APPLICATION OF ION EXCHANGE TO ACID MINE DRAINAGE TREATMENT

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INTRODUCTION

Coal is returning to prominence as the nation's primary energy resource. Expansion of mining operations and increases in production are stressed almost daily by energy officials in response to the current energy crisis. As mining operations expand, the quantities of pyritic materials in the strata surrounding the coal seams that are exposed to natural oxidation forces are similarly increased; this increased exposure creates additional concern over the problem of acid mine drainage production.

The Environmental Protection Agency (EPA), in cooperation with industry and the scientific community, began several years ago to investigate acid mine drainage treatment processes that were capable of producing potable effluents. Reverse osmosis and ion exchange were foremost among these more sophisticated processes.

This paper will briefly discuss several ion exchange treatment schemes conceived for the production of a potable water from acid mine drainage and will present specific data from research on one of these processes currently under study by EPA at the Crown Mine Drainage Control Field Site near Morgantown, West Virginia.

Ion exchange is defined as a "reversible exchange of ions between a solid and a liquid in which there is no substantial change in the structure of the solids. In this definition, the solid is the ion exchange material (resin)" [1].

CURRENT APPLICATIONS OF ION EXCHANGE TO ACID MINE DRAINAGE

SUL-BISUL PROCESS [2,3]

The Commonwealth of Pennsylvania has notably been the pioneer in the development and implementation of acid mine drainage treatment technology. Pennsylvania has constructed two full-scale ion exchange plants on acid mine drainage (AMD). A third plant is in the planning stage. The first of these plants was built in 1969 for the Smith Township community and was designed for the production of 500,000 gallons per day (gpd) of potable water. The plant went on-line in 1971. Although the water problem in the Smith Township was degraded by mining, the water to be treated turned out to be more brackish than acidic. The major problems were high sulfate and manganese levels.

The Sul-biSul process was chosen for this application. A continuous countercurrent regeneration system (the Higgins System) was utilized to provide a continuous supply of water to the Township. The Higgins System is a doughnut-shaped column in which the resin is hydraulically moved from one section to another for backwash, regeneration, rinsing and service. Some quantity of resin is always in service to provide a constant supply of product.

In the Sul-biSul process, the sulfate form of a strong-base anion exchanger is used. The acidic condition of AMD converts the sulfate on the resin to the monovalent bisulfate ion, which frees one resin exchange site that may then be occupied by another anion (sulfate or bisulfate):

$$R_2 \cdot SO_4 + H_2SO_4 \rightleftharpoons R_2 \cdot (HSO_4)_2$$

Regeneration of this resin requires a shift of equilibrium to convert the bisulfate back to the sulfate form. This is accomplished by an alkaline rinse causing:

$$R_2 \cdot (HSO_4)_2 \rightarrow R_2 \cdot SO_4 + H_2SO_4$$

At Smith Township, a strong-acid cation exchanger is coupled to the Sul-biSul anion exchanger (Figure 1). Sulfuric acid is used to regenerate the cation column. The effluent from the cation process (primarily sulfuric acid) is treated by the Sul-biSul anion column to remove free mineral acidity. Lime-neutralized water is used to regenerate the anion column. The end product is chlorinated and meets potable standards.

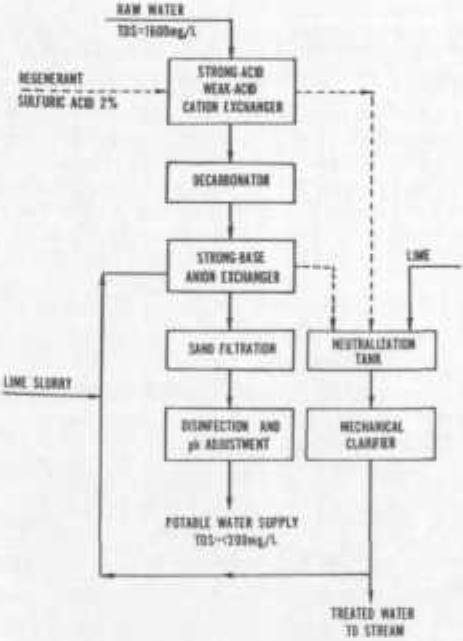

Figure 1. Sul-biSul continuous ion exchange flowsheet for the potable water treatment system at Smith Township, Pennsylvania.

