

A Review on Different Active Treatment Methods for Acid Mine Drainage

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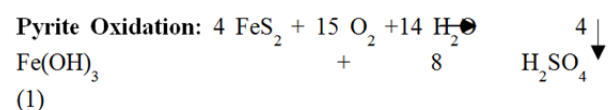
Abstract—Acid mine drainage (AMD) is an unavoidable problem generating from different active and abandoned mines. The untreated acidic drainage possess serious threat for the environment as it pollutes the surface as well as underground water body. Acidic drainage contains several toxic heavy metals that leave negative impact on the environment. There are different methods available for the treatment of AMD by removing potentially hazardous metals form the solution. These methods are broadly divided into two groups i.e. abiotic (can be controlled) and biotic (occurs naturally, cannot be controlled). Furthermore, these two classes are subdivided into two classes, as active and passive. This paper reviews the status of different active remediation techniques available for the treatment of AMD. It also represents the advantage and disadvantage among the different methods as well as the metal removal efficiency from AMD solution

Keywords: Acid Mine Drainage, Pyrites, Active Treatment

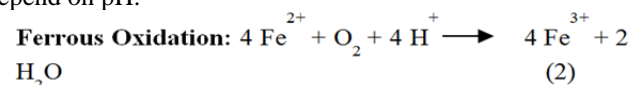
1. INTRODUCTION

Acid Mine Drainage (AMD) termed as the effluent of acidic water from active or abandoned metal mines or coal mines. Discharged wasters from the mines are often extremely acidic in nature[1]. As the acidic drainage contains higher concentration of different heavy and toxic metals, so it is very harmful to the living organisms. However, iron is considered, as the prime metal present in AMD that can be present in the form of ferrous and ferric ion. Generally, the colour of AMD depends on the pH and the concentration of iron present in the drainage. As an example, for extremely acidic AMD water whose pH ranges from 2.3 – 4 and concentration of ferric iron is approximately 650 mg/l, makes the AMD typically red in colour. While in case of streams with a pH 5 - 6.5 and iron concentration of approximately 160 mg/l [8] orange-yellow ferric iron-rich sediments (“yellow boy”) are found [2]. Surface waters affected by AMD can be identified by low pH (2-4), enhanced concentrations of iron, sulfate, total dissolved solids (TDSs) 4000-5000mg/l [3] and other heavy metals, most of them are harmful to living organisms. Although the impact of AMD on ground water is less in comparison to the surface water. Because the buffering reactions with different ions such as carbonate, hydroxide and aluminosilicate minerals present in aquifers [4] and due to the dissolution of

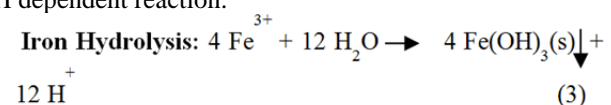
large amount dissolved oxygen and abolition of air in the subsurface environments [5]. Though mostly surface waters are impacted by AMD, but due to the infiltration of AMD into the groundwater through crushed mill tailings and waste rock piles, it can contaminate the groundwater as well [6]. Johnson [7], has reported that there are series of geo-chemical and microbial reactions are responsible behind the formation of AMD. These reactions takes place when sulphide minerals exposed to atmospheric oxygen and come contact with water. Oxidation of this sulphide minerals accelerated due to the presence of some onsite microorganisms. Iron and sulphur oxidized to ferric iron and sulfate, respectively, and hydrogen ions are produced during the oxidation process [7]. AMD generation from pyrite can be elaborated with the three different chemical reactions such as pyrite oxidation, oxidation of ferrous ion and hydrolysis of iron[8]. When the pyrite oxidation takes place (Eq. (1)) sulphur converted to sulphate and ferric iron released. Equation (1) is the beginning step for the pyrite oxidation in presence of atmospheric oxygen. Sulphuric acid so formed (Eq. (1)), make the drainage extreme acidic.



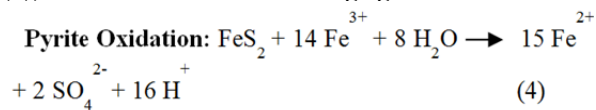
Conversion of ferrous iron into ferric ion (Eq. (2)) leads to consume one mole of protons. The reaction rate is totally depend on pH.



The final step of the series of reactions is the hydrolysis of iron (Eq. (3)). In this reaction, three moles of protons generated beside the formation of ferric hydroxide precipitate, which is solid in nature, and orange in colour. This is also a pH dependent reaction.

