

Ion exchange system design for removal of heavy metals from acid mine drainage wastewater

R. W. Gaikwad¹, V. S. Sapkal² and R. S. Sapkal²

This paper discusses the methodology used to determine the optimal ion-exchange column size to process all separate batches of feeds from acid mine drainage wastewater.

The optimal design ensures the best utilization of resin material and therefore results in a minimum amount of spent resins.

Ion exchanger materials have been studied for removing heavy metals from a metal bearing wastes. For the current treatment, a facility has been designed for the removal of heavy metals from the acid mine drainage (AMD) waste by the ion-exchange technology.

Key words: Heavy Metals, Acid Mine Drainage, Ion Exchange, Resins, Column, Design

Introduction

Water is essential to life on our planet. A prerequisite of sustainable development must be to ensure uncontaminated streams, rivers, lakes and oceans. We often take the presence of clean water for granted, forgetting its importance and assuming that it is always available. Unfortunately, the law and technology to protect this vital resource remains far from perfect. Increasingly, human activities threaten the water sources on which we all depend. Mining is one such activity. In fact, water has been called “mining's most common casualty”.

Acid mine water is an unavoidable by-product of the mining and mineral industry, especially as far as the oxidation of sulphide minerals is concerned. Acid mine waters typically contain high concentrations of dissolved heavy metals and sulphate, and can have pH values as low as 2. These conditions may prohibit discharge of untreated acid mine waters into public streams, as they have a detrimental effect on the aquatic plant and fish life. Similarly, the ground water pollution caused by the drainage of acid mine water is an equally serious problem.

Traditionally, acid mine water is neutralized by treatment with lime, resulting in the concomitant precipitation of iron, aluminium and other metal hydroxides.

The removal of heavy metals from waste waters with sulphide precipitation processes have consequently gained considerable importance in the last few decades [1-7]. Unfortunately, the sulphide precipitation has a tendency to form toxic H₂S at low pH values.

The precipitation process results in the removal of most of the heavy metals to within prescribed limits, but yields an effluent with a high salinity and limited use. The main problem in treating the limed effluent is that the dissolved salts have to be reduced to acceptable levels with an incurring undue cost. Existing technologies for the removal of salt include, among other, the evaporation, reverse osmosis, electrodialysis and the ion exchange.

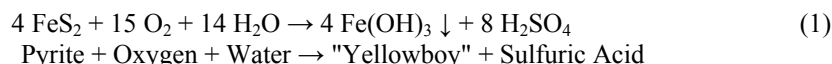
The evaporation entails both the natural and forced evaporation. Despite its low cost, the natural evaporation is time-consuming and requires large ponds to be effective. In contrast, the energy-driven evaporation is more efficient but also significantly more expensive. Reverse osmosis [8, 9] is a technology in which water containing dissolved salts is pumped under high pressure through membranes that allow selective permeation of water, while retaining the dissolved salts, thereby producing purified water and brine. However, sparingly soluble calcium sulphate concentrated in the brine effluent limits water recovery by causing scaling of equipment.

It is also possible to extract dissolved salts from water by passing it through beds of ion-exchange resins. This is well-established technology for producing very pure water from water containing low levels of dissolved salts [10] The dissolved salts in many of the polluted mine waters are mainly calcium and magnesium sulphate. Various authors [11, 12] have investigated the elution of calcium and magnesium ions from cation-exchange resins with sulphuric acid, and the elution of sulphate ions from the anion-exchange resins with lime.

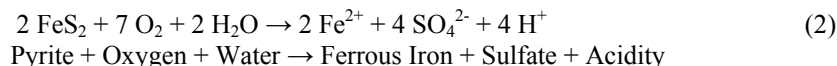
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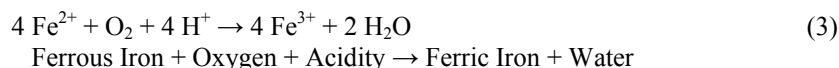
The general chemical reactions explaining the oxidation of pyrite and the production of acidity are given by the following equations. There are four commonly accepted chemical reactions that represent the chemistry of pyrite weathering to form AMD. An overall summary reaction is as follows:



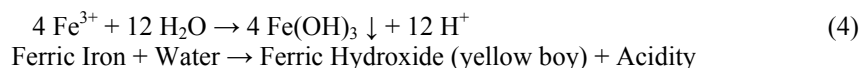
The first reaction in the weathering of pyrite includes oxidation of pyrite by oxygen. Sulfur is oxidized to sulfate and ferrous iron is released. This reaction generates two moles of acidity for each mole of pyrite oxidized.



