Ion Exchange Processes for the Reclamation of Acid Mine Drainage Waters

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■ A 3000-p.p.m. (as $CaCO_3$) synthetic acid mine drainage water (AMD) may be processed to yield a water of quality suitable for industrial, agricultural, and domestic purposes. A basic process, possessing considerable flexibility, has been developed, which our laboratory studies show to be practical. It is based on the use of the conventional gel anion exchange resin, Amberlite IRA-68, which, used in a column operation, functions in the bicarbonate cycle. The effluent water is aerated and subsequently clarified to give useful water, whose quality may be further improved through lime softening prior to clarification. In the clarification step, improved clarification and sedimentation rates may be obtained using an anionic polyelectrolyte such as Primafloc A-10.

The discharge of acid mine drainage (AMD) waters from coal mines has received considerable attention within recent years. The seriousness of the problem is reflected by numerous laws being enacted on federal, state, and municipal levels. Under the current Pennsylvania Clean Streams Laws, after January 1, 1967, discharge of AMD waters into streams or other waterways is limited to waters that have an iron content below 7 p.p.m. and a pH between 6 and 9. It is estimated that at least 80% of all the mine water effluents in Pennsylvania must be subjected to some sort of treatment before discharge to meet state requirements. The mine water drainage problem is nothing new; it has existed ever since coal mining operations were first begun several centuries ago. The AMD waters present a serious pollution problem which has been increasing because of the existence of an ever larger number of mines, operational and abandoned in the coal mining regions. In effect, the problem is not limited to the United States. Besides Ohio, West Virginia, and Pennsylvania, Western Europe (Wales, the Ruhr, etc.) is plagued with a similar problem. If one were to add to the list the coal mining regions located in the Eastern European countries, the world-wide seriousness of the pollution problem that exists would be greatly magnified. In the Pennsylvania area alone, close to 1.4 billion gallons of acid mine waters are discharged daily.

The extent to which AMD waters become a source of pollution is variable. Though it is difficult to define a typical mine water, one feature common to practically every mine water is its sulfate content. Both acidic and alkaline mine drainage waters occur, though acid waters predominate and cause the greatest inconveniences. The presence of sulfate in AMD waters arises principally from the oxidation of inorganic sulfur-containing substances found in the seams of the mines; pyrite (FeS_2) is one of the principal constituents. When the pyrites come into contact with water in the presence of air the following reaction takes place:

$$FeS_2 + H_2O + 3\tfrac{1}{2}\, O_2 \rightarrow FeSO_4 + H_2SO_4$$

Upon being discharged into streams, further oxidation unavoidably occurs:

$$2\, FeSO_4 + H_2SO_4 + \tfrac{1}{2}\, O_2 \rightarrow Fe_2(SO_4)_3 + H_2O$$

The ferric sulfate so produced hydrolyzes readily (pH 3) to give:

$$Fe_2(SO_4)_3 + 6\, H_2O \rightarrow 2\, Fe(OH)_3 \downarrow\ + 3\, H_2SO_4$$

The ferric hydroxide from the hydrolysis reaction is insoluble and is deposited along banks and beds of streams. The sulfuric acid from the hydrolysis reaction then becomes the main source of pollution. It reduces the natural alkalinity of streams and may damage aquatic animal and vegetable life. The pH of the waters is also decreased and there usually is an accompanying increase in the total water hardness. Consequently, water treatment costs are increased if these waters are processed for domestic or industrial use.

The concentration and types of ions found in AMD waters depend on the geological composition of the coal seam. Among other factors, volume and residence time of the waters in the mines, the original ionic composition of the waters before entering the mines, and flow rate become important variables influencing the compositional character of the waters. Besides ferrous ions, originating from the pyrites, AMD waters usually abound in Ca^{+2}, Mg^{+2}, and Al^{+3}. Also found in lesser quantities are manganese and silicate ions. The free mineral acidity of "acid" mine waters, contrary to general belief, is very low, if any acid is present. The acidity values usually reported in reference to a particular AMD water are in actuality a measure of the acidity contributed to the waters by the total dissolved ionic species and not solely of the dissolved free acids.