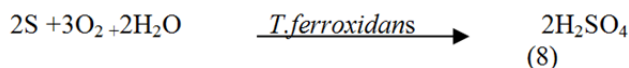
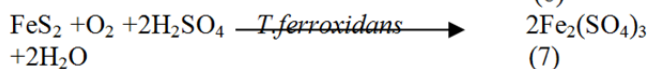
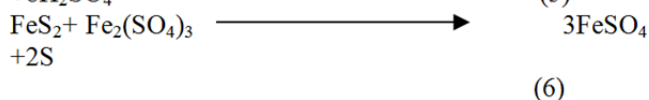
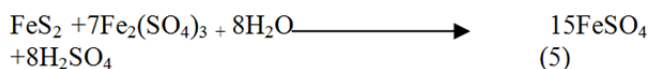


Reduction of ferric ions also leads to the oxidation of pyrite (Eq.(4)). Iron behaves as an oxidising agent in this reaction.



Production of Fe^{3+} ion through equation 2, is regenerative in nature and reaction 2 is considered as a prime reaction for the oxidation of mineral. Because, the process is repetitive and quick in nature and it continues until and unless ferric iron or pyrites is totally depleted[9]. pH plays a vital role for the series of reactions. When the value of pH is above 4, the reaction is chemically or biologically mediated. However, if the pH is below 4, iron-oxidising bacteria are become active for the formation of AMD and abiotic oxidation become less significant [2]. According to Hassett (1998) [10] pyrite is the key mineral for the generation of final product. This final product forms the contaminants termed Acid rock Drainage (ARD) according to the chemical reaction below:

Drainage (ARD) according to the chemical reaction below:



Equation (7) and (8) is solely dependent on microbial activity that proceed to the oxidation of ferric ion. It has been reported from literature that the native bacteria (*Thiobacillus ferrooxidans*), consumes sulphur as their source of energy. They are autotrophic by nature. They obtain their fundamental food resources and nutritional needs from the atmosphere (nitrogen, oxygen, carbon dioxide and water) and from minerals (sulphur and phosphorus)[9]. They considered as very essential factor for the generation of AMD. It is assumed that in absence of bacteria, reaction (5),(9) and (10) become very dominant. After the completion of the series of reactions, products are sulphuric acid and ferric sulphate. As sulphuric acid is produced, so the overall pH of the drainage going down to the extreme acidic level. Sometimes the pH ranges from 2.5-3.0 [9]. Table 1 shows the characteristics of a typical Acid Mine drainage [11]. As AMD is highly acidic, so it help

to solubilize the other toxic heavy metals in to it, that make it extreme severe. If untreated AMD is discharged into the environment, than it raise several difficulties including water, soil pollution. Because of its acidic nature, flora and fauna present in the fresh water cannot survive any more if the water contaminated with AMD. Problem of AMD is not only limited to the living organism, but it has negative effect on the property. Acidic drainage is highly corrosive that causes heavy corrosion in pipes, pumps and machineries used in industries.

Table 1: Characteristics of a typical Acid Mine Drainage [11]

Parameters	Value
pH	2.19
EC(ms/cm)	15.77
Acidity(mg/L CaCO ₃)	14,450
B	10.3
Na	102.9
Mg	399.4
Al	453.4
Si	99.2
Ca	146.9
Mn	95.8
Fe ⁺²	4444.9
Fe ⁺³	2065.6
Ni	6.16
Cu	7.1
Zn	15.71
Co	4.3
Se	0.39
Sr	1.95
Mo	0.014
Ba	0.018
Pb	0.455
SO ₄ ²⁻	24,880
Cl ⁻	370
NO ₃ ⁻	90

All the values are given in mg/l unit except pH and EC

2. TREATMENT OPTIONS FOR AMD

There are several methods available for treating the acidic drainage including primary prevention (that inhibit the acid-generation process), secondary control (ceased the movement of acidic drainage after its formation) and tertiary control (treatment of the acidic effluent after collection). However, due to the limitation of the first two process, primary and secondary control is not possible. Such as the acid generation process cannot be controlled and composition and concentration of different heavy metals in AMD vary widely from place to place [12]. Therefore, tertiary control has been implemented for the treatment of generated AMD. Tertiary treatment is widely divided in two group, active treatment and passive treatment. Both of these treatments further categorized in to two category, such as abiotic active treatment and biotic active treatment. In this paper, active treatments are critically and widely reviewed for the treatment of AMD.

2.1 Active Abiotic remediation technology

Active treatment includes the treatment of AMD with some alkaline material to enhance the pH of the water to neutralize the acidity as well as to precipitate out the metals from the solutions. Active treatment includes aeration, addition of alkaline material, addition of natural zeolites, electro dialysis, reverse osmosis, ion-exchange etc. Before implementing the active treatment system, flow rate, pH total suspended solids, acidity-alkalinity, concentration of different toxic metals, availability of man-power, electrical power are to be determined [13].

