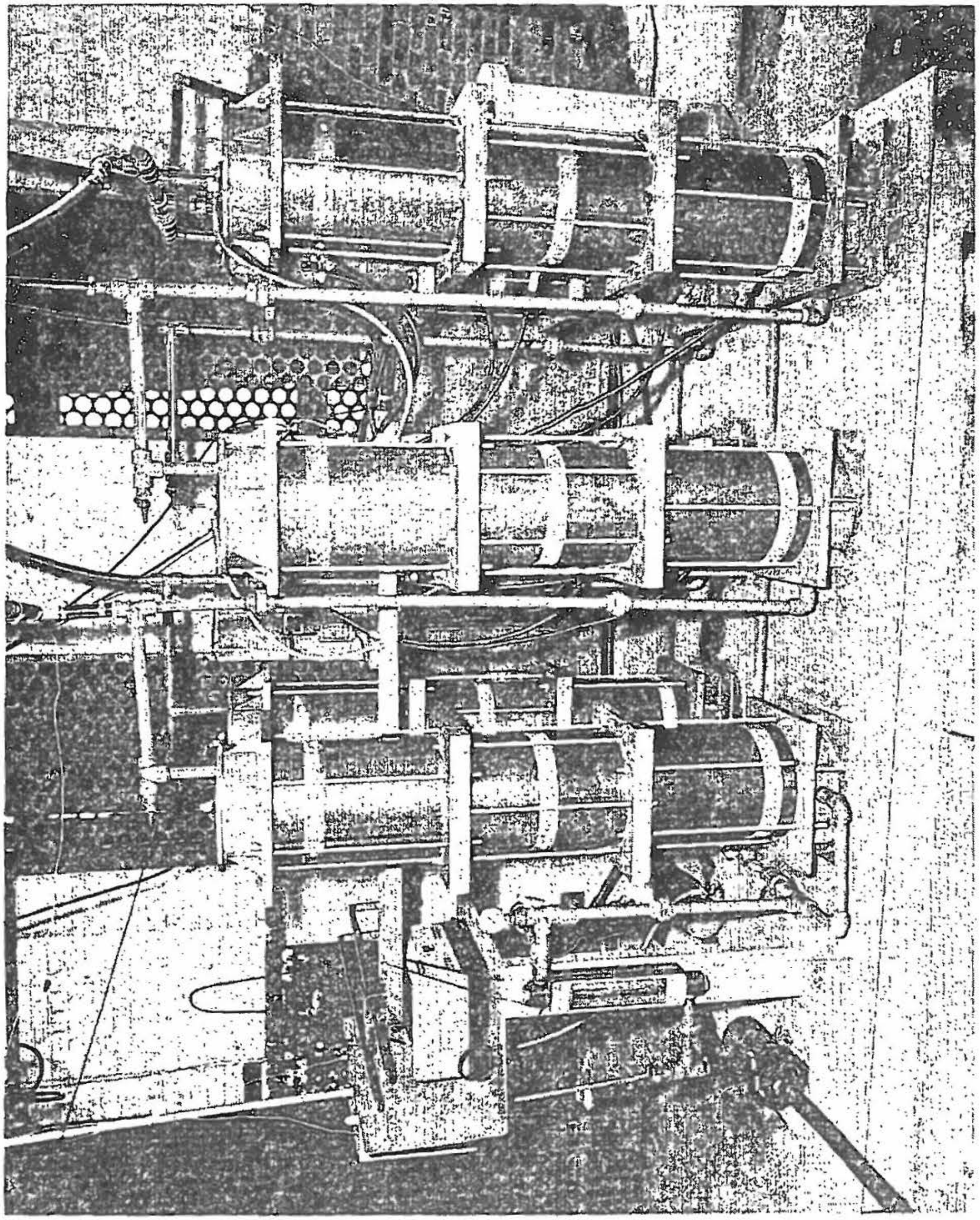

FIGURE 18. Complete Electrochemical System

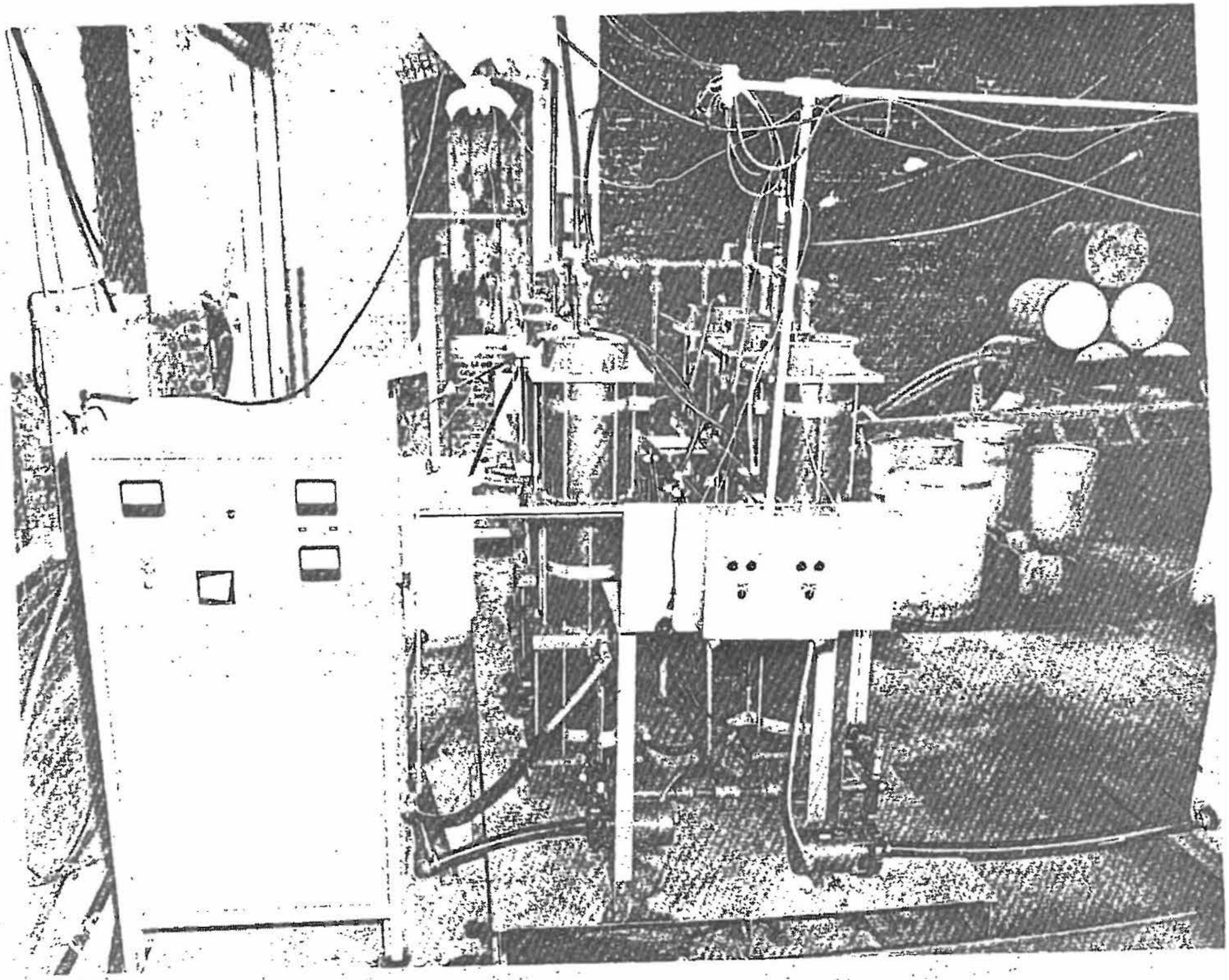

FIGURE 19. Power Section of Electrochemical Plant

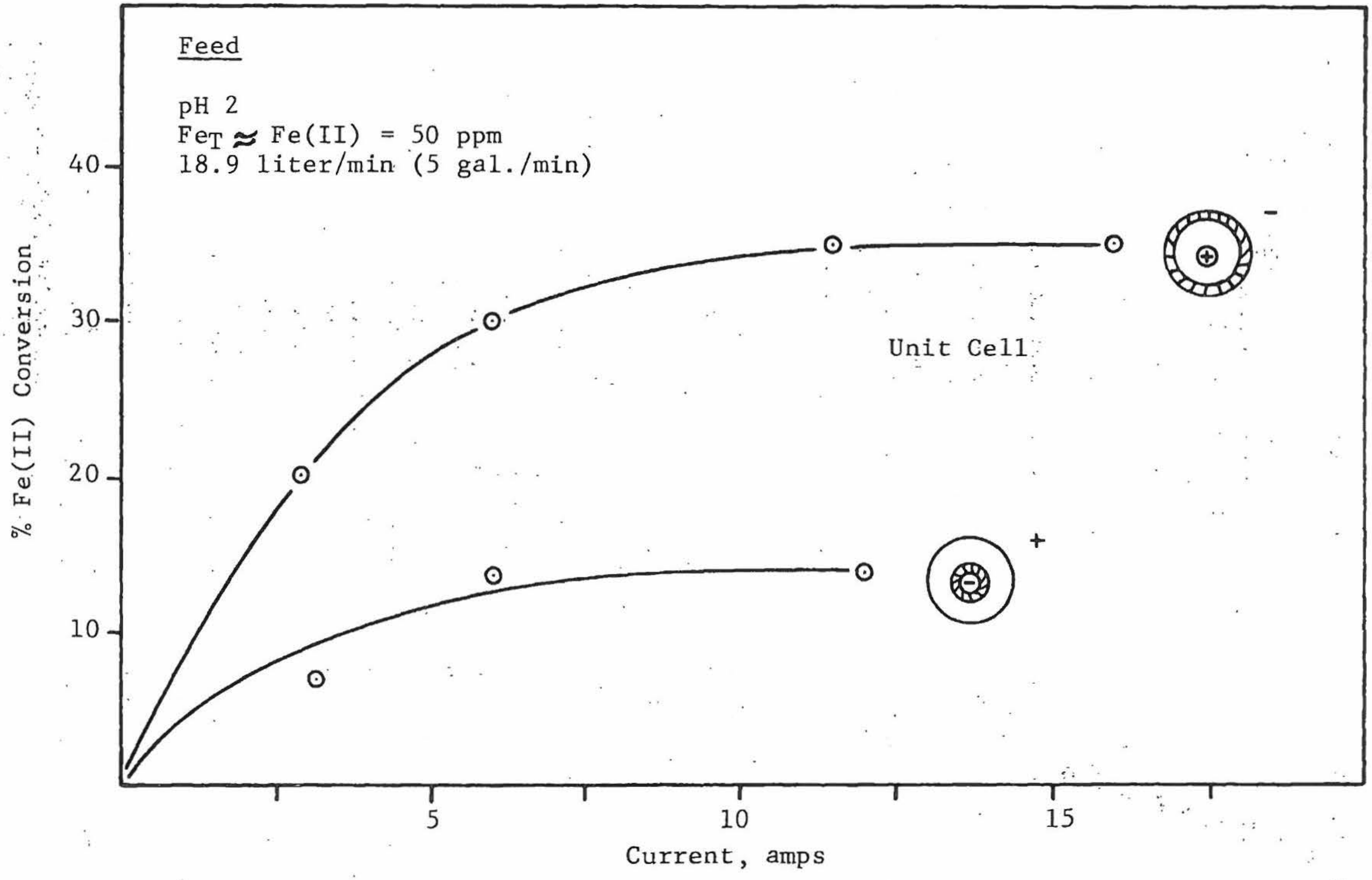

FIGURE 20. Effect of Electrode Polarity on Fe(II) Conversion

The next series of runs were performed to further investigate the difference between a compact and expanded bed in the circular cells. For these tests four 3-stage cells were used, two with compact beds and two with sectionalized beds with space provided for bed expansion. Feed with 250 ppm Fe(II) and pH 2 was processed at 3.8 and 18.9 liter/min (zero and one percent expansion of the free beds). As shown by curves in Figure 21, at the limiting current values the percent conversions of Fe(II) on the compact and loose beds were approximately equal at 3.8 liter/min (1 gal./min), a flow rate below the threshold value for bed expansion. For the 18.9 liter/min (5 gal./min) flow (Figure 22) the expanded bed effected about 25% higher conversion than the compact system. Also, the optimum conversion at 18.9 liter/min (5 gal./min) with the expanded bed was approximately equal to the maximum conversion at 3.8 liter/min (1 gal./min). The latter result further emphasized the beneficial effect of bed expansion in view of the higher mass loading with the 18.9 liter/min (5 gal./min) flow.

