# Ion Exchange
# Treatment of Acid Mine Drainage

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## INTRODUCTION

Mine water pumped from active mines and flowing from abandoned mines frequently contains relatively high concentrations of dissolved iron (both ferrous and ferric) and acidity as well as other dissolved ions such as aluminum, calcium, and magnesium. Recent legislation by the Commonwealth of Pennsylvania requires the treatment of acid mine drainage (AMD) from active mines to meet the effluent standards established by the Pennsylvania Sanitary Water Board. The key items in this set of standards are: no greater than seven mg/l iron, alkalinity greater than acidity, and pH between 6.0 and 9.0.

Lime neutralization of AMD is one treatment that is known to be effective and is currently being used (1). However, the resulting precipitate settles to a final thixotropic sludge which contains hydrated ferric and aluminum hydroxides and may be more than 99 per cent water, i.e., less than one per cent solids. The volume of the sludge produced may amount to more than 10 per cent of the original AMD discharge, depending on the original concentrations of iron and aluminum. The disposal or storage of this sludge, which dries and compacts poorly, represents the most difficult aspect of AMD treatment via lime neutralization. The large storage lagoons, which will be needed to contain this production of sludge, will take the land out of productive service and will be hazardous for many years after being filled.

As part of a broad research program directed toward developing more effective and economical methods for handling the AMD problem, we undertook experimental and pilot plant studies of ion exchange as a means for producing a concentrated waste stream which would contain the iron, aluminum, and other cations in AMD and could be handled more conveniently and economically than the sludge from lime neutralization. The estimated regenerant cost for a minimum-volume, concentrated waste stream as well as the solids concentration of sludges obtained by treatment of this waste stream are stated for the particular AMD treated.

## PILOT PLANT TEST PROGRAM

Preliminary experimental work with small fixed beds of ion exchange resins in one-half and one in. diameter glass columns showed that it was technically feasible to remove iron from AMD by ion exchange. On the other hand, the low efficiency of regenerating the resin in the small fixed-bed apparatus made it impractical to determine minimum regenerant requirements or to obtain a highly concentrated waste stream. To overcome the limitation imposed on regeneration efficiency by fixed-bed operation, we investigated the feasibility of using another major alternate, i.e., continuous countercurrent ion exchange. However, existing theoretical studies of countercurrent ion exchange had not yet developed practical equations from which one could calculate regenerant utilization from equilibrium measurements for a complex mixture of cations such as exists in AMD.

Therefore, experimental work on an actual mixture of this type was required before one could establish the feasibility and operating parameters of the continuous countercurrent ion exchange method. To this end, we conducted a series of tests in a pilot-sized continuous countercurrent ion exchange unit of the Higgins type with AMD pumped from a mine shaft. The resin used was a strong acid, cation exchange type consisting of a styrene base, cross-linked with eight per cent divinyl benzene.

## PILOT PLANT EQUIPMENT AND FLOW SHEET

The pilot plant equipment is presented schematically in Figures 1 and 2. The contractor unit, shown in Figure 1, consists of two-in. ID glass piping arranged