2.1.1. Aeration

In case of aeration, air is introduced into the water. When water is oxidized it helps the metals to be precipitate out at lower pH values. Mechanical surface aeration introduces atmospheric oxygen into water with the help of blades. Basically oxygen is absorbed by the water and then react with iron and other reduced compounds in the water. Aerator creates the turbulence and dispersed air bubbles keep the iron floc in suspension form. If aeration and oxidation are introduced into the improved treatment system, than the chemical treatment efficiency will be increased [13].

2.1.2. Neutralizing Material

The most extensive methodology used to treat acidic effluents is an active treatment process involves continuous application of a chemical-neutralizing agent[1]. Although there are various alkaline materials applied for the treatment of AMD, but six chemicals such as calcium carbonate, ammonia, caustic soda, pebble quicklime and hydrated lime are widely used to raise the pH. Sufficient alkalinity must be introduced in order to neutralize the acidity of the AMD that dissolved metals will be precipitate out from the water of AMD¹³. In this process, iron-sludge is produced as a final product that contains other various metals based on the reaction chemistry between the AMD and various alkaline agents. All the above mentioned alkaline agents are different by means of cost and effectiveness. Sodium hydroxide is 1.5 times (approx.) efficient than lime, but the cost of lime is nine time less than the cost of sodium hydroxide[1]. Lime is very effective for the treatment of AMD. It removes the unwanted and harmful metals and ions by neutralization and precipitation methodology. But the problem to use of lime for the treatment of AMD is clogging problem in the reactor and generation of bulk amount of sludge. Trapzene (CaO₂) is a chemical compound formed from calcium peroxide. It has oxidation and acid neutralization capability as well. Lilly and Ziemkiewicz (1992) found that trapzene can successfully water contaminated with Mn including raising the pH from 3.5 to 7.5. they also reported that the metals such as Fe, Mn, and Al removal efficiency was much higher by the trapzene in comparison with NaOH [14].

2.1.3. Flocculants/Coagulants

Coagulants and or flocculants are the chemicals that often used for the treatment of AMD. Basically flocculants/coagulants enhance the particles settling efficiency. There are number of cogualnats /focculants are available such as Aluminium Sulfate, Ferrous Sulphate, Ferric Sulphate, Sodium Aluminate, Polyampholytes etc. These type of chemicals are utilized where a specialized treatment system is required for the unique metal composition in the acidic drainage, or aeration and residence time in the setting pond are not capable enough for the complete metal precipitation. Coagulants minimize the repulsive forces at particle surface, and help to associate the smaller particles into bigger one. Whereas, flocculation combines the particles by making channel between the particles with chemical[13].

2.1.4. Reverse Osmosis

In case of osmosis, when the two solutions of different concentrations are separated from each other by a semi-permeable membrane, then the solvent will flow form more dilute solution to the more concentrated solution until an equilibrium concentration is achieved. But during reverse osmosis, direction of flow can be reversed with the help pf applying pressure to the more concentrated solution. Solvent leaves the solution with more concentrated solutes. It has been reported in literature that reverse osmosis is able to separate the Ca, Mg, Zn, Mn, Cu, Al, and Fe as nitrate, chloride, and sulphate salts from acid mine water. Metals removal efficiency by reverse osmosis was reported as 95-99 % [15]. This process produces a high quality effluent water suitable directly for potable and industrial use [13].

2.1.5. Ion Exchange

Ion exchange is defined as interchange of ions between a solid medium and the aqueous solution. It is basicaaly used in case of softening the hard water for domestic purpose. Hardness of water generally caused by Ca²⁺ and Mg²⁺ ions. The hard water solution is passes through the ion- exchange bed material, that with charged with monovalent sodium ions. The resins where ion-exchange takes place consist of a chemically-inert polymer matrix with functional group attached for exchange [13]. It has been reported that ion-exchange is able to remove the heavy metal ions from the AMD by precipitation along with lime followed by ion-exchange process [15].

2.1.6. Electrodialysis

It is the system consist of a number of tiny compartments or sections separated by very closely spaced membranes. Each and every section is separated by cation and anion membranes. Electrodes are generally located at opposite ends of the unit. After filling the channels between the membranes with the solution, electrodes are energized and the ions moves towards the positive or negative poles and are collected on the membranes [13].