Finally, the complete system shown in Figure 18 was assembled. In view of the favorable results obtained with the previous runs, provision was made for bed expansion in each of the 18 unit cells. With all six columns in operation tests were conducted with 250 ppm (Fe(II)-pH 2 AMD at flow rates of 3.8 liter/min (1 gal/min), 11.4 liter/min (3 gal./min), 18.9 liter/min (5 gal./min), and 26.5 liter/min (7 gal./min). The data obtained for the first three flow rates are plotted in Figure 23 as percent Fe(II) conversion versus the applied current, expressed as a percentage of the theoretical current required for complete conversion of 250 ppm ferrous iron[30]. Maximum conversion at 3.8 liter/min (1 gal./min.) was slightly higher than at 18.9 liter/min. (5 gal./min) as expected based on a consideration of contact time. However, conversion at 11.4 liter/min (3 gal./min) was less than at 18.9 liter/min. The optimum combination of residence time and degree of bed expansion most likely occurred at 18.9 liter/min , the designed loading for this system, since at 26.5 liter/min (7 gal./min) an Fe(II) conversion higher than 10% could not be attained regardless of the power applied.

Although conversion was maximized at 5 GPM as per scale-up, the highest degree attained with the 250 ppm Fe(II) feed was 76%. One possible reason for the lower than expected conversion is the occurrence of back reduction of Fe(III) by

