A review on treatment of acid mine drainage with waste materials: A novel approach

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Abstract

The present study systematically and comprehensively reviewed different aspects of treating Acid Mine Drainage (AMD) with active treatment and waste materials. The work also critically reviews the status and the factors associated with the treatment process. Although, conventional active methods are very efficient but they are mainly associated with costly material as well as high maintenance cost which enhances the cost of entire treatment system. Waste materials such as fly ash, metallurgical slag, zero valent iron (ZVI), cement kiln dust (CKD), organic waste such as peat humic agent (PHA) and rice husk can be efficiently used for the treatment of AMD. However, efficiency of different waste material varied from each other due to the variation in their physical and chemical characteristics. The results from the investigation showed that fly ash, metallurgical slag and CKD raise the pH of acidic solution more, in comparison to ZVI and organic waste, due to their richness in lime content. Furthermore, fly ash can be efficiently converted and utilized in its other derivative such as chemically modified fly ash and zeolite. Efficiency of ZVI is hindered by the presence of higher concentration of total dissolved solids. PHA can treat AMD that is mild acidic in nature. Besides, long retention time is required for the removal of heavy metals and sulfur with organic waste and sulfate reducing bacteria (SRB). The study also potentially reviewed that metal removal from AMD varied due to composition of AMD and the characteristics of waste materials. However, waste materials demand more attention for its practical applicability in field conditions due to its richness, higher possibility for recycling and reuse, low installation cost and harmless nature towards the environment.

Keywords: Acid Mine Drainage; Active Treatment; Fly Ash; Metallurgical Slag; Zero Valent Iron; Organic waste.

1. Introduction

Acid Mine Drainage (AMD) refers to the effluent generated from active as well as abandoned mines. The exposure of rocks consisting of ferrous or ferric sulfide minerals to water and oxygen results in generation of AMD.

The reason behind AMD generation is the presence of sulfide mineral, in form of iron sulfide-aggregated rocks and exposure of these minerals to water and oxygen (Akcil and Koldas, 2006).

This phenomenon is more prominent in abandoned mines than active mines, as in latter case water tables are kept low by continuous pumping system. However, in case of abandoned mines, pumping systems are disabled and the voids generated due to mining are filled with water. This water than reacts with the pyrite present in the rocks of these mines and generates acidic drainage, thereby contaminating the groundwater (Johnson and Hallberg, 2005; McCarthy, 2011). However, the reason behind the AMD production is not only restricted to the mining activities, it can also takes place in the highway, tunnel construction and other deep excavations. The primary and secondary sources of AMD are presented in Table 1 (Akcil and Koldas, 2006).

Table 1. Sources of Acid Mine Drainage (Akcil and Koldas, 2000)

Primary sources	Secondary sources
Mine rock dump	Treatment sludge pounds
Tailings impoundment	Rock cuts
Underground and open pit mine workings	Concentrated load-out
Pumped/nature discharged underground water	Stockpiles
Diffuse seeps from replaced overburden in rehabilitated areas	Concentrate spills along roads
Construction rock used in roads, dams etc.	Emergency ponds

Figure 1 illustrates the process of AMD generation. It shows that pyrite oxidation can take place through several pathways including surface interactions with dissolved O_2, Fe^{3+}, and other mineral catalysts such as MnO_2 (Buzzi *et al.*, 2013). Oxidation of pyrite (FeS_2) through (1(a) and 1(b)) is key reaction for AMD generation. Pyritic oxidation

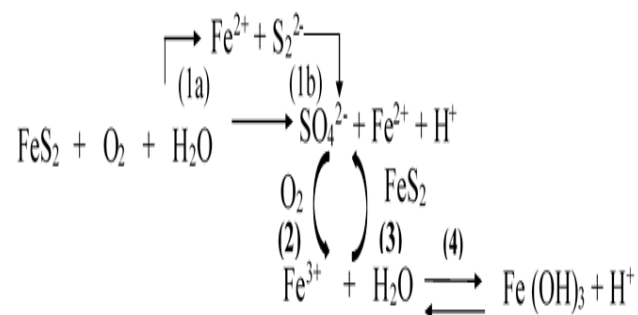leads to the formation of dissolved iron, sulfate and hydrogen (1).

$$FeS_2 + O_2 + H_2O \xrightarrow{(1a)} Fe^{2+} + S_2^{2-} \xrightarrow{(1b)} SO_4^{2-} + Fe^{2+} + H^+$$

$$Fe^{3+} + H_2O \xrightleftharpoons{(4)} Fe(OH)_3 + H^+$$

Figure 1. Model for oxidation of pyrite (Buzzi *et al.*, 2013)

Fe^{2+}, SO_4^{2-}, H^+ are dissolved into the drainage and act as the key indicator for the increasing total dissolved concentration of metals and acidity of the drainage. H^+ helps to reduce the pH of the drainage. Fe^{2+} undergoes further oxidation (2) if there is favorable oxidizing condition prevails in terms of oxygen concentration, pH, and microbial activity (Akcil and Koldas, 2006). Ferric iron precipitates as ferric hydroxide ($Fe(OH)_3$) and jarosite if the pH value of the reaction lies between 2.3-3.5 (4) (Akcil and Koldas, 2006; Simate and Ndlovu, 2014). Ferric hydroxide, so formed, is not stable when the solution pH is less than 2, and Fe^{3+} remains in the solution (Dold, 2010). Remaining Fe^{3+} present in the solution, that cannot be converted into ferric hydroxide (precipitated) form, acts as an oxidizing agent for further pyrite oxidation through (3) (Akcil and Koldas, 2006). Fe^{2+} produced from the similar reaction aids to continue the reaction (2) and (4) until entire ferric iron or pyrite is exhausted.

AMD is highly acidic in nature; pH ranges from 2-3 with elevated concentration of different heavy metals, ferrous and non-ferrous metal sulfate (McCarthy, 2011). Qualitative information about the nature of AMD can be identified through the visual examination of rock and effluent. Organic stains and cloudy water indicates about the presence of iron with pH value above 3.5 whereas wine-colored stains with clear effluent is strong indicator of iron with pH value less than 3.5. Presence of aluminium (Al) can be detected by white color stains with pH value above 4.5. However, chocolate brown to black stains clearly specify the presence of manganese in the effluent at a pH level greater than 7 (Fripp *et al.*, 2000). Although the concentration of the metals and pH of the AMD varies, but sulfate concentration remains higher in all effluents generated from various mines.

It causes major environmental pollution. Approximately 7000 km of streams in Unites States of America (USA), was severely damaged by AMD; 8000-16000 km of streams in the USA are in worst condition and extremely contaminated by AMD (Acid report 2010; USEPA 1995). An investigation in metal mine and industrial-mineral tailings in Canada indicated that 6 billion tons of waste rock and 7 billion tons of tailings; 750 billion tons of waste rock and 1.9 billion tons of tailings respectively, have potential to generate acidic drainage (Acid report 2010). Groundwater present in the mining district of Johannesburg, South Africa is massively polluted and extremely acidified because of oxidation of pyrite present in mine tailings dumps (Naicker *et al.*, 2003). Also, in the areas of Witwatersrand goldfield, which is also known as the rand, underground mine voids, surface mine tailings dumps, waste rocks, created in the course of mining, milling and processing of ores are the key source of acid mine drainage generation (Ochieng *et al.*, 2010; Merkel and Mandy, 2011). Water pollution including AMD in Loskop Dam, Vaal river catchment and the Olifants River Catchment area, due to Mpumalanga coalmines, has been reported (Acid Report 2010; Manders *et al.*, 2009; Merkel and Mandy, 2011). McCarthy *et al.* (2011) also reported that acidic drainage from Witbank and Middelburg coalmines contaminated the tributaries of the Olifants river. In India, Makum coal fields in Assam, Jaintia coalfield in Meghalaya, Western Coalfield (WCL), Northern Coalfiled (NCL), north-eastern coalfield are prone to generate AMD by the oxidation of pyrite present in coals (Baruah *et al.*, 2006; Equeenuddin *et al.*, 2010; Sahoo *et al.*, 2012; Tiwary, 2001).

If this acidic drainage is not treated then it can contaminate the surface as well as ground water, destroy the plant, aquatic and human life. AMD has severe negative impact on the environment. Therefore, AMD must be treated to ensure the safety and to minimize the environment and health risk.

Treatment of AMD is divided into two categories, i.e. active and passive. To adopt the treatment options, economic factors and technical factors are always considered. Economic factor comprises of price of reagents, labor, machineries, equipment, time scale for treatment and rate of interest. Technical factors include acidity levels, influent flow, type and concentration of heavy metals present in AMD wastewater (Skousen *et al.*, 2000). Active treatment refers to the continuous application of alkaline materials into the drainage water to neutralize acidic mine waters and to precipitate metals. Whereas, passive treatment is the process where natural and constructed wetlands are used to treat the acidic drainage (Johnson and Hallberg, 2005).