Methods for Treating AMD Waters

Numerous methods and approaches have been suggested, and some practiced. Recognizing the active role of oxygen (oxidation) in polluting the mine waters, the technique of sealing off abandoned mines (mine sealing), so as to exclude oxygen from the mines, has been practiced with varying degrees of success. Though oxidation is retarded and minimized in many instances, the technique has not generally been effective, especially where the coal seam is above drainage level. Methods that probably have received the greatest attention in recent years are based on the chemical neutralization of the

AMD waters themselves. Neutralization techniques, in general, leave much to be desired. Besides the cost aspect, the processed waters are suitable for neither industrial nor domestic use. Neither the sulfate nor the calcium content of the AMD water is reduced to any significant degree. Actually, in most cases, if lime is employed, the calcium content increases because of the solubility of $CaSO_4$. Most neutralization processes only reduce the acidity, iron, and heavy metal content of the mine water, making it acceptable for discharge into streams, thus satisfying state requirements.

Since iron in acid mine water contributes heavily to pollution, several investigators have been concerned principally with the removal of iron rather than total or partial deionization of the acid mine waters. Simpson and Rozelle (1965) briefly discussed methods of removing iron from solution: precipitation (neutralization), electrolysis, aeration-filtration, and ultrasonic methods. They also investigated the use of ozone on both synthetic solutions and actual AMD waters. A combination ozone-activated carbon process is currently in use for removing iron and manganese from Rhine river water (Schenk, 1962). Treatment with ozone oxidizes iron(II) to (III) and manganese to permanganate. A layer of activated carbon is then used to filter out the hydrous iron(III) oxide and reduce the permanganate to dihydroxymanganese(IV) oxide, which may also be filtered out. The iron and manganese oxides can then be backwashed from the activated carbon into a settling basin. Lowell *et al.* (1965) have also taken the neutralization approach, suggesting the use of coal, fly ash, red dog, preparation plant refuse, waste products from the lime-consuming industries, and limestone for this purpose. Two United States patents (Magill, 1941; Rodman, 1933), which were issued in the middle thirties and early forties, make claim to the use of materials comprising coal and carbonaceous coke alone or in conjunction with inorganic chemicals for treatment of waters to render them potable. Using these coal materials, Lowell *et al.* found that the pH of acid mine waters could be increased and the acidity and iron content decreased. However, the response of different coals varied widely and sulfur was not removed from the aqueous system despite changes in pH, acidity, or iron content. Other methods such as flash distillation and electrodialysis have been suggested, but the practicability and economics of such processes are highly questionable.

Ion Exchange Process

The use of weak base resins such as Amberlite IRA-68, operated conventionally in the free base cycle, is not a practical system for processing an AMD water, since hydrous metal oxide is unavoidably precipitated in the resin beds during the anion exchange neutralization. On the other hand, the use of the weak base resin operated in the bicarbonate cycle circumvents this problem. In the process, advantage is taken of the fact that the metal sulfates, which usually represent almost the entire soluble anion content of typical AMD waters, are readily converted to the soluble bicarbonates, with subsequent deposition of a significant portion of the metallic ions as the insoluble hydrous oxides by the ion exchange of the AMD waters with Amberlite IRA-68 operated in the bicarbonate cycle. The following conversion occurs:

$$M_x(SO_4)_x + 2\ RHCO_3 \rightleftharpoons R_2SO_4 + M(HCO_3)_x$$

where

$$R = \text{Amberlite IRA-68}$$

$$M = Fe^{+2}, Al^{+3}, Mn^{+2}, Ca^{+2}, Mg^{+2}, \text{etc.}$$

Upon aeration of the effluent waters, carbon dioxide is expelled, precipitating iron, aluminum, and manganese as the insoluble hydrous oxides. A certain portion of the calcium and magnesium is also coprecipitated or occluded with the hydrous oxides as $CaCO_3$ and $Mg(OH)_2$. Ferrous and any other easily oxidizable ions present in solution are also oxidized, while the bulk of the calcium and magnesium remains solubilized as the bicarbonates. In essence, what remains after aeration is a bicarbonate water (pH 8.0 to 8.2) containing calcium and magnesium hardness. Should further deionization be required, a cold lime-softening treatment at this point is rather effective. Lime treatment of the aeration waters results essentially in the following reaction:

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

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

After lime treatment, a complete deionization will not be achieved, since $CaCO_3$ and $Mg(OH)_2$ both have limited solubilities in water. After aeration or after lime treatment, should this step be made an integral part of the process, clarification of the waters is facilitated through the use of an anionic polyelectrolyte. The over-all process is diagramatically represented in Figure 1.