The plant, however, did not meet design capacity specifications and is currently not operating because of pending litigation.

MODIFIED DESAL PROCESS [2,3,4]

The Hawk Run facility was the second ion exchange plant to be constructed in Pennsylvania for drinking water use. A moderately severe acid mine drainage stream is treated at the Hawk Run plant. This plant was designed at 500,000 gpd and utilizes the modified Desal process.

The modified Desal process incorporates a weak-base anion exchange resin that operates in the bicarbonate form. To achieve the bicarbonate form, the weak-base resin is first regenerated with ammonium hydroxide to the free-base (OH^-) form; then, in a second step, the resin is charged with a carbon dioxide solution to convert the resin to the bicarbonate (HCO_3^-) form. This bicarbonate form of the resin is capable of converting metal sulfates to their respective carbonate salts. For example, ferrous sulfate ($FeSO_4$) in the AMD reacts with the anion resin (R_a) as follows:

$$2\,R_a \cdot HCO_3 + FeSO_4 \rightarrow (R_a)_2 \cdot SO_4 + Fe(HCO_3)_2$$

The sorbed sulfate ion occupies two exchange sites on the resin. Acidity in the AMD is removed as follows:

$$2R_a \cdot HCO_3 + H_2SO_4 \rightarrow R_{a2} \cdot SO_4 + 2H_2CO_3$$

The soluble constituents in the effluent from this stage of treatment will be the bicarbonate salts of calcium, magnesium, ferrous iron, manganese and sodium. With the removal of acidity and increase in pH, aluminum and ferric iron will precipitate. Subsequent aeration and lime treatment are required for the removal of the remaining cations (except for sodium) as follows:

$$2\,Fe(HCO_3)_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow \underline{2Fe(OH)_3} + 4CO_2$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow \underline{2CaCO_3} + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow \underline{2CaCO_3} + \underline{Mg(OH)_2} + 2H_2O$$

$$Mn(HCO_3)_2 + \tfrac{1}{2}O_2 + 2Ca(OH)_2 \rightarrow \underline{2CaCO_3} + \underline{MnO_2} + 3H_2O$$

To accomplish the removal of these metals, it is necessary to increase the pH to approximately 10. It is therefore necessary to posttreat with an acid to reduce the pH to acceptable potable levels and to apply chlorination for bacteria control.

Several optimizing modifications have been made on the Hawk Run plant to increase its efficiency. Such modifications as precarbonating the AMD have contributed to a significant increase in capacity (from 500,000 to 800,000 gpd). A schematic of the process is shown in Figure 2. The waste regenerant is composed of an ammonium sulfate solution. This is lime treated to form calcium sulfate, which is removed by filtration. The filter effluent is sent to a distillation process where 92 to 95% of the ammonia is recovered for reuse as the first-stage regenerant.

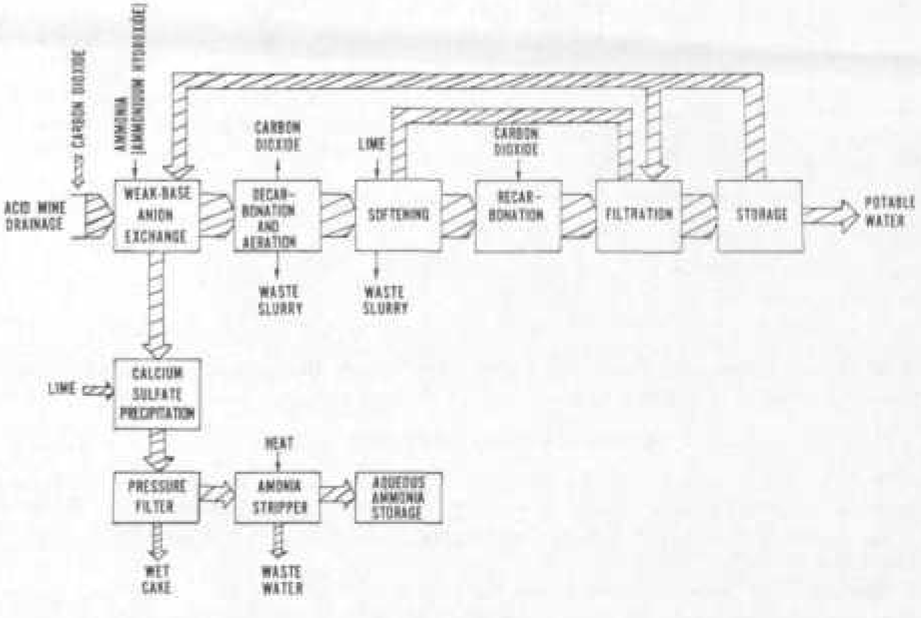

Figure 2. Acid mine drainage treatment plant at Philipsburg, Pennsylvania using the modified Desal process.

