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SUMMARY AND CONCLUSIONS

The Water Quality Office, EPA, Mine Drainage Field Site at Norton, West Virginia, has successfully demonstrated that the combination of two known mine drainage treatment processes can produce over 98 percent water recovery and less than two percent of easily disposed inert sludge.

In the past the Environmental Protection Agency, (EPA) Water Quality Office (WQO), and the Office of Saline Water (OSW) have cooperated in studies of the application of reverse osmosis to mine drainage in which the reverse osmosis unit and technical assistance have been supplied by OSW and feed water treatment and technical operation by WQO. This cooperative project had successfully demonstrated that reverse osmosis could recover up to 80 percent of the water from acid mine drainage, but left unanswered the problem of disposal of the concentrated waste product, brine.

At the conclusion of the first joint project, WQO initiated another project to solve the brine problem. OSW continued to cooperate by providing the reverse osmosis unit. During this project, WQO technologists demonstrated in a 380 hour test run that 90 percent water recovery through reverse osmosis, was possible. Calcium sulfate fouling of the membranes was overcome through pressure variation techniques.

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At the same time the Norton Field Site, WQO, had been conducting studies in neutralizing acid mine drainage and into the disposal of the sludge which results from this process. A combination of the neutralization and reverse osmosis process was conceived by the Norton staff and experiments implemented. Brine from the reverse osmosis unit was cycled through the neutralization plant and the clarified water blended into the reverse osmosis feed. The resulting process, which has been dubbed "neutrolosis" by the staff, extracts 98+ percent of the water from acid mine drainage and produces a sludge suitable for disposal through permanent landfill. Salt rejection exceeded 99 percent. The breakthrough for this process was treatment of the acid mine drainage with (a) 98+ percent water recovery and (b) elimination of the brine as a disposal problem.

Specific conclusions drawn from this study were:

(1) A reverse osmosis-neutralization process can obtain 98 percent water recovery when operated on a high ferric to ferrous ratio iron acid mine drainage water.

(2) A high quality water and an inert sludge with no brine stream is produced by this combination process.

(3) A reverse osmosis unit can treat a high ferric iron acid mine drainage at a 91 percent water recovery without resulting in permanent fouling of the modules.

(4) Salt rejection exceeding 99 percent can be obtained.

(5) The major unknown yet to be resolved in the reverse osmosis-neutralization treatment of acid mine drainage is the long-term effect of the process on membrane life and performance.

BACKGROUND

The feasibility of treating acid mine drainage with a high ferric to ferrous iron ratio (greater than 4:1) by reverse osmosis to produce a water suitable for domestic use had been demonstrated through cooperative research by the Office of Saline Water (OSW) and the WQO, EPA.[1][2]* During these initial studies OSW supplied the equipment and a consultant and WQO operated the equipment and made the test runs. Most of these studies were conducted at water recovery rates** between 50 and 75 percent (although one test was as high as 80 percent) because of the fear of fouling the membranes with iron and/or calcium sulfate. At recoveries of greater than 70 to 75 percent, calcium sulfate was above the saturation concentration and a potential danger of fouling the membranes was present.

It was concluded from these studies that water recoveries up to 80 percent could be accomplished without uncontrollable iron or calcium sulfate fouling of the membranes and that between 97 and 99 percent salt rejection*** could be obtained.[2] Typical performance data are shown in Table 1. These studies did not consider the major potential pollution problem associated with the disposal of the brine.

The WQO was deeply concerned with the disposal and pollution problems associated with the waste brine that constituted from 20 to 25 percent of the water treated in the reverse osmosis plant. One proposed solution

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* Numbers in parenthesis refer to references listed at end of report.
** Water Recovery (%) = Product Water Produced X 100/Water Treated.
*** Salt Rejection (%) = Concentration in Feed Water Minus Concentration of Ion in Product Water X 100/Concentration of Ion in Feed Water.