2.1.7. Natural Zeolites

Natural zeolites are hydrous aluminosilicates that used to exchange ions for the treatment of AMD. Sodium ions is the dominant ions present naturally in the natural zeolites are preferred for the exchange for the metal ions. When the natural zeolites are used for the treatment of wastewater, it eventually loaded with exchanged metal cations. Therefore, to regenerate the efficiency of natural zeolite, sodium chloride solution is used to remove the metal cations from the aluminosilicate matrix [13]. Schultze et.al., (1994) [16] reported that natural zeolites behaves as an excellent adsorbing material in reducing the metal concentration in AMD to drinking water standards¹⁶.

2.2. Active biological system: Sulfidogenic Bioreactors

Sulfidogenic bioreactors show a potential approach for the treatment of AMD. These systems have some advantages over the passive remediation: i) performance of this system can be controlled and can be predictable (ii) sulphate ion concentration is very low in treated waters; and (iii) they has the capability to recover and reuse the heavy metals (copper, zinc, arsenic) present in AMD [1]. In case of alkalinity generation, sulfidogenic bioreactor consume the biogenic hydrogen sulphide, so that the metals present in AMD is removed is the form of insoluble sulphides. The aforesaid process occurs in compost bioreactors and Permeable Reactive Barriers (PRBs), even though off-line sulfidogenic bioreactors are designed and operated in a manner that the production of hydrogen sulphide is optimized. Sulphate Reducing Bacteria (SRBs) are evry sensitive to the moderate acidity, therefor eteh system is operated in a way that the reactor is capable to protect the microorganism from direct exposure of influent acidic drainage, which led to death of the organism. One of the technologies used in off-line sulphidogenic bioreactors is Biosulfide process. The Biosulfide system has two sections, one is biological and the other one is chemical, which can be operated independently[17] Before coming into the biological compartments, first the acidic influent enters into the chemical compartment. Hydrogen sulphide is produced in the biological compartment. Therefore, when the AMD enters into the biological unit, it get contacted with hydrogen sulphide. Metal sulphide present in AMD can be separated by optimizing the pH and other parameters that influence the reaction chemistry in the bioreactor. After successful separation of the sulphide metal from the partially treated water, it transfers to the other unit for additional advance treatment. Some amount of treated AMD recirculated in to biological unit in order to provide the sulphide source to the microorganism. The recirculated AMD contains a mixed culture of SRB. Although, SRB is able to produce the alkalinity required for their growth and to maintain the raction condition in the bioreactor, but sometime alkali must be added to ensure the smooth ans successful operation of the reactor. The other technology used in these bioreactors is Thiopaq process. This process is different from the biosulphide process by two different means: i) conversion

of sulphate sulphide with the help of SRB followed by precipitation of metal sulfides and (ii) utilising sulfide-oxidising bacteria, surplus amount hydrogen sulfide converted to elemental sulfur. It has been reported that Thiopaq process has been running successfully for the treatment of groundwater contaminated with zinc at the Budelco zinc refinery in the Netherlands since 1992 [18].

3. CONCLUSION

From the above detailed discussion it can be concluded that there are lots of economic as well as environmental factors that determine for adapting the treatment option for the AMD. Basically when huge amount of the effluent that is acidic in nature has to be treated, active abiotic system are used. Although the mentioned abiotic processes such as reverse osmosis, ion-exchange, electro dialysis are efficient, but they incurred huge amount of installation as well as maintaining cost. After the solvents are separated from the solutes in reverse osmosis, concentrated AMD sludge is become very hazardous to be disposed off. Because there is no neutralization of acidity has occurred and no metal hydroxide have been formed [19, 20]. Hilton(1989) [21] found that although electro dialysis process worked well in ponds of acid mine drainage, but membranes got clog very rapidly with the mtral ions. Poweel and Vickland (1968) [22] also observed that iron quickly fouls the membranes and causes problems for disposal²². On the other side neutralizing chemicals such as lime, sodium hydroxide, quick lime, hydrated lime all these are cheeper agents for the treatment of AMD. These also consumes much less cost that the other system. Though now a day's extensive researches are continues for finding the suitable technique to treat the AMD. Reseachers are also focused to enhance efficiency and concentrated on optimising the treatment processes. However, it is not reported anywhere in the literature but every remediation techniques requires some maintenance and management that must be included in cost-benefit analysis. Finally field condition of the treatment site, characteristics of AMD, financial status of the industry and the legislation become the prime and challenging aspects to choose the suitable remediation technique for the treatment of AMD.

4. ACKNOWLEDGEMENT

The authors are thankful to the Ministry of Human Resource Development, Government of India. We are also grateful to the Department of Environmental Science and Engineering, Indian School of Mines, Dhanbad for the logistic support.

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