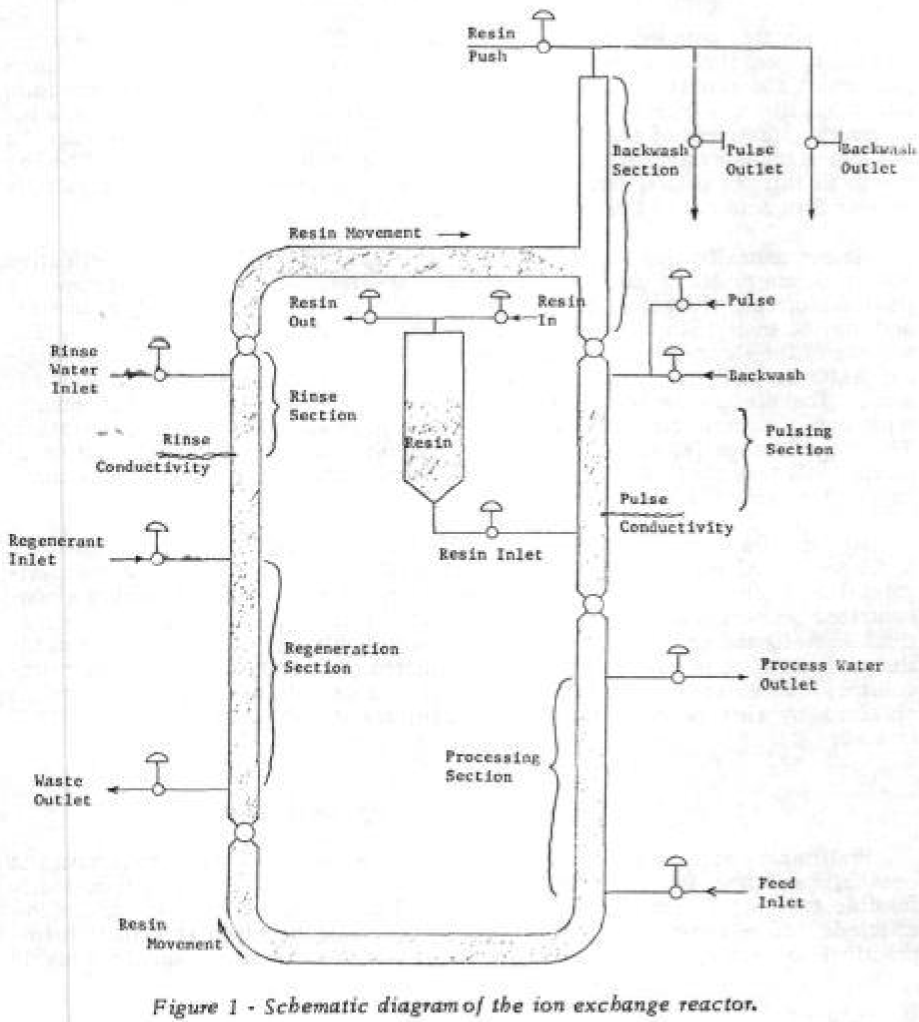


*Figure 1 - Schematic diagram of the ion exchange reactor.*

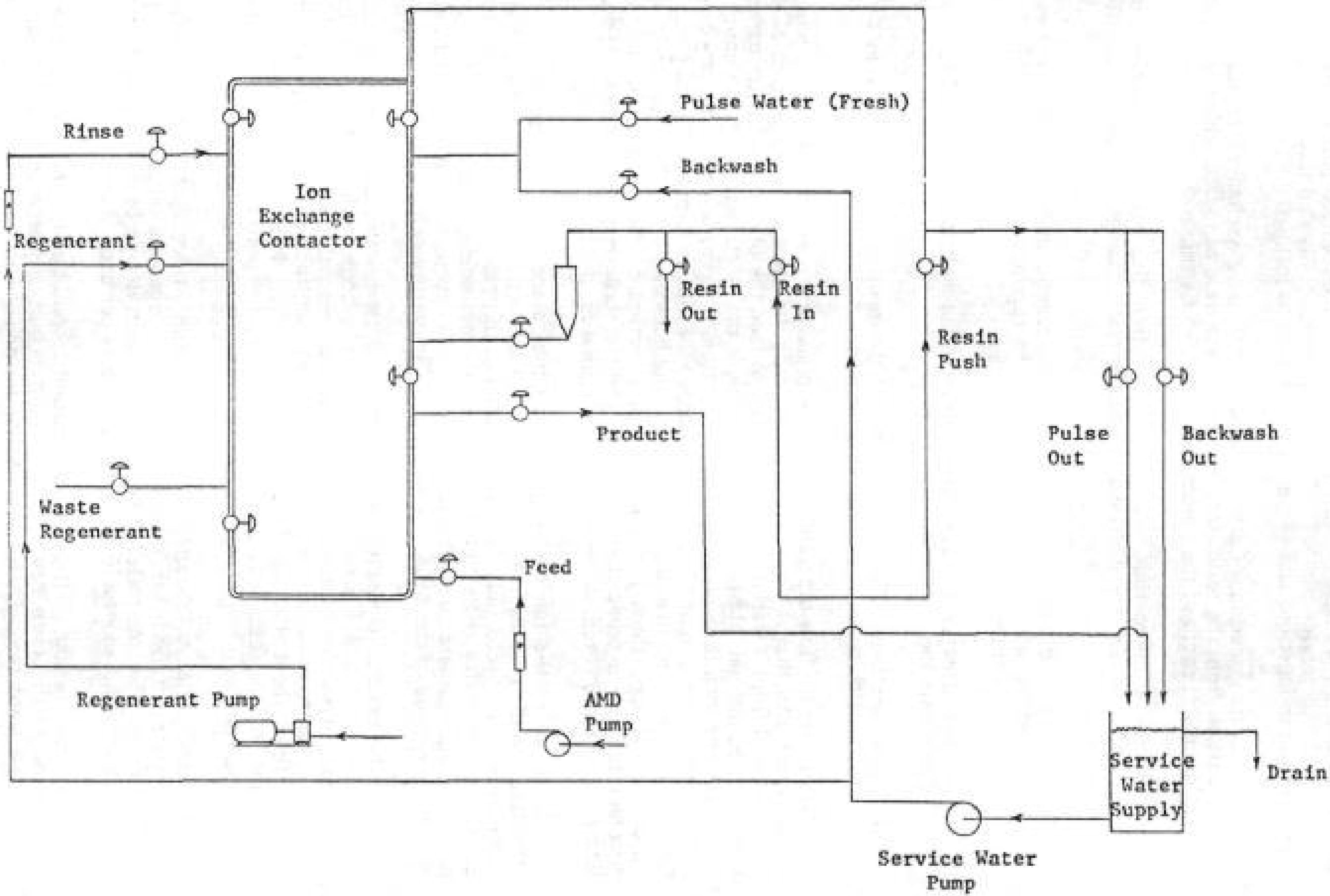


*Figure 2 - Flow diagram -- ion exchange pilot plant.*

in a rectangular loop approximately 15 ft high and 20 ins. wide and mounted vertically on a steel framework which also supports the control panel, the control valves, and the service piping. The contactor unit is divided into five operating sections, whose functions and key dimensions were as follows:

1. Processing section. Cations from the AMD were exchanged for regenerant cations from the resin (sodium ions, in the case of sodium chloride regenerant). Length of the processing section -- 74 ins.

2. Regeneration section. Regenerant ions from the regenerant solution were exchanged for the AMD cations on the resin. Length of the regeneration section - 76 ins.

3. Rinse section. Rinse water displaced the regenerant solution that was carried along with the resin bed leaving the regeneration section. Length of the rinse section -- 32 ins.

4. Backwash section. Backwash water provided additional rinse and removed fines from the resin bed.

5. Pulse section. This section moved the resin bed periodically in short pulses clockwise around the contactor loop.

Figure 2 is the flow diagram of the pilot plant as a whole and shows the piping arrangement and the values used for controlling the operations. A portion of the AMD pumped from a working mine was used to feed the pilot plant. After passing through a 5,000 gal plastic-lined storage tank the AMD was pumped through a rotameter and then through the processing section of the resin bed. The processed AMD flowed into a receiving tank; a portion of the processed AMD was pumped from this tank as service water for rinsing and backwashing. The regenerant solution was pumped through the regenerating section of the resin bed from a regenerant tank by a proportioning pump, and the waste regenerant stream flowed into a catch tank. Fresh domestic water was used for pulsing.