TABLE I

Typical Performance Data at 74.4 Percent Water Recovery[2]

	Raw Feed	Product Water	Percent Rejection
pH	2.7	4.4	--
Conductivity, Micromhos/cm	1,350	55	97.9
Acidity ($CaCO_3$), mg/l	604	4	99.8
Ca, mg/l	115	2	99.3
Mg, mg/l	38	0.9	99.2
Al, mg/l	39	3.1	97.3
Fe, mg/l	153	0	100
SO_4, mg/l	936	4.2	99.8

to this problem was increasing the recovery rate to a maximum, thus producing the smallest volume of brine. With this goal in mind, WQO entered into a contract with Gulf Environmental Systems, Incorporated[3] to evaluate ultra high water recovery. OSW assisted by supplying the reverse osmosis equipment. WQO conducted the studies with the consultation of Gulf Environmental Systems.

This study showed that the reverse osmosis unit could be operated at 91 percent $\pm$ 1 percent for extended periods of time.[4] Although fouling of the membranes at the discharge end of the plant did occur, these calcium sulfate scales could be removed by operating the unit at 50 percent recovery for short periods of time, thus flushing them from the membranes.

The Norton Mine Drainage Field Site also has an active research program in the neutralization of acid mine drainage. The staff conceived that the reverse osmosis process could be combined with the neutralization process to produce a maximum amount of high quality water and a minimum volume of waste products. The process conceived was the operation of the reverse osmosis unit at maximum recovery, neutralization of the brine, and

recycle of the neutralized brine water back to the reverse osmosis unit. This system would produce only product water plus a small amount of sludge containing the iron, calcium, sulfate, aluminum, etc. The process was named neutrolosis (a combination of neutralization and reverse osmosis).

PROCEDURES

The reverse osmosis equipment was a 10,000 gpd rated unit manufactured by Gulf Environmental Systems, Incorporated.* The unit utilized five 4-inch by 10-feet long pressure vessels. Each pressure vessel contained three type 3009-A modules, which are two leaf, fabric-backed modules 3 feet long, 3.75 inches in diameter, and contain 50-square feet of high-selectivity modified cellulose acetate membrane. A pressure vessel contained 150 square feet of membrane for a unit total of 750 square feet of membrane area.

A flow diagram of the reverse osmosis unit is presented in the top portion of Figure 1. Pressurized sand filters and 10 micron cartridge filters were used to remove suspended solids from the raw feed water before the water entered the reverse osmosis unit. This precaution was necessary as suspended solids can plug the small brine channels in the spiral-wound reverse osmosis configuration.

The pressure vessels were arranged in a 2-2-1 array in order to maintain as nearly as possible a uniform brine flow through each vessel. The first two vessels were in parallel. Brine from these vessels was combined to be the feed water for vessels 3 and 4, then combined and served as feed to vessel 5.

*Mention of commercial products is for clarification only and does not imply endorsement by the Environmental Protection Agency.

In order to reach a recovery rate of 91 percent and not have insufficient flow in the final vessel, it was necessary to recycle part of the brine. A brine flow of 3.0 gpm through each module was felt necessary to minimize membrane fouling due to boundary layer problems.