The Hawk Run facility was originally constructed to augment a degrading water supply; lately, however, water quality has improved to the point that the plant is not currently needed. The facility has been placed in the standby mode for future use as required. While it was operating, it performed extremely well.

STRONG-ACID/WEAK-BASE TWO-RESIN PROCESS

In 1972, the U.S. Environmental Protection Agency contracted with Culligan International Company [3] to conduct bench-scale feasibility studies on various schemes of ion exchange treatment of acid mine drainage. Two processes were chosen from the studies as having the greatest potential for use in AMD treatment; *i.e.*, the two-resin process and the Modified DeSal process. Since Pennsylvania was already investigating the Modified DeSal process, EPA chose to conduct pilot-plant studies on the two-resin process and performed these studies in-house at the EPA Crown Field Site.

Ion Exchange Process at Crown

The ion exchange process investigated at Crown involves the use of a 2-resin system; the first resin being an H^+-form, strong-acid cation exchanger and the second resin being a weak-base anion exchanger in the free-base (OH^-) form.

In the cation column, H^+ ions are exchanged for the metal ions (iron, aluminum, magnesium, calcium, manganese, sodium, etc.) in the AMD. Since the only anion in Crown AMD is sulfate, the cation effluent becomes predominantly H_2SO_4 with residual concentrations of metals.

The basic reversible reaction involved in the strong-acid cation process is illustrated in the following example using manganese; R_c represents the cation resin and sulfuric acid is the regenerant:

$$\mathrm{MnSO_4} + 2\mathrm{H^+R_c} \underset{\leftarrow \text{ Regeneration}}{\overset{\text{Exhaustion} \rightarrow}{\rightleftharpoons}} \mathrm{Mn \cdot 2R_c} + \mathrm{H_2SO_4}$$

The concentration of residual metals is largely governed by the amount (dosage) of regenerant used initially to charge the cation resin with hydrogen ions. Thus, by regulating regenerant dosage, it is possible to establish the degree of residual metal concentration remaining in the cation effluent. Removal of residual metals and regenerant dosage are not linearly related , however, and the utilization efficiency of the regenerant drops drastically as the dosage is increased and process costs skyrocket accordingly. The choice of cation regenerant dosage then becomes largely an economic one and the intent is to operate the column at the largest residual metal level consistent with the objectives of product end-use and thereby minimize both regenerant requirements and cost.

The effluent from the cation column (predominantly sulfuric acid) then enters the weak-base anion exchanger where the acid is totally absorbed by the resin. A weak-base anion exchanger can only absorb acid; it cannot split neutral salts. Some carryover therefore exists of metal salts that were not removed by the cation exchanger and passed unaffected through the anion column. Because of the alkaline nature of the anion exchanger, some precipitation of iron and aluminum residuals can be expected. The effect of this accumulation on anion resin efficiency and capacity must be investigated during this study. The basic weak-base anion exchange reactions are illustrated using sodium hydroxide as the regenerant; R_a designates the anion resin and H_2SO_4 is the cation effluent:

Exhaustion: $\mathrm{R_a + H_2SO_4 \rightarrow R_a \cdot H_2SO_4}$

Regeneration: $\mathrm{R_a \cdot H_2SO_4 + 2NaOH \rightarrow R_a + Na_2SO_4 + 2H_2O}$

Iron precipitation[1]: $\mathrm{Fe_2(SO_4)_3 + 3R_a + 6H_2O \rightarrow 2Fe(OH)_3\downarrow + 3R_a \cdot H_2SO_4}$

As the anion effluent contains residual levels of ferrous iron and manganese, it must be further treated to meet potability requirements. This is accomplished by lime neutralization to pH 9 or 10, followed by filtration, and then followed by pH readjustment back to neutral levels. A small portion of the cation effluent is added to the filtered effluent to reduce the pH to acceptable values.