This manuscript critically reviews different active treatment methods that uses waste materials as the main component in the process. It also provides a comparative analysis among different waste materials with respect to metal percentage removal efficiency and a detailed knowledge about the waste materials that can be used successfully for the treatment of AMD.

2. Treatment technology for AMD

Owing to the difficulties in controlling the AMD at source, it is rather an alternative approach to collect and treat AMD, thereby minimizing the impact of AMD on receiving streams, river and other environmental components.

2.1. Active treatment

The most extensively used methodology to mitigate AMD is active treatment that includes various processes such as aeration, addition of neutralizing agents, reverse osmosis, ion exchange, electro dialysis and natural zeolites (Ali, 2011).

Aeration is done to introduce air into water, which facilitates the oxygen to combine with metals and forms metal oxides, which gets precipitated. Different type of aerators are available for this process, but mechanical surface aerators are used for hydrated lime treatment plants for the treatment of highly acidic and reduced water. Mechanical surface aeration helps to incorporate oxygen into water by rotating its blades located beneath the water in aeration basins. Aerator creates turbulence that disperses air bubbles and keeps the iron floc in suspension. High velocity spray nozzles are used for in-line aerators to improve the contact between air and water. However, the efficiency of aeration in terms of ferrous ion oxidation depends on pH, as inorganic oxidation reaction is slow below pH 5. Therefore, this oxidation process is combined with the addition of base, to neutralize pH (Skousen *et al.*, 1998; Skousen *et al.*, 2000).

For neutralization and treatment of AMD, some chemicals such as limestone, hydrated lime, pebble quick lime, soda ash briquettes, caustic soda, ammonia, magnesium hydroxide, magna lime are widely used. Enhancement of pH of the solution to precipitate the insoluble metals as hydroxides or carbonates and for rapid chemical oxidation of ferrous iron is done by providing sufficient amount of alkalinity in the solution. Most of the metal ions except Fe^{3+}, precipitate from water in a pH range of 6-9. Therefore, appropriate neutralizing agents are chosen for specific condition. Table 2 summarizes the characteristics as well as the advantages-disadvantages of using different neutralization materials.

Figure 2 shows conventional treatment plant that uses lime for the treatment of AMD (Aubé and Eng, 2004). Lime is added to the reactor filled with AMD to enhance the pH of AMD which facilitates the precipitation of metals present in AMD. Than flocculent is added and stirred into flocculent reactor to encourage the floc formation and enhance the settling rate of the precipitated metals in form of larger particles. Than the treated water is taken out from the flocculent reactor and sludge disposed of.

AMD when treated by reverse osmosis produces high quality effluent water which is suitable for potable or industrial use, while the concentrated acidic brine solution left behind contains Fe and sulfate (Skousen *et al.*, 1998). Ultra Pressure Reverse Osmosis (ULPRO) attains 97% and 96% rejections of heavy metal and total conductivity in comparison to Nano filtration (NF) with 90% and 48% rejection, respectively (Zhong *et al.*, 2007). However, the major disadvantage of this process is less water recovery efficiency (13.8%-15.3%). High pressure is essential for more water recovery, which in turn enhances treatment cost. Researchers have also reported about the fouling of

membrane for longer operational time. Moreover, this process is only useful for the AMD laden with low metal concentrations. Therefore, the applicability of RO and nanofiltration needs to be investigated further for the treatment of AMD with high metal concentrations as well as requirement for the pre or post treatment or another stage of reverse-osmosis treatment for complying the environmental standards (Sastri, 1979).
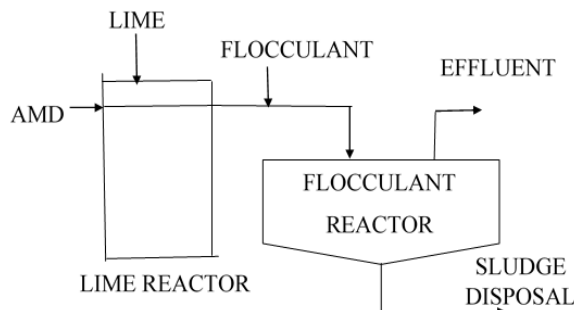

Figure 2. Conventional AMD treatment plant

Ion exchange is the reversible interchange of ions between a solid medium and the aqueous solution. Ion exchange resins or materials comprise of chemically inert polymer matrix with functional groups that are anionic or cationic. For treatment of hard water, water is passed through a bed of ion exchange material, which is charged with monovalent cations, such as sodium. Treatment of South African gold mines acidic drainage was done by heavy metal precipitation using lime followed by ion exchange for calcium and magnesium with sodium ions. (Skousen *et al.*, 1998; Feng *et al.*, 2000). Although, ion-exchange generates 98% water recovery, but it requires some pre-treatment that increases the cost of treatment process. Feng *et al.* (2000) reported that an ion exchange plant with a capacity 2.5 ML/d treating AMD effluent, requires 2.5 kg/m^3 acid for regeneration of resin, 2.5 kg/m^3 of lime and produces 98% of water recovery. For the whole operation, estimated cost is US$0.40/m^3. On other side, Gaikwad *et al.* (2010) carried out the performance and design of ion exchange column treating the AMD contaminated with copper. It was evaluated that for treatment of 5.137x10^{-3} m^3/cycle of water and resin capacity of 36 kg/m^3, required 9.8175 x 10^{-4} m^3 of resin. It was also reported that the diameter of the ion-exchange column was approximately 0.05 m and the amount of water required for backwashing was 0.4594 m^3/hr.

Electrodialysis (ED) unit consists of number of narrow compartments separated by closely spaced membranes and its each compartment is divided with cation and anion membranes. Positive and negative electrodes are placed at extreme opposite end of the unit. After filling the channels with solution, electrodes are energized and the ions in solution migrate towards the charged poles and ions are collected on the membranes (Skousen *et al.*, 1998, Buzzi *et al.*, 2011). Buzzi *et al.* (2013) has studied the effectiveness of electrodialysis for the pretreated acidic drainage with microfiltration. However, if AMD contains Fe, than it forms a precipitates at the surface of cation-

exchange membranes, which requires increase of membrane voltage in continuous manner. Therefore, removal of Fe is considered as a pre-treatment for ED process to treat the acidic water.

Table 2. Characteristics of different neutralization materials used for the treatment of AMD

Sl. No.	Name of acid neutralization	Saturation pH	Solubility (mg/L) in cold water	Advantage	Disadvantage	References
1.	Limestone	8-9.4	14	Inexpensive material, safe and easy to handle	Low solubility in cold water, generate external coating or armouring	Skousen *et al.* (1996); Skousen *et al.* (1998); Skousen (2002); Taylor *et al.* (2005)
2.	Hydrated Lime	12.4	1300-1850	Cost effective reagent for high flow and highly acidic AMD solution	Being hydrophobic, it requires mechanical aerator for mixing	Skousen *et al.* (1996); Skousen *et al.* (1998); Skousen (2002); Taylor *et al.* (2005)
3.	Pebble Quick Lime	12.4	1300-1850	Cost effective neutralizing agent	It is very reactive, so metering equipment needed to ensure proper mixing	Skousen *et al.* (1996); Skousen *et al.* (1998); Skousen (2002); Taylor *et al.* (2005)
4.	Soda Ash Briquettes	11.6	75,000	Useful for low flow and low amounts of acidity and metals	Soda ash briquettes absorbs moisture, expand and thereby stick to the corners of hopper in basket-hopper system.	Skousen *et al.* (1996); Skousen *et al.* (1998); Skousen (2002); Taylor *et al.* (2005)
5.	Caustic Soda	14	450,000	Can be used in remote location Very soluble and easily disperse in water	Incurred high cost, not safe to handle and generates high sludge volume	Skousen *et al.* (1996); Skousen *et al.* (1998); Skousen (2002); Taylor *et al.* (2005)
6.	Ammonia	9.2	900,000	Reactive and easily soluble Incurred 50-70% less cost than caustic soda	Cannot be handle easily, increasing the concentration of hazardous nitrate, specialized persons are required for safe handling of ammonia	Skousen *et al.* (1996); Skousen *et al.* (1998); Skousen (2002); Taylor *et al.* (2005)
7.	Magnesium Hydroxide	9.5-10.8	1-50	Cost effective reagent for high flow and highly acidic AMD solution	Being hydrophobic, it requires mechanical aerator for mixing	Skousen *et al.* (1996); Skousen *et al.* (1998); Skousen (2002); Taylor *et al.* (2005)
8.	Magna Lime	9.5-10.8	1-50	Cost effective neutralizing agent	It is very reactive, so metering equipment needed to ensure proper mixing Dissolution kinetics is marginally lower than quick lime.	Skousen *et al.* (1996); Skousen *et al.* (1998); Skousen (2002); Taylor *et al.* (2005)

