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# Project Summary

# Pilot Plant Treatment of Acid Mine Drainage by Reverse Osmosis

G. Lansing Blackshaw, Alfred W. Pappano, Garth E. Thomas, Jr., and Shun-Yung Cheng

**Studies were conducted at the EPA Crown Mine Drainage Control Field Site (a) to examine the performance of a 227,000 lpd (60,000 gpd) reverse osmosis (RO) unit at recovery levels of 50 percent through 90 percent for a variety of dominantly ferrous iron acid mine drainage (AMD) feed qualities, (b) to evaluate the feasibility of using the neutrolosis process to treat AMD, and (c) to determine the AMD treatment capability of a coupled 18.9 lpm (5 gpm) sodium cycle cation exchange (CIX)/RO system.**

**Neutrolosis studies were conducted using both 227,000 lpd (60,000 gpd) and 15,100 lpd (4,000 gpd) spiral-wound membrane module RO units utilizing lime, soda ash, and lime-soda ash combinations as the neutralizing agents. The neutrolosis process did not increase system recovery beyond the maximum recovery levels attainable by once-through RO treatment of AMD. Precipitate fouling and osmotic pressure phenomena associated with neutrolosis caused an increased frequency of system operational and shutdown problems.**

**Using the coupled CIX/RO system, a greater than 90 percent recovery operation was achieved by the RO unit when the AMD feed was pretreated by the CIX unit.**

**This report represents the second phase of RO process research pertinent to AMD treatment at the EPA Crown Mine Drainage Control Field Site in fulfillment of Contract Number 68-03-0245 by West Virginia University under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period May 1973 to November 1975.**

***This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).***

## Introduction

The discharge of Acid Mine Drainage (AMD) from both active and abandoned coal mines throughout the coal-producing areas in the United States has resulted in a serious water pollution problem since the first coal mining operation in Pennsylvania began in 1761. The problem is especially present in the Appalachian region, where acid mine discharges have contaminated many freshwater streams, and has diminished the available water supplies. As a result, the control of this serious problem has become a regional as well as a national concern.

The formation of AMD is principally due to oxidation of iron sulfide minerals (pyrite or marcasite) that are found in coal seams. After coal is mined, the $FeS_2$ is oxidized in the presence of air and dissolved by water to form ferrous sulfate and sulfuric acid. Further oxidation of the ferrous sulfates produces ferric sulfate. Then, through subsequent hydrolysis, more sulfuric acid is produced along with the formation of ferric hydroxide. Therefore, a large quantity of iron sulfate is present in the AMD, and the sulfuric acid formed decreases the pH value of the acid mine water. This wastewater infiltrates surface waters and other groundwaters, thus lowering the pH and increasing their dissolved solids content. However, the resulting pH is generally high enough to cause the precipitation of ferric hydroxide, which in turn deposits in stream beds and aquifiers and increases the turbidity of the water. The acid mine water also abounds in other metallic pollutants, such as aluminum, manganese, calcium and magnesium. Moreover, it is found that the relative pollutant concentrations and the temperature of AMD vary considerably with climatic conditions, and the extent to which acid mine waters become a source of pollution is also variable in different coal mining areas.

Although various neutralization treatment schemes can provide effluents of sufficient quality to meet discharge standards into natural waterways, they normally cannot produce potable water. The purpose of studies conducted by West Virginia University has been the pilot-plant investigation of both Reverse Osmosis (RO) and coupled Ion Exchange/Reverse Osmosis (CIX/RO) processes that do have the potential of yielding potable water from AMD.

This document summarizes the results of both analytical and experimental work conducted during the period May 1973 through November 1975 concerning treatment of AMD by RO- and CIX-based techniques to produce a high quality product water. The basic studies have involved pilot-plant scale operations at the U.S. Environmental Protection Agency (EPA) Crown Mine Drainage Control Field Site, Rivesville, West Virginia, and focused on:

- Evaluation of the operating performance of a 227,000 lpd (60,000 gpd) rated produce output RO unit, containing spiral-wound cellulose acetate membrane modules, in terms of its ability to treat AMD at unit recoveries of 50 to 60 percent.
- Determination of the feasibility of using lime, soda ash, and combined lime-soda ash neutrolosis (a combination of RO and neutralization) processes to treat AMD focusing on enhanced overall systems recovery and low-volume waste yields.
- Examination of coupled sodium cycle co-current CIX/RO systems as a potentially high recovery AMD treatment process.

