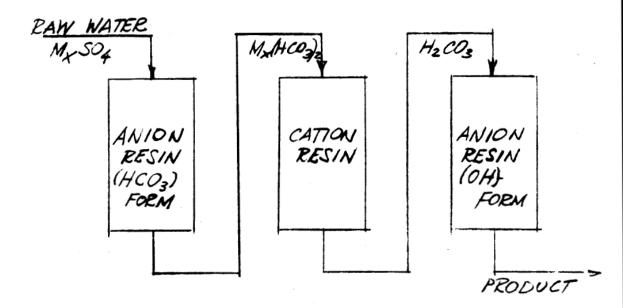
PROCESS DEVELOPMENT

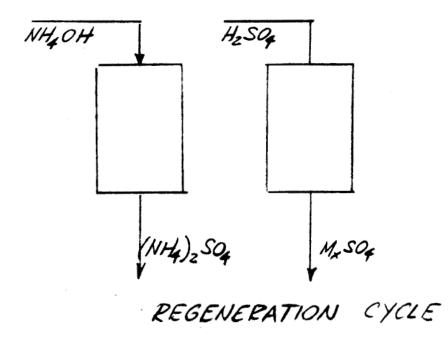
In 1962 R. Kunin and B. Vassiliou of Rohm and Haas first described a new ion exchange technique which utilized weak electrolyte resins. Typically these resins were used in a three bed system. The first and third beds contained weak base anion exchange resins and the middle bed contained weak acid cation exchange resin. The resin in the first column has previously been converted to the bicarbonate form and was therefore exchanging anions in the raw water for bicarbonates. The middle column was exchanging cations for hydrogen ions. In the last column weak base anion resin was converted from the free base form into the bicarbonate form. The process can be expressed by the following set of reactions:

$M_{x}SO_{4} + R_{A} (HCO_{3})_{2} \longrightarrow M_{x} (HCO_{3})_{2} + R_{A}SO_{4}$	(Anion exchange)
$M_x(HCO_3)_2 + 2R_cH \longrightarrow 2H_2CO_3 + 2R_cM_x$	(Cation exchange)
$R_A SO_4 + 2NH_4 OH \longrightarrow (NH_4)_2 SO_4 + R_A (OH)_2$	(Anion regeneration)
$2R_{c}M_{x} + H_{2}SO_{4} \longrightarrow M_{x}SO_{4} + 2R_{c}H$	(Cation regeneration)
$R_{A} (OH)_{2} + 2H_{2}CO_{3} - R_{A} (HCO_{3})_{2} + 2H_{2})$	(Anion alkalization)

Upon completion of the exhaustion cycle, the first unit is regenerated back to the free base form with ammonia, caustic or lime. The middle unit is converted back to the hydrogen form by regeneration with sulfuric or hydrochloric acid. Since the last column is now in the bicarbonate form, the flow pattern is reversed for the next cycle and the third column becomes the first column and the first column, now in the free base form, is converted to the bicarbonate form. The process is shown in Exhibit I.



EXHAUSTION CYCLE



19

EXHIBIT 1

The above process has been patented by Rohm and Haas and is offered for licensing under the name of "Desal Process." Its primary advantages over conventional ion exchange processes is that it utilizes low cost regenerants, that the rinse requirements are substantially lower and that regeneration efficiencies close to the minimum stoichiometric amounts can be obtained.

Further research by Kunin and F. Pollio of Rohm and Haas has indicated that a modification of the Desal Process can be applied to the treatment of acid mine waters. In this modification only a single column of the weak base anion exchange resin is utilized. Following regeneration with ammonia, the column is converted into the bicarbonate form with carbonic acid and acidic mine drainage water is then passed through this column to effect an exchange of sulfate and chloride ions for bicarbonate ions. In a subsequent aeration step the bicarbonate breaks down into the heavy metal hydroxide and carbonic acid. The latter is expelled from the water as carbon dioxide.

The hydroxides are largely insoluble and can be removed by settling. During the ion exchange process step, the service flow is in an expanded bed, upflow mode in order to minimize deposition of any precipitates that might be formed. This step must be performed under pressure to prevent the carbon dioxide from escaping and to maintain the bicarbonate concentration on the resin. The waste regenerant, primarily a weak solution of ammonium sulfate can either be sold for fertilizer or treated with lime to recover the ammonia. Ammonium sulfate has a relatively low market value. On the other hand, ammonia for regeneration is a major cost element of the process. This ammonia reuse step is the key to the economic feasibility of this ion exchange treatment process. The ammonia recovery operation produces a calcium sulfate precipitate which is easily dewatered and disposed by conventional means.

Some of the advantages of the modified Desal Process which make it attractive for the treatment of acid mine drainage are as follows:

1. High resin capacities are obtained with weak-base ion-exchange resins when treating sulfates. Amberlite IRA-93 capacities of 21 kgr/ft²

20

as CaC03 have been achieved with simulated and natural AMD waters. This compares with a capacity of 18 kgr/ft² when treating neutral salts when no free acid is present.

2. Conversion of dissolved heavy metals, iron, aluminum and manganese ions to their respective bicarbonates permits their precipitation and removal as hydroxides without need for liming.

3. Sludge volumes are less than obtained from direct liming because the sulfates are concentrated in the resin beds.

4. The product water is low in hardness and in total solids and can therefore be used as either municipal or industrial source of supply. 5.

Chloride ion removal and concentration is also effected. This is not accomplished by neutralization treatments.

6. Small amounts of turbidity can be tolerated by the resin without extensive pretreatment. This is due to the upflow expanded bed operation.