

1

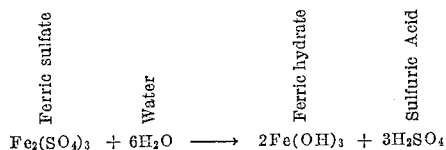
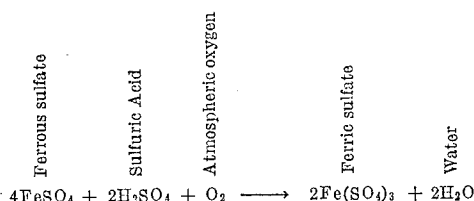
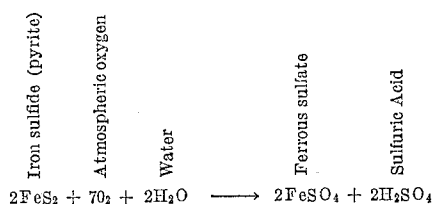
3,388,058

TREATMENT OF ACID MINE WATER WASTE
Louis F. Wirth, Jr., Western Springs, Ill., assignor to
Nalco Chemical Company, Chicago, Ill., a corporation
of Delaware
No Drawing. Filed Aug. 3, 1966, Ser. No. 569,840
9 Claims. (Cl. 210-32)

When coal deposits are exposed to natural weathering and erosion, the iron sulfides contained in the coal and adjacent strata oxidize to form new compounds, primarily ferrous sulfate and free sulfuric acid. The ferrous sulfate is then oxidized to ferric sulfate by means of oxygen in the atmosphere. In an excess of water, the ferric sulfate hydrolyzes to insoluble iron hydrates known as "yellow boy" and sulfuric acid. The above is accelerated by removal of the coal bed through mining whereby large surface areas are exposed to oxidation. Mining may also drain ground water from the surrounding strata and this seepage will dissolve the acid salts formed in the mine and transport them to the streams. The acid mine drainage problem is particularly present where there is extensive coal mining, an abundance of rainfall which produces large quantities of rainwater and run-off, a low natural alkalinity of streams and presence of pyrite in coal.

With more specific regard to this problem, coal associated with iron disulfide usually is isolated from oxygen and water from its natural environment in the earth. However, mining the coal seam removes support from the overlying strata, inducing cave-in. Water and air influx together with exposure of traditional acid-producing materials, co-act to produce the acidic waste waters. The problem is particularly severe when mining activity is ceased. In these abandoned mines, water continues to flow indefinitely. For example, in one small abandoned underground mine, it was found, via random sampling, that the total acid load, in terms of the mine discharge over a period of 182 days, was equal to 41 tons of sulfuric acid. The acid load for the entire year would equal approximately 80 tons, which acidity flowed directly into a major river.

The reactions which occur in formation of acid mine waters are not exactly known. However, the following reactions have been generally accepted as typical of the chemical change occurring in the coal seam itself and surrounding rock strata in presence of air and water.



Additional ions such as silica, aluminum, manganese, cal-

2

cium and magnesium are also present in a typical acid mine water, and these ions are thought to accelerate formation of acid. The above reactions generally occur when ground water percolates downward through the overburden of the mine, passes through the mining workings and then drains into streams or rivers.

As is readily apparent, the acid mine drainage causes a severe problem of pollution and particularly causes extensive fish kill. The drainage from mine sites usually reaches the larger rivers via small tributaries. In many states, the acidic mine drainage waters have been classified as an industrial waste and disposal of such waters into streams clean or polluted has been prohibited. Millions of gallons of mine water containing sulfuric acid, ferrous sulfate and ferrous hydroxide are discharged annually into bodies of water in varying amounts of acidity up to about 5,000 p.p.m. It is therefore evident that the problem is one of some magnitude.

A number of proposals have been made in an effort to overcome this problem. For example, it has been advocated that sufficient coal be permitted to remain in place to prevent cave-in. However, there is a severe economic loss in coal left behind. Also in many coal seams, systematic pulling of pillars and controlled caving yield the only practical method of relieving excessive rock pressures. The excavations, of course, materially contribute to the problem of production of acid mine waters.

Another proposal made involves sealing of abandoned mines to exclude air and prevent oxidation of sulfide material. However, the high infiltration rate and permeability of the overburden to water has made this suggestion a poor solution to the problem at hand.