Operation of the ion exchange column took place as a cyclic series of steps separated by short delays to allow valves and relays to operate. The timing and sequence of the cycle and of the steps within each cycle were controlled by timers and conductivity cells through a series of interlocking relays that activated solenoids which operated pneumatic valves. The cycle took about 2-1/2 minutes and consisted of the following sequence of operating periods:

a. Pulse period. Hydraulic pressure from the fresh water main forced the entire resin bed a short distance around the loop. The distance the bed moved was about nine and one-half ins. per pulse and was controlled by the pulse conductivity probe. This operation took about five secs and required about 640 ml of fresh water per cycle. With a total length of 353 ins. for the resin bed, it required about 37 cycles to complete a circuit of the bed.

b. Rinse period. Processed AMD provided the service water to rinse residual regenerant from the resin bed above the regeneration section. This operation was controlled by the rinse conductivity probe and required about 20 secs and about 370 ml of service water per cycle.

c. Process period. Filtered AMD passed upward through the processing section of the resin bed, while, simultaneously, regenerant solution passed downward through the regenerating section. This operation, fixed at two mins by a timer, took about 6400 ml of AMD and from 58 to 156 ml of regenerant per cycle. During the first 15 secs of this period, resin in the backwashed section was backwashed with about 930 ml of service water.

## TEST PROCEDURE AND OPERATING DATA

Both sulfuric acid and sodium chloride were selected as possible regenerants for the treatment of AMD. Several runs were attempted with various concentrations of $H_2SO_4$ as the regenerant, but continuous operation with sulfuric acid proved impractical due to the continual precipitation of gypsum in the regenerating section of the column. Backwashing removed little of the precipitated gypsum representing the calcium from the AMD stream.

The NaCl tests were run at three concentrations, 10, 15 and 20 per cent, and various flow rates of the regenerant. A run consisted of establishing equilibrium conditions and then operating the unit for one complete circuit of the resin loop (30-40 cycles) at steady conditions. The flow rates of AMD and regenerant were recorded for every cycle, and samples of product water and waste regenerant were taken periodically for chemical analysis. In addition, the resin movement per cycle as well as the volumes of rinse water, pulse water and backwash were measured. Samples of rinse water, pulse water and backwash were taken every run for subsequent analysis. Before starting a run, the pilot plant was operated at uniform cyclic conditions for at least two complete circuits of the loop (about three hours) in order to establish equilibrium.

Averaged operating data for each NaCl run are summarized in Table I. The AMD flow rate and the quantity of resin moved per pulse changed somewhat from run to run. However, the variations within any particular run were too small to affect the equilibrium of the pilot plant. There was little variation in the chemical composition of the AMD from week to week. The iron in the AMD drawn from the storage tank was nearly all ferric.

Waste regenerant from one of the 15 per cent NaCl runs was neutralized with 10 per cent $Ca(OH)_2$ slurry at room temperature and at 190 F. Settling tests were made by allowing the neutralized mixtures to stand at neutralization temperatures in 1000 ml graduated cylinders for 24 hrs and noting the final level of the settled solids. Vacuum filter tests were made at neutralization temperatures on the unsettled suspensions resulting from the precipitation tests using standard filter test procedures with a 0.1 sq ft filter leaf using nylon filter cloth.

## RESULTS

Table II summarizes averaged cation compositions of the AMD and regenerant streams entering and leaving the ion exchange unit. These data show that regenerant cations were exchanged not only for $Fe^{+++}$ but also for $Al^{+++}$, $Ca^{++}$ and $Mg^{++}$. Although the AMD used for these tests is not typical of all AMD streams, some of which may contain more ferrous iron, the exchange of regenerant cations for AMD cations was found to be relatively indiscriminate with regard to species of AMD ions. In view of this finding, the results obtained in this study can be used for approximating regenerant requirements for treating any similar AMD stream by continuous countercurrent ion exchange using NaCl regenerant. Table III presents the calculated utilization of the sodium regenerant for exchange with ferric ions and for exchange with all of the AMD cations. The overall efficiency in utilization of the sodium for ion exchange was high, the removal of iron from the AMD accounting for about 20 per cent of the regenerant used, and the remaining sodium being used for exchanging with the other cations.