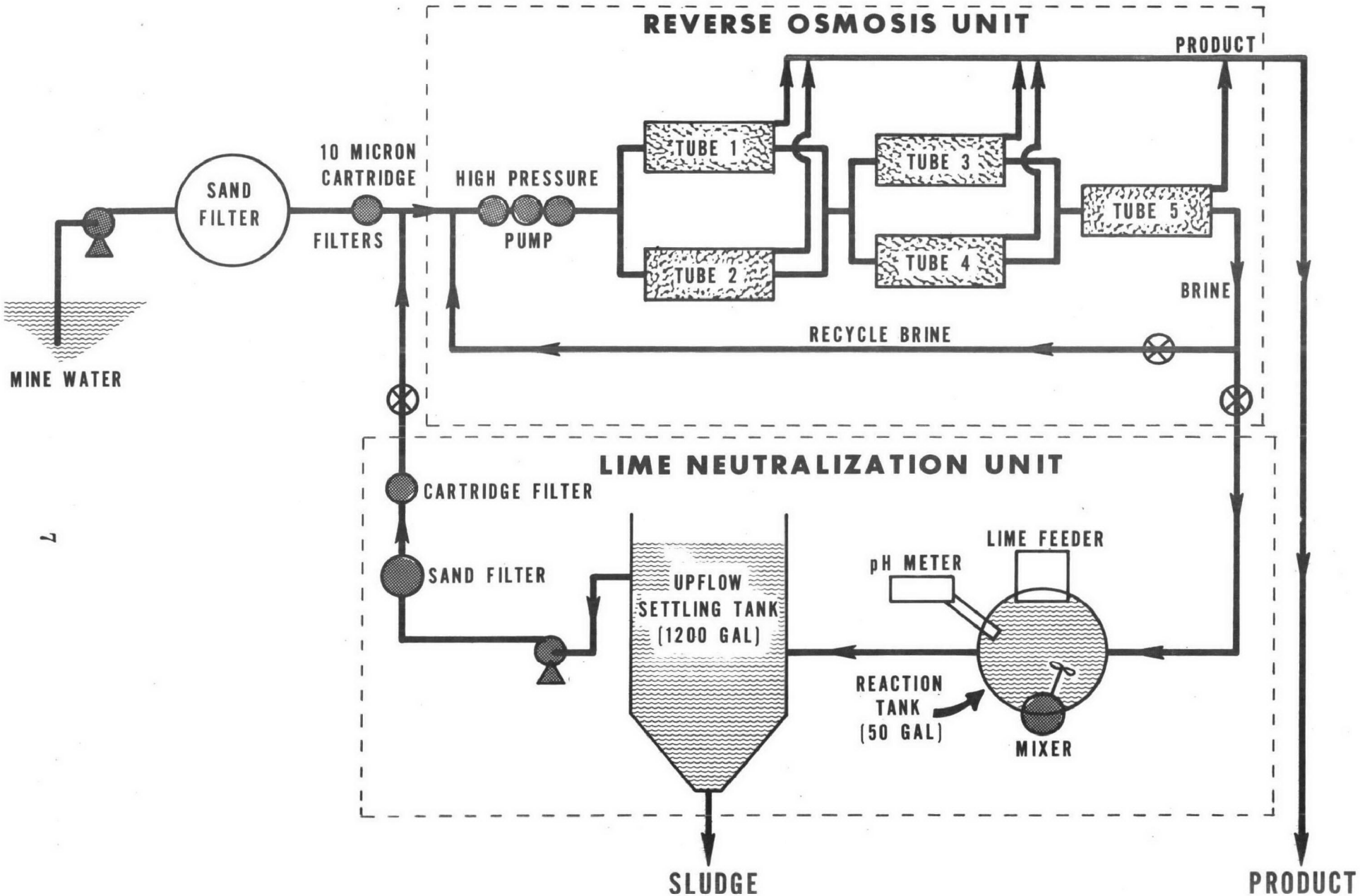
For neutrolosis operation, brine from the reverse osmosis unit passed into a 50-gallon stainless steel reaction tank where lime was added (see lower portion of Figure 1). The water was neutralized to a pH of only 4.3 to 4.5 because past experience had shown that at this pH most of the iron and aluminum were removed.(5) If the pH were raised too high, a danger existed that when the neutralized water was recycled instantaneous iron precipitation would occur resulting in fouling of the membrane vessels.

The neutralized brine passed from the reactor to an upflow settling tank, where the suspended solids were removed. The supernatant water was then filtered to remove any remaining suspended solids and then recycled to the reverse osmosis unit.

Two high recovery reverse osmosis runs (without neutralization) were made. For 100 hours the unit was operated at 91 percent recovery. The second run was for 281 hours at 91 percent recovery during the day and 85 percent at night. The latter operation was necessary because personnel were not available for 24 hour surveillance and the unit was left unattended at night. During the run, operational and water quality data were collected regularly. The test was terminated because the high pressure pump failed.

Three "neutrolosis" runs were made. The first run was a feasibility study for 29.5 hours with the primary reverse osmosis unit operating at 91 percent water recovery. The second was for 99.6 hours, again at 91 percent recovery. The third run was for 130.6 hours at 80 percent primary

F URE 1
FLOW DIAGRAM FOR NEUTROLOSIS TESTS



water recovery. The latter test was made to determine if ultra high recoveries were needed during the first pass in order to obtain maximum overall water recovery.