## Conclusions

The following major conclusions are based on the results of the investigations of RO-based AMD treatment techniques conducted on ferrous mine discharge waters at the EPA Crown Mine Drainage Control Field Site, Rivesville, West Virginia:

- The 227,000 lpd (60,000 gpd) RO unit, which represents a significant scale-up compared to previous RO studies of AMD treatment, is fully capable of treating ferrous AMD discharges to produce high quality water with few operational difficulties. Automated regulation of product flow rates at preset levels functioned reliably during more than 4500 hours of operating time. Module failures were minimal (4 out of 84) during the period, and were the result of cracked module casings. No deterioration of membrane performance in terms of flux decline or deterioration of ion rejection was noticed during normal operations at 50 through 90 percent unit recoveries. With proper acidification of AMD (pH 2.8-3.0), and known recovery limitations of the AMD feed based on its cited characteristics, no iron or gypsum fouling will occur. Automatic low pressure shutdown and acidified backflushing systems worked well. The RO unit met all design and operating specifications. The only major problem encountered was erosion/corrosion of the stub tubes connected at 90° angles to the inner surface epoxy-coated pressure vessels. This resulted in pin-hole leaks in the stub tubes themselves. Welding and epoxy recoating of the defects was only a short-term maintenance measure, and the pressure vessels may eventually have to be replaced.
- Lime neutrolosis proved to be both technically and operationally unfeasible, primarily due to excessive $CaSO_4$ concentrations in the neutralized supernatent recycled to the RO unit. Several case studies and experiments demonstrated that when compared to once through RO recovery operations on an AMD with specified chemical characteristics, lime neutrolosis is not competitive when examined from either an operational or economic perspective.
- Soda ash neutrolosis appeared to be a feasible process, if care was taken to raise pH levels to greater than 9.5 to remove calcium hardness. The economics of the process are questionable for Crown AMD, with chemical costs running in excess of 53 cents per 1000 liters ($2.00 per 1000 gallons) of AMD treated.
- Lime-soda ash neutrolosis was also an operationally viable treatment method. Costs were reduced since lime may be used to elevate the RO brine to pH 8.0 before using soda ash softening to raise pH levels to 9.5-10.0, which removes better than 90 percent of the calcium. Cost estimates of chemicals show that it would require approximately 40 cents per 1000 liters ($1.50 per 1000 gallons) to treat Crown AMD, plus the expense of maintaining accurate pH control in both the lime and soda ash additive steps of the process.
- In both the soda ash and lime-soda ash neutrolosis processes, a problem of $NaSO_4$ concentration buildup in the supernatant occurred during the run periods. Even for the small amounts of recycle conducted in the studies, the increases in the RO brine osmotic pressures due to this effect were large. The net result to maintain a pre-set product flow under these conditions must be to increase feed pressure, and hence operating costs, at a possible sacrifice of overall product quality.
- The coupled sodium cycle CIX/RO process showed an excellent capability to function as a high recovery AMD treatment system without membrane fouling. The $Na_2SO_4$ laden waste brine from the process was utilized to provide up to 40 percent of the regenerating capacity of the resin bed, thus reducing NaCl requirements in regeneration. Again, with such a high recovery (greater than 90 percent) mode of operation, substantial osmotic pressures existed within the RO system,

tending to reduce product flux which must be compensated for by increased feed pressure on the RO system. Product water quality from the coupled system met potable water standards except for low pH, which could be easily buffered to pH 7.0.

## Recommendations

Based on the results and conclusions of the investigations, the following recommendations are made for additional studies related to RO-based and coupled CIX/RO treatment of AMD:

- The economics of once-through RO treatment of AMD should be fully investigated to include capital, operating, and maintenance costs for a complete treatment system including the RO unit and all peripheral unit processes and hardware, with special emphasis on waste brine disposal costs.

- The cost-effectiveness of soda ash and lime-soda ash neutrolosis should be determined to establish whether they are viable processes for treatment of AMD, and to find any advantages over a once-through maximum recovery type RO operation.

- A counter-current CIX system coupled with RO should be studied, because there is reason to believe that even higher system recoveries can be attained owing to reduced hardness leakage from the ion exhange side of the system. Also, more detailed investigations should be made to optimize regenerant utilization when the CaCl- $Na_2SO_4$ tandem regeneration procedure is utilized. In this respect, the goal would be to minimize NaCl consumption, and maximize $Na_2SO_4$ usage. The addition of a chemical antiprecipitant agent to the $Na_2SO_4$ regenerant aid should be investigated to inhibit the onset of $CaSO_4$ precipitation.

- A detailed study of the process economics of a CIX/RO treatment system should be performed, and a comparative cost analysis made with other types of RO-based treatment techniques.

- A Manual of Practice pertinent to treatment of AMD by RO techniques should be prepared to serve as a practical AMD treatment guide for design and operating personnel in the field. There appears to be sufficient information developed to date to produce such a document.

- Membranes having high sodium rejection should be used to raise the sodium concentration in the waste brine to determine the effect of this increase upon the waste brine as a regenerant aid and simultaneously improve the product quality by decreasing sodium concentration .

- A determination of capacity as a function of time should be done at various NaCl dosages to find the degree of the resin degradation during long-term operations. This experiment would permit the quantification of fouling to be expected when dealing with the concentrations of iron encountered in this study.