Figure 3 is a log-log plot of the ratio of AMD to regenerant versus the total iron concentration in the treated water for various concentrations of regenerant. This graph shows that regeneration with 15 per cent NaCl resulted in the largest output of processed AMD per volume of regenerant. At this optimum regenerant concentration, one volume of regenerant would be required for the treatment of 59 volumes of AMD to produce effluent containing seven mg/l of iron and 70 mg/l acidity. The waste stream produced at this AMD-to-regenerant flow ration would contain 12,000 mg/l Fe and 55,000 mg/l free acidity.

TABLE I

SUMMARY OF OPERATING DATA OF ION EXCHANGE PILOT PLANT FOR TREATING AMD

| Run No. | Regenerant Concentration | AMD Flow ml/Cycle | Regenerant Flow ml/Cycle | Flow Ratio of AMD to Regenerant | Pulse Distance, Ins. | Pulse Water Volume ml/Cycle | Backwash Volume ml/ cycle | Rinse Volume ml/Cycle | Product Temp., °F | Cycles Per Run |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 10% NaCl | 6060 | 109.0 | 55.6 | 7.2 | 1500* | | --- | --- | 59 |
| 2 | 10% NaCl | 5970 | 155.6 | 38.4 | 7.6 | 540 | --- | 320 | --- | 42 |
| 3 | 10% NaCl | 5940 | 156.1 | 38.1 | 8.0 | 580 | 875 | 340 | --- | 45 |
| 5 | 15% NaCl | 5870 | 85.7 | 68.5 | 9.8 | 640 | 980 | 300 | 52 | 37 |
| 6 | 15% NaCl | 6640 | 129.6 | 56.1 | 7.8 | 670 | 930 | 280 | 50 | 37 |
| 7 | 15% NaCl | 7170 | 113.7 | 63.1 | 10.6 | 600 | 950 | 360 | 50 | 31 |
| 8 | 20% NaCl | 6950 | 57.7 | 120.4 | 11.5 | 650 | 1010 | 400 | 49 | 31 |
| 9 | 20% NaCl | 6960 | 107.3 | 64.8 | 9.0 | 560 | 990 | 350 | 51 | 31 |
| 10 | 20% NaCl | 7000 | 132.7 | 52.8 | 10.2 | 640 | 970 | 400 | 57 | 36 |
| 11 | 20% NaCl | 5820 | 122.8 | 47.4 | 10.1 | 760 | 900 | 410 | 60 | 31 |

* Combined pulse and backwash water.

TABLE II

SUMMARY OF CHEMICAL ANALYSES OF MAJOR PILOT-PLANT STREAMS

| Run No. | Regenerant | Flow Ratio of AMD to Regenerant | Total Fe, mg/l | | | Free Acidity,* mg/l $CaCO_3$ | | | Al, mg/l | | | Ca + Mg, mg/l | | | Na, mg/l | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | AMD | Product | Waste Regenerant | AMD | Product | Waste Regenerant | AMD | Product | Waste Regenerant | AMD | Product | Waste Regenerant | AMD | Product | Waste Regenerant |
| 1 | 10% NaCl | 55.6 | 217 | 52 | 8,100 | 870 | 272 | 32,200 | --- | --- | --- | --- | --- | --- | -- | --- | --- |
| 2 | 10% NaCl | 38.4 | 217 | 10.5 | 8,860 | 870 | 127 | 33,400 | 112 | 3 | 5,400 | 461 | 66 | 7,890 | 35.6 | 891 | 1,290 |
| 3 | 10% NaCl | 38.1 | 217 | 3.6 | 7,800 | 870 | 81 | 32,300 | 112 | 1.5 | 3,530 | 461 | 18 | 6,820 | 35.6 | 817 | 6,410 |
| 5 | 15% NaCl | 68.5 | 269 | 20.5 | 13,600 | 935 | 105 | 56,900 | 121 | 7 | 6,420 | 320 | 108 | 10,980 | 32.6 | 891 | 2,016 |
| 6 | 15% NaCl | 56.1 | 269 | 3.6 | 12,640 | 935 | 61 | 59,200 | 121 | 4 | 6,180 | 320 | 44 | 13,120 | 32.6 | 1,211 | 4,450 |
| 7 | 15% NaCl | 63.1 | 269 | 16 | 12,500 | 935 | 98 | 57,800 | 121 | 10 | 5,960 | 320 | 131 | 11,590 | 32.6 | 1,187 | 3,500 |
| 8 | 20% NaCl | 120.4 | 269 | 126 | 13,600 | 935 | 460 | 58,400 | 121 | 37 | 7,200 | 320 | 306 | 10,500 | 32.6 | 588 | 1,226 |
| 9 | 20% NaCl | 64.3 | 269 | 27 | 13,620 | 935 | 127 | 67,800 | 121 | 7 | 8,100 | 320 | 60 | 15,850 | 32.6 | 1,119 | 5,730 |
| 10 | 20% NaCl | 52.8 | 269 | 7.1 | 13,500 | 935 | 63 | 64,100 | 121 | <5 | 6,400 | 320 | 30 | 15,800 | 32.6 | 1,280 | 14,060 |
| 11 | 20% NaCl | 47.4 | 269 | 5.0 | 12,920 | 935 | 65 | 57,400 | 121 | <5 | 5,900 | 320 | 28 | 13,250 | 32.6 | 1,280 | 19,580 |