As in other AMD reclamation processes, the problem of sludge disposal is always present. The goal then is to obtain as low a volume of sludge and as great a recovery of water as possible. It has been demonstrated, at least on a laboratory scale, that the volume of sludge produced by the proposed ion exchange process is substantially less than obtained during the lime-neutralization treatment of an identical synthetic AMD water. As a result, even though the ion exchange process does not completely eliminate the sludge problem, it does go a long way toward reducing the disposal problem. Since a smaller amount of sludge is produced, less lagooning area will be necessitated, should lagooning be a preferred disposal practice. Should the sludge be combined with coal refuse, the coal refuse requirements will be considerably reduced, as would be the abandoned mine space required for disposal by this alternative means.

Experimental

Amberlite IRA-68 (Rohm and Haas Co.) is the anion exchange resin of choice in the process, since it may be effi-

Table I. Synthetic AMD Water

pH	3.1
Sp. resist., ohm cm.	310
Ca^{+2}, p.p.m. as $CaCO_3$	964
Mg^{+2}, p.p.m. as $CaCO_3$	480
Fe^{+2}, p.p.m. as $CaCO_3$	895
Al^{+2}, p.p.m. as $CaCO_3$	556
Mn^{+2}, p.p.m. as $CaCO_3$	91
Free mineral acidity, p.p.m. as $CaCO_3$	118
SO_4^{-2}, p.p.m. as $CaCO_3$	3104

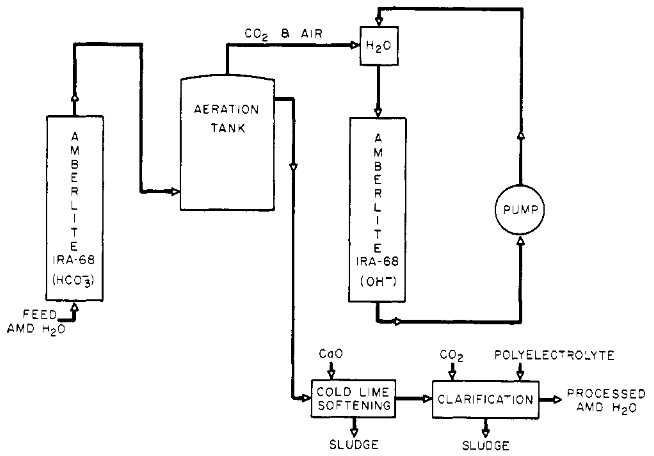

Figure 1. IER process for treatment of AMD waters

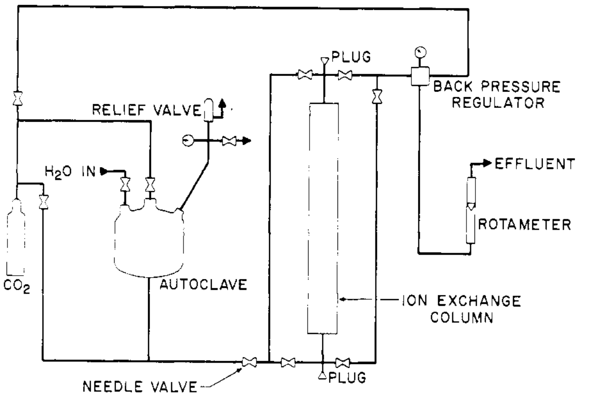

Figure 2. Schematic drawing of pressurized ion exchange system for treatment of AMD water

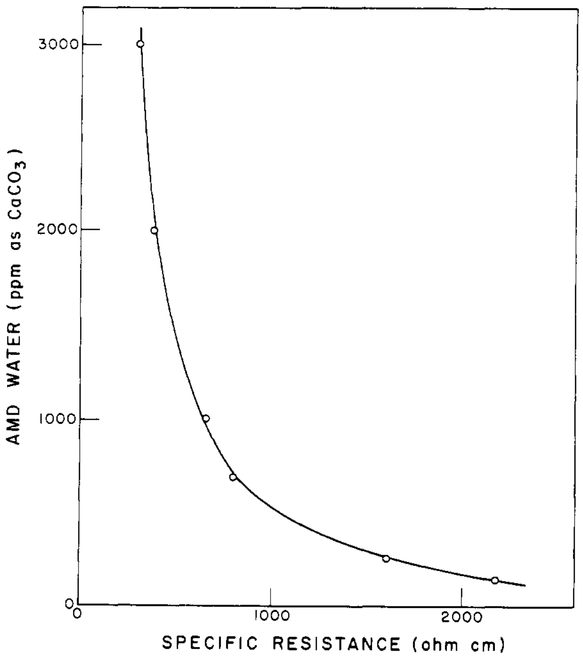

Figure 3. Standard curve relating specific resistance and total dissolved solids of synthetic AMD water

ciently converted to the bicarbonate form using a carbonated water. It is a weak polyamine anion exchange resin. The particular resin employed in our studies had a volume exchange capacity of 1.63 meq. per ml.