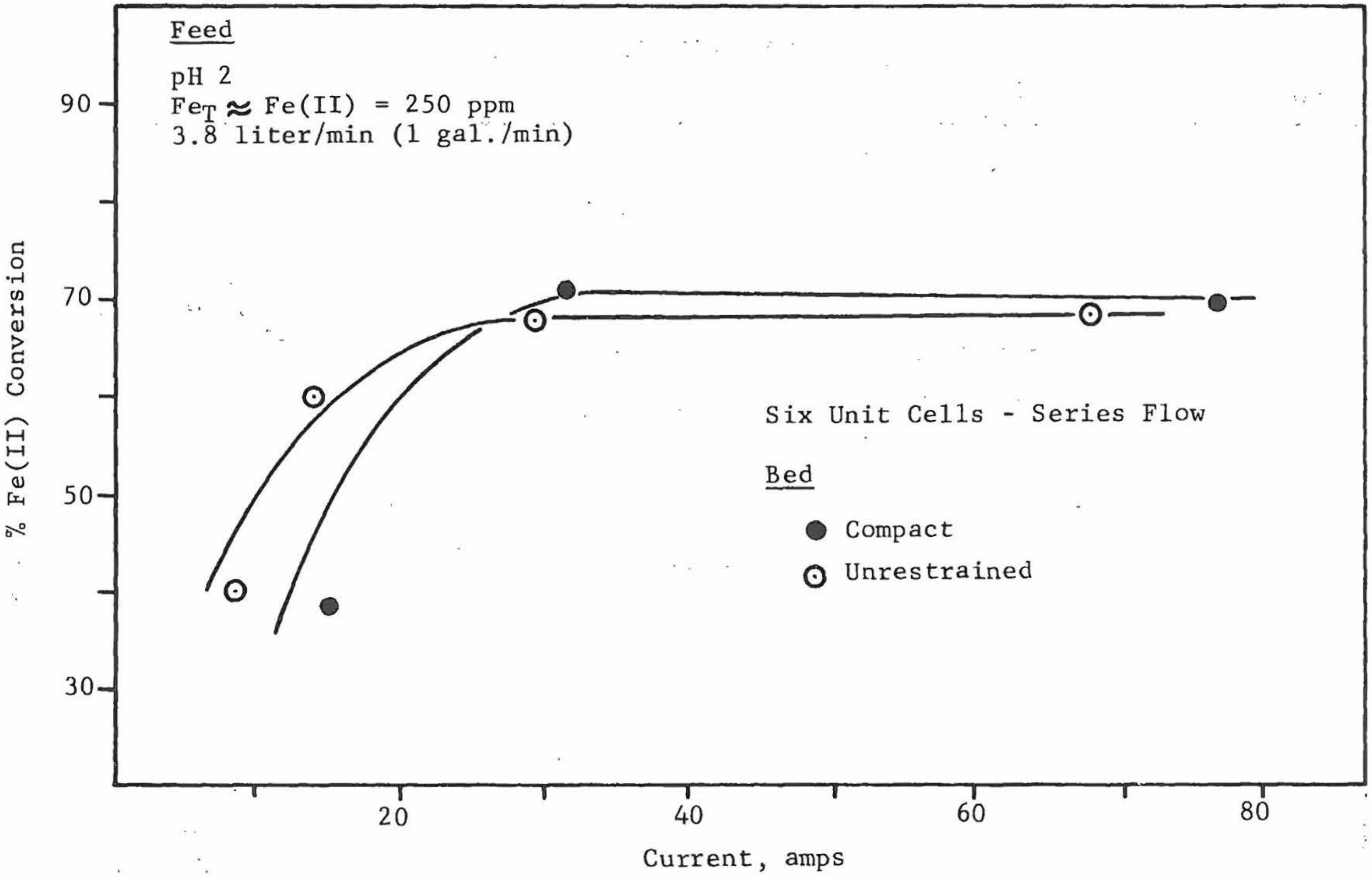

FIGURE 21. Effect of Bed Compaction for Four Liter Per Minute Feed

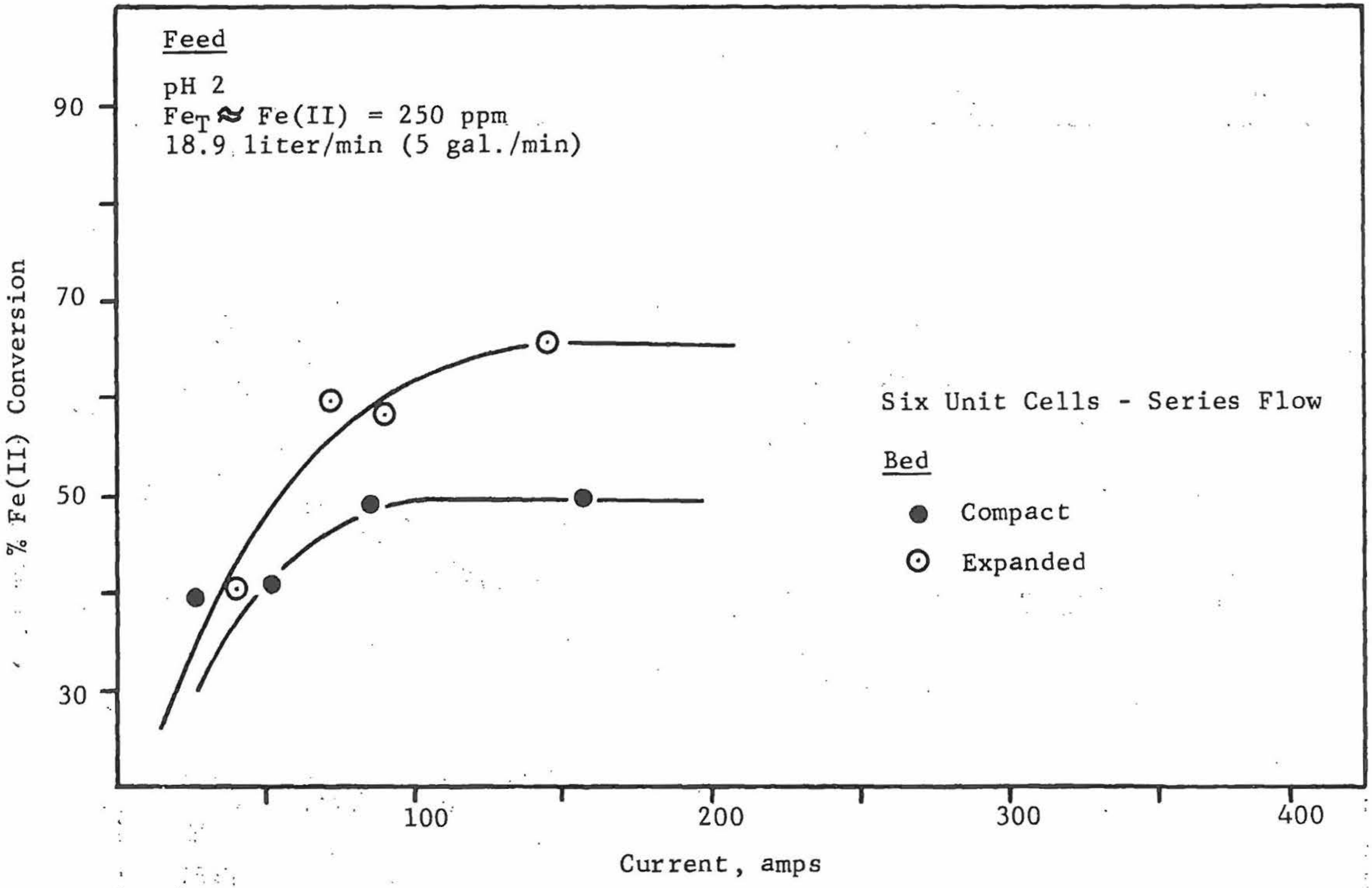

FIGURE 22. Effect of Bed Compaction for Nineteen Liter Per Minute Feed

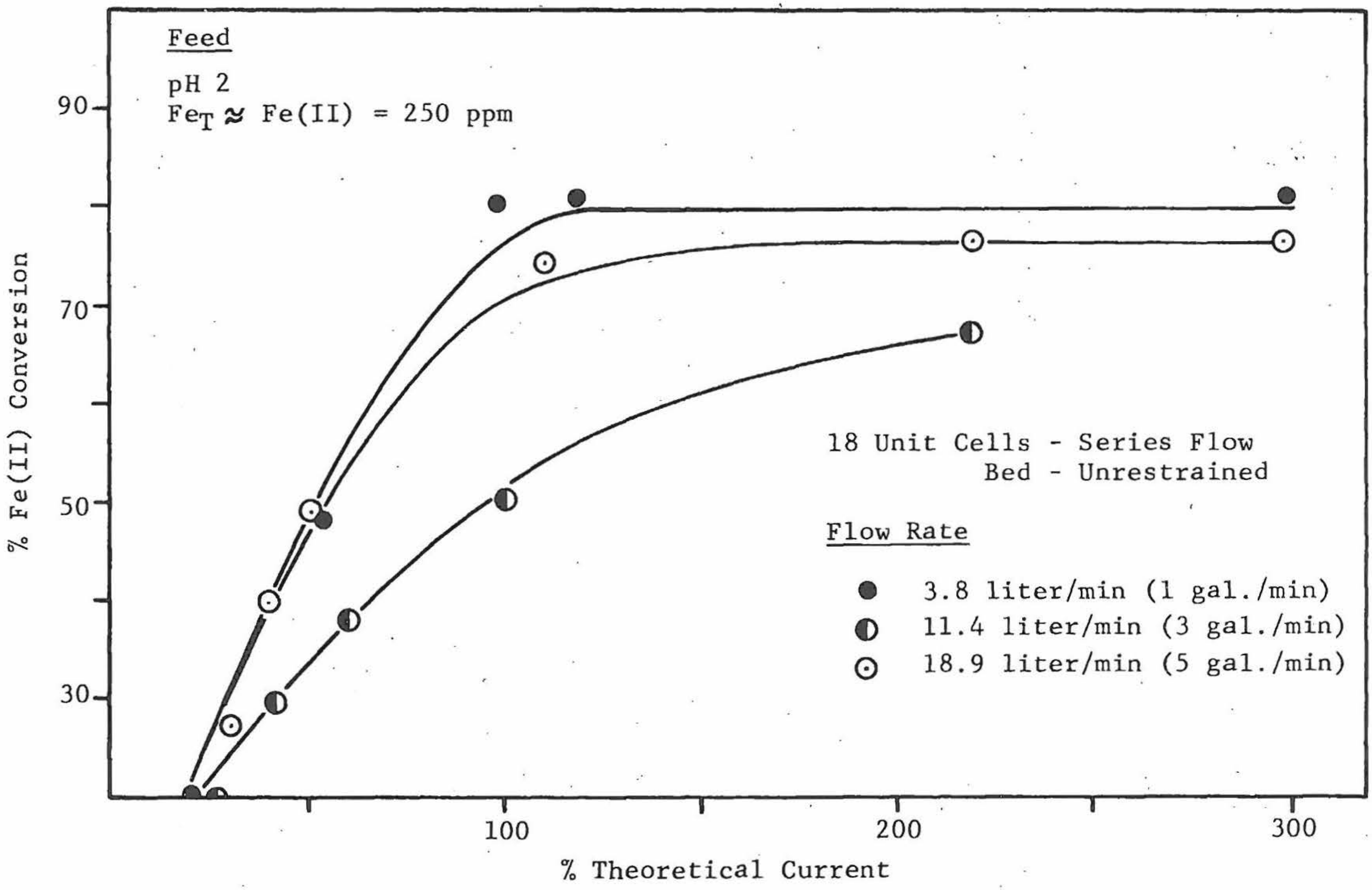

FIGURE 23. Effect of Flow Rate on Fe(II) Conversion

hyrdrogen generated in the pH 2 water. In order to decrease the volume of hydrogen accumulated as the liquid flowed through the cells, vent pipes were installed in the exit line of each cell. Repetition of the 18.9 liter/min (5 gal./min) run with this modification resulted in an increase in percent Fe(II) conversion to 85. This figure represents the highest degree of Fe(II) oxidation attainable by electrolysis alone during this study.

Final Electrolysis and Aeration Runs

In order to generate cost figures for electrochemical treatment, pH 2 and pH 5 AMD with Fe(II) concentrations of 40 and 250 ppm were processed at the rate of 18.9 liter/min. (5 gal./min). Comparative 18.9 liter/min aeration runs were conducted with the high ferrous AMD at pH 2 and 5.