* Titrated to pH 4.5 with 0.02N NaOH

TABLE III

UTILIZATION OF SODIUM CATIONS FOR REGENERATION

| Run No. | Regenerant | Flow Ratio of AMD to Regenerant | Sodium Utilization, Per Cent | |
|---|---|---|---|---|
| | | | Exchange With Fe | Exchange With All Cations |
| 2 | 10% NaCl | 28.4 | 21.7 | 96.9 |
| 3 | 10% NaCl | 28.1 | 22.8 | 84.8 |
| 5 | 15% NaCl | 68.5 | 22.4 | 96.9 |
| 6 | 15% NaCl | 56.1 | 20.3 | 93.2 |
| 7 | 15% NaCl | 63.1 | 21.0 | 94.6 |
| 8 | 20% NaCl | 120.4 | 21.9 | 98.6 |
| 9 | 20% NaCl | 64.8 | 18.5 | 93.7 |
| 10 | 20% NaCl | 52.8 | 19.7 | 84.4 |
| 11 | 20% NaCl | 47.4 | 20.9 | 78.3 |

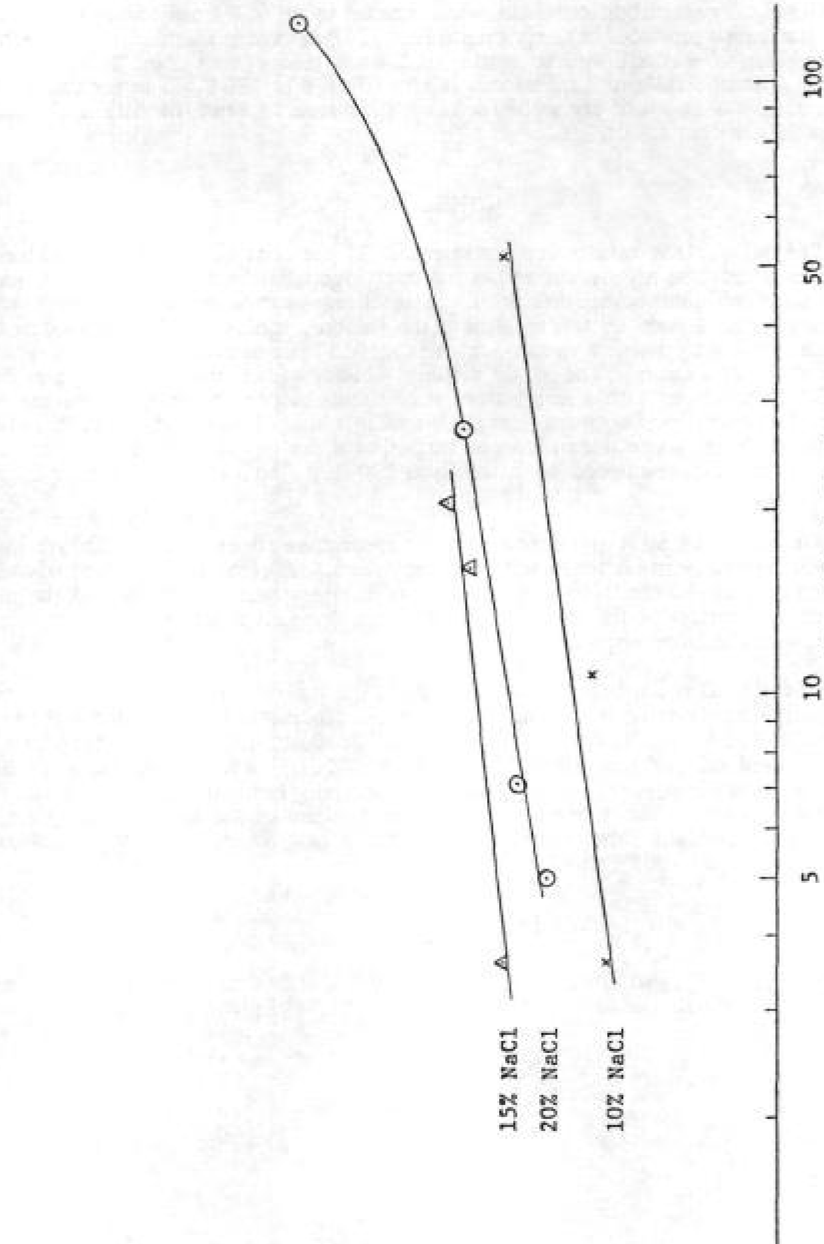


*Figure 3 - Total iron in product versus ratio of AMD to regenerant flow.*

Hot lime neutralization of the waste stream to pH 7.0 from one of the 15 per cent NaCl runs produced a slurry containing 3.4 per cent suspended solids. When this suspension was allowed to settle, the final sludge contained 10.5 per cent solids. The neutralized suspension was also filtered at 190 F. The measured filtering rate was 14 lbs of dry solids/sq ft of filter area/hr, and the filter cake contained 25 per cent solids.

## CONCLUSIONS

The pilot plant results demonstrate that 15 per cent aqueous sodium chloride solution is feasible regenerant for an ion exchange treatment of AMD in a process to produce effluent complying with the discharge standards of the Pennsylvania Sanitary Water Board. By this treatment the cations, including dissolved iron, are concentrated into a waste stream which is