As the working solution in the process studies, a synthetic AMD water was prepared which was considered to be fairly representative of typical AMD waters commonly encountered in the field. In Table I are listed the compositional features of the water, pH, and specific resistance.

Stability of the water was excellent for as long as 3 to 4 weeks if the water was initially prepared to contain some free mineral acidity. No detectable change in pH, specific resistance, or total dissolved solids was apparent over this period. A water prepared without any significant free mineral acidity (pH 3.6), on the other hand, showed considerable instability after only a few days, then became discolored (yellow-brown) and considerable finely dispersed turbidity particles were evident.

Apparatus

Since use of pressurized carbonated water allows a greater solubilization and effective utilization of carbon dioxide during the carbonation step of the alkalization operation, a pressurized ion exchange unit was used to convert Amberlite IRA-68 to the bicarbonate form and alkalize the acid mine drainage waters. The pressurized alkalization unit is schematically diagrammed in Figure 2. The configuration of the equipment allows either conventional or upflow operation of the ion exchange column during the exhaustion cycle and for either internal (carbonation) or external (NH_4OH) regeneration. The column was approximately 36 inches long and had an internal diameter of 1 inch. It was adapted with two stainless steel fine wire mesh screens at both ends. To minimize obstruction of the screen openings and loss of resin, the resin bed consisted of a +40-mesh (U.S. Standard sieve) resin cut of Amberlite IRA-68. Using a 200-ml. resin bed volume, enough head room was available in the column to allow for at least a 100% expansion of the bed during the upflow exhaustion operation. When the resin needed to be regenerated with NH_4OH, the column could be isolated from the rest of the system by manipulating the appropriate valves. Two plugs at the end of the column were removed and the ammonia regeneration could then be performed by gravity. To convert the resin to the bicarbonate form, 2-liter quantities of water were introduced into the autoclave, saturated with CO_2 gas at 75-p.s.i. pressure, and then passed (downflow) through the pressurized column using a 50-p.s.i. CO_2 head pressure. Once regenerated, the AMD water could be introduced into the autoclave and in turn passed upflow through the column under a 50-p.s.i. CO_2 head pressure.

Analysis

The unit operations of the over-all process were followed by pH, specific resistance, alkalinity, or a combination of these. Specific resistance and alkalinity measurements were particularly useful in checking the effectiveness of the treatments at various stages of the process. Specific resistance measurements gave an approximate measurement (±10%) of the total dissolved solids still remaining in the processed waters. A plot of specific resistance *vs.* total dissolved solids (as $CaCO_3$) (Figure 3) was prepared by making appropriate dilutions of the synthetic AMD water with deionized water and then measuring the specific resistance of the diluted samples. Alkalinity measurements gave a means of following the extent of the $SO_4^{-2} \rightarrow HCO_3^{-1}$ conversion during the alkalization step.

Total cations remaining in the final processed waters were obtained by an ion exchange procedure by passing a water sample through a small column containing Amberlite IR-120 (H), a sulfonic cation exchange resin. After the effluent water from the column had been collected, the acidity generated was titrated to the methyl orange end point with standard NaOH and the titration value in turn related to the metal sulfate (and carbonate) content of the original sample. A second sample of the processed water was titrated with acid (M.O. end point) to obtain the metal bicarbonate alkalinity. The total cations in the processed water were equal to the summation of these two values. Total hardness and total calcium were determined by the standard EDTA titration. Total magnesium was obtained from the difference between the two values and consequently magnesium values reported may not be fully reliable. Iron, aluminum, and manganese were measured using specific spectrophotometric procedures. Though sulfates were not determined *per se*, the maximum level present in a particular water could be estimated, being no greater than the total cations determined by the ion exchange technique using Amberlite IR-120 (H).

Process Studies

In the initial phase of the study, Amberlite IRA-68 was used to convert the metal sulfates of the synthetic AMD water to the soluble bicarbonates, using the pressurized unit described. Prior to treatment of the AMD water, the Amberlite IRA-68 (free base form) was converted to the bicarbonate form using an excess volume [(in our laboratory studies, 30 bed volumes (BV)] of D.I. (deionized) water, previously saturated with CO_2 at 75 p.s.i. After conversion of the resin to the bicarbonate form, alkalization ($SO_4^{-2} \rightarrow HCO_3^{-1}$ conversion) of the AMD water was carried out upflow at a flow rate of 2 gallons per cu. foot per minute. The upflow operation minimized the deposition of precipitates that could have formed had some of the resin sites still have been in the free base form after the carbonation step. The effluent waters emerging from the ion exchange column were collected and aerated vigorously for 1 hour or less—that is, until the pH of the slurries rose above 8 and remained essentially constant with continued aeration. The red-brown liquid slurries that resulted were clarified at this point or processed further by subjecting them to a lime-softening treatment.