The raw acid mine drainage treated in these studies has the following typical characteristics:

Acidity ($CaCO_3$)	-	600 mg/l
Total Iron	-	100 mg/l (95% ferric)
Calcium, Ca,	-	100 mg/l
Magnesium, Mg	-	40 mg/l
Aluminum	-	40 mg/l
Sulfate	-	900 mg/l
pH	-	2.7
Conductance		950 micromhos/cm

RESULTS

In Table II, the results of the high recovery test at 91 percent are reported. The overall rejection and product water quality were not as good at 91 percent recovery (Table II) as at 75 percent (Table I). However, because of the brine recycle the membranes were receiving a feed water with much higher concentration (see feed water versus blended feed water in Table II). As the concentration of the feed increases, the concentration in the effluent also increases. When rejection was determined on the basis of blended feed water, the rejections are the same magnitude at 91 percent recovery as at 75 percent recovery. In a fullscale plant, brine recycle would not be necessary and thus, better product water quality would be expected, probably similar to that reported in Table I.

The flux decline during the 100 hour run was from 11.6 to 9.8 gallons per square foot per day. At the end of the run, the water recovery was reduced to 50 percent, thereby, forcing more water through the brine channels. This process was found to restore the flux to 11.0, probably by the removal of calcium sulfate. To further evaluate the flushing of membrane fouling materials, samples were taken immediately before and 30

minutes after lowering the recovery rate from 91 to 85 percent. A mass balance revealed that at 91 percent recovery, the quantity of all constituents entering the unit were within analytical error of being the same as those leaving. Thus, the buildup on material on the membrane occurred at a slow rate. After leaving the recovery to 85 percent, the mass balance showed that approximately 30 percent more calcium, sulfate, iron, aluminum and magnesium were being discharged than entered the unit. This result showed that flushing was occurring and that the material building up in the unit was more than just calcium sulfate.

The results obtained during the 91 percent day-85 percent night water recovery operating mode was similiar to those reported in Table II. Less membrane fouling occurred at 85 percent than at 91 percent recovery however, the flux rate could be recovered in both cases by flushing.

The conclusion drawn from these tests was that the reverse osmosis unit could be operated at 90 percent recovery and not have uncontrollable membrane fouling. The problem of disposing of the brine still remained.

A summary of the first "neutrolosis" test run is presented in Table III. During this run the primary water recovery was established at 91 percent. Past research[5] had shown that the acidity, iron and aluminum were almost entirely removed when the acid mine drainage was neutralized to a pH of 4.5. Thus, the brine was neutralized to pH 4.7. Raising the pH to a higher level might result in instantaneous precipitation of the iron and plugging of the membrane. As seen in Table III, the neutralization process reduced the acidity, aluminum, calcium, iron and sulfate but did not completely remove them. Therefore, the continued recycling of these

TABLE II

Summary of 91 Percent Water Recovery Test

Average Water Recovery, Percent - 91.2
Range of Water Recovery, Percent - 90.6 to 93.1
Average Pressure, psi - 606
Average Feed Water Temperature, ^{o}F - 44
Water Flux Rate, Corrected to 10^{o}C, gal./sq. ft./day: start of run - 11.6, end of run - 9.8, range 9.5 - 13.4
Length of Run, Hours - 100

	Raw Water	Blended[a] Feed Water	Brine	Product	Tube[b] Rejection Percent	Overall[b] Rejection Percent
Conductance, Mmhos/cm	1,190	4,210	9,600	248	95	79
pH	2.7	2.2	2.0	3.4	--	--
Acidity ($CaCO_3$), mg/l	633	2,584	5,914	116	96	82
Ca ($CaCO_3$), mg/l	266	1,206	2,756	7.5	99	97
Mg ($CaCO_3$), mg/l	134	750	1,671	2.8	99	98
SO_4, mg/l	810	4,024	9,542	16.8	99	98
Fe, mg/l	110	528	1,190	2.8	99	97
Al, mg/l	35	172	398	1.1	99	97

[a]Blended feed was the mixture of raw water and recycled brine actually pumped to the reverse osmosis unit.

[b]Tube rejection is the percent decrease in concentrate based on the water the membranes were actually receiving, e.g., blended feed - product X 100/blended feed. Overall rejection is the efficiency of the whole process, e.g., feed water - product water X 100/feed water.

neutralized brine would not cause a buildup on these ions. Manganese which is not removed at a low pH will continue to build up until its saturation point is reached. This buildup may be too great for good reverse osmosis performance and a periodic blow down will be necessary.