## Description of the Pilot Plant Facility

The Crown Mine Drainage Control Field Site is located at the intersection of Stewarts Run and Little Indian Creek on 10 acres of land at Crown, West Virginia, which is approximately 20 km (12 miles) southwest of Morgantown, West Virginia. The mine drainage feed source, which is capable of delivering more than 567,000 liters/day (150,000 gallons/day), originates from a 156-mm (6-inch) bore hole pump situated 366 m (1200 ft) from the pilot plant location. The acid mine waters are transported to the pilot plant through a 78-mm (3-inch) polyvinylchloride (PVC) pipeline.

The 227,000 lpd (60,000 gpd or 60 K) and 15,000 lpd (4,000 gpd or 4 K) RO units, and the twin-bed sodium-cycle CIX system are located in a 12.2 m x 30.5 m (40 ft x 100 ft) light gauge steel building which was erected by West Virginia University at the Crown Mine Drainage Control Field Site.

### *Reverse Osmosis*

The RO process utilizes a semipermeable membrane through which almost pure water (permeate) is transported from a concentrated solution (brine) to a dilute solution by applying a pressure which is greater than the natural osmotic pressure. Since the membrane essentially rejects (is impermeable to) the dissolved ions, they are retained in the concentrated brine solution. In this manner a feed such as AMD can be demineralized to produce a quantity of permeate separated from a volume of concentrate that contains almost all of the pollutants originally present. The water flow rate (flux) through the membrane is proportional to the difference between the net applied pressure and the natural osmotic pressure of the concentrate, while salt transport across the membrane surface depends primarily on the salt concentration gradient which is relatively independent of the pressure.

The membrane is truly the key component of an RO system. Many variables can affect membrane performance, and therefore, RO performance.

Based on the success of previous investigators to utilize RO to produce nearly potable water from AMD and simultaneously minimize iron fouling problems, EPA decided to initiate pilot-plant scale studies to further examine the applicability of using RO-based processes to treat AMD. In 1971, work was started to install a 227,000-lpd (60,000-gpd) spiral-wound RO membrane system demonstration plant at the Crown Mine Drainage Control Field Site, Rivesville, West Virginia, to provide data on the RO systems scale-up and its ability to sustain long-term operations. Also to be studied was the feasibility and reliability of neutrolosis (a combination of RO and neutralization) as a high recovery/low waste treatment process for ferrous iron type AMD. In 1973, a 240-hour continuous shakedown run was conducted at Crown using the 227,000-lpd RO unit operating at a 50-percent recovery on a once-through basis. It was concluded that the RO unit did demonstrate the capability of successfully treating Crown AMD at this recovery level without membrane fouling or major operational difficulties.

### 60K Reverse Osmosis System

The 60K RO unit, manufactured by Gulf Environmental Systems, Inc., has been designed to nominally deliver a constant product water output of 227,000 lpd (60,000 gpd). This is basically accomplished by pneumatically operated automatic flow control valves in the feed and brine lines which, when preset to flow rates to yield 2.65-lps (42 gpm) product flow, will work in conjunction to adjust system operating pressures to maintain constant product output and recovery. The feed stream volume flow rate may vary from 6.56 to 2.90 lps (104 to 46 gpm), which corresponds to designed operational recoveries ranging from 40 percent to 90 percent. The system is composed of four major assemblies: (1) pretreatment, and product storage and blending, (2) membrane-module pressure vessels and high pressure pump assembly, (3) sampling and pressure measurement assembly, and (4) instrument console.

Acid mine feedwater from the bore hole pump enters the pilot plant facility and is piped to a 9500-liter (2500-gallon) holding tank. Then it is transferred by a centrifugal pump to the pretreatment skid where sulfuric acid is added to adjust the pH to 2.9. The feed is subsequently filtered by 20-micron cartridges to remove suspended solids prior to entering the main high pressure feed pumps.

The volume discharged from these pumps is automatically controlled by means of a differential pressure flow controller and control valve. The feed is then distributed via manifolding to the series-parallel array of 14 pressure vessels, each containing six spiral-wound ROGA®* modules. The concentrate flow is controlled similarly to the feed flow, so that once the two controllers are set, the unit will then operate at constant recovery, and the unit pressure will vary to maintain constant product flow rates.

The product from each pressure vessel is piped to a sampling panel where it can be measured independently. Provisions for measuring the osmotic pressure of each tube, as well as the pressure and $\Delta P$ of each bank of vessels are included. The product streams are collected downstream of the sampling valves and piped to the 1330-liter (350-gallon) elevated product water storage tank. The product flow is measured by means of an orifice-type rotameter and the water pH is adjusted just prior to entering the tank. This water can then be used to dilute the feed stream at recovery levels above that where calcium sulfate precipitation is expected, or utilized for flushing the pressure vessels during unattended or scheduled shutdown.

A centrifugal pump, manual valve, and orifice-type rotameter are used to determine the amount of product water blended with the feedwater. The flushing system includes a normally open valve and electric-pneumatic controls. The flushing sequence will begin at a preset number of minutes after shutdown. A ball valve in the line can be closed when flushing is not desired.