Either hydrochloric acid or sulfuric acid may be used for regenerating the cation column. Sulfuric is generally preferred because it is considerably cheaper. A potential problem of gypsum (calcium sulfate) precipitation is present with the use of sulfuric acid as the regenerant; no precipitation problems are anticipated with hydrochloric acid. The waste stream during regeneration with sulfuric acid will consist of excess sulfuric acid plus iron, aluminum, sodium, manganese, calcium and magnesium sulfates.

The anion exchanger is regenerated with sodium hydroxide (caustic). The anion regenerant waste stream consists mainly of sodium sulfate.

The Basic Ion Exchange Unit

The operating specifications for the basic ion exchange unit designed for Crown are given in Table I. The system included individually adjustable timers and adjustable flow controls for each operating cycle. Both the cation and anion column operated in the downflow mode (Figure 3). The regeneration sequence could be initiated either manually or automatically (by sensing changes in conductivity).

Table I. General Specifications for EPA Ion Exchange Treatment Unit (Two-Resin System)

	Cation Exchanger	Anion Exchanger
Type	strong acid	weak base
Resin	Duolite C-20	Dowex WGR
Volume of resin, m^3	0.93	0.54
Approximate tank size, cm	91 x 213	76 x 213
Approximate tank area, m^2	0.65	0.45
Service flow rate, liters/min	40	40
Service flow rate, liters/min/m^3	43	74
Service flow direction	downflow	downflow
Backwash flow rate, liters/min	115	100
Backwash flow rate, liters/min/m^2	180	190
Backwash flow direction	upflow	upflow
Bed expansion during backwash, %	50	75
Regenerant flow rate, liters/min	100	40
Regenerant flow rate, liters/min/m^2	150	90
Regenerant flow rate, liters/min/m^3	110	74
Regenerant flow direction	downflow	downflow
First rinse flow rate, liters/min	100	40
First rinse flow rate, liters/min/m^3	110	90
First rinse flow direction	downflow	downflow
Second rinse flow rate, liters/min	115	100
Second rinse flow rate, liters/min/m^3	120	190
Second rinse flow direction	downflow	downflow
Regenerant	sulfuric acid	sodium hydroxide
Regenerant concentration, wt %	2	3 to 5

STUDY RESULTS

The AMD quality (Table II) at Crown was significantly worse than that of Hawk Run. The high sodium levels at Crown proved to be important in this investigation. These studies on the process basically characterized system performance under different conditions of cation regenerant dosage. Typical pollutant concentration trends during each cycle of the treatment process are shown in Figures 4 and 5 for the cation and anion columns respectively.

Typical operational data from the treatment process for three sets of cation dosage conditions (48, 96 and 144 g of 100% sulfuric acid per liter of resin) are given in Tables III, IV and V.

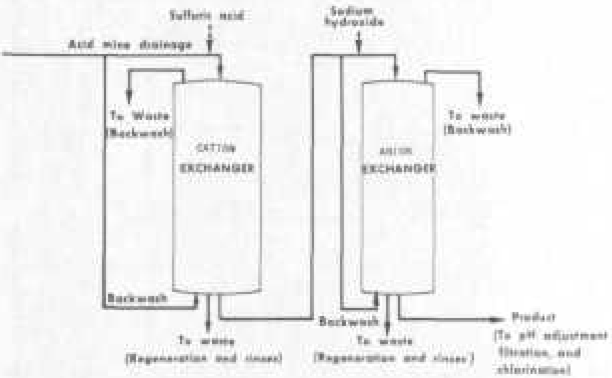

Figure 3. Flow diagram of EPA 2-resin ion exchange unit.