Zeolites are known to be naturally occurring hydrated aluminosilicate minerals. They are closely related to the group of minerals known as "tectosilicates". The formation of natural zeolites is due to alteration of glass rich volcanic rocks by fresh water or by seawater. Three-dimensional frameworks of SiO_4 and AlO_4 formed the backbone of zeolite structure. Size of aluminium ion is very tiny to occupy the central position of the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+}, which in turn produce negative charge in the lattice. This net negative charge is balanced with the exchangeable cation (sodium, potassium or calcium). Cations are also interchangeable with some cations that are present in the solution (Pb^{2+}, Cd^{2+}, Zn^{2+}, and Mn^{2+}). The best part in case of zeolite is ions, which are exchangeable and comparatively harmless which makes them a suitable component for treating the heavy metal laden wastewater (Erdem et al., 2004).) Adsorption rate of heavy metal ions from solution follow the progression: Fe^{3+} >Zn^{2+}>Cu^{2+}>Mn^{2+} (Motsi et al., 2009). However, the efficiency of natural zeolites is exhausted after few adsorption cycles. Table 3 summarizes the advantage and the difficulties associated with reverse osmosis, ion exchange, electrodialysis and natural zeolites during treatment of acid mine water.

2.2. Treatment of AMD with waste materials

The above mentioned chemical treatments for the neutralization of AMD are associated with high cost of the adsorbents. Besides this, armoring of limestone by ferric hydroxides is a major issue which hinders the treatment efficiency of oxic limestone drains and the active limestone treatment systems. All these difficulties lead researchers to find efficient and cost effective neutralization materials (Gitari et al., 2008). Extensive research has been done for the treatment of AMD by various industrial wastes such as fly ash, steel slag, ZVI, CKD, organic waste through combination of reactions such as neutralization, adsorption and precipitation.

2.2.1. Fly ash

Fly ash is a low cost, environment friendly, unconventional and alternative adsorbent for activated carbon (Ceptin and Pehlival, 2007). It can remove different heavy metals from wastewater (Polat et al., 2002; Erol et al., 2005; Heechan et al., 2005). Researchers have reported that it can be used as pretreatment agent as an alternative to dolomite and limestone (Potgieter-Vermaak et al., 2006). It has been extensively used for the treatment of AMD. It was reported that fly ash can decontaminate the acidic water by removing heavy metals such as iron (Fe), aluminium (Al), manganese (Mn), calcium (Ca), magnesium (Mg), zinc (Zn), copper (Cu), cadmium (Cd), nickel (Ni), and cobalt (Co) (Gitari et al., 2008; Reynolds, 2004; Bäckström and Smarts, 2011; Jianping and Haito, 2014; Pradhan and Deshmukh, 2008). Removal percentage of different heavy metals with fly ash is presented in Table 4. Iron removal takes place at pH greater than 7. If the solution has pH from 4-4.5, Fe^{3+} is

removed as $Fe(OH)_3$ and as schwertmannite ($Fe_8O_8(OH)_6(SO_4).nH_2O$). For aluminium (Al) at pH 3.96-5.9, jurbanite controlled the Al concentration at the beginning stages of the neutralization process (Gitari et al., 2008). Although, many researchers have reported higher removal percentage of Cu, Zn and Cd (Gitari et al., 2008; Reynolds, 2004; Bäckström and Sartz, 2011) but low percentage removal of Cu, Zn and Cd was also reported (Jianping and Haito, 2014). The differences in removal efficiency is attributed to the characteristics of the fly ash. Fly ash utilized by Gitari et al. (2008) and Reynolds (2004) was rich in calcium content (CaO 2.1-8.43%) than the fly ash used by Jianping and Haito (2014) (CaO 1.22%). However, higher content of magnesium oxide (MgO 2.67%), was found for the fly ash used by Gitari et al. (2008) in comparison to the fly ash utilized by Reynolds (2004) and Jianping and Haito (2014). Therefore, CaO content plays the major role for enhancing the pH of the solution and thereby removal of metals from the solution. Precipitation of different metals from the solution occur at different pH. Manganese oxide (Mn^{2+}) at pH 5-5.5 and Cu and Zn at pH greater than 5-5.5 are cemented on the precipitated aluminium (oxy) hydroxide and iron (oxy) hydroxides. The concentration of Ca and Mg initially increases in the solution due to the leaching of Ca^{2+} and Mg^{2+} from surface of fly ash. However, after initial increment, Ca concentration decrease due to formation of gypsum and anhydrite, which takes over the control of calcium concentration in the solution. Gypsum formation at pH >5.5 and adsorption of high concentration of sulfate by iron hydroxides at pH >6.0 are attributed for the reduction of sulfate in the solution (Gitari et al., 2008). Fly Ash is not only effective for the treatment of AMD but it is also efficient adsorbent for the treatment of circumneutral mine water (CMW) which, contains lower concentration of Fe and Al but rich in Ca and Mg (Madzivire et al., 2010). CMW is produced by AMD's partial neutralization due to the surrounding geology. This process also results in precipitation of some metals while sulfate get precipitates in the form of gypsum or adsorbed on precipitating metal hydroxides. However, unlike AMD treatment with FA which removes significant amount of sulfate, treatment of CMW with FA is not so effective at pH <10. Treatment of CMW with FA followed by seeding of gypsum and amorphous $Al(OH)_3$, at pH 12.25, reduced sulfate concentration from 4800 ppm to 1043 ppm due to the dissolution of CaO from FA. CaO present in FA, dissolves and reacts with sulfate ions according to the Eq. (1) and Eq. (2) (Madzivire et al., 2010).

$$CaO + H_2O \longrightarrow Ca^{2+} + 2OH^- \tag{1}$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \longrightarrow CaSO_4.2H_2O \tag{2}$$
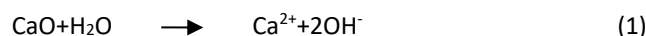
Thereafter, with addition of amorphous $Al(OH)_3$, the sulfate concentration was further reduced to 213 ppm from 1043 ppm as shown in Eq. (3)

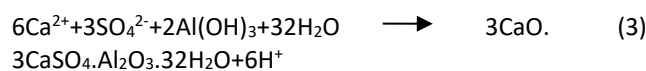$$6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_3 + 32H_2O \longrightarrow 3CaO.3CaSO_4.Al_2O_3.32H_2O + 6H^+ \tag{3}$$

Table 3. Different active treatment technology

Sl. No.	Methodology	Membrane used	Experimental condition	Percentage removal	Remarks	Reference
1.	Reverse Osmosis	Cellulose acetate membrane	Product rate 26.2 g/hr Operating pressure 300 psig	95-99% metal separation efficiency	Further reverse osmosis required for treated water	Sastri, 1979
2.	Reverse Osmosis	Polyamide Ultra-low-pressure reverse osmosis	Feed rate at 1200 L/hr 0.9-1.0 Mpa	Removal percentage of Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} was 97.41%, 97.73%, 97.89% and 98.06% respectively	No pre and post treatment required. However, higher pressure required to enhance the water recovery, that give additional treatment cost	Zhong *et al.*, 2007
3.	Filtration	Nanofiltration membrane	Feed rate at 1200 L/hr 0.9-1.0 Mpa	Removal percentage of Ni^{2+}, Cu^{2+}, Zn^{2+} and Pb^{2+} was 92.45%, 93.24%, 94.37% and 95.19% respectively	No pre and post treatment required. However, higher pressure required to enhance the water recovery, that give additional treatment cost	Zhong *et al.*, 2007
4.	Ion Exchange	-	Gel type strong acidic cation exchange resin of the sulphonated polystyrene, porous medium base anion exchange resin with an acrylic matrix	100% Metal removal and 98% of water recovery	different pre-treatment stages required, such as oxidation, neutralization and precipitation with lime and combination with different pre-treatment stages required, such as oxidation, neutralization and precipitation with lime and combination with	Feng *et al.*, 2000
6.	Electrodialysis	HDX 200 anion-exchange and cation exchange membrane	-	Metal removal efficiency was 97%	Requires pre-treatment such as microfiltration. Cannot able to treat AMD with higher Fe concentration	Buzzi *et al.*, 2013
7.	Natural Zeolites	-	6 hrs of reaction time with dose of 37 g/L.	Removal efficiency of Fe^{3+}, Mn^{2+}, Zn^{2+}, and Cu- was 80%, 95%, 90%, and 99% respectively.	Adsorption of elements decreases if initial pH of the AMD solution is lower.	Motsi *et al.*, 2009

Mg concentration decreased below detection limit when the pH was increased to 12.25 because of the formation of $Mg(OH)_2$. Treatment of mine water with FA also reduced Mn concentration below detection limit as Mn precipitates in the form of $Mn(OH)_2$ at pH 8.5-9.5 (Madzivire *et al.*, 2014). Along with various heavy metals, sometimes AMD contains different radioactive materials such as uranium (U) and thorium (Th) from the associated bedrock (Madzivire *et al.*, 2014). FA interacted with U and Th present in the water and form UO_2 at ph≥3 and ThO_2 at pH >5. Formation of these compounds helps to remove more than 90% of U and Th from the water. This in turn reduces the alpha and beta radioactivity by 88% and 75% respectively. FA behaves like a sink for these radioactive materials. It was also reported that treatment of AMD with FA, can remove 90% of Ra and Pb. Hence, it can be used as a safe adsorbent to treat contaminated gold mine water as no leaching of radioactive materials from coal fly ash to acidic water was reported (Madzivire *et al.*, 2014).