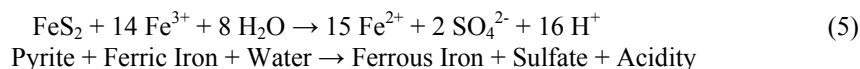
The second reaction involves the conversion of ferrous iron to ferric iron. The conversion of ferrous iron to ferric iron consumes one mole of acidity. Certain bacteria increase the rate of oxidation from ferrous to ferric iron. This reaction rate is pH dependant with the reaction proceeding slowly under acidic conditions (pH 2-3) with no bacteria present and several orders of magnitude faster at pH values near 5. This reaction is referred to as the "rate determining step" in the overall acid-generating sequence.



The third reaction which may occur is the hydrolysis of iron. Hydrolysis is a reaction which splits the water molecule. Three moles of acidity are generated as a byproduct. Many metals are capable of undergoing hydrolysis. The formation of ferric hydroxide precipitate (solid) is pH dependant. Solids form if the pH is above about 3.5 but below pH 3.5 little or no solids will precipitate.



The fourth reaction is oxidation of additional pyrite by ferric iron. The ferric iron is generated in the reaction steps 1 and 2. This is the cyclic and self propagating part of the overall reaction and it takes place very rapidly and continues until either ferric iron or pyrite is depleted. Note that in this reaction iron is the oxidizing agent, not oxygen.



The presence of iron-oxidizing microorganisms as catalysts affects the rate of AMD forming reactions. These bacteria are indigenous to many environments including sulfide ore bodies. As discussed above, the iron oxidizing autotrophic bacteria, *T. ferrooxidans*, greatly increases the oxidation of ferrous to ferric iron, which causes the reaction 4 to quickly proceed. The reaction 4 produces 16 equivalents of hydrogen ions, further lowering pH and causing more ferric iron to be oxidized. At low pH levels (pH 2 to 4) these bacteria thrive and multiply, further increasing reaction rates. Sulfide-oxidizing bacteria, such as *T. thiooxidans* may also increase the AMD formation, although to what extent is less known.

Mineral sulfides vary in their reactivity. This is due to the physical and chemical characteristics of various sulfide minerals. For example, some metal sulfides (i.e., copper, lead, and zinc) have a tendency to form low solubility minerals which encapsulate them and prevent further oxidation. The crystal structure of the sulfide minerals is an important factor for two reasons: (1) certain crystalline structures are more stable and resist weathering (oxidation); and (2) due to the increased surface area, smaller crystals react faster.³ The rate of AMD formation depends upon the particle size and surface area of rocks containing the sulfide minerals. Smaller particles have increased the surface area that can contact the weathering agents. Therefore, rock tailings (very fine particles) will weather faster than large boulders. Rates of weathering and production of AMD are dramatically increased in processed materials (e.g, crushed tailings from mineral processing or leaching), due to the increased amount of surface area. The rate of AMD formation is also dependent on pH and temperature. The chemical reaction rate is higher at low pH because the solubility of metals increases and biological oxidation peaks at a pH of about 3.5. Therefore, it is generally true that as more sulfuric acid is released and the pH decreases, more intense leaching occurs. A proposed facility is being designed for the treatment of Acid Mine Drainage wastewater.

For the current treatment, design of the Ion Exchange Treatment Plant (IETP), the removal of heavy metal-copper acid mine drainage waste (AMD) is achieved by the ion exchange technology based on **Indion 730** (14 BSS) and **Indion 236** (Ion Exchange of India Limited) resins. The proposed design of the facility consists of two packed columns (i.e., a cation exchange column followed by an anion exchange column). During a operation, upon reaching a specified copper concentration criterion at the exit of the cation column, the operation is switched to the second column. The copper-loaded column is processed (i.e., washed and eluted).

This paper analyzes the performance of proposed ion-exchange columns using the **Indion 730** (14 BSS) and **Indion 236** material for the removal of copper from the acid mine drainage waste. The main objectives of this analysis is to design an ion exchange facility for the removal of heavy metals- copper from the acid mine drainage waste

Design of Ion Exchange Column

For the packed bed study, an Ion Exchange column has been designed:

STEP 1, Determine the amount of water to be treated per cycle and the amount of heavy metal to be removed.