Table II. Crown Water Quality Data, 8/76 Through 3/77

Parameter	Mean	Maximum	Minimum	Standard deviation
pH	5.1	6.1	3.5	0.6
Specific conductance, µmho/cm	2790	4000	2350	540
Acidity as $CaCO_3$, mg/l	420	610	260	90
Calcium, mg/l	340	400	310	20
Magnesium, mg/l	110	130	96	7.2
Total iron, mg/l	210	270	140	32
Ferrous iron, mg/l	200	270	120	33
Sodium, mg/l	360	470	290	40
Aluminum, mg/l	7.6	18	0.5	3.9
Manganese, mg/l	5.1	6.6	3.6	0.7
Sulfate, mg/l	2500	3040	2100	200
Alkalinity, mg/l	20	100	0	25
Total dissolved solids, mg/l	3540	4260	3040	270
Temperature, °C	17	25	14	1.7
Exchangeable cations as $CaCO_3$, mg/l	2510	3060	2180	180

The regeneration system on the ion exchange unit was interlocked so that both the cation and anion columns were sequentially regenerated. This was necessary to insure that both units did not attempt simultaneous regeneration because the cation unit needed to be on-stream to provide water for the anion regeneration process. This interlocking, however, worked to a disadvantage in evaluating and optimizing anion column performance. Since the anion column was totally dependent upon the cation column, it was essential that the cation exhaust first and thus initiate regeneration. The anion column was, therefore, necessarily overdosed to assure a greater capacity than the cation column. Because of this, it must be emphasized that the anion capacities and efficiencies in Tables III, IV and V were not optimized and the apparent changes largely reflect the differences in cation capacities.

Chemical data from the studies are given in Table VI. As the cation dosage increased, the concentrations of each of the pollutants in the cation effluent tended to decrease. Very little removal of sodium was achieved, however. Passage through the anion column effectively removed all acidity and imparted alkalinity. Precipitation of iron within the

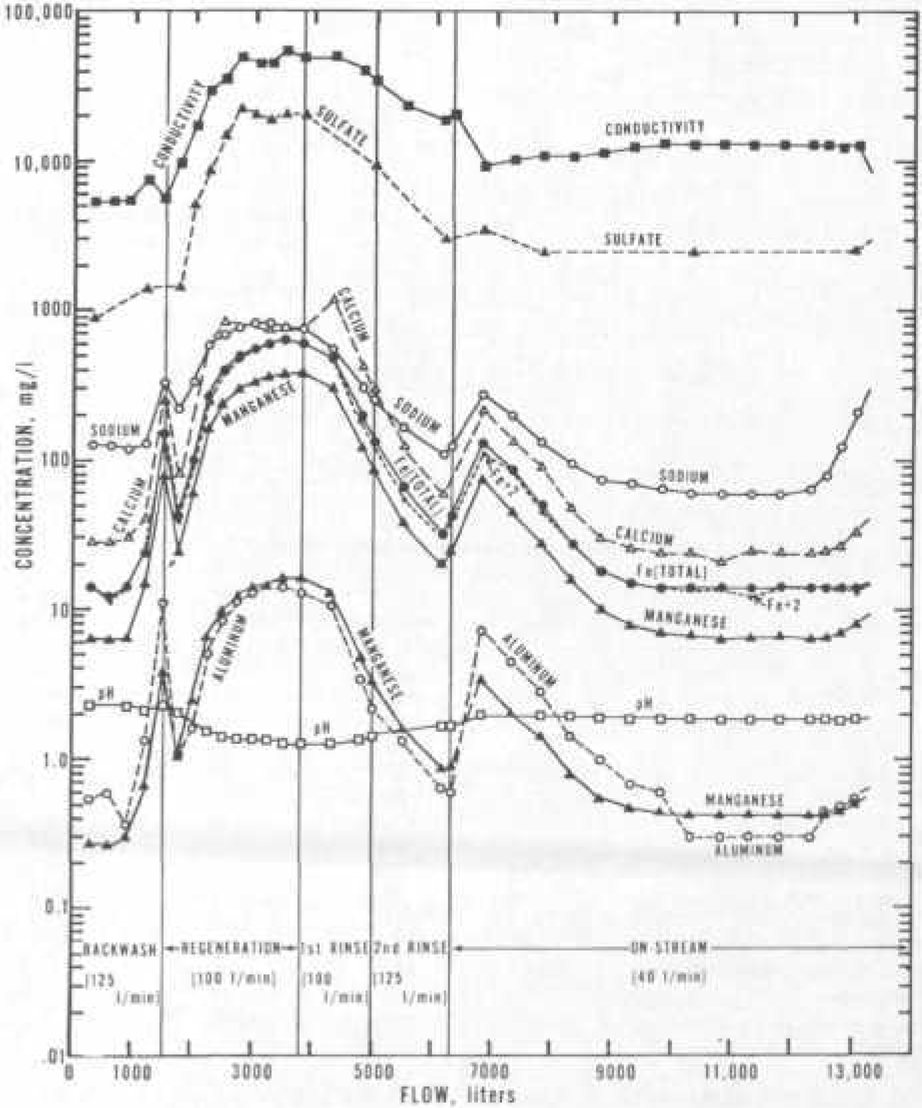

Figure 4. Trends of pollutant concentration throughout a typical cation service cycle at 48 g/liter (3 lb/ft^3) sulfuric acid regenerant dosage.