Product water in excess of that needed to maintain a proper inventory in the storage tank has its pH raised to 6.5 before discharging to a floor drain outlet to Little Indian Creek. When not conducting specific neutralization or neutrolosis studies, waste brine is usually lime-neutralized in a 2300-liter (600-gallon) reactor vessel to pH levels of 5.5 to 6.5, and then pumped to the Crown Mine Drainage Control Field Site sludge settling pond.

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use

## 4K Reverse Osmosis System

The 4K RO unit, manufactured by Gulf Environmental Systems, Inc., has been designed to produce a nominal output of 15,000 lpd (4000 gpd) of high quality product water. The feed stream volume can vary from 0.44 to 0.19 lps (7 to 3 gpm), which corresponds to recoveries of 40 percent to 90 percent. This system is also composed of four major assemblies: (1) pretreatment assembly, (2) membrane-module pressure vessels and high pressure pump assembly, (3) sampling and pressure measurement assembly, and (4) instrument console.

AMD feedwater is withdrawn from the same 9500-l (2500-gal) holding tank utilized by the 60K RO system. This feedwater is then transferred by a centrifugal pump to the 4K RO unit. Sulfuric acid is added to adjust the feed pH to 2.9 in order to maintain iron constituents in solution and control iron fouling of the membranes. If a precipitation inhibitor is to be used, it is also added at this point. The feed is then filtered in the 10-micron cartridge filters to remove any suspended solids.

The feed pressure to the unit is controlled by passing a portion of the feed through a valved bypass line. The overall unit recovery is adjusted by altering the amount of the brine to be recycled with the fresh feed to the unit, where increasing the brine recycle also increases the unit recovery of product water. The resulting product water is adjusted to pH 6.5 before it is discharged to the drain. The waste brine is lime neutralized, or it may be used as feed to another process.

## *Reverse Osmosis Systems Operations*

One major aspect of the work conducted at the Crown Mine Drainage Control Field Site was the examination of RO pilot plant performance under a variety of AMD feed conditions. Studies focused on the production of high quality permeate from Crown AMD using the 60K RO unit at 50 to 90 percent recovery levels, the investigation of chemical pretreatment of AMD to alleviate or retard precipitate fouling of RO membranes, and the documentation of operations maintenance problems (including repair efforts) created by long-term sustained usage of RO equipment in the field.

As noted above, when a feed water under applied pressure continuously moves through an RO unit, water is transported through the membrane. This increases the salt concentration of the water not passing through the membrane. The percentage of the feedwater collected as a permeate is defined as the recovery.

At 90-percent permeate recovery, the brine concentration is 10 times that of the original feed. Thus, attempts to attain high product recoveries can cause problems of product quality deterioration, elevated osmotic pressure, and ever-increasing feed pressures.

During a 150-hr, 50 to 90 percent recovery checkout operation with the 60K RO unit, operational difficulties were minor in nature: a leak in the product water recycle pump, sticking of the brine flow controller, a malfunction of the product recycle rotameter, and several low suction pressure shutdowns due to loss of raw AMD feed at the bore hole. In all cases of automatic shutdown due to low ($<10$ psig) feed pressure, the automated backflushing operations with pH 2.5 to 3.0 phosphoric acid solution functioned well, as evidenced by the return to pre-shutdown operating conditions (flow rates, system pressures, water quality) when the RO unit was restarted.

Repairs for the most part were satisfactory; however, the incidence of erosion-corrosion defects continued to accelerate during the course of the two-year investigations. The vendor has noted that another of its RO units, having identical pressure vessel design and being utilized in brackish water treatment, was experiencing erosion-corrosion problems similar to those at Crown. The vendor's recommendation was that newly designed fiberglas pressure vessels having end entry-exit feed-brine ports be installed to replace the current pressure vessel system.

Some comments should be made concerning the performance and durability of the spiral-wound cellulose acetate membrane-modules used in the 60K RO unit. During more than 4,500 hours of operation, the RO unit experienced only four module failures due to cracks in the module casing. No modules had to be replaced because of inherent loss of membrane rejection capability. Occasionally, modules were removed and dissected to examine iron or gypsum fouling patterns, and other times, the central axis product tubes were broken due to improper loading procedures. When one considers the types of investigations being conducted that often resulted in potential $CaSO_4$ fouling situations and deliberate iron fouling of the membranes, and the numerous deliberate and unintentional shutdown, membrane cleaning, and start-up operations, the track record of modular durability, performance and lifetime must be rated as excellent.

## Coupled Reverse Osmosis/ Neutralization Studies

The RO treatment of AMD often produces a considerable volume of concentrate which must undergo treatment and disposal processes, even though a significant amount of the feed may be recovered as a high quality permeate. In the majority of applications of AMD treatment by RO, the RO unit most likely would be utilized as an adjunct to neutralization processes to produce a given quantity of high quality water for a particular purpose. The concentrate in this case subsequently would be treated in the neutralization/clarifier train before a discharge to surface waters. However, if it was desirable or necessary to alleviate concentrate disposal problems, a possible solution might be to recycle some portion of the neutralized brine to the RO unit for additional treatment. Ideally, such a coupled technique could yield a high permeate recovery of the raw AMD and a small amount of waste effluent. In some cases, the only waste might be a sludge which could be dried or disposed of in a landfill.