The results of electrochemical treatment followed by neutralization are shown in Table 15. Table 16 contains the data obtained by aeration after neutralization. Except for the Al, Mn, Ca, and Mg values, the numbers represent averages of many measurements taken over a forty-hour period after an equilibrium condition had been reached during electrolysis treatment, and over a twenty-hour period in the case of the aeration series. Toward the end of each run the feed, cell effluent, neutralization and neutralization-aeration overflows were samples for Al, Mn, Ca, and Mg analyses. These were performed by personnel in the Water Quality Laboratory of Wilkes College in Wilkes-Barre. All samples including the neutralization overflows were filtered through medium porosity paper before analysis.

Considering first the results of electrolytic processing alone (feed and cell effluent values in Table 15), it is seen that for treatment of the low ferrous AMD, the cell system as designed produced an expected effluent containing less than 10 ppm Fe(II). The results for the high ferrous waters are short of the design value especially in the case of the pH 5 AMD. As discussed previously, the lower conversion in the high pH system is believed to be due to the deleterious coating of ferric hydroxide on the electrode bed. The 18.9 liter/min (5 gal./min) liquid flow apparently was not vigorous enough to aid in expelling the solids from the cells.

TABLE 15. AMD TREATMENT BY ELECTROLYSIS AND NEUTRALIZATION

AMD[a]							CELL EFFLUENT[a]							% CONV	NEUTRALIZATION OVERFLOW[a]						
pH	Fe(II)	Fe(III)	Al	Mn	Ca	Mg	pH	Fe(II)	Fe(III)	Al	Mn	Ca	Mg	Fe(II)	pH	Fe(II)	Fe(III)	Al	Mn	Ca	Mg
(18.9 liter/min , 7.5 Volts, 220 Amps)[b]															(Lime Feed Rate, 1.3 g /liter)						
2.0	38.8	2.2	0.92	4.1	140.0	97.9	2.0	5.0	36.0	0.34	3.9	(300)	79.9	87.5	7.6	0	0	1.12	1.9	500	87.6
(18.9 liter/min , 10 Volts, 350 Amps)															(Lime Feed Rate, 2.2 g /liter)						
2.0	250.0	5.0	1.0	4.2	95.0	85.0	2.0	37.0	218.0	0.54	3.8	(130)	80.0	84.8	7.3	0	0	0.54	1.6	1,000	125.0
(18.9 liter/min , 12.5 Volts, 350 Amps)															(Lime Feed Rate, 0.38 g /liter)						
5.4	35.0	0	0.35	3.5	100.0	94.9	5.4	7.5	27.5	0.20	3.3	(110)	95.0	78.0	7.1	0	0	0.52	1.5	330	98.3
(18.9 liter/min , 28 Volts, 380 Amps)															(Lime Feed Rate, 0.66 g /liter)						
5.4	245.0	10.0	1.0	4.6	100.0	102.0	4.8	110.0	28.0	0.96	4.3	84	104.0	55.2	7.1	0	0	0.52	2.3	240	148.0

[a] All metal concentrations measured as ppm or mg /liter.