2.2.2. *Modified fly ash*

Although raw coal fly ash is an alternative for the chemical treatment of acid mine drainage, but sometime it shows insufficient adsorption capacity, and poor pH enhancing capability. Presence of higher amounts of Al and Si reduces the efficiency of fly ash. Therefore, to enhance the efficiency, coal fly ash is often modified by soaking in acid or alkaline solution. This chemically modified coal fly ash (MFA) results with greater surface area, lower amounts of Al and Si, higher pH value, enhanced pore volume, more loss of ignition and higher percentage metal removal efficiency (Sahoo *et al.*, 2013; Jianping and Haitao 2014; Hsu *et al.*, 2008). 120 g/L and 180 min was optimized as dose and reaction time, respectively, for AMD neutralization by MFA (Sahoo *et al.*, 2013). Table 4 presents the metal removal percentage by MFA. It also enhances the removal efficiency of heavy metal ions like Cd^{2+}, Cu^{2+}, Zn^{2+} due to higher specific surface area and small pore diameter (Jianping and Haito, 2014). Figure 3 depicted the reaction chemistry behind the metal removal by fly ash/modified fly ash. It shows that metal removal is due to adsorption of some metals such as Cu, Pb, Ni, Zn, Cd, Mn on the surface of adsorbent. Hydrolysis and precipitation of several metals in the form of $CaSO_4$, $CuSO_4$, $Cr(OH)_3$, $Fe(OH)_3$, $Mn(OH)_2$, $Al(OH)_3$ and co-precipitation of some metals in the form of $Fe(OH)_3$, Cu^{2+}, $Al(OH)_3$, Zn^{2+}, Mn^{2+} also play a major role for the metal removal process. Adsorption of metals (Cu^{2+} and Zn^{2+}) and anion such as SO_4^{2-} on the surface of secondary precipitated phases such as ferric hydroxide and aluminium hydroxide is the another major pathway for metal uptake by fly ash/MFA. However, removal efficiency gradually weakened with prolonged reaction time.

2.2.3. *Fly ash synthesized zeolites*

Zeolites can be produced from coal fly ash (CFA) by hydrothermal methods (Nascimento *et al.*, 2009). CFA contains huge amount of silica (Si) and aluminium (Al), which makes it suitable material for formation of zeolites.

Moreover, solid residue generated after treatment of AMD with fly ash can also be converted into synthetic zeolites. It has wide application such as alkylation, isomerization, catalysis for hydrogenation and acts as an excellent adsorbents for the removal of contaminants (heavy metals, toxic gas, organic pollutants such as benzene and alcohol) (Apiratikul and Pavasant, 2008). Synthetic zeolites from CFA shows adsorption capacity 2-25 times higher than the original CFA (Nascimento *et al.*, 2009) and 3-5 times greater than natural zeolites (Lee *et al.*, 2000), along with 100% removal of heavy metals (Koukouzas *et al.*, 2010). Ríos *et al.* (2008) studied the removal of heavy metals from AMD by different adsorbents such as coal fly ash (CFA), natural clinker (NC) and synthetic zeolites such as Natural Clinker Based Faujazite (NCF), Natural clinker-based Na-phillipsite (NCZ), Coal fly ash faujasite (CFAF) made from natural clinker, coal fly ash. NCF enhanced the pH to maximum 9.43 due to the presence of free CaO inside the faujasite network (Ríos *et al.*, 2008). The order of the adsorbents with respect to pH enhancement capability followed the trend NCF>CFAF>CFA>NCZ>NC. Besides the pH enhancing capability, NCF and CFAF also showed higher metal removal efficiency because of lower SiO_2/Al_2O_3 content that brings more terminal Al-OH species at zeolite-water interface during entire reaction. The enhancement in the hydrophilic nature of zeolite increases the metal exchange capacity. The principal mechanism associated with metal removal by the adsorbent is precipitation. With increasing pH, metal concentration decreases, which reveals the precipitation of metals on the surface of the sorbents (Ríos *et al.*, 2008).
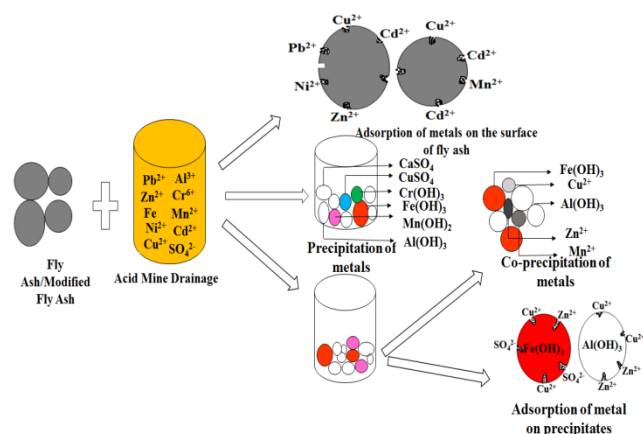

Figure 3. Removal of heavy metals by fly ash/modified fly ash

Extensive literature review demarcates that fly ash, natural zeolites and zeolites synthesis from fly ash has potential to decontaminate the AMD. However, disposal of this fly ash-solid residue after treatment is a matter of concern, as it contains heavy metals on its surface that has environmental impacts like water pollution, soil pollution, etc. Therefore, safe disposal of the solid residue is necessary. Zeolites synthesized from the solid residue, recovered after the treatment of fly ash and AMD, is reported as a very effective adsorbent for the treatment

of AMD (Petrik *et al.*, 2003; Gitari *et al.*, 2005; Somerset *et al.*, 2008; Vadapalli *et al.*, 2010). Gitari *et al.* (2005) synthesized ion-exchange adsorbents, in form of zeolites, through high temperature hydrothermal reaction from this solid residue. It was used for comparative analysis for the removal of Ni, Zn and Pb with commercial zeolite. Although removal of Zn was not significant, however Ni and Pb removal efficiency with the synthesized adsorbent was higher than the commercial zeolites. Somerset *et al.* (2008) studied removal efficiency of zeolite synthesis from fly ash and solid residue. It was found that zeolite produced from solid residue has the ability to remove lead and mercury from acidic wastewater with removal percentage of 95% and 30%, respectively. While, zeolites synthesized from raw fly ash removed lead up to 88%, but was unable to reduce the mercury concentration. Vadapalli *et al.* (2010) also investigated about the reuse of the solid residue synthesized product, zeolite-P for the treatment of CMW up to four number of treatment cycle. The product had a high cation exchange capacity (178.7 meq/100 g) and surface area (69.1 m^2/g). Percentage removal efficiency of zeolite-P presented in Table 4. Metals such as K, Ca, Sr, and Ba were efficiently removed by zeolite-P in the first phase of treatment. However, removal of Mg was insignificant. Although, it was able to remove heavy metals successfully for the first treatment cycle, but removal efficiency exhausted and the pH decreased from 8.3 to 7.5 with subsequent and rapid treatments, which may be attributed to the competition and adsorption of the other materials on the surface of zeolite. Sodium (Na) was the most important exchangeable cation presented in the zeolite-P product as there was continuous release of Na found during the experiments. Therefore, solid residue could be effective in the form of synthetic zeolites for the treatment of acidic waste water laden with high concentration of heavy metals.