In Table II are listed alkalinity data obtained during the exhaustion cycle and other pertinent information pertaining to a typical run. The fact that the level of alkalinity formed during the run was less than the influent concentration does not mean that the conversion was incomplete; however, as the effluents were collected some decomposition of the ferrous bicarbonate occurred [$Fe(HCO_3)_2 \rightarrow 2\ CO_2 + Fe(OH)_2$], resulting in a loss of alkalinity.

Three composite samples of the fractions collected from the Amberlite IRA-68 column were prepared. Fraction 1 was a composite of the first 28 bed volumes, Fraction 2 the first 32 BV, and Fraction 3 all 36 BV collected. These samples were then further processed (aeration, lime softening, and clarification-sedimentation). The samples were aerated for 75 minutes, and then limed for 1 hour at room temperature, using a quantity of lime corresponding to the residual M.O. alkalinity present in samples of the clarified waters after the aeration operations. Evaluation data were obtained for the aerated and lime-softened slurries after clarifying each with the aid of a few parts per million of Primafloc A-10. The data are reported in Table III.

The effect of using different levels of lime during lime softening of the aerated slurries was investigated. The completeness of the liming operation was determined when quantities

Table II. Alkalization of AMD Water with Amberlite IRA-68 (HCO_3^-)

Resin bed volume. 200 ml.
Bed height. 18 inches

CO_2 driving pressure. 50 p.s.i.
Exhaustion flow rate. 2 gal./cu. ft./min.

Bed Volumes Collected	M.O. Alkalinity, P.P.M. as $CaCO_3$
1–4[a]	1350
5–8	2250
9–12	2230
13–16	2230
17–20	2280
21–24	2290
25–28	2290
29–32	1100
33–36	0

[a] Contains approximately 1½ BV of sweetening-off carbonated water from column and lines.

Table III. Evaluation Data for Processed AMD Waters

After aeration	28-BV Composite	32-BV Composite	36-BV Composite
pH	8.45	8.30	8.0
Sp. resist., ohm cm.	1320	1260	880
M.O. alkalinity, p.p.m. as $CaCO_3$	420	420	300
SO_4^{-2}, p.p.m. as $CaCO_3$	0	. . .	<630
Ca^{+2}, p.p.m. as $CaCO_3$	390	420	680
Mg^{+2}, p.p.m. as $CaCO_3$	50	40	40
After lime softening			
pH	8.80	8.65	8.20
Sp. resist., ohm cm.	3600	2000	1160
M.O. alkalinity, p.p.m. as $CaCO_3$	180	170	70
SO_4^{-2}, p.p.m. as $CaCO_3$	0	<125	<375
Ca^{+2}, p.p.m. as $CaCO_3$	160	290	470
Mg^{+2}, p.p.m. as $CaCO_3$	5	10	10

Table IV. Processed Amberlite IRA-68 (HCO_3) Waters as a Function of Lime-Softening Level

Lime used, % of residual alk. after aeration	25	50	100
pH	8.00	8.10	8.20
Sp. resist., ohm cm.	850	960	1160
M.O. alk., p.p.m. as $CaCO_3$	280	190	70
M.O. alk. removed, %	18	44	80