[b] Conversion factors:

liters x 0.264 ≡ gallons
grams/liter x 0.00834 ≅ pounds/gallon

TABLE 16. AMD TREATMENT BY NEUTRALIZATION AND AERATION

AMD[a]								Lime Feed	Aerator Blower	NEUTRALIZATION - AERATION OVERFLOW[a]						
Flow (liter/min)	pH	Fe(II)	Fe(III)	Al	Mn	Ca	Mg	(g /liter)	(liter/min)	pH	Fe(II)	Fe(III)	Al	Mn	Ca	Mg
18.9	5.2	228	2.0	0.72	4.5	135	89	0.48	453	7.5	3.0	9.0	2.17	1.8	740	102
18.9	1.9	245	5.0	0.44	4.6	140	93	1.0	453	6.2	2.5	0	1.04	3.8	600	104

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[a] All metal concentrations measured as ppm on mg /liter.

[b] Conversion factors:

liters x 0.264 ≡ gallons
grams/liter x 0.00834 ≡ pounds/gallon
cubic feet x 28.3 ≡ liters

After the runs with the pH 5 waters were completed, attempts were made to clean the beds by pumping dilute sulfuric acid through the cells while periodically reversing the polarity of the major electrodes. Analysis of the effluent acid solution showed mainly ferric and very little ferrous iron in the wash. Following this treatment, pH 5 high ferrous AMD was passed through the cells while no D.C. potential was applied to the electrodes. When the effluent pH and Fe(II) concentration equaled the feed values, power was applied. Analysis of the effluent during a few hours' operation at 18.9 liter/min (5 gal./min) showed a significant improvement in Fe(II) conversion over the value indicated by the data in Table 15. These observations suggest that for electrolytic treatment of high pH AMD, a periodic bed maintenance procedure as described above might have to be included in the operation of a large-scale plant in order to maintain the required degree of Fe(II) oxidation.

It is difficult to draw definite conclusions regarding the effect of electrolysis on aluminum and manganese in view of the low concentrations of these metals in the raw AMD. However, it appears from the analytical data that reductions in aluminum concentration of 40 to 60% might have been attained except during treatment of pH 5 - high ferrous AMD when, along with the relatively low Fe(II) conversion, the reduction in aluminum value dropped to 4%. Manganese concentrations were reduced by 5 to 10% in accordance with the laboratory results. No explanation other than analytical error can be offered for the apparent anomaly of higher calcium concentrations in the cell effluent than in the feed. In view of the fact that lime was used for neutralization, this anomaly was not further investigated.

Natural aeration of the cell effluent during lime addition and neutralization resulted in complete oxidation of residual ferrous iron, as this species was not detected in the neutralization overflow (see Table 15). Also, essentially all of the iron was removed from the overflow by filtration. Manganese concentrations were further reduced during neutralization. The increase in aluminum values is believed to be due to impurities in the lime used.

Approximately 10 times the stoichiometric amount of air was fed to the mine water during the neutralization-aeration runs (Table 16). Both ferrous and ferric iron were detected in the filtered overflow. Manganese concentrations were reduced by 50%, while the aluminum values increased with lime addition.

A comparison of the lime feed rates for high ferrous AMD in Tables 15 and 16 shows that the lime demand for neutralization after electrolysis was higher than for aeration, more so for the pH 2 than for the pH 5 runs. In this regard, it should be noted that two different batches of lime were used for these tests. An older lot which had been stored in the Yellowboy Van from previous projects was depleted during the electrochemical runs. A new batch obtained from the D.E.R. was used for the aeration studies. It is possible that the older lot had deteriorated on standing. Thus, the apparent higher lime demand of the electrolyzed water. In addition to this factor, the significantly higher lime uptake of the electrolyzed versus aerated pH 2 AMD most likely occurred as a consequence of pH adjustment of the raw mine water. This was done essentially by pH titration. Since the required pH of 2 lies on the standard acid-base titration curve in the region where significant changes in volume of added acid have only a small effect on pH, more acid might have been used in adjusting the pH of AMD treated in the cells than added to the mine water treated by aeration, which was done on a different day.

During electrochemical treatment of the pH 5 AMD, the dark red and apparently crystalline solid observed during the laboratory runs was formed with the usual ferric hydroxide precipitate. However, the volume fraction of the desired solid generated in the actual AMD was no greater than found in the laboratory. X-ray patterns of the isolated solid again showed no evidence for a crystalline material.

Characteristics of the sludges formed after lime treatment of the electrolysed and aerated AMD were compared. Although final volumes and percent solids (9.7) of the settled sludge were approximately the same for each case, the curves in Figure 24 indicate a definite improvement in sludge settling rate when the AMD was electrolysed before lime treatment.