2.2.4. *Slag*

Slag is considered as waste product from steel making industry. Iron ore or scrap metals are added in molten form with limestone, dolomite or lime in different combination during steel making process. All these calcium components combine with aluminium, silicon, and phosphorous to form slag. Matrix of slag solubilize to release calcium and magnesium oxides which in turn enhance the pH of dissolving fluid up to 10-11 and help the metals to precipitate in the slag leach bed when AMD passes through it. The neutralization potential (NP) of steel slag is in the range of 45 to 78%. For in-situ AMD treatment, the effluent from the leach beds can infiltrate directly into a spoil or refuse-pile (Ziemkiewicz and Skousen, 1998). Feng *et al.* (2004) conducted a study using metallurgical by product, slag (Iron slag and Steel slag) for the treatment of gold mine AMD which was highly acidic (pH 2.03) and contained high concentration of different heavy metals. Iron slag, showed much higher adsorption capacity with greater increase in pH in comparison with

steel slag. Optimum pH value for the metal sorption was 3.5-8.5 for steel slags and 5.2-8.5 for iron slag. Metal adsorption increased as soon as the pH of iron slag increased (>4.8), due to the enhancement of negative charge on the surface of slag which increases the metal removal by adsorption, precipitation and co-precipitation represented in Figure 4. It illustrates that adsorption of some metals such as Cu^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}; precipitation of several metals in their hydroxide form ($CaSO_4$, $CuSO_4$, $Cr(OH)_3$, $Fe(OH)_3$, $Mn(OH)_2$, $Al(OH)_3$) as well as the co-precipitation of some metals in form of $Fe(OH)_3$, Cu^{2+}, $Al(OH)_3$, Zn^{2+} and Mn^{2+} are the significant metal removal processes from AMD. Moreover, the adsorption of metals (Cu^{2+}, Zn^{2+}) and anion such as SO_4^{2-} on the surface of secondary precipitated phases such as ferric hydroxide and aluminium hydroxide is one of the reason for metal removal as well. In case of steel slag similar phenomenon occurs at ph >3.2. Name and Sheridan (2014) investigated the efficiency of two type of slag, Basic Oxygen Furnace slag (BOF) and Stainless Steel (SS) slag for the treatment of AMD. Metal removal efficiency for different metals are listed in Table 4. 30 g/L of slag dose and 24 hrs of reaction time was optimum to enhance the pH to 6.68 and 6.32 for iron slag and steel slag, respectively, with greater sulfate removal in iron slag (Feng *et al.*, 2004). 100 g/L dose of BOF slag not only enhances the pH to a greater value in comparison with SS slag, but also results in higher sulfate removal (Name and Sheridan, 2014). From the comparative study, it was evident that as the dose of steel slag or BOF slag was enhanced percentage reduction of sulfate decreased (Table 4). So, the variation in pH enhancement and sulfate reduction was attributed to the characteristics of slags used for the treatment. Calcium content was more in case of iron slag (46.3%) than steel slag (37.5-38.7%) and SS slag (36%). Because of higher calcium content in iron slag higher reduction in sulfate was was observed due to precipitation as gypsum (Gitari *et al.*, 2008). Metal removal efficiency of iron slag was more than BOF slag because of its higher surface area 31.929 m^2/g than BOF slag 22.333 m^2/g (Feng *et al.*, 2004). Therefore, the sequence of the adsorbents with respect to metal removal was iron slag>BOF slag> SS slag. Although, the experimental results of batch experiments for the treatment of AMD with slags were very impressive, but AMD treatments in slag leach beds sometimes proves ineffective for prolonged period of reaction time. This might be due to limitation of dissolvable calcium compounds on the surface of slag particles that lead to low alkalinity loadings. Accumulation of thick layer of precipitation in the effluent piping as well as formation of precipitates within slag resulted in lower alkalinity values (Goetz and Riefler, 2014).

2.2.5. *Zero valent iron particles*

Zero valent iron (Fe^0) is one of the common reducing agent, used for the removal of contaminants from wastewater. It behaves as a strong reducing agent as well as it is cost effective and readily available material to reduce the sulfate and enhance the metal precipitation of highly stabilized metal sulfides. Even the corrosion of iron

promotes the generation of Fe^{2+} ions that in turn sequester excess sulfide and the effluent contains minimum concentration of toxic metals. It can neutralize the acidity of AMD by generating alkalinity (Eq. (4)) through the corrosion of ZVI (Ayala-Parra et al., 2016).
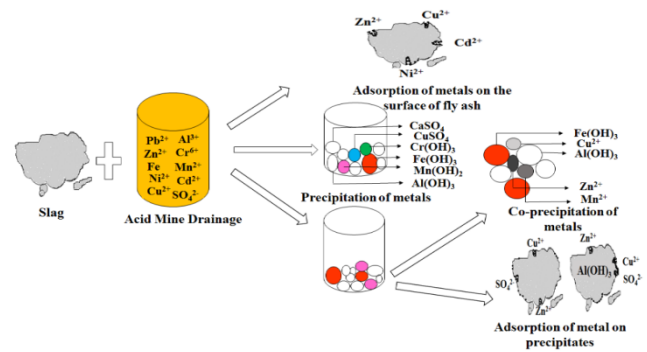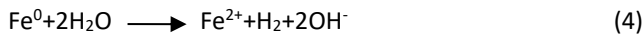
$$Fe^0 + 2H_2O \longrightarrow Fe^{2+} + H_2 + 2OH^- \qquad (4)$$

Figure 4. Removal of heavy metals by Slag

Table 4. Removal percentage of metals with different waste material

Sl no	Used material	Optimum Mixing ratio/ Dose	Initial pH	Final pH	Reaction Time	Percentage removal of metals	References
1.	Fly Ash	1:3	2.78	9.1	1440 mins	Greater than 90% for toxic metals, 78% for sulfate	Gitari et al., 2008
2.	Coal Fly Ash	-	4	7.0	12 hrs.	60.4% sulfate, 53.4% Chemical Oxygen Demand	Jianping and Haitao, 2014
3.	Fly Ash	-	2.88	12.0	-	Removal of 97.0% Al, 99.9% Fe, 99.98% Mn and 96.42% Zn	Reynolds, 2004
4.	FA followed by seeding with gypsum crystals and the addition of amorphous $Al(OH)_3$	1:2	6.6 ± 0.21	12.25	-	Removal of 79.57% sulfate	Madzivire et al., 2010
5.	Alkaline Ash Leachates	-	3.3-5.0	8.0	7 days	Removal of 99.97% of Cu, 99.78% of Zn, 90.2% of Cd, 99.94% of Pb, 62.71% of Ni and 99.41% of Co.	Bäckström and Sartz, 2011
6.	Modified Fly Ash	120 g/L	1.6	2.8-6.6	180 min	89%, 92%, 94%, 96%, 60%, and 99 % for Ni, Zn, Pb, Fe, Mn, and Al respectively	Sahoo et al., 2013
7.	Modified Fly Ash	-	4		36-120 hrs	82.4% of Cd^{2+}, 91.85% of Cu^{2+}, 57.2% Zn^{2+}	Jianping and Haitao, 2014
8.	Natural Clinker-Based Faujasite	0.25 gm and 1 gm in 20 ml	1.96	4.29-9.43	24 hrs	Approximately complete removal of Fe, As and ammonium. Partial removal of Cu and Zn.	Ríos et al., 2008
9.	Synthetic Zeolite	20 g/L	2.64	4.25-4.88	1 hr	Removal efficiency for lead is 88%	Somerset et al., 2008
10.	Synthetic zeolites (Zeolite-P)	1 g/100 ml	6.2	8.3	1 hr	Removal of Al, Fe, Mn, Zn, Cu, Ni, Mg as (68%-77%), (99.1%-99.9%) (8%-64%), (58%-69.2%), (54%-88.9%),(43%-68.6%), and (7%-13%) respectively	Vadapalli et al., 2010
11.	Basic Oxygen Furnace	30 g/L	2.03	6.32	24 hrs	Greater than 90% removal of heavy metals and anions	Feng et al., 2004