anion column was particularly apparent from the data. An increase in sodium imparted by the anion column was also noted.

The process, as is, will not produce a potable effluent from the Crown AMD because of the unusually high sodium level in the influent AMD. The sodium concentration and its equivalent quantity of sulfate exceed the 500 mg/l total dissolved solids standard for potability. If the sodium were not present in the AMD, the effluent could be posttreated and filtered for residual iron and manganese removal and chlorinated to meet potability requirements.

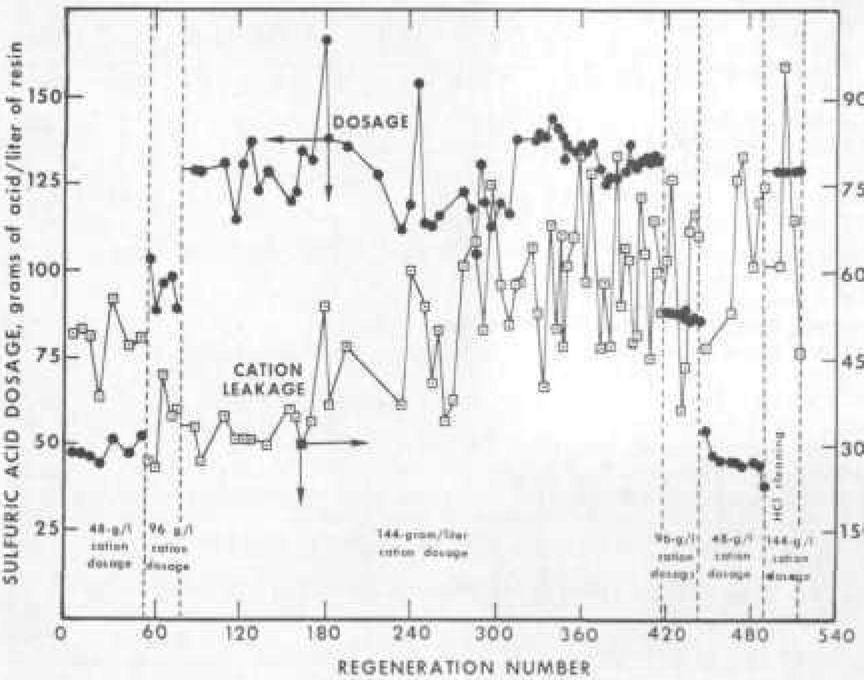

Figure 5. Relationship between cation dosage and leakage during the EPA studies.

Table III. Ion Exchange System Performance at 48 g/l Sulfuric Acid Dosage

	Cation	Anion
Regenerant	H_2SO_4	NaOH
Bulk regenerant cost, ¢/kg	7.72	11.0
Bulk solution concentration, wt %	93	20
Desired regenerant concentration, wt %	2.0	3.0
Desired dosage, grams of regenerant/liter of resin	48	40
Desired dosage, pounds of regenerant/ft^3 of resin	3	2.5
Influent load, mg/l as $CaCO_3$	2710	1770
Effluent load (leakage), mg/l as $CaCO_3$	780	0
Effective removal, mg/l as $CaCO_3$	1930	1770
Average actual dosage, grams of regenerant/liter of resin	45	44
Average actual regenerant concentration, wt %	1.95	3.71
Exchanger capacity, grams/liter of resin as $CaCO_3$	27.7	19.0
Exchanger capacity, kilograins/ft^3 of resin as $CaCO_3$	12.1	8.3
Regenerant utilization efficiency, %	60	34
Regenerant cost, ¢/m^3	39	98
Regenerant cost, ¢/1000 gal	150	370
Total volume to waste, liters/regeneration	6400	3280

Present studies are investigating the long-term effects of the iron precipitation on the anion resin. After 400 regeneration cycles to date, no effects are apparent. The use of the low-pH cation effluent for backwashing appears to remove substantial quantities of iron during each regeneration cycle.