Previous work with RO/neutralization processes was conducted by the EPA staff at Norton, West Virginia. The name 'neutrolosis' was applied to the coupled process in which the RO concentrate was lime neutralized and recycled to the RO unit. Although the Norton study showed a an overall systems recovery of greater than 98 percent, it was not clearly determined how a long-term neutrolosis operation would function with respect to calcium sulfate fouling within the process loop, nor was the overall feasibility of operating in a neutrolosis mode explicitly evaluated.

A major purpose of this study was to carefully examine neutrolosis concepts. Three variations of the coupled RO/neutralization process were studied using lime, soda ash, and combined lime-soda ash as the respective neutralizing agents. These processes were evaluated from both theoretical considerations and on the basis of experimental results.

### *Lime Neutrolosis*

In the neutrolosis process, concentrate from the RO unit is reacted with lime to raise the pH of the concentrate to a specified level. The reactor effluent is then aerated to oxidize the iron to facilitate its removal, and subsequently clarified to produce a sludge and a low turbidity supernatant. A large portion of the supernatant is blended with the raw AMD for further treatment in the RO unit, which results in much of the concentrate being continuously recycled in the coupled system (Figure 1). The basis for lime neutralization as a water treatment process is that lime reacts with several metals to yield fairly insoluble hydroxides. The lime addition raises the pH so that the solubility equilibrium is shifted and the metals are precipitated from the water.

All of the lime neutralization reactions form calcium sulfate as one of the products. In order to remove most of the reactable components in AMD waters, it would be necessary to add a considerable amount of lime, thus greatly increasing the calcium sulfate loading. For example, in a typical sample of Crown water more than 1.55 kg of hydrated lime must be added to each 1000 liters of RO concentrate neutralized. This is enough to gypsum-saturate the water by itself, but when added to the calcium sulfate already present, a supersaturated condition arises. Such a highly saturated concentrate stream poses the great problem with a lime neutrolosis type of operation: namely, scaling of the membranes with gypsum when the recycle stream is introduced to the RO unit.

In order to examine the performance of an RO system when an actual lime neutrolosis recycle operation occurs, several experimental runs were conducted. The calcium sulfate brine saturation factor was selected as a significant variable, since its limiting value of 1.4 (based on ionic interference solubility calculations) appeared widely applicable to the RO treatment of a diversity of AMD feeds. In an evaluation of RO systems operation, it is the fouling potential of the brine in the last bank of modules which is of critical importance. For Crown AMD, the 1.4 calcium sulfate saturation factor represented $CA^{++}$ concentrations of 750-800 mg/l in the brine stream. It should further be noted that based on non-ionic

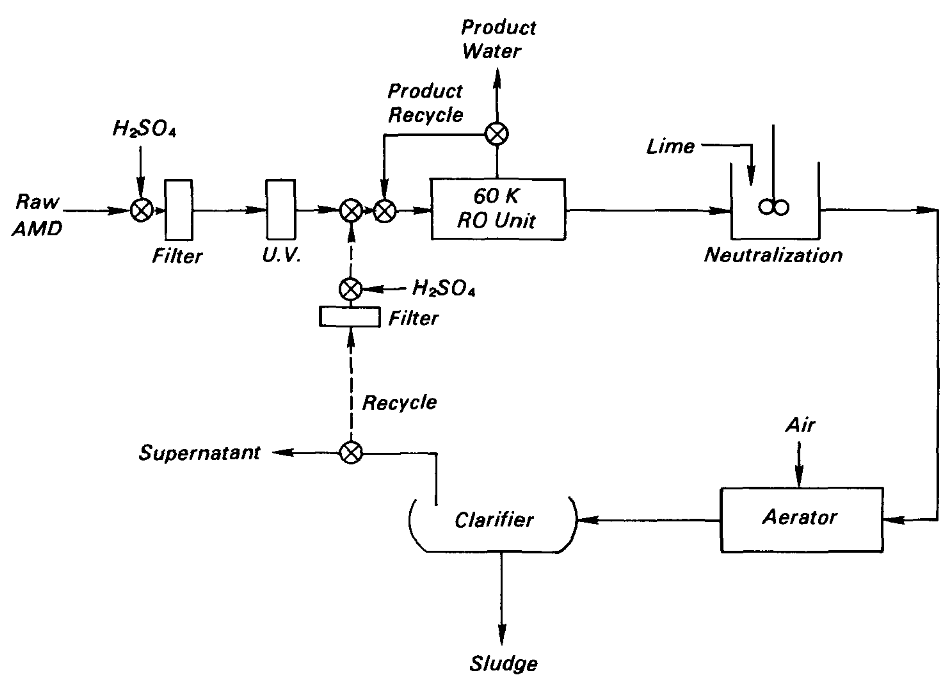


*Figure 1. Process schematic for lime neutrolosis studies.*

interference calculations (comparison of solubilities of $CaSO_4$ in brine with $CaSO_4$ solubility in distilled $H_2O$), the 1.4 value cited above corresponded to a non-ionic interference $CaSO_4$ saturation factor of 2.45. These calculations are described in detail in the main body of the report.