	Slag/Steel Slag						
12.	Iron Slag	30 g/L	2.03	6.68	24 hrs	Greater than 90% removal of heavy metals and anions	Feng *et al.*, 2004
13.	Stainless Steel slag	100 gm/L	2.5	5.9	240 mins	Removal of 63.6% iron,39.8% sulfate	Name and Sheridan, 2014
14.	Basic Oxygen Furnace Slag/Steel Slag	100 gm/L	2.5	11.3	240 mins	Removal of 99.7% iron,75% sulfate	Name and Sheridan, 2014
15.	Colloidal Iron	3%(w/v)/1.25 L	2.3	6.5	250 hrs.	99.6% of Al, 64.4% of As, 97.1% of Cr, 98.5% of Zn and 19.5% of Sulfur	Shokes and Moller, 1999
16.	Granular Iron	3%(w/v)/1.25 L	2.3	5	250 hrs.	97.7% of Al, 29.6% of As, 8.2% of Cr, 3.33 % of Zn and 4.43% of Sulfur	Shokes and Moller, 1999
17.	Zero Valent Iron	0.23 gm/ml	2.3	5.7	24 hrs.	Removal of 99.90% Al, 97.7% Hg, 99.42% As, 98.4% Cd, 99.98% Cu, 99.78% Ni and 9.81 % of Zn	Wilkin and McNeil, 2003
18.	Zero Valent Iron and mixtures of Organic carbon	-	4.5-4.8	6.38-6.87	60 days	Removal of Fe (91.6–97.6%), Zn (>99.9%), Cd (>99.9%), Ni (>99.9%),Co(>99.9%) Al (>99.9%),Mn (89.9-90.6%)and Pb (94.6-96.9%)	Lindsay *et al.*, 2008
19.	Zero Valent Iron	-	4.8	7.32-7.61	60 days	Removal of 31.3% Fe, 76.75% Co, 98.2% Zn, 99% Ni and Cd, and Pb (94.6-96.9%)	Lindsay *et al.*, 2008
20.	Cement Kiln Dust Slurry	25% of CKD slurry	(2.4 ±0.1)	9.5	1 minute	98% of zinc and 97% of iron	Mackie and Walsh, 2012
21.	Rice Husk	1:10	2.3	4.0	24 hrs.	99% Fe^{3+}, 98% Fe^{2+},98% Zn^{2+} , 95% Cu^{2+}	Chockalingam and Subramanian, 2006
22.	Peat Humic Agent	1:500	2.7	3.1	1 hr	Removal of 36% Fe, 26% Al, 20% Zn, 35% Cu, 43% Cd, 98% Pb, 40% Ni, 21% Co	Bogush and Voron, 2010
23.	Peat Humic Agent	1:500	4.1	5.3	1 hr	Removal of 95% Fe, 99% Al, 21% Zn, 23% Cu, 23% Cd, 15% Ni and 18% Co	Bogush and Voronin, 2010
24.	Peat Humic Agent	1:500	4.8	7.1	1 hr	Removal of 94% Fe, 99.9% Al, 96% Zn, 99% Cu, 76% Cd, 61% Ni and 57% Co.	Bogush and Voronin, 2010

Abiotic removal of metals take place by different processes such as adsorption onto the surfaces of Fe^0 and precipitation. Iron has proved as an effective material in changing the chemistry of acidic system towards conditions promoting immobilization of dissolved heavy metals, increase in pH, and decrease in redox potential (Shokes and Moller, 1999). Extensive studies were carried out with Fe^0 in the form of iron fillings, iron chips and used in batch study as well as in permeable reactive barrier for the removal of different toxic metals such as chromium (Cr), mercury (Hg), nickel (Ni), copper (Cu) and organic compounds from contaminated water (Blowes *et al.*, 1997; Puls *et al.*, 1997; Weisener *et al.*, 2005; Sinha and Bose, 2009; Moraci and Calabrò, 2010). Complete removal of radioactive metal such as uranium was also reported with iron particles (Gu *et al.*, 1998). Shokes and Moller (1999) carried out their study with diversified form of Fe^0 such as, colloidal iron and granular iron. Wilkin and McNeil (2003) used granular iron of two different mesh size; peerless iron of (-8+50) mesh particle size and fisher iron of (-100) mesh particle size for their experiment. Both the iron particles showed the enhancement of pH from

2.3 to 5.7-6.5. AMD solution with lower initial pH, such as 3.5 and 4.5 reached to higher final pH of 9.6-10.0 after several hours of reaction (Wilkin and McNeil, 2003). Metal removal efficiency for both the experiments is presented in Table 4. However, metal removal efficiency of colloidal iron is better than granular iron because of their specific surface area. Surface area of colloidal iron was 0.3 m^2/g whereas 0.005 m^2/g for granular iron. As the surface area was much less therefore, granular iron does not have adequate surface area to enhance the pH to 7 or to maintain a reducing environment by generating hydroxyl ions (Shokes and Moller, 1999). Shokes and Moller (1999) reported Ni removal percentage with colloidal iron and granular iron was 74.5% and 7.1%, respectively. Whereas, Wilkin and McNeil (2003) reported the removal percentage as 99.78% with granular iron. Similarly for Zn, removal percentage was observed to be 98.5% and 3.33% with colloidal iron and granular iron, respectively (Shokes and Moller, 1999), in comparison to 98.81% for peerless iron and 99.78% for fisher iron, respectively (Wilkin and McNeil, 2003). The variation in the results might be due to the specific surface area of both the granular iron. Specific surface area of peerless iron and fisher iron was reported as 3.05 m^2/g and 0.05 m^2/g (Wilkin and McNeil, 2003), which is more than reported by Shokes and Moller (1999). However, there was no significant difference in percentage removal for peerless iron and fisher iron. This may be due to the same pH attained by both granular irons and precipitation of the metals took place according to their own precipitating pH values. Removal of sulfate by Fisher iron was two times more than the reduction by pearless iron at same dose level. However, Mn removal by ZVI was insignificant (Wilkin and McNeil, 2003). This may be due to release of Mn ions from ZVI at low pH values. Ni and Zn removal took place due to the formation of complexes with hydroxide and sulfate. Removal process for antimony (Sb) was very slow and it took several hours to achieve 86% of removal. It was reported that the oxidation state of As does not changed by ZVI, it remain in As(V) form in the solution (Wilkin and McNeil, 2003). It forms complexes with iron oxide and removed by co-precipitation with sulfides, iron oxides and iron oxy-hydroxides. Cd and Cu bind on the surface of the iron by reduction into its elemental metal form. Al precipitate as Al(OH)$_3$ (Wilkin and McNeil, 2003; Shokes and Moller, 1999). Figure 5 depicted the removal process of metals by ZVI. Adsorption is considered as the initial and most rapid metal uptake mechanism. Cu^{2+} and Cd^{2+} reduced by ZVI and adsorption of elemental Cu and Cd take place on the surface of ZVI itself. Similarly, precipitation of metals according to their hydroxide form such as Cr(OH)$_3$, Fe(OH)$_3$, Al(OH)$_3$, Mn(OH)$_2$, Ni(OH)$_2$ occur. Sulfate may be removed from the solution by precipitation of metal sulfur compounds such as metal sulfate (NiSO$_4$, CuSO$_4$), metal hydroxide compounds Fe$_6$(OH)$_{12}$SO$_4$.nH$_2$O or co-precipitate as metal hydroxide (M$_6$(OH)$_{12}$SO$_4$). Iron corrodes in acidic solution and formed iron oxy hydroxide and iron oxides and co precipitated on the metal surface. As^{5+} co-precipitated with iron oxide or iron oxy hydroxide or cemented on the surface of ferrihydrite (Fe$_5$HO$_8$.4H$_2$O).

Ni^{2+} and Zn^{2+} form complex with hydroxide and sulfate or cemented on the surface of ferrihydrite.

Under anaerobic condition sulfate reduction leads to the corrosion of Fe^0 and forms Fe (II) along with OH$^-$ and H$_2$ (Eq. 4). Molecular H$_2$, is utilized by some sulfate reducing bacteria (SRB) species as an electron donor for SO$_4^{2-}$ reduction (Eq.5) (Karri *et al.*, 2005; Ayala-Parra *et al.*, 2016).

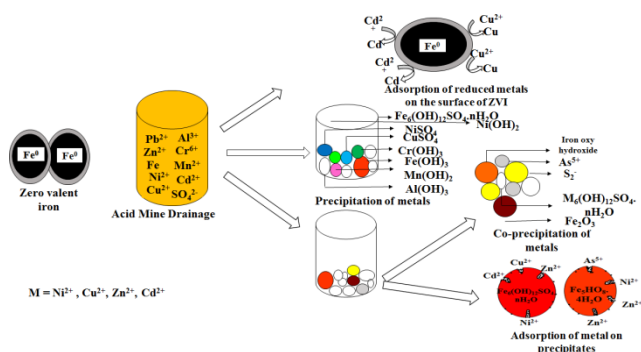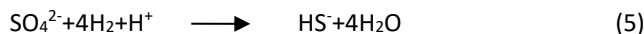$$SO_4^{2-}+4H_2+H^+ \longrightarrow HS^-+4H_2O \qquad (5)$$

Figure 5. Removal of heavy metals by Zero Valent Iron

Table 5. Composition of reactive mixtures expressed as dry weight percentages (dry wt.%) (Lindsay *et al.*, 2008)

Reactive mixture	Reactive mixture composition (dry wt. %)				
	OC	Fe^0	Inoculum	Limestone	Silica Sand
RM1	50	0	2	16	32
RM2	48	2	2	16	32
RM3	45	5	2	16	32
RM4	40	10	2	16	32
RM5	0	50	2	16	32