Table V. Primafloc A-10 Flocculation Tests

Primafloc A–10 Dosage, P.P.M.	Rate,[a] Lb./Ton	Lb. of Primafloc A–10/ 1000 Gal.	Remarks
Aerated Composite, 36 BV Aerated Solids, 2600 P.P.M.			
0.5	0.38	0.0042	Small flocs, slight haze
1.0	0.77	0.0083	Fair flocs and settling, sl. haze
3.0	2.31	0.0249	Good flocs and settling, clearer
3.5	2.69	0.0290	Very good flocs and settling; clear
4.0	3.08	0.0332	Optimum, excellent floc and clarity
4.5	3.46	0.0374	Excellent floc and clarity
Lime-Softened Composite, 36 BV (Lime Used Equivalent to 25% of Measured Alkalinity after Aeration) Limed Solids, 2850 P.P.M.			
0.5	0.351	0.0042	Some fine flocs, sl. haze, good settling
1.0	0.702	0.0083	Large flocs, sl. haze, good settling
1.5	1.053	0.0125	Very good flocs, clear, very good settling
2.0	1.404	0.0166	Optimum, excellent clarity and settling
3.0	2.106	0.0230	Excellent clarity and settling
4.0	2.808	0.0332	Excellent clarity and settling
Lime-Softened Composite, 36 BV (Lime Used Equivalent to 50% of Measured Alkalinity after Aeration) Limed Solids = 3020 P.P.M.			
0.5	0.331	0.0042	Good flocs, sl. haze, good settling
1.0	0.662	0.0083	Very good flocs, sl. haze, very good settling
1.5	0.993	0.0125	Optimum, excellent clarity and settling
2.0	1.324	0.0166	Excellent clarity and settling
Lime-Softened Composite, 36 BV (Lime Used Equivalent to 100% of Measured Alkalinity after Aeration) Limed Solids, 3290 P.P.M.			
0.5	0.304	0.0042	Very good flocs, sl. haze, very good settling
1.0	0.608	0.0083	Optimum, excellent clarity and settling
2.0	1.216	0.0166	Excellent clarity and settling

[a] Pounds of flocculant per ton of solids

of lime corresponding to 25 and 50% of the residual alkalinity were used (Table IV). Prior to the lime-softening treatments, a clarified portion of the aerated slurry exhibited a pH of 8.0, a specific resistance of 880 ohm cm., and a M.O. alkalinity value of 340 p.p.m. as CaCO$_3$.

An almost linear relationship exists for the amount of alkalinity removed *vs.* the level of lime employed when lime is used in quantities below the stoichiometric (100%) residual alkalinity value during the lime-softening operations.

Clarification-Sedimentation

During the clarification of the slurries that result from either the aeration or lime-softening step, clarification and sedimentation rates are significantly improved when an anionic polyelectrolyte is employed. Primafloc A-10 (Rohm and Haas Co.) was found to be a most effective flocculant for this purpose. In Table V, flocculation data obtained during treatment of the 36-BV composite of Amberlite IRA-68 (HCO$_3$) processed AMD water (Table III) are summarized, with data for flocculation tests performed on the aerated slurries with and without lime softening. In the case of the lime-softened slurries, flocculation tests were conducted on the slurries previously lime-softened with quantities of lime equivalent to 25, 50, and 100% of the M.O. alkalinity originally present in the aerated slurries (Table IV). The polyelectrolyte dosages are the levels of flocculant used per total volume of slurry. During the tests, Primafloc A-10 was used as a 0.1% active (sodium salt) solution in all cases.

Larger optimum dosage levels of Primafloc A-10 are required for the aerated slurries than the limed slurries (Table V). This is to be expected, since the effectiveness of Primafloc A-10, and of most other anionic polyelectrolytes, improves with increased suspended solids content and pH.

Since the existence of a sludge disposal problem is recognized in the case of direct lime neutralization methods for the processing of AMD waters, the amount of sludge resulting during a typical ion exchange resin process run was measured, primarily to ascertain whether the ion exchange resin process offers any improvement over the direct lime neutralization techniques by producing a smaller amount of sludge. Accordingly, 100-ml. volumes of Amberlite IRA-68–treated waters, aerated and lime-softened at various levels with lime, were treated with Primafloc A-10 and allowed to settle in graduated cylinders. For comparison, additional AMD water was treated by the direct lime neutralization method at pH 6.6, 7.3, and 8.2 with subsequent aeration. The aerated slurries (100-ml. volumes) were in turn treated with Nalco 670, a nonionic flocculant especially effective as a settling aid for direct lime-treated AMD waters, and allowed to settle likewise in graduated cyclinders.

In Table VI, the time required for 50% of the sludge to settle is recorded along with the per cent volume of sludge that settled out after a 24-hour period.

Table VI. IER and Lime Neutralization Processes Sedimentation Comparative Data

Process	Time, Hr., 50% Settling	Final Sludge Volume, Vol. %
IER		
No lime	<0.30	4.5
50% lime	<0.30	5.5
100% lime	<0.30	6.0
Lime neutralization		
pH = 6.6	≅1.00	23.5
pH = 7.3	≅1.00	24.0
pH = 8.2	≅1.00	26.0

Though some increase in sludge volume resulted with the use of Primafloc A-10 (IER process), the sludge volume obtained was still significantly less than found through direct lime neutralization. In fact, a few laboratory scale continuous runs have demonstrated that if the aerated waters from the ion exchange process are transferred to a settling tank and only the overflow waters flocculated using Primafloc A-10, the volume of sludge that results (settling tank and flocculation tank) is essentially equal to the sludge volume obtained had no flocculant been employed (approximately 3%).