The "tap water neutrolosis" study again provided evidence that the lime neutrolosis mode of operation is not comparable to a once-through recovery process. Operational problems were also encountered with respect to increased acid consumption for feed pH adjustment of the blended feed to the RO unit, and more frequent replacement of cartridge filters was due to the precipitation of gypsum present in the supernatant. These problems had been anticipated, and, in fact, proved to be recurrent in all lime neutrolosis schemes attempted.

In summary, the lime-based neutrolosis process caused an intolerable membrane fouling rate when attempting to sustain a long-term, high overall RO system recovery operation. Although numerous attempts were made to run lime neutrolosis experiments, all were rather short-lived and unsuccessful due to prefiltration system fouling and/or deterioration of product water flux rates, even when precipitation inhibitors were introduced to the process.

## Soda Ash Neutrolosis

Because of the gypsum fouling which resulted from lime neutrolosis, attempts were made to use soda ash (sodium carbonate) as the neutralization agent in place of the lime. It was expected that calcium sulfate hardness could be removed with the soda ash and thus circumvent the principal difficulty which was associated with lime neutrolosis. Operating experience with soda ash neutralization of AMD indicated that soda ash was a very effective neutralizing agent but that its cost was prohibitive compared to lime and limestone.

Soda ash ($Na_2CO_3$) is used to raise the pH of the water and thus acts to precipitate the metals as insoluble hydroxides. As discussed in the section on lime neutrolosis, the pH is controlled to remove most of the various metals present. Addition of soda ash to proper pH levels allows the iron, manganese, aluminum, and magnesium to be removed to the same extent as in the lime process. The great differences between the two processes have to do with the hardness removal and cost.

Bench-scale neutralization tests on Crown AMD indicated that soda ash neutralization of the RO brine to a pH level of greater than 9.5 would be capable of removing 90 percent of the calcium hardness. This was the neutralization bench mark pH value for the "closed loop" experiment which followed, using the 60K RO unit.

Chemistry analyses for each day of the four-day operation are shown in Table 1. It can be seen that for a supernatant pH of 9.6, the calcium removal was better than 95 percent; however, the $Na_2SO_4$ buildup in the supernatent increased tenfold during the operating period. This verified the hypothesis that increased sodium concentrations in the soda ash neutrolosis mode of operation will occur.

An evaluation of soda ash consumption during the "closed loop" operation indicated that the neutralization chemical costs themselves were greater than \$0.53 per $m^3$ (\$2.00 per 1,000 gal) of treated AMD, which supported the earlier contention that soda ash neutrolosis (at least from Crown AMD) would be an expensive process.

## Combined Lime-Soda Ash Neutrolosis

The lack of operational success of lime neutrolosis and the high cost of soda ash neutrolosis led to a brief preliminary examination of a lime-soda ash neutrolosis process, whereby waste brine from the RO unit was neutralized to pH 8.0 with lime, and then raised to pH 10.0 by adding more soda ash. These pH values were established by bench-scale experiments conducted with Crown AMD RO waste brine, with the objective to remove at least 90 percent of the calcium from the supernatant.

The basic chemical reactions which would be involved in lime-soda ash neutralization have already been discussed. In this type of process the concentrate is first lime-treated to remove many of the metals with the cheaper lime. The more expensive soda ash is then added to remove the residual calcium as calcium carbonate; the goal is to take advantage of the best features of the two neutralization agents. Lime-soda ash treatment has been utilized extensively for the treatment of both industrial water and drinking water. However, application to AMD treatment is very recent, and there have been no other reported studies of a neutrolosis

*Table 1. Chemistry Analysis for "Closed Loop" Soda Ash Neutrolosis (All Concentrations in mg/l)*