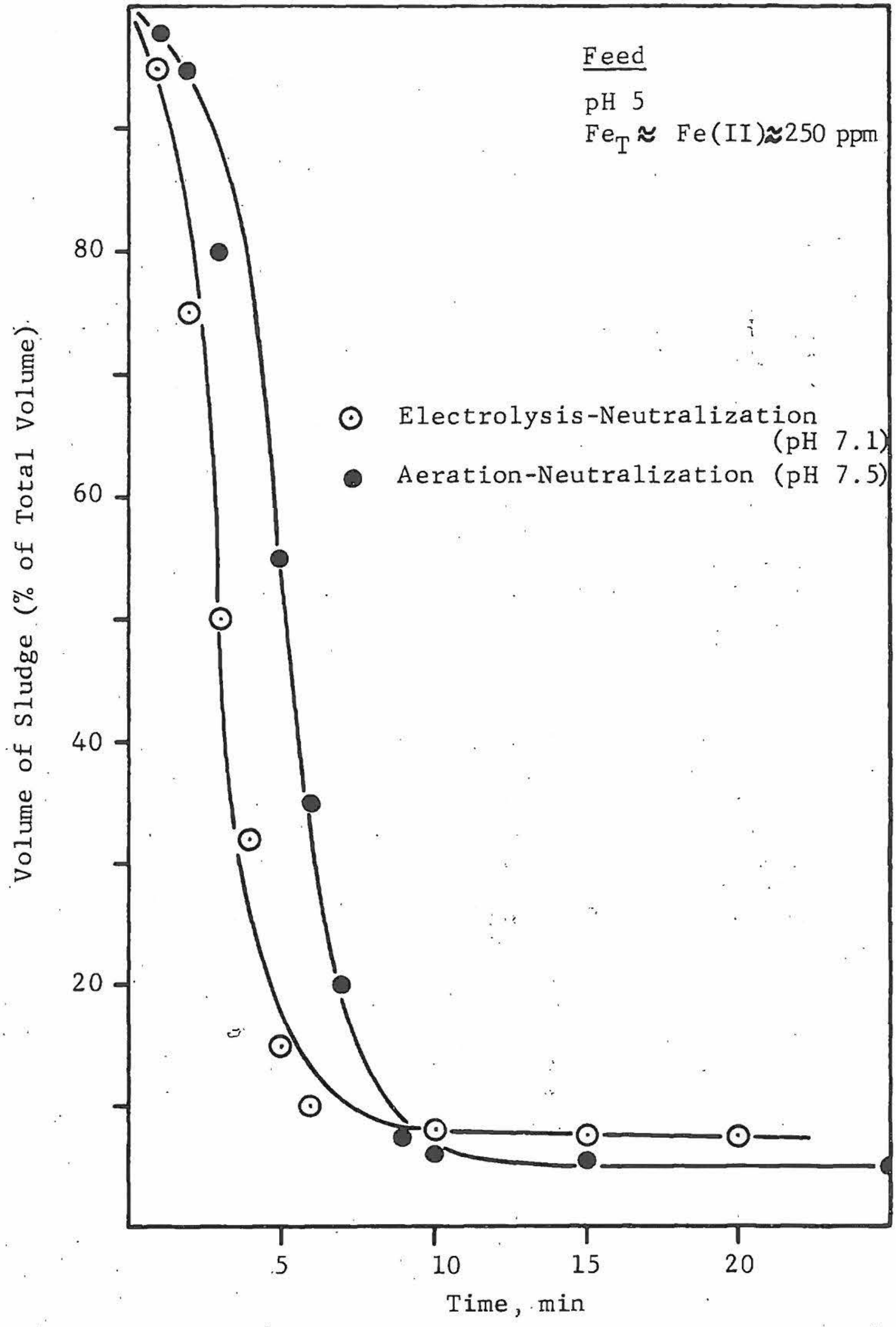

FIGURE 24. Sludge Settling Rates

SECTION VI

COST ANALYSIS AND DISCUSSION

Based on the data in Tables 15 and 16, estimates were made of the capital and operating costs for 473 liter/min (125 gal./min) plants treating pH 2 AMD (95% oxidation of Fe(II)) by electrochemical oxidation and by aeration. It is realized that some degree of lime tratement must precede aeration in order to provide the appropriate pH for rapid oxidation of Fe(II). However, in view of the lime demand discrepancy between the pH 2 runs discussed earlier and since costs of lime neutralization for both treatment systems should be approximately the same, these costs were not included in the present analysis. Further bases for scale-up are that the cells system be constructed as one piece of equipment and that power could be scaled up linearly from the 18.9 liter/min (5 gal./min) data. Tables 17 and 18 show the capital cost estimates for electrochemical treatment and aeration respectively. Operating costs are compared in Table 19. As indicated by these figures, the electrochemical system is more expensive in fixed capital requirements and in operating costs.

The difference in operating costs between the two processes can be lessened if total treatment including neutralization is taken into account. It is known that whereas high ferric AMD can be satisfactorily neutralized with limestone, neutralization-aeration of high ferrous drainage requires the addition of the more expensive lime in order to attain the appropriate pH for rapid oxidation of ferrous iron[30]. Limestone could not be used for this project because of the nature of the apparatus in the Yellowboy Van (lime screw feeder). However, limestone is the preferred material for neutralizing the effluent from the electrochemical cells. Although hydrogen production was not studied during the present project, further cost savings for operation of a large-scale electrochemical plant might ensue from the recovery and sale of by-product hydrogen.