Regeneration

The Amberlite IRA-68 resin, previously exhausted during the treatment of 36 BV of AMD water, was subsequently regenerated. To convert the resin back to the free base form, a quantity of 1*N* NH_4OH solution was used which corresponded to a 50% excess of the resin exchange capacity utilized during the $SO_4^{-2} \rightarrow HCO_3^{-1}$ exchange. To obtain an accurate measurement of the capacity realized during the treatment of the AMD water, the total regeneration effluent consisting essentially of NH_4OH and $(NH_4)_2SO_4$ was collected. By passing an aliquot sample through a small column of Amberlite IR-120(H) the amount of H_2SO_4 generated was determined by titration and related directly to the SO_4^{-2} content displaced from the Amberlite IRA-68 during the ammonia regeneration.

After converting the resin to the bicarbonate form, a second alkalization cycle was performed to ascertain whether or not the resin had been fully regenerated. In Table VII, the data obtained for the two alkalization runs are compared. The column capacities reported were measured experimentally using the ion exchange technique described.

Though lime may not be used directly to regenerate the sulfate-exhausted Amberlite IRA-68 due to $CaSO_4$ formation, it may be used to recover ammonia from spent regenerant solution. The recovered ammonia, containing from 1.0 to 1.5 grams of soluble $CaSO_4$ per liter, may be reconstituted and used effectively for additional regenerations. In Table VIII are reported alkalization data for both fresh resin and resin regenerated with lime-recovered ammonia.

Chemical Characteristics of Processed Water

The processed water obtained from several additional treatments of the AMD water contained from 150 to 600

Table VII. Comparative Data on Alkalization of AMD Water Using Amberlite IRA-68 (HCO_3^-)

Bed Volumes Collected	Alkalization Cycle 1	2
	Alkalinity, P.P.M. as $CaCO_3$	
1–4	1350	1490
5–8	2250	2290
9–12	2230	2270
13–16	2230	2330
17–20	2280	2280
21–24	2290	2280
25–28	2290	2280
29–32	1100	1390
33–36	0	0
Column capacity, kgr./cu. ft.[a]	33.9	33.0
Evaluation of Processed H_2O (after Aeration, Lime Softening, Clarification) (32-BV Composite)		
pH	8.65	8.20
Sp. resist., ohm cm.	2000	1650
M.O. alk., p.p.m. as $CaCO_3$	170	200
SO_4^{-2}, p.p.m. as $CaCO_3$	<125	<130
Ca^{+2}, p.p.m. as $CaCO_3$	290	420
Mg^{+2}, p.p.m. as $CaCO_3$	10	20
Total hardness, p.p.m. as $CaCO_3$	300	440

[a] Kilograins per cu. foot.

Table VIII. Comparative Data on Alkalization of AMD Water Using Amberlite IRA-68 (HCO_3^-) Regenerated with Fresh and Reconstituted Lime-Recovered NH_4OH

Bed Volumes Collected	Alkalization Cycle Fresh Resin	Regenerated Resin
	Alkalinity, P.P.M. as $CaCO_3$	
1–4	1700	1800
5–8	2200	2350
9–12	2280	2280
13–16	2250	2290
17–20	2290	2280
21–24	2280	2310
25–28	2300	2270
29–32	1380	1420
33–36	0	0

Table IX. Evaluation of Selected Processed Water Samples for Metallic Ions

Sample	Treatment	P.P.M. Al	Fe	Mn
1	Amberlite IRA-68 (HCO_3^-) treated; aerated, no lime	0.2	0.12	<0.05
2	Amberlite IRA-68 (HCO_3^-) treated; aerated, limed	0.5	<0.1	<0.05

p.p.m. of dissolved solids (as $CaCO_3$) in the case of waters clarified after aeration or after further processing (lime softening). In all cases, the predominant ions remaining solubilized in the processed waters were calcium, bicarbonate, and carbonate. Magnesium ions were present at a much lower concentration than calcium ions. When the alkalization treatment was not 100% complete, the processed waters contained varying quantities of sulfate ions. Processed waters characterized by pH values greater than 8.5 (due to excess lime during lime softening) also exhibited small levels of soluble calcium hydroxide. Essentially no iron, aluminum, or manganese was present, based on the analysis of a selected series of processed water samples. Values were well below 1 p.p.m. in the case of all three ions. Analytical data pertinent to typical samples have been tabulated in Table IX.