A heavy metal to be removed from water requires the use of cation – exchange resin operated in the sodium form to exchange the heavy metal cations for sodium regenerated with the aqueous sodium chloride solution. The total amount of water to be treated is,

$$(1.248 \times 10^{-3} \text{ m}^3/\text{hr})(4 \text{ hr/cycle}) = 5.137 \times 10^{-3} \text{ m}^3/\text{cycle}$$

In determining the quantity of heavy metal to be removed, neglect 1-ppm allowable heavy metal in the effluent (this is a conservative simplification) and complete the heavy metal removal. Since the influent heavy metal is expressed as parts per million (equivalent as CaCO_3). It is necessary to convert it to units consistent with the resin manufactures capacity data, usually expressed as kilo grains (as CaCO_3) per cubic foot of resin. A total of 200 ppm heavy metal is to be removed. Convert this to kilograins as CaCO_3 . Thus,

$$(200\text{ppm}) (5.137 \times 10^{-3} \text{ m}^3/\text{cycle}) / (17.1 \text{ ppm/gr/gallon}) = 0.0601 \text{ kgr as CaCO}_3 \text{ per cycle}$$

STEP 2, Establish the regeneration level and the resin capacity.

An optimal level of regeneration exists for each heavy metal to be removed by the application. This relates the level of regeneration (pounds of regenerant per cubic foot of resin), the leakage (ions not exchanged and thus appearing in the effluent) and the operating capacity. In the present case, the desired information is given (based on the information from the resin manufacturer).

The optimal regeneration level is 68 kg NaCl per cubic meter (4 lb NaCl / ft³).

$$\text{Deareation factor} = 0.9$$

$$\text{The optimal regeneration level} = \text{Resin Exchange Capacity} \times \text{Deareation factor} = 68 \times 0.9 = 61.2$$

STEP 3, Determine the volume of resin needed.

The heavy metal load per cycle is 0.036 kg per cycle from the step1 and the resin capacity is given as 36 kg/m³. So, the amount of resin needed is

$$\frac{0.0601}{61.2} = 9.8175 \times 10^{-4} \text{ m}^3$$

However, if the water production must be continuous, two units must be used so that one can be regenerated while the other is in service. An alternative is to supply the storage facilities for several hours by the production of water at $1.148 \times 10^{-3} \text{ m}^3/\text{hr}$.

STEP 4, Determine the column diameter, pressure drop and the backwash requirement.

The normal linear velocity is equivalent to 9.75 to 24.4 m³/(hrm³) [4-10 gal/(min.ft²)]

If the pressure drop is too high, it is excessive; if it is too low the velocity can cause a poor distribution of flow through the units. As per bed depth, it should normally be 0.9 to 0.8 m. given these norms of the column dimension are usually done by trial and error. Thus, assume the bed height of 50 cm.

$$\text{Cross-sectional Area} = \frac{\text{Resin required}}{\text{Bed Height}} = \frac{9,8175 \times 10^{-4}}{0,5} = 1,9635 \times 10^{-3} \text{ m}^2$$

$$\begin{aligned} \text{Column Diameter} &= \sqrt{[\text{Cross-sectional Area} \times (4 / \Pi)]} \\ &= \sqrt{[1,9635 \times 10^{-3} \times (4 / \Pi)]} = 0,05 \text{ m} \end{aligned}$$

In establishing the column height, allow an adequate headspace or a free board, to permit backwashing. A good allowance is 100 % of the bed height. Thus, the column height is twice the bed height or 3.05 m. The pressure drop per meter of bed depth is assumed to be 4.14 kpa.

Thus the total pressure drop = $4.14 \times 0.5 = 2.07$ kpa. This excludes the pressure drop due to the liquid distribution and collectors in the column as well as due to auxiliary fitting and valves.

Backwashing is necessary to keep the bed in the hydraulically classified condition, to minimize the pressure drop and to remove the resin fines and suspended solids that have been filtered out of the influent water. A normal practice is to backwash at the end of each run for about 15 min., so as to obtain about 50-75 % bed expansion. The flow rate required to achieve this expansion is obtained from the manufactures data.

The appropriate flow rate is $15.6 \text{ m}^3 / (\text{hrm}^2)$.

Total backwash rate is thus $15.6 \times 1.9635 \times 10^{-3} = 0.0306 \text{ m}^3 / (\text{hr})$.

Then, the total water requirement is

$$0.0306 \times (1/60) \times 15 = 7.657 \times 10^{-3} \text{ m}^3 / \text{min.} = 0.4594 \text{ m}^3 / (\text{hr}).$$

STEP 5, Determine the regenerant requirement and the flow rate.

The NaCl regeneration level necessary to hold leakage 1 ppm is $64 \text{ NaCl} / \text{m}^3$ (4 lb NaCl per ft^3).

The requirement is 100 %, then $64 \times 1 \times 10^{-3} = 0.064 \text{ kg NaCl} / \text{cycle}$.