Table IV. Ion Exhcnage System Performance at 96-Grams/Liter Sulfuric Acid Dosage

	Cation	Anion
Regenerant	H_2SO_4	NaOH
Bulk regenerant cost, ¢/kg	7.72	11.0
Bulk solution concentration, wt %	93	20
Desired regenerant concentration, wt %	2.0	5.0
Desired dosage, grams of regenerant/liter of resin	96	40
Desired dosage, pounds of regenerant/ft^3 of resin	6	2.5
Influent load, mg/l as $CaCO_3$	2410	1730
Effluent load (leakage), mg/l as $CaCO_3$	650	0
Effective removal, mg/l as $CaCO_3$	1730	1730
Average actual dosage, grams of regenerant/liter of resin	88	46
Average actual regenerant concentration, wt %	1.92	4.77
Exchanger capacity, grams/liter of resin as $CaCO_3$	29.2	26.5
Exchanger capacity, kilograins/ft^3 of resin as $CaCO_3$	12.7	11.6
Regenerant utilization efficiency, %	33	46
Regenerant cost, ¢/m^3	59	67
Regenerant cost, ¢/1000 gal	230	250
Total volume to waste, liters/regeneration	8720	2890

Table V. Ion Exchange System Performance at 144-Grams/Liter Sulfuric Acid Dosage

	Cation	Anion
Regenerant	H_2SO_4	NaOH
Bulk regenerant cost, ¢/kg	7.72	11.0
Bulk solution concentration, wt %	93	20
Desired regenerant concentration, wt %	2.0	5.0
Desired dosage, grams of regenerant/liter of resin	144	40
Desired dosage, pounds of regenerant/ft^3 of resin	9	2.5
Influent load, mg/l as $CaCO_3$	2480	1800
Effluent load (leakage), mg/l as $CaCO_3$	520	0
Effective removal, mg/l as $CaCO_3$	1960	1800
Average actual dosage, grams of regenerant/liter of resin	129	46
Average actual regenerant concentration, wt %	1.95	4.94
Exchanger capacity, grams/liter of resin as $CaCO_3$	29.4	29.1
Exchanger capacity, kilograins/ft^3 of resin as $CaCO_3$	12.8	12.7
Regenerant utilization efficiency, %	22	51
Regenerant cost, ¢/m^3	91	63
Regenerant cost, ¢/1000 gal	350	240
Total volume to waste, liters/regeneration	10,270	2810

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Table VI. Summary of Ion Exchange System Chemical Analyses[a]

Sample	Cond	Acid Alk	pH	Ca	Mg	Total Iron	Fe^{2+}	Na	Al	Mn	SO_4	TDS	Exchangeable Cations
Operation at 48-g/l (3-lb/ft^3) Dosage of Sulfuric Acid													
Raw feed	2870	410	4.9	400	110	210	190	360	9.3	5.0	2600	3690	2670
Cation eff.	8890	1780	1.54	42	12	23	22	260	0.6	0.6	2460	2790	760
Anion eff.	1230	280	9.4	38	12	3.1	0.3	320	0.1	0.4	610	980	860
Operation at 96-g/l (6-lb/ft^2) Dosage of Sulfuric Acid													
Raw feed	2870	410	5.1	330	110	200	190	340	8.7	5.0	2430	3410	2410
Cation eff.	8910	1730	1.55	29	6.0	14	13	240	0.6	0.3	2380	2670	650
Anion eff.	1370	340	9.3	21	5.3	2.4	0	380	0.3	0.2	570	970	890
Operation at 144-g/l (9-lb/ft^3) Dosage of Sulfuric Acid													
Raw feed	2790	430	5.0	340	110	210	200	350	7.8	5.2	2470	3500	2480
Cation eff.	9700	2000	1.58	24	5.6	16	13	190	0.7	0.8	2280	2550	520
Anion eff.	1430	290	9.5	19	4.5	1.4	0	400	0.5	0.2	730	1150	950

[a] All units are mg/l except for conductivity (μmho/cm) and pH. Acidity, alkalinity and exchangeable cations are expressed as $CaCO_3$.