The samples in Table IX refer to the 36-BV composite of AMD water previously treated with Amberlite IRA-68 (HCO_3^-) (Table III). When the 28- and 32-BV composites of the same run were analyzed, aluminum was absent; the iron was less than 0.01 p.p.m. and the manganese less than 0.05 p.p.m.

Cost Estimate

The operating costs of the AMD water purification process based on the use of Amberlite IRA-68 have been calculated for plant sizes of 100,000 and 1,000,000 gallons per day.

For calculation purposes, it was assumed that the AMD had a 3000-p.p.m. SO_4^{-2} (as $CaCO_3$) content and that a 34-kgr. (as $CaCO_3$) per cu. foot capacity would be realized during alkalization. For the lime-softening operation, cost calculations, with regard to consumption of lime, were based on the assumption that approximately 15% (400 to 500 p.p.m.) of the influent SO_4^{-2} content would still be solubilized as alkalinity in the aerated slurries after aeration and an equivalent amount of lime corresponding to the residual solubilized alkalinity would be used during lime softening.

In Table X, the costs calculated for each of the individual phases of the operation are listed, including grand total cost values for both the 100,000 and 1,000,000 gallons per day installations.

Since the cost of the chemicals used greatly influences the operational costs, any chemical cost reduction due to availability or other factors will considerably improve the economics of the operation. For example, if CO_2 could be generated from the burning of coal at the actual operational site, the price of CO_2 could be as low as $20 per ton. Another important factor is the total anion content of the AMD water. With increased anion content, the length of the alkalization cycle will diminish and therefore more regeneration cycles will be needed per day, increasing daily processing costs. For economic reasons, therefore, the present AMD ion exchange process, based on the use of Amberlite IRA-68, should be limited to AMD waters characterized by anion contents below 4000 p.p.m. as $CaCO_3$.

Table X. Cost Estimate for AMD Water Reclamation Process

	$ Cost/1000 Gal.	
	100,000 gal./day	1,000,000 gal./day
Alkalization	0.285	0.246
Carbonation[a]	0.149	0.134
Degasification	0.009	0.003
Lime softening[b]	0.032	0.032
Clarification[b]	0.014	0.014
Grand total	0.489	0.429

[a] Includes CO_2 make-up.
[b] Chemicals only, does not include equipment.

Discussion

Since some precipitation may occur during alkalization it has been necessary to operate in an unconventional upflow manner during the ion exchange step. Amberlite IRA-68 has performed remarkably well under these conditions during numerous laboratory runs. No noticeable pressure drop nor deposition of precipitates into the resin bed has been experienced. In addition, essentially theoretical utilization of the resin exchange capacity (33 to 34 kgr. per cu. foot) has been achieved in each instance.

The total cost to process an average AMD water has been calculated to be well within the range of 25 to 50 cents per 1000 gallons, the actual cost depending primarily on regenerant costs, the quality of processed water desired, and the anion content of the AMD waters.

Disposal of the waste regenerant from the ion exchange unit might present a BOD problem unless the regenerant, consisting primarily of ammonium sulfate, can be used as a fertilizer or put to some other use. Recent experimentation has demonstrated that one way of circumventing the problem would be to treat the waste regenerant with lime, forming a $CaSO_4$ precipitate and NH_4OH. The precipitate would then be combined with the process sludge and the NH_4OH solution re-used during subsequent regenerations.

The process possesses much flexibility and a water of practically any desired quality may be obtained, something that direct lime neutralization methods have not achieved. For example, at a relatively insignificant increase in cost, the processed waters may be completely deionized by further subjecting them to a dealkalization treatment. Amberlite IRC-84, a weak cation exchange resin, is particularly useful for this purpose. In essence, this places the process in a unique position in the spectrum of mine effluent treatment systems now available to the coal mining communities.

Acknowledgment

The authors acknowledge the assistance of Thomas Doherty in conducting the experimental portion of this study.

Literature Cited

Lowell, H. L., Falconer, R. A., Lachman, R. I., Reese, R. D., "Control of Mine Drainage Pollution by Removal of Impurities from Drainage Streams," Symposium on Acid Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., **92-8** (1965).
Magill, R. R., U. S. Patent **2,251,748** (Aug. 5, 1941).
Rodman, H., *Ibid.*, **1,933,567** (Nov. 7, 1933).
Schenk, P., *Gas-Wasserfach* **103**, 791-8 (1962).
Simpson, D. G., Rozelle, R. B., "Studies on the Removal of Iron from Acid Mine Drainage," Symposium on Acid Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., **64-82** (1965).

Received for review December 1, 1966. Accepted March 9, 1967.