It would be of extreme advantage to the art if a method were discovered of somehow treating acid mine discharge waters whereby particularly the iron and acidity were removed therefrom prior to discharge of these waste waters into streams or rivers. If such acid mine discharge waters could be somehow purified prior to drainage into major tributaries, the problem of water-pollution of many bodies of water could be overcome to a substantial degree.

Therefore, it becomes an object of the invention to purify acidic mine discharge waters containing iron and sulfuric acid impurities.

A specific object of the invention is to purify the above mine waters via a unique ion exchange system and thereby avoid pollution of bodies of water into which said mine waters generally feed.

In accordance with the invention, a method of purifying acidic mine discharge waters has been discovered. These waters which contain as impurities at least iron and sulfuric acid have been purified via the method of the invention by contact with ion exchange resins. More particularly, the discharge waters are purified by bringing them in contact with an anion exchange resin in the sulfate form, whereby the sulfuric acid content is reduced. The waters are also contacted with a cation resin having on its exchange sites cations selected from among calcium, magnesium, sodium and potassium which are capable of being replaced by iron ions whereby the iron content in the waters is reduced.

The contact of water with resins may be carried out in any sequence. That is, the water may be first contacted with the anion resin followed by treatment with cation resins. The reverse procedure may also be carried out. In yet another embodiment, a mixed bed of cation and anion resins may be utilized. The method of the invention is particularly adaptable to treating acidic mine discharge waters which have an iron content ranging from about 5 to about 5,000 p.p.m., expressed as Fe and a free mineral acid content of 1-5,000 p.p.m., expressed as CaCO_3 .

In a preferred embodiment, the free mineral acidity, chiefly sulfuric acid, is removed by a first contact with the

anion resin in sulfate form. The type of the anion resin may vary widely, and the resin itself may be either a strongly basic or weakly basic liquid or solid material. The primary requisite is that the anion exchanger be in sulfate form.

Preferred anion exchange resins used in the practice of the invention are strongly basic anion exchange resins, i.e. anion exchange resins which in the hydroxide form are capable of converting inorganic salts in aqueous solution directly to hydroxides. Thus, a strongly basic anion exchange resin is capable of converting an aqueous solution of sodium chloride directly to an aqueous solution of sodium hydroxide. A strongly basic anion exchange resin can also be defined as one which on titration with hydrochloric acid in water free from electrolytes has a pH above 7.0 when the amount of hydrochloric acid added is one-half of that required to reach the inflection point (equivalence point). A weakly basic anion exchange resin under the same conditions has a pH below 7.0 when one-half of the acid required to reach the equivalence point has been added. The strongly basic anion exchange resins which are available commercially are characterized by the fact that the exchangeable anion is a part of a quaternary ammonium group. The quaternary ammonium group has the general structure:



wherein R_1 , R_2 and R_3 represent alkyl or substituted alkyl groups, and X^- is a monovalent anion.

Examples of the strongly basic anion exchange resins which can be employed in the practice of the invention are those resins disclosed in U.S. Patents 2,591,573, 2,597,440, 2,597,494, 2,614,099, 2,630,427, 2,632,000 and 2,632,001.

Strongly basic insoluble anion exchange resins include reaction products of a tertiary alkyl amine and a vinyl aromatic resin having halo methyl groups attached to aromatic nuclei in the resin which resins are subsequently converted to the sulfite form. Another class of strongly basic anion exchange resins suitable for the practice of the invention are the reaction products of tertiary carbocyclic or heterocyclic amines and vinyl aromatic resins having halo methyl groups attached to aromatic nuclei in the resin which resins are subsequently converted to the sulfite form.

The vinyl aromatic resins employed as starting materials in making the anion exchange resins employed in the preferred practice of the invention are the normally solid benzene-insoluble copolymers of a monovinyl aromatic compound and a polyvinyl aromatic compound containing from 0.5 to 40% by weight, preferably from 0.5 to 20% by weight of the polyvinyl aromatic compound, chemically combined with 99.5% to 60% by weight of the monovinyl aromatic compound. Examples of suitable monovinyl aromatic compounds are styrene, alpha methyl styrene, chlorostyrenes, vinyl toluene, vinyl naphthalene, and homologues thereof, capable of polymerizing as disclosed, for example, in U.S. Patent 2,614,099. Examples of suitable polyvinyl aromatic compounds are divinyl benzene, divinyl toluene, divinyl xylene, divinyl naphthalene and divinyl ethyl benzene. These resins are halo methylated as described, for instance, in U.S. Patent 2,614,099, preferably to introduce an average of 0.2 to 1.5 halo methyl groups per aromatic nucleus in the copolymer and then reacted with a tertiary amine to introduce a quaternary ammonium anion exchange group. Examples of suitable tertiary amines are trimethyl amine, triethyl amine, tributyl amine, dimethyl propanol amine, dimethyl ethanol amine, methyl diethanolamine, 1-methylamino-2,3-propane diol, dioctyl ethanolamine, and homologues thereof.