only 1.7 per cent of the volume of the original AMD stream. The slight residual acidity of the product water is eliminated by treatment with a small amount of lime. Larger amounts of lime are required to neutralize the waste stream, and this should be done at about 180 F. The neutralized waste stream can be settled to a sludge containing 10.5 per cent solids or can be dewatered by filtering at 180-190 F to a cake containing 25 per cent solids.

Although the pilot plant tests did not recombine supernatant or filtrate from the neutralized waste stream with the processed AMD, the combination of these two streams could result in some precipitation of gypsum, depending on the sulfate concentration of the raw AMD. However, gypsum settles readily and would not present a sizable disposal problem.

Since AMD streams vary widely in chemical composition, the material costs given here apply only to the particular AMD processed in this pilot plant program: \$0.166 for NaCl, \$0.109 for CaO, and \$0.019 for heating per 1000 gals of AMD, based on NaCl at \$0.007/lb, CaO at \$0.01/lb and natural gas at \$0.50/1000 scf. The quantity of lime required for neutralizing both the waste stream and the residual acidity of the processed AMD stream would be the same as the quantity required for straight lime neutralization of the raw AMD, i.e., approximately 10.9 lbs CaO per 1000 gals of AMD.

## REFERENCES

1. Young, E. F., Steinman, H. E., "Coal Mine Drainage Treatment," *Proc. 22nd Ind. Waste Conf.*, Purdue University, 22, 477 (1967).