Total system water recovery was 99 percent. For every 100 gallons treated, 99 gallons of product water were produced and one gallon of sludge. Membrane fouling occurred at the very high primary water recovery (91 percent) utilized during this run. Flushing the unit every 20 to 24 hours was successful in restoring the flux rate.

TABLE III

Summary of Neutrolosis Test I

Reverse Osmosis Unit Water Recovery	-	91 percent
Total Water Recovery "Neutrolosis" System	-	99 percent
Pressure, psi	-	602
Water Temperature, °F	-	58
Raw Water Flow, gpm	-	5.02
Product Water Flow, gpm	-	4.97
Brine Water Flow, gpm	-	0.48
Neutralized Brine Recycled, gpm	-	0.43
Average Water Flux, gal/sq. ft/day at 77°F	-	15.4
Length Run, Hours		99.6

	Raw Water	Blended[a] Feed	Brine	Neutralized Brine Recycled	Product Water	Salt[b] Rejection Percent
Conductance, Mmhos/cm	1720	5160	10,000	3680	335	93
pH	2.7	2.2	20	4.7	34	-
Acidity, Mg/l	657	2680	6030	462	130	95
Magnesium, Mg/l	38	271	547	312	2	99
Calcium, Mg/l	100	473	1130	755	3	99
Aluminum, Mg/l	38	187	405	65	1	99
Iron, Mg/l	117	516	1210	2	2	99
Sulfate, Mg/l	982	4680	11,100	2160	21	99
Alkalinity, Mg/l	0	0	0	1	0	-

[a] Blended feed was a mixture of raw water, recycled brine and recycled neutralized brine. This water was pumped to the reverse osmosis unit.

[b] Salt rejection % = blended feed concentration minus product water concentration X 100 divided by blended feed concentration.

In order to relieve some of the fouling problem, the second "neutrolosis" test run was made at 82 percent water recovery. A summary of this test run is presented in Table IV. The "neutrolosis" process water recovery was 98.7 percent or essentially the same as with 91 percent unit water recovery. Fouling of the membrane was less than at the high recovery and less flushing was necessary. Salt rejection was approximately 99 percent for all multivalent

TABLE IV

Summary of Neutrolosis Test II

Reverse Osmosis Unit Water Recovery	- 82 Percent
Total Water Recovery "Neutrolosis" System	- 98.7 Percent
Pressure, psi	- 600
Water Temperature, ^{o}F	- 61
Raw Water Flow, gpm	- 4.83
Product Water Flow, gpm	- 4.77
Brine Water Flow, gpm	- 1.31
Neutralized Brine Recycled, gpm	- 1.25
Average Water Flux, gal./sq.ft/day at 600 psi at $77^{o}F$	- 12.3
Length Run, Hours	- 130

	Raw Water	Blended[a] Feed	Brine	Neutralized Brine Recycled	Product Water	Salt[b] Rejection Percent
Conductance, Mmhos/cm	1660	3000	5640	2500	213	93
pH	2.7	2.5	2.3	4.9	3.7	-
Acidity, Mg/l	585	1150	2430	175	36	97
Alkalinity, Mg/l	0	0	0	7	0	-
Calcium, Mg/l	133	460	939	845	2	99
Aluminum, Mg/l	43	91	189	30	1	99
Iron, Mg/l	101	214	459	7	1	99
Sulfate, Mg/l	1340	3010	6380	3490	18	99
Magnesium, Mg/l	32	118	254	131	1	99

[a]Blended feed was a mixture of raw water, recycled brine, and recycled neutralized brine. This water was pumped to the reverse osmosis unit.

[b]Salt rejection % = blended feed concentration minus product water concentration x 100 divided by blended feed concentrate.

ions. The product water quality was also better because a less concentrated feed water was introduced. In a larger sized unit where brine recycle would not be necessary, the product water at 91 and 82 percent recovery would be the same.

The optimum primary water recovery has not yet been determined. The reduced fouling at lower water recovery must be balanced with the higher capital cost of a larger neutralization system. Total system water recovery, salt rejection and chemical costs for neutralization would be approximately the same.

The "neutrolosis" concept is a significant breakthrough in reverse osmosis technology. Converting 99 percent of the acid water into a high

quality product water and the remaining one percent into a dense wet sludge is a dramatic result. Further studies on this process are being carried out by the Water Quality Office.

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