| | Ca | Mg | Total Fe | $Fe^{+2}$ | Na | Al | Mn | $SO_4$ |
|---|---|---|---|---|---|---|---|---|
| *Day 1* | | | | | | | | |
| Brine | 470 | 140 | 230 | 220 | 2700 | 9.2 | 5.7 | 8900 |
| Supernatant | 17 | 95 | 0.7 | 0 | 1500 | 2.2 | 0.14 | 6000 |
| Product | 0.35 | 0.2 | 0.3 | <1.0 | 14 | 1.0 | <0.01 | 46 |
| *Day 2* | | | | | | | | |
| Brine | 420 | 230 | 230 | 230 | 3400 | 8.6 | 5.6 | 11000 |
| Supernatant | 16 | 140 | 6 | 0 | 3000 | 2.2 | 0.16 | 7200 |
| Product | 0.65 | 0.3 | 0.5 | <2.9 | 20 | 0.6 | <0.01 | 48 |
| *Day 3* | | | | | | | | |
| Brine | 450 | 230 | 240 | 200 | 3500 | 5.6 | 4.4 | 11000 |
| Supernatant | 18 | 150 | 2.20 | 0 | 12000 | 3.2 | 0.17 | |
| Product | 0.66 | 0.37 | 0.32 | <2.9 | 32 | 0.6 | <0.01 | 74 |
| *Day 4* | | | | | | | | |
| Brine | 470 | 210 | 350 | 270 | 10000 | 10.0 | 6.2 | |
| Supernatant | 17 | 160 | 2.2 | 0 | 17000 | 2.2 | 0.26 | |
| Product | 0.60 | 0.34 | 0.6 | <1.0 | 50 | 1.0 | <0.01 | 112 |

type process which utilizes both lime and soda ash.

Lime and soda ash consumption during the study was calculated to cost approximately $0.40 per $m^3$ ($1.50 per 1,000 gal) of Crown AMD waters treated. Although less than soda ash neutrolosis itself, it is still quite costly. Again, the economics of the situation need to be evaluated before any decision is made to promote lime-soda ash neutrolosis as a cost-effective technology. In any neutrolosis process, there will be added equipment costs and involved operational and control procedures which must be carefully monitored, e.g., accurate pH control in neutralization procedures and maintenance of low turbidity conditions in supernatant effluents from clarifiers.

## Acid Mine Drainage Treatment by Ion Exchange

Ion exchange (IX) has been widely used for many years to produce limited quantities of potable water from brackish water, but its application to AMD treatment is relatively recent. Based on the promising results of previous coupled IX/RO systems studies, investigations were conducted at the Crown Mine Drainage Control Field Site to determine the applicability of such coupling processes for AMD treatment. A sodium form strong acid ion exchanger was used as a softening pretreatment step prior to purification in a spiral-wound membrane 15,000-lpd (4,000-gpd) RO unit. The exhausted resin was regenerated by both NaCl solution and by a combined $NaCl/Na_2SO_4$-loaded waste brine from the RO unit. The specific goal of the studies was to determine the recovery potential of the coupled system, and the effect of utilizing $Na_2SO_4$ waste brine as a regenerant aid to NaCl for capacity restoration of the exhausted IX resins.

### *Twin-Bed Ion Exchange System*

The heart of this system is a twin-bed sodium-form IX unit, manufactured by Culligan International Company, that consists of two pressure tanks, 0.61 m (24 inch) in diameter and 2.43 m (8 ft) high, each containing 0.41 $m^3$ (14.5 $ft^3$) of resin. The tanks are hot rolled steel rated at 690 $kN/m^2$ (100 psi) with a 0.1-mm vinyl-ester lining for corrosion resistance. AMD feed is transferred to the IX unit from the indoor holding tank by means of a centrifugal pump. Before the AMD is fed to the IX column in service, the pH is adjusted to 2.8 by addition of sulfuric acid in order to prevent iron precipitation in the resin bed. The AMD passes through the servicing exchanger at a flow rate of 0.22 to 0.25 lps (3.5 to 3.9 gpm).

During the downflow exhaustion process, samples of softened water from the ion exchanger are taken at intervals to obtain leakage and free mineral acidity (FMA) data. In addition, a representative sample (AMD composite) of the average influent water to the resin is continually collected at hourly intervals throughout the entire exhaustion run. This composite sample is used to calculate the average cationic loading to the coupled Ion Exchange (CIX), and with the total service time, is used to compute the IX capacity.

After the exhaustion process of the in-service IX column is completed, the alternate tank on standby simultaneously goes into service, thus maintaining a continuous AMD treatment process. The exhausted ion exchanger is then backwashed by sending a strong flow of AMD upward at the rate of 1.0 - 1.1 lps (4.3 gpm) in the downflow direction. After the regenerant has passed through the resin, a slow rinse, followed by a fast rinse, is applied to complete the regeneration cycle and return the exchange resin bed to a standby service mode. The operation is classified as co-current, since it utilizes both regeneration and exhaustion in a downflow mode.

The IX process is defined as a reversible replacement of the exchangeable cations between a resin and the feed solution, where the exchange resin contains ionic groups which are chemically linked to the polymer structure of the resin in which the reactions occur. The polymeric portion of the resin must be highly cross-linked so that the solubility of the resin is negligible. Moreover, the resin structure must be chemically stable so that essentially no degradation occurs during use.

A complete IX operation cycle contains the following four steps:

(1) Exhaustion Process - During exhaustion, the AMD to be treated is continuously fed through the bed of IX resin, and the softening capability of the ion exchanger is gradually depleted.

(2) Backwash Process - Effective backwash is required to maintain a clean resin bed. The purpose of the backwash process is to expand the IX bed and to break up any channels that may have formed in the column.