The anion exchange resins can also be prepared by halogenating the molecule of the resin and then introducing an anion exchange group as described in U.S. Patent 2,632,000 and subsequently converting them to

the sulfite form, with or without admixture with the hydroxide form of the resin.

Specific anion exchange resins that can be used as starting materials in practicing the invention include Dowex SAR and Dowex SBR. Dowex SBR is a styrene-divinylbenzene resin containing quaternary amine ion exchange groups in which the three R groups are methyl groups. This resin consists of spherical particles of 20 to 50 mesh and containing about 40% water. The divinylbenzene content is approximately 7.5%. The total exchange capacity is approximately 1.2 equivalents per liter, wet volume. Dowex SAR is similar to Dowex SBR except that one of the methyl groups in the quaternary amine salt structure is replaced by a hydroxy ethyl group. Dowex SBR is somewhat more basic than Dowex SAR.

From a regeneration or conversion standpoint, the $HSO_3 \rightleftharpoons SO_3^-$ reaction is independent of the anion resin used. For this reason both strong base anion exchange resins and weak base anion exchange resins are contemplated within the scope of this invention. The commercially available products Dowex WGR and Dowex WBR are examples of polyamine-type weak base resins. Such resins usually contain a mixture of primary, secondary, and tertiary amine groups.

The cation exchange resins are employed to remove or reduce the iron content in the waste water. In one preferred embodiment, the cation resin is utilized subsequent to employment of the anion exchange resin described above. The cation resin should have on its exchange sites a cation selected from the group consisting of calcium, magnesium, potassium and sodium. Of these, it is most preferred that the cation resin be in calcium form. Use of such calcium form resin in an ion exchange process is believed to be unique, since the usual water-softening procedure involves the opposite from what is to be carried out here. That is, generally hardness such as calcium is removed from water via contact with cation exchange resin in alkali metal form such as sodium. In the instant invention, just the contrary is taking place; that is, the calcium is being exchanged for iron and hardness is being introduced into the mine water. However, introduction of hardness-containing constituents by calcium exchange into the treated water is not a drawback in the instant invention, since the purified water, when finally fed into a river or stream will be subsequently softened if utilized for consumer use. Thus, it is believed that this is the first use of the calcium form cation exchange resin as a means of purification of water.

The cation exchange resins themselves are known in the prior art. One of the most common types is a sulfonated resin. Nalcite HCR-W is a typical resin of this type, and is a sulfonated styrene divinyl benzene strongly acid cation exchanger of the type described in U.S. 2,366,007. Thus, all that is necessary in order to utilize this resin is to put it in a calcium or other suitable form.

Another suitable form of cation exchange resin is a sulfonate acid phenol-formaldehyde resin, such as a resin derived by condensing a phenolsulfonic acid with formaldehyde. In general, resins having a plurality of sulfonic acid groups are the most suitable cation exchange resins suitable for this invention. Synthetic zeolites may also be used in this step.

After a certain period of use, the anion resin becomes exhausted and regeneration is necessary. Any method of conventional regeneration of anion resins may be utilized, as long as the bisulfate form of the exhausted resin is converted to the useful sulfate form. One preferred method is to rinse the exhausted anion bed with water. The water can be flowed either downwardly or upwardly through the anion exchange resin. In a particularly preferred embodiment, the purified acid mine water is utilized as an anion exchanger regenerant, thus making the overall process more attractive economically.

The conversion of anion exchange resin bisulfate to the sulfate form can be accelerated by using an alkaline

rinse water, whether the source of water be the purified acid mine water or another source of rinse water. A greatly preferred alkaline compound used as the make-up for the alkaline rinse water is lime, preferably in slurry form. Other alkaline compounds may also be used such as, for example, ammonium hydroxide, sodium bicarbonate, sodium hydroxide, potassium bicarbonate and potassium hydroxide. The use of an alkaline compound accelerates the regeneration step, although untreated water may also be usefully employed.