Now, it is typically administrated as a 10 % solution at the rate of $4.023 \text{ kg} / \text{m}^3$. Thus the volumetric requirement is

$$\frac{0.066}{0.1 \times 8.94 \times 0.45 \times 1.248 \times 10^{-6}} = 131.455 \text{ m}^3 / \text{cycle} = 32.864 \text{ m}^3 / \text{hr.}$$

This should be fed at the rate

$$\frac{1.248 \times 10^{-3} \times 9.8175 \times 10^{-4}}{(0.305)^3} = 4.318 \times 10^{-5} \text{ m}^3 / \text{hr.}$$

STEP 6, Determine the required volume of rinse water.

The resin bed must be rinsed with water following the regeneration with salt. Rinse water requirements are obtained from the manufacturers literature; in the present case they are

$$25 \text{ to } 50 \text{ gal} / \text{ft}^3 [94.5 \text{ to } 189 \text{ lit} / \text{ft}^3].$$

At 35 gal/ ft^3 [132.48 lit / hr^3] the total rinse required is

$$\frac{1.3248 \times 9.8175 \times 10^{-4}}{(0.305)^3} = 0.0458 \text{ m}^3 / \text{cycle} = 0.0114 \text{ m}^3 / \text{hr.}$$

Selection of the column dimensions and the direction of the flow

It is a common fact that the column dimensions and the direction of flow have profound effects on the heavy metal removal in continuous mode applications, particularly for a proper operation. Channeling is one of the most significant operational problems encountered in the column operations packed with porous sorbent materials.

Channeling is often encountered in larger columns rather than smaller ones ($L_c/D_c > 20$) and in down-flow operations when relatively higher volumetric flow rates are employed. Therefore, narrower columns are generally employed and the introduction of feed solution to columns is generally conducted in the up-flow mode in order to warrant perfect wetting of resin and, accordingly, to maximize the contact between resin and heavy metal ions in the feed solution.

Elimination of clogging and selection of influent Cu^{2+} concentration

As mentioned in the Materials and Methods part of this study, rinsing was applied for resin samples prior to the use in column studies. The reason for rinsing was to eliminate the fine particles associated with resin grains and consequently to prevent the packed bed column from clogging. Nevertheless, in some cases, rinsing alone cannot be a remedy for the clogging problem. A low ionic strength of the feed solution and/or considerably high flow velocities may results in clogging in column operations. For the low ionic strength and high flow rate cases, the particle release is driven by the electrostatic repulsion and the flow induced by shear forces, respectively.

Experimental set up

The schematic diagram of the experimental set up is shown in fig. 1 based on above the calculations. It consists of the tank T1 which contains the metal stock solution. This tank is connected to a pump which pumps the solution through the rotameter in to the anion exchange column. The outlet at the top of the column helps to withdraw the treated solution. A manometer is connected across the column for the pressure measurement. RT1 is the tank containing the regenerating solution placed right on the top of the column. The solution after regeneration is collected in the tank T3. For the cation exchange column, the solution is pumped from the tank T3 into it. The treated sample is collected in the tank T5. The rotameter for the flow measurement and the manometer for the pressure measurement is provided for the column. RT2 is the tank containing regenerating solution placed right on the top of the column. The solution after regeneration is collected in the tank T4. Both exchange columns are of 50 mm diameter and 1000 mm height. The material of construction is borosil glass.