(3) Regeneration Process - The regeneration process is applied to restore the capacity of the ion exchanger by passing a regenerant solution through the exhausted resin bed.

(4) Rinse Process - After the regenerant solution has been applied to the ion exchanger, the water or liquid to be treated is used to rinse the IX bed before it is returned to the exhaustion process. The purpose of the rinse process is to complete the contacting and remove spent regenerant from the ion exchanger.

### *Coupled Cation Exchange/ Reverse Osmosis and Treatment Systems*

Due to an inability to use RO as a single unit process to treat Crown AMD (or mine drainages of similar quality) at recoveries greater than 50 percent, the failure of lime neutrolosis as a feasible AMD treatment alternative and the apparent high cost of soda ash and lime-soda ash neutrolosis processes, an AMD treatment scheme which offered a potential for high recovery performance was investigated. One promising process appeared to be a coupled CIX/RO system in which an ion exchanger operating on a sodium cycle removes calcium and other +2 valence and +3 valence cations from the AMD, replaces them with sodium ions yielding essentially an $Na_2SO_4$ solution, and transfers this calcium-free effluent to an RO unit to be processed at high recovery.

Because of the high product water recovery that can now be obtained from the coupled IX/RO process, the volume of the waste brine obtained is also decreased. Moreover, the concentration of $Na_2SO_4$ in this waste brine is high enough to assist with the regeneration of the exhausted IX resin. In this mode, the brine is stored and later recycled back to the IX unit to make up a portion of the regenerant stream.

Observations of the experimental work indicated that high permeate recoveries (90 to 93 percent) could be maintained in the RO unit throughout the period of operation without any evidence of membrane fouling. The performance of the coupled system can be analyzed using Table 2, which presents a representative chemical analysis of AMD feed, softened feed, blended feed, brine, and product at salt dosage of 240 $kg/m^3$ (15 lb $NaCl/ft^3$).

*Table 2. Representative Chemistry Analysis at a Salt Dosage of 240 kg/m³ (15 lb/ft³)*

| Component | AMD Water | Softened Feed (SF) | Blended Feed (BF) | Brine | Product | Salt Rejection * in SF (%) | Salt Rejection* in BF (%) | Salt Rejection* in AMD (%) |
|---|---|---|---|---|---|---|---|---|
| Ca | 380 | 6.0 | 45 | 71 | 0.2 | 96.7 | 99.6 | >99.9 |
| Mg | 110 | 0.6 | 4.6 | 7.0 | 0.01 | 98.3 | 99.8 | >99.9 |
| Al | 4.4 | 0.2 | 0.9 | 1.2 | trace | >99.9 | >99.9 | >99.9 |
| Ferrous Fe | 250 | 2.5 | 12 | 18 | trace | >99.9 | >99.9 | >99.9 |
| Mn | 4.5 | 0.02 | 0.2 | 0.4 | trace | >99.9 | >99.9 | >99.9 |
| Na | 480 | 1,200 | 8,200 | 12,000 | 58 | 95.2 | 99.3 | 87.9 |
| Total Fe | 270 | 2.6 | 12 | 19 | 0.01 | 99.6 | 99.9 | >99.9 |
| $SO_4$ | 2,900 | 2,900 | 28,000 | 48,000 | 260 | 91.0 | 99.1 | 91.0 |
| Conductance | 3,800 | 5,500 | 27,000 | 40,000 | 650 | 88.2 | 97.6 | 82.9 |
| pH | 4.5 | 2.8 | 2.7 | 2.5 | 3.4 | | | |

*All units are mg/l except pH and conductance (Mmhos/cm)*

$$\text{*Salt Rejection (\%)} = \frac{\text{Feed (SF, BF, AMD) - Product}}{\text{Feed (SF, BF, AMD)}} \times 100\%$$

Table 2 also presents the salt rejections for each specific ion.

The results obtained in these studies demonstrated that the coupled sodium-form exchanger and 4K RO unit were capable of high-recovery treatment of AMD at Crown, WV. When compared to the use of each treatment system separately, it was found that not only was the RO water recovery effectively enhanced by using IX pretreatment, but also NaCl regenerant savings were realized with the aid of $Na_2SO_4$ waste brine discharged from the RO unit.

*G. L. Blackshaw, A. W. Pappano, G. E. Thomas, Jr., and S-Y Cheng are with Department of Chemical Engineering, West Virginia University, Morgantown, West Virginia 26506*
***Robert B. Scott** and **Roger C. Wilmouth** are the EPA Project Officers (see below).*
*The complete report, entitled "Pilot Plant Treatment of Acid Mine Drainage by Reverse Osmosis," (Order No. PB 83-191 437; Cost: $14.50, subject to change) will be available only from:*
*National Technical Information Service*
*5285 Port Royal Road*
*Springfield, VA 22161*
*Telephone: 703-487-4650*
*The EPA Project Officers can be contacted at:*
*Industrial Environmental Research Laboratory*
*U.S. Environmental Protection Agency*
*Cincinnati, OH 45268*

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