Again, when the cation resin becomes exhausted, a regeneration step is also necessary. One mode of cation regeneration is treatment of the cation exchange resin with an aqueous sulfuric acid whereby a cation hydrogen form resin is realized. This resin is then put in an alkali metal or alkaline earth metal form. However, the most efficient way of carrying out the cation resin regeneration is by contact of the resin having a majority of its sites attached to iron ions with an alkaline earth or alkali metal salt or hydroxide. The most preferred procedure is to treat the exhausted cation exchanger with a source of calcium ions such as by treatment with calcium hydroxide or calcium chloride. The most efficient mode of regeneration is contact of the cation exchange resin with an aqueous solution of a calcium salt such as calcium chloride.

A greatly preferred system of purifying acid mine waters including regeneration of resins employed is as follows: A series of four reactors are provided. These contain anion resin, regenerant for anion resin, cation resin and regenerant for cation resin.

The regenerant reactor for the anion resin is first filled with a source of neutral water which can be periodically replenished with effluent from the service run of the cation exchange resin. To this water is then added lime, preferably in slurry form consisting of dissolved lime and lime suspended in aqueous medium. The lime slurry preferably has a concentration range of about 2,000 to 10,000 p.p.m., and most preferably 2,500 to 4,000 p.p.m., total alkalinity as CaCO_3 . After the anion exchange resin is exhausted, approximately $\frac{1}{2}$ of the lime to be utilized as regenerant is added to the neutral water and this regenerant solution is passed up-flow through the exhausted anion exchange resin. The effluent from the regenerant run is returned to the regenerant solution and the remainder of the lime slurry added to regenerant solution. The regenerant solution thereby becomes saturated with calcium sulfate which precipitates out of solution and is drawn off in some manner such as in form of a filter cake or sludge or slurry cake from a centrifugation operation. The calcium sulfate cake is then disposed of in some manner. The filtrate or concentrate is, of course, available for subsequent regenerations.

Again, the regenerant used for the cation exchange resin may be a source of neutral water. To this is added calcium chloride, and this calcium chloride solution is also flowed upward through the exhausted cation resin. The regeneration effluent is again added back to the reactor containing regenerant solution. To replenish the source of calcium, lime is added to the cation regenerant solution. This causes the iron now present to precipitate as an iron hydroxide. Generally, a source of oxygen is also added to this regenerant solution in order to convert the iron from ferrous to ferric form, thereby causing precipitation of the iron. The ferric hydroxide may then be used as a suitable source of iron in a steel making operation.

When additional water is needed to replenish the regenerant solutions, the purified acid mine water may be utilized. Thus, once the process has been set up, it may be run in a continuous manner without need to resort to fresh regenerant solutions upon each regeneration of anion and cation resin. As is evident, the process then is one which is extremely attractive both from technical and economic viewpoints.

The following example relates to a typical procedure of the invention in purifying acid mine water waste. It is understood, of course, that this example is merely illustrative and that the invention is not to be limited thereto.

EXAMPLE I

A synthetic test water was prepared to simulate the composition of a typical acid mine water. Analysis of this acidic waste water is as follows:

Free mineral acid (FMA) -----	880 p.p.m. as CaCO_3 .
Iron (total $\text{Fe}^{+2} + \text{Fe}^{+3}$) -----	516 p.p.m. as Fe.
Iron, Fe^{+3} -----	11 p.p.m. as Fe.
Calcium hardness -----	980 p.p.m. as CaCO_3 .
Sulfates, total -----	1920 p.p.m. as SO_4 .
Chloride -----	15 p.p.m. as NaCl.
Aluminum -----	24 p.p.m. as Al.
Manganese -----	16 p.p.m. as Mn.
Sodium -----	17 p.p.m. as CaCO_3 .
Magnesium -----	34 p.p.m. as CaCO_3 .
pH -----	2.15.

A 3 inch inner diameter tube was filled with 4 liters (0.141 cu./ft.) of a strong base anion resin (Dowex SBR) in sulfate form. The resin bed height was 35". The acid mine water was then flowed through the anion resins until exhausted. Random sampling of the effluent, throughout the bulk of the run, indicated that the free mineral acidity was reduced to essentially 0 p.p.m. The service run was carried out by passage of the acidic water downflow through the anion resin at a flow rate of 0.9 g.p.m. per cu. ft. resin at a temperature of 78°-80° F. Under these experimental conditions and operating with an acid water of 880 p.p.m. of free mineral acidity, a throughput capacity of 80-85 gallons of mine water per cu. ft. of resin was obtained. The run was terminated and resin regenerated when the effluent reached an acidity of 200-250 p.p.m. free mineral acid, expressed as CaCO_3 .