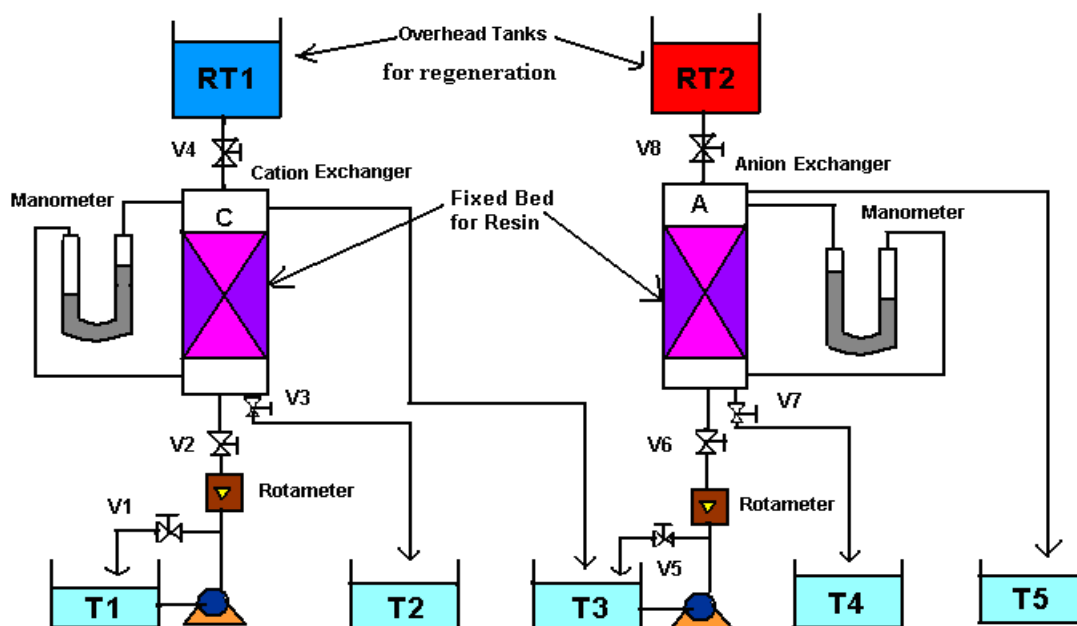


Fig. 1. Experimental Set Up.

Experimental Procedure

The water is pumped in to the column prior to resin is being added. The resin was then added as wet slurry. This was to prevent air bubbles from being trapped between the particles, hence poor contacting in the column during each cycle.

A, Service cycle of cation exchanger

The solution containing a metal is filled in the **tank T1** and pumped through the rotameter into the cation exchanger. The rotameter measures the flow rate and the manometer the pressure drop. The treated sample from the column is taken out from the top of the column and collected in the **tank T3** and analyzed for the metal content from time to time. The process continues until the metal content reaches the discharge limit. Once this stage is reached, the supply of metal solution is stopped. Now, the regeneration process is carried out before the exchanger column is backwashed by water.

Regeneration of cation exchanger

For regeneration, the regeneration solution HCl, from the tank RT1 is allowed to flow through the exchange column drop by drop for 3 hrs. regenerant removes the cations adsorbed during the service cycle and converts the resin to the hydrogen form for the next service cycle. This solution is collected in the bottom **tank T2**. The recovery of the metal is achieved in this step.

Monitoring of pH during the regeneration process

The pH value of the prepared metal solutions (influent) was 5 and it was monitored during the regeneration process. At the breakthrough point, a rapid change in the pH value may occur, coinciding with the rapid increase in the metal concentration according to the breakthrough curve. At the exhaustion point, the pH value of the effluent became equal to the pH value of the influent. This is due to the increased metal concentration in the effluent and its hydrolysis [13],[14]. Therefore, if the pH value in the effluent is continuously monitored, one can predict the breakthrough and exhaustion points [15].

Back washing of cation exchanger

For backwashing, the tank T1 is filled with water, the valves V3 and V4 are closed and the valves V1 and V2 are opened. Water from the tank T1 is pumped into the column with a force for 10 minutes and taken out from the top of the column.

B, Service cycle of anion exchanger

The solution from the tank T3 is pumped in to the anion exchanger. During this, the valves V5 and V6 are opened and the valve V7 and V8 are closed. The flow rate is measured by the rotameter and the pressure drop by the manometer. The treated solution is taken out from the top of this column and collected in the tank T5 and analyzed for acidity of the sample by the titration method.

The solution collected from the H-type resin column is fed to the OH type anion resin column for a conversion where acidity of wastewater is neutralized.

Regeneration of anion exchanger

For regeneration, the regenerative solution NaOH from the tank RT2 is allowed to flow through the exchange column drop by drop for 3 hrs. The regenerant removes anions adsorbed during the service cycle. This solution is collected in the bottom tank T4.

Back washing of cation exchanger

The column is backwashed with water after the regeneration cycle is completed. The backwash step removes the particulate matter filtered out by the exchanger during the service and also regrades the bed eliminating any channels which may be formed.

Sorption Studies

A successful application of the ion exchange technique demands for the innovation of cheap, non toxic, easily available ion exchangers. The knowledge of the optimal conditions would proclaim the better design and modeling process. Thus, the effect of some major factors, viz. pH, time, flow rate, dosage, initial concentration, and bed height is to be studied. Experiments should be carried out at different conditions keeping one parameter constant and varying the other parameters to study the effect of

- different concentrations on removal,
- pH of solution,
- types of resins,
- flow rates,
- different Bed heights.

Conclusion

Using the dimensions, a pilot plant for the treatment of acid mine drainage waste water has been designed for the heavy metal (copper) removal. The optimal size of the ion exchange column in the 2-column design system is determined to be approximately **0.05 m** in diameter. In establishing the column height, an adequate headspace or free board, is allowed to permit backwashing. A good allowance is 100 % of the bed height. Thus, the column height is twice the bed height or 3.05 m.

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