It should be mentioned here that based on scale-up calculations from laboratory data obtained with small packed bed electrode cells, engineers at Tyco Laboratories have estimated the cost of a 378 liter/min (100 gal/min) plant to be about 1/5 the figure shown in Table 17 [30]. However, in view of the large

TABLE 17. CAPITAL COST ESTIMATE FOR ELECTROCHEMICAL SYSTEM (473 liter/min, 125 gal./min)

Purchased Equipment		
Cells & Pump	$32,500	
Installation @ 22%	7,150	
Piping @ 40%	13,000	
Instrumentation @ 5%	1,625	
		$ 54,275
Electrical		
DC Power (100 KW Installed)	2,600	
Buss Bars Installed	1,300	
Plant Electrical @ 10%	3,250	
		7,150
Buildings @ 35%		11,375
Land and Improvements @ 10%		3,200
Carbon Bed @ 50¢/lb		5,400
Physical Plant Cost		81,400
Engineering and Construction @ 25%		20,350
Direct Plant Cost		101,750
Contractor's Fee @ 8%		8,140
Contingency @ 15%		15,260
Fixed Capital		$125,150

BASIS: pH 2, 250 ppm Fe(II), 95% Conversion.
Cells system designed as one piece of equipment.
Linear power scale-up.
Neutralization equipment not included.

TABLE 18. CAPITAL COST ESTIMATE FOR AERATION SYSTEM (473 liter/min, 125 gal./min)

Purchased Equipment		
4,000 gal. Capacity Tank	$ 5,000	
Pump	1,000	
Aerator	1,000	
		$ 7,000
Installation @ 22%		1,540
Piping @ 40%		2,800
Instrumentation @ 5%		350
Electrical @ 10%		700
Building @ 35%		2,450
Land and Improvements @ 10%		700
Physical Plant Cost		15,540
Engineering and Construction @ 25%		3,885
Direct Plant Cost		19,425
Contractor's Fee @ 8%		1,555
Contingency @ 15%		2,915
Fixed Capital		$23,895

BASIS: pH 2, 250 ppm Fe(II), 95% Conversion.
Neutralization equipment not included.

TABLE 19. ESTIMATES OF OPERATING COSTS FOR ELECTROCHEMICAL AND AERATION SYSTEMS (473 liter/min, 125 gal./min)

	Electrochemical Oxidation	Aeration Aeration
Raw Materials (Annual Bed Replacement)	$ 2,000	-
Power	13,480	5,200
Maintenance and Supplies @ 5% Fixed Capital	6,260	1,200
Labor	12,000	12,000
Indirect Labor @ 40%	4,800	4,800
Total Annual Costs	$38,540	$23,200
¢/1,000 gal.	71.4	43.0

BASIS: 95% Conversion, pH 2 AMD
24-hour day, 300 days/year.
Labor, 4 men at 40% time to both systems.
Neutralization costs not included.

scale-up factor involved (1.25 liter/min or less to 378 liter/min), pilot plant tests with a 378 liter/min system should be conducted.

The foregoing discussion pertains to the removal of iron from AMD. There are currently no regional requirements for manganese and aluminum concentrations. However, it is expected that most states experiencing the AMD problem will adopt the proposed EPA standard of less than one ppm total heavy metals. The effluents generated during total electrochemical-lime treatment of the Delaware Pump water showed a reduction in manganese levels from 4 to 2 ppm, but most of this occurred in the neutralization step. The apparent higher reduction in aluminum concentration must be further substantiated in view of the low feed values encountered in this case. Studies should be conducted with AMD containing these metals in much higher concentration than found in the Delaware water in order to obtain more definite data on the electrolytic removal mechanism. The deleterious effect of manganese on Fe(II) oxidation observed during the laboratory study should also be investigated further in regard to the treatment of AMD containing high manganese levels.

The elusive "crystalline" solid generated during electrolysis of AMD at pH 3 or higher continues to be merely a laboratory phenomenon. Formation of small quantities of this solid in a laboratory cell was clearly demonstrated before the EPA and DER project officers during an early meeting on the progress of Phase I activity. However, all attempts to generate large amounts of the material and to identify it were not successful. Formation in significant quantities might require closer control of operating conditions. The solid may be a coagulated form of the hydroxide, which by a mechanism involving, for example, some appropriate value of zeta potential, can only exist in an electric field.

It is not known whether the presence of small amounts of the crystalline solid or some other effect is responsible for the noted higher settling rate of the sludge generated by lime neutralization of the cell effluent. Whatever the explanation, further investigation in this area is warranted, as anyone familiar with the usual AMD neutralization sludges can well appreciate a process involving simultaneous oxidation of Fe(II) and conversion to a rapid settling and readily filterable form. The application of operating conditions which promote formation of the desired solid should effect an improvement in the electrochemical oxidation of Fe(II) in high pH AMD by eliminating deleterious coating of the electrode bed by the usual gelatinous hydroxide precipitate.

In conclusion, from scale-up estimates for a 473 liter/min (125 gal./min) loading based on data obtained from the pilot tests, this electrochemical system does not appear to offer a more economical approach to AMD treatment than conventional neutralization-aeration. In connection with other applications related to AMD treatment, work is currently being done in this laboratory on re-evaluation of scale-up methods and on the engineering of improved high-flow cells for efficient bed distribution, gas expulsion, and precipitate removal. Sectionalized power application is also being considered. During the AMD pilot runs, all of the cells were connected in parallel to the same rectifier. However, as the solution flows through the cells, voltage and especially current requirements decrease because of a decrease in the Fe(II) concentration. The use of multi-output rectifiers to provide the appropriate power to different sections of the cell system should result in operating costs savings which would more than offset the added capital expense associated with these rectifiers.

Assuming that developments currently under study will show significant improvements over the economics that were generated during this project, a 378 liter/min (100 gal./min) portable plant should be built and operated for several months at sites providing high and low acidity AMD with high and low ferrous, manganese and aluminum concentrations. In addition to the bed regeneration technique described in a previous section of this report, removal of high pH precipitate by purging with an inert gas should be evaluated as a periodic maintenance procedure. Because of the complexities in scaling up an electrochemical system of this type, the data generated during operation of the 378 liter/min (100 gal./min) plant will provide a firmer base than the 18.9 liter/min (5 gal./min) figures for economic predictions involving a full-scale plant, e.g., a 22,710,000 liter/day (6,000,000 gal./day) system.

SECTION VII

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