The effluent from the anion exchange resin was then passed through a 1500 ml. resin column of a strong acid cation exchanger completely in the Ca^{++} form at a flow rate of 2.4 g.p.m. per cu. ft. of cation resin (Dowex HCR-W). The capacity for iron was 0.814 pound of iron, expressed as Fe, per cu. ft. of cation resin.

When exhausted, the anion exchange resin was regenerated and put back in sulfate form by treatment with lime water. More specifically, the regeneration was carried out by first purifying the resin with 3.5 to 4 gallons of deionized water per cu. ft. resin to remove acid mine water entrapped in the resin column. Lime water containing 2250 p.p.m. of calcium hydroxide, expressed as calcium carbonate, was then passed upflow through the resin to obtain a 20% expansion or at a flow rate of 0.85 g.p.m. per cu. ft. of resin. Any excess lime water left in the column was displaced by downflow wash with 3.5 to 4 gallons of deionized waters before starting a new exhaustion run of acid mine water.

The iron exhausted cation resin was regenerated in the following manner. The resin was first purified with deionized water to a 50% expansion until all precipitated iron was removed. This iron was collected and analyzed: 0.017 pound of Fe was found. The resin was then regenerated with 50 pounds of calcium chloride per cu. ft. of resin, applied as a 10% solution of calcium chloride. This solution was passed through the resin at 0.6 g.p.m. per cu. ft. This amount of calcium chloride eluted 0.687 pound of iron per cu. ft. resin or 84.4% of the iron on the resin. The elution of total amount of iron on the resin was then contemplated by contact of the resin with 3 normal hydrochloric acid solution at 180° F. until no more iron was found in the effluent. The amount of iron removed in this step was 0.11 pound per cu. ft. resin.

In addition to removing iron, the process of the invention also removes other contaminant metal ions from acid mine water waste such as manganese and aluminum.

The invention is hereby claimed as follows:

1. A method of purifying acidic mine discharge water which contains as impurities at least iron and sulfuric acid which comprises bringing said water into contact with a strong base anion exchange resin in the sulfate form to reduce said sulfuric acid content, and with a cation resin having on its exchange sites cations selected from the group consisting of calcium, magnesium, potassium and sodium which are capable of being replaced by iron ions whereby said iron content in said water is reduced.

2. The method of claim 1 wherein the iron content in said mine water ranges from about 5 to about 5000 p.p.m., expressed as Fe, and said waters, also contain 1-5000 p.p.m. of free mineral acid, expressed as CaCO_3 .

3. The method of claim 1 wherein said contact is effected sequentially by treatment with said anion resin followed by treatment with said cation resin.

4. The method of claim 3 wherein the iron content in said mine water ranges from about 5 to 5000 p.p.m., expressed as Fe, and said waters also contain 1-5000 p.p.m. of free mineral acid, expressed as CaCO_3 .

5. The method of claim 1 wherein said anion resin and said cation resin are in mixed bed form.

6. The method of claim 1 wherein said anion exchange resin is selected from the group consisting of a strongly basic solid anion exchanger, a weakly basic solid anion

exchanger, a strongly basic liquid anion exchanger and a weakly basic liquid anion exchanger.

7. A method of purifying acidic mine discharge water which contains as impurities at least iron and sulfuric acid which comprises bringing said water into contact with an anion exchange resin in the sulfate form to reduce said sulfuric acid content, and with a cation resin in calcium form whereby said iron content in said water is reduced, regenerating said anion resin by contact with water, and regenerating said cation resin by contact with a water-soluble calcium salt.

8. The method of claim 7 wherein said water regenerant is an aqueous dilute base and said calcium salt is calcium chloride.

9. The method of claim 8 wherein said basic regenerant is selected from the group consisting of lime solution and lime slurry.

References Cited

UNITED STATES PATENTS

2,628,165	2/1953	Bliss	210-38 X
2,660,558	11/1953	Juda	210-32 X
2,738,322	3/1956	Baumanet al.	210-32
2,954,276	9/1960	Hazen	210-38 X

SAMIH N. ZAHARNA, *Primary Examiner*.