It was reported that some heterotropic bacteria such as *Desulfovibrio desulfuricans* oxidize H$_2$ but it requires some organic carbon (OC) source for their growth (Ehrlich, 2002). Permeable reactive barrier (PRB) contained mixture of Fe^0 and OC that promotes the growth of SRB, which in turn reduces sulfate with buffering of pH and enhanced removal of metals/trace elements (Lindsay *et al.*, 2008; Ayala-parra *et al.*, 2016). Enormous studies have been done to find the effectiveness of zero valent iron and combination of zero valent iron along with organic carbon mixtures for the remediation of AMD (Lindsay *et al.*, 2008; Ayala-parra *et al.*, 2016). Compositions of reactive-mixtures (RM) are presented in the Table 5. Experimental results showed rapid decrease in metal concentration and sharp increase in pH within 1 day. Although, metal removal under sulfate reducing condition takes place due to metal-sulfide precipitation, but other mechanisms such as (oxy) hydroxide precipitation, co-precipitation and surface complexation also acts as key

mechanisms for metal removal. Similar sulfate reduction rate (SRR) was observed for RM3 and RM4. Manganese (Mn) concentration eventually increase (28.3%) in RM5, at ph<8 as Mn-hydroxide was not precipitated. From the results it is inferred that except Fe and Mn, removal efficiency for all heavy metal was almost similar when Fe^0 was used either solely or in combination with OC. Ayarapara *et al.* (2016) reported similar observation, with respect to using limestone (LS) and ZVI for the treatment of AMD. LS aids as buffer as well as inorganic food for lithoptropic SRB that can utilize CO_2 as a carbon source. Increasing sulfate reduction observed in ZVI-LS column than ZVI column, where sulfate reduction ceased after small reaction time in LS column. Metal removal efficiency in all the columns was more than 98%. In ZVI column, metal removal took place due to the formation of metal sulfides. It was observed from the solid-phase analyses that heavy metals precipitated with biogenic sulfide in the columns packed with ZVI. However, in absence of ZVI, heavy metals were also significantly removed due to precipitation with hydroxide and carbonate ions released from limestone, though LS surfaces are super saturated after a while. Therefore, in case of permeable reactive barrier (PRB), small amount of Fe^0 can make the system efficient and cost effective. ZVI acts as an efficient reducing agent for treatment of AMD, specifically for sulfate reduction when associated with PRB system (Ayala-parra *et al.*, 2016).

It is concluded that zero valent iron is effective to decontaminate the acid mine drainage through various reaction mechanism from its soluble toxic metals as well as anions such as sulfate, chloride etc. However, if groundwater is contaminated with sulfate rich ground water then the prime corrosion product of zero valent iron is green rust. Regular adsorption of green rust on the top of the iron corrosion products, co-precipitation with corrosion products or combination of both makes the metal uptake process much slower. Another important factor that also hinders the efficiency of ZVI, is the presence of high concentration of total dissolved solid loads (TDS). Loss of permeability and high rates of mineral precipitation, due to high loads of TDS, also acts as barrier for the efficiency of ZVI (Wilkin and McNeil, 2003).

2.2.6. *Cement klin dust*

Cement Klin Dust (CKD) is known as caustic-material, which is produced during the cement production in cement klin. In cement production, the raw materials such as limestone along with quicklime, eventually converts into lime by removal of carbon dioxide within klin. Pollution control devices such as Bag house filter and electrostatic precipitator (ESP) remove the small particles of CKD, present in the exhaust gases generated from cement kiln. This waste product contains 8-61% (weight %) of total CaO (Mackie and Walsh, 2012). Extensive literature studies reported that CKD is able to remove the pollutant and toxic heavy metals from the wastewater with approximately 100% removal percentage (El-Awady and Sami, 1997; Zaki *et al.*, 2007). Mackie and Walsh (2012) conducted a bench-scale study to evaluate the

efficiency of CKD for acid mine water treatment. Four type of CKD sample (CKD-A, CKD-B, CKD-C, and CKD-F) whose particle sizes were 34-73% smaller and specific surface areas 2-3 times greater than the quicklime samples were used in this study. Treatment of mine water with 25% of CKD (w/v) removed 98% of total zinc and 97% of total iron concentration. Metal removal percentage are presented in Table 4. Surface adsorption, hydrolysis and precipitation of the heavy metals are the removal mechanism of toxic metals (Figure 6). It illustrates that adsorption as well as the precipitation of metal (Cu, Pb, Cd, Zn) as their hydroxide ($Cu(OH)_2$, $Cr(OH)_3$, $Fe(OH)_3$, $Al(OH)_3$ $Pb(OH)_2$) and sulfate form ($CaSO_4$) are major metal removal path followed by CKD. However, among all the CKD samples, CKD-F has the highest free lime content. Therefore, removal efficiency of CKD-F is slightly better than other CKDs. All CKD samples were able to achieve more than 98% and 97% precipitation of soluble Zn and Fe concentration, respectively. Moreover, CKD-treated samples generated less sludge by volume (50%-60%) than the sample treated with quicklime slurry. Therefore, CKD is a promising treatment option to reduce acidity, precipitate and remove metals as they generate only 50-60% of sludge compared to lime. However, increasing settling time or polymer doses might be needed to meet the treatment requirements. Even though the treatment results are significant, but to treat the mine water with CKD, much higher volumes of slurry is required to reach the target pH of 9 with respect to quicklime slurry.
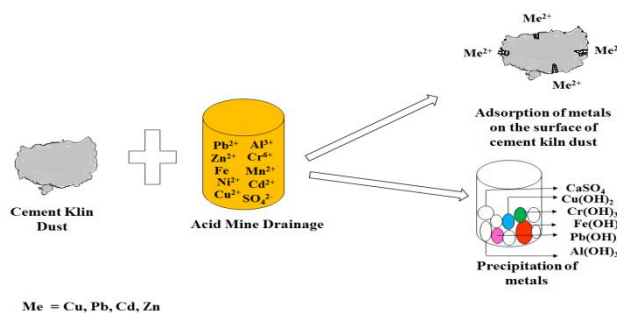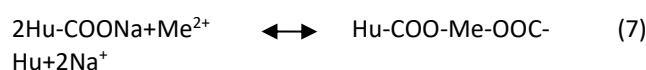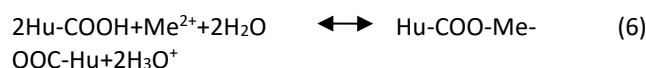

Figure 6. Removal of heavy metals by Cement Klin Dust

2.2.7. *Organic waste material*

Organic substrates such as rice husk and peat humic agent (PHA) are also considered as potent adsorbents for the metal ions. Humic agents are high molecular complex organic compounds formed due to the decomposition of vegetative and animal residue by microorganisms and abiotic factors (Orlov, 1990). Carboxyl group present in humic agent in the form of humic acid (Hu-COOH) and sodium humate (Hu-COONa) produce humate ion, a hydroxonium ion and a sodium ion via dissociation. This humate ion form humate complex by reacting with metal ions (Eq. (6) and Eq.(7)) (Bogush and Voronin, 2010).

$$2Hu\text{-}COOH + Me^{2+} + 2H_2O \longleftrightarrow Hu\text{-}COO\text{-}Me\text{-}OOC\text{-}Hu + 2H_3O^+ \tag{6}$$

$$2Hu\text{-}COONa + Me^{2+} \longleftrightarrow Hu\text{-}COO\text{-}Me\text{-}OOC\text{-}Hu + 2Na^+ \tag{7}$$

Organic materials and humic agents consist of carboxyl, hydroxyl, carbonyl, amide and phenolic group, attached to larger organic molecules, which in turn bind the metal ions (Bogush *et al.*, 2007). Organic compounds act as an excellent energy source for the SRB. These organic compounds can be utilized as an adsorbent for the removal of heavy metals from wastewater. Chockalingam and Subramaniam (2006) studied the metal ions removal and sulfate reduction using rice husk and SRB (*Desulfotomaculum nigrificans*) for the remediation of AMD. AMD and simulated AMD with pH 2.3 were pre-treated with rice husk (10 gm/100 ml) in the study. After pre-treatment, pH of AMD and simulated mine water increased to approximately 4.5 and 6.1 respectively. For sulfate reduction tests, acid mine water of pH 2.3 were interacted with 10, 16 and 20 g of rice husk for 1 hour so that the final pH values became constant at 4.6, 5 and 5.3 respectively. There was no significant sulfate removal after 24 hours. However, after inoculation of *D. nigrificans* into AMD, sulfate reduction increased to 40% from 21% at pH 5.3 after 31 days by using rice husk filtrate in addition with nitrogen and carbon contents. In case of simulated AMD, sulfate removal percentage was observed to be 73% after 35 days. However, concentration of sulfate again increased after the point of its reduction for both the cases. This might be due to the co-precipitation of sulfate and ferric (oxy) hydroxides in the acid mine water sample and its subsequent dissolution in reducing conditions (Christensen *et al.*, 1996). Metal removal process by rice husk is represented in Figure 7.

The figure 7 clearly depict that adsorption of metals (Cu^{2+}, Pb^{2+}, Fe^{2+}, Zn^{2+}) and conversion of sulfate to sulfide by SRB is the major metal removal process of rice husk associated with SRB. Moreover, the co-precipitation of metals with iron oxy-hydroxide as well as sulfate is the other metal uptake procedure form AMD contaminated water.
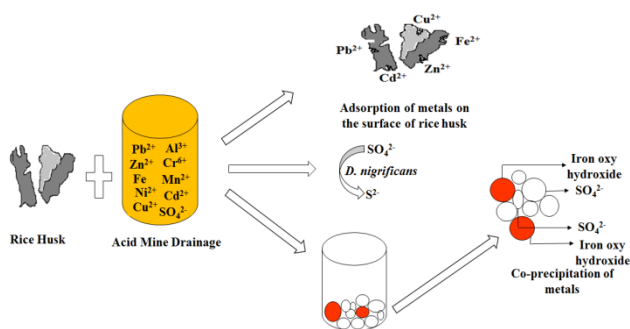

Figure 7. Removal of heavy metals by Rice Husk

Treatment of acid mine drainage with peat humic agent was carried out by Bogush and Voronin (2010). Three PHA/AMD ratios (1:100, 1:500 and 1:1000) and three different type of AMDs with three different initial pHs (2.7, 4.1, and 4.8) was used for this study. It was observed that PHA has the ability to remove heavy metals from the mildly acidic AMD and contains moderate metal concentration by hydrolysis, physical adsorption and co-precipitation of metals on the surface of ferric hydroxide, presented in Figure 8. Adsorption of metals (Pb^{2+}, Cu^{2+},

Cd^{2+}, Ni^{2+}, Zn^{2+}) on the surface of PHA and the precipitation of metals ($Cu(OH)_2$, $Cr(OH)_3$, $Fe(OH)_3$, $Mn(OH)_2$, $Al(OH)_3$) in its hydroxide form are the key mechanism for the metal removal from AMD. However, co-precipitation of the metals as well as the adsorption of metals on the metal precipitates such as $Fe(OH)_3$ are also considered for the metal removal process of PHA. Furthermore, AMD with pH 4.8 was treated with PHA at 1:500 ratio, it removed more than 90% toxic and other metals and pH was enhanced to 7.1. Therefore, the order of AMD that can be treated with PHA was as follows, AMD with pH 4.8>AMD with pH 4.1>AMD with pH 2.7. Metal removal percentage is presented in Table 4. Although, PHA are very stable in nature, not prone to biodegradation and thermal destruction, however, in comparison with rice husk, it can only treat mildly acidic water. Therefore, PHA is not beneficial for treating the highly acidic AMD.
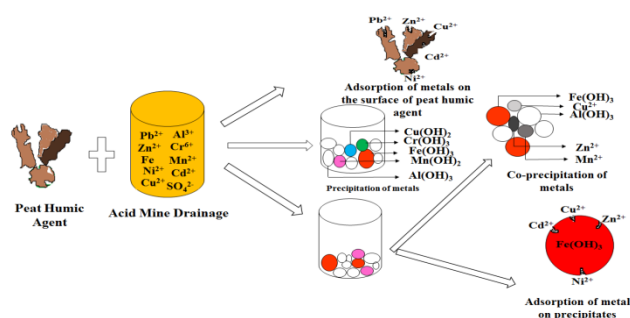

Figure 8. Removal of heavy metals by Rice Husk

3.   Discussion

3.1. Enhancement of pH by different type of waste material

The prime objective to treat AMD is to increase the level of pH from acidic to neutral or basic. Researchers have used various waste materials to enhance the pH of the wastewater.

Fly ash, modified fly ash, metallurgical slag and cement kiln dust have the ability to enhance the pH of AMD from 2.00 to the range of 8-12 (Gitari *et al.*, 2008; Reynolds, 2004; Bäckström and Sartz, 2011; Ríos *et al.*, 2008; Name and Sheridan, 2014). However, BOF slag has more potential to enhance the pH from 2.5 to 12.1 than SS slag, which enhance the pH from 2.5 to 6.6 (Name and Sheridan, 2014). Natural clinker and ZVI are unable to increase the pH to higher alkaline pH values. They can enhance the pH only up to 3.86-5.7 from an initial value of 2.5. Raw fly ash is not able to enhance the pH of AMD if it contains low lime content. Sahoo *et al.* (2013) modified the fly ash for the treatment of AMD due to its poor pH enhancing property. It was reported that fly ash can enhance pH up to 5.3 without any modification whereas with modification, pH value can be enhanced to 11.5. After the conversion of fly ash into zeolites, pH of the acidic water can be turned into alkaline range i.e. 8.41-12 (Koukouzas *et al.*, 2009; Ríos *et al.*, 2008). However, organic waste such as rice husk and PHA have very low

capability to enhance the pH. They can enhance the pH from 2-3 to 3.7-4 (Bogush and Voronin, 2010; Chockalingam and Subramanian, 2006). Lindsay *et al.* (2008) reported that the treatment of AMD with combination of ZVI and organic carbon enhances pH from 4.5 to 7.32 within 11 days. The difference in enhancement of pH in acidic solution, by different adsorbents, might be due to the variation of calcium and magnesium oxide content available within adsorbents and due to their ability to reduce water and produce hydroxide ions.

3.2. Effect of dose of adsorbents

Although all the adsorbents have the ability to decontaminate AMD, but percentage removal for the heavy metals depends on the optimum doses of the adsorbing material. Gitari *et al.* (2008) carried out the study of AMD treatment with two different ratio of FA:AMD i.e. 1:3 and 1:1.5, respectively. It was evaluated that the maximum percentage removal of heavy metals (Mg, Mn, Al, Si. Total Fe, Zn and Cu) was at ratio of 1:1.5. Sahoo *et al.* (2013) evaluated that the maximum removal efficiency of metals with modified fly ash was observed at 120 g/L out of 25 g/L, 50 g/L, 80 g/L, 120 g/L, and 150 g/L. When the dose of NCF increased from 0.25 g/20 ml to 1 g/20 ml, pH of the solution enhanced to 9.43 from 1.96 and the metal removal efficiency increased (Koukouzas *et al.*, 2010). Metallurgical slags such as basic oxygen slag and stainless steel slag were tested with different ratios such as 20, 40, 60, 80, 100, 120 and 140 g/L for the treatment of AMD. Finally, it was concluded that for both the material, 100 g/L is optimum for maximum removal of metals (Name and Sheridan, 2014). In case of ZVI, Wilkin and McNeil (2003) carried out study with different dose of iron, i.e, 0.02 g/ml to 0.23 g/ml where maximum percentage removal was observed at 0.23 g/ml of iron dose. PHA was used as adsorbent with three different PHA: AMD ratio of 1:1000, 1:500 and 1:100 and 1:500 ratio was the most efficient dose for the treatment of mild acidic AMD (Bogush and Voronin, 2011).

3.3. Effect of initial pH values of AMD

Acidic effluent can be converted into neutral effluent with the adsorbents. However, initial pH of the AMD plays an important role in the attainment of alkaline conditions and neutralization of AMD. Wilkin and McNeil (2003) investigated that when the AMD has initial pH of 2.3, ZVI was able to enhance the pH up to 5.7-6. However, when the initial pHs of the solution were 3.5 and 4.5, enhancement of the pH took place up to 9.8-10. At this increased pH, higher percentage of metal removal occurred. Bogush and Voronin (2010) investigated that the AMD with initial pH 2.7, reached to pH 2.9-3.1 only with PHA. However, when initial pH of the effluent was 4.8, PHA enhanced the pH values to 8.2. Lindsay *et al.* (2008) showed that, pH enhanced to 6.38 when the initial pH of AMD was 4.5 with OC associated with ZVI.

4. Conclusion

This paper critically reviewed the application and selection of waste materials for the treatment of AMD. Although, active treatments are effective, but they incur high installation and adsorbent cost. Beside this, some active treatment such as reverse osmosis, ion exchange, electrodialysis need pre-treatment of the influent, which enhances the whole treatment cost. Waste material on other side reduces environmental load and are economically viable alternative for the treatment purpose. After consideration and reviewing different studies, it can be concluded that among all the waste material, fly ash and its derivatives such as modified fly ash and fly ash synthesized zeolites, slag, CKD can be preferred among all the waste material for the treatment of extreme acidic AMD. They have more potential to enhance the pH of extreme acidic solution as well as removal of pollutants from the solution. On the other side, ZVI and organic waste can be used if the AMD is mild or less acidic in nature. OC along with ZVI and SRB can be considered as potential option if the sulfate concentration in AMD is high. However, specific surface area, pH enhancing capacity, adsorption capability, retention time, leachability of different metals from adsorbents into the treated water, cost effectiveness, environmental impact must be taken into consideration prior to the selection of the waste material as an adsorbent. This study will be beneficial for the readers to choose suitable and specific waste material for field condition as well as it will facilitate future research requirements for the treatment of AMD.

Acknowledgement

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