Recent Patents on Chemical Engineering, **2009**, *2*, 238-252

Acidic Rock Drainage Treatment: A Review

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Received: May 4, 2009; Accepted: July 22, 2009; Revised: July 23, 2009

Abstract: Acidic rock drainage (ARD) is naturally produced through a series of chemical and biochemical reactions at abandoned mine sites. ARD containing acidity and a broad range of heavy metals is classified as hazardous, and must be properly treated. Many technical advances have been developed in recent years towards prediction, control, prevention, and treatment of ARD. This paper focused on the ARD treatment reviews on more than 85 patents filed mainly since year 2000. The patents surveyed are classified into four main types of ARD treatment: chemical precipitation process, adsorption method, biological system, passive treatment and others. The advanced technologies are discussed and evaluated. The key inventors and attractive applications are addressed. An assessment is made about current and future development of ARD treatment technologies.

Keywords: Acidic Rock Drainage, heavy metals, metal adsorption, metal removal, sludge stability and immobilization, water treatment, passive treatment, biological system.

1. INTRODUCTION

Acidic rock drainage (ARD) is naturally produced at abandoned mine sites when geologic materials containing metal sulfides are exposed to oxidizing conditions [1-5]. There are many types of metal sulfide, but iron sulfides, pyrite (FeS_2) and pyrrhotite (FeS), are the predominant ARD producers. Through a series of chemical reactions catalyzed by existing bacteria (thiobacillus ferrooxidans) [6-8], sulfuric acid and free ferric ions are formed as shown in Eq. (1). Thus, sulfuric acid will dissolve some heavy metal carbonate and oxide materials, but has little reactive effect on heavy metal sulfides. At acidic conditions ($pH < 4$), ferric ions become the dominant oxidizing agent for many heavy metal sulfides [9,10], including those of lead, copper, zinc and cadmium, to liberate heavy metals from their sulfide minerals into ARD as shown in Eq. (2). Once the ARD process has taken place, it is extremely difficult to reverse or stop. ARD commonly contains proton and mineral acidity respectively corresponding to a low pH level and a broad range of heavy metals. In a few cases, the mine drainage is close to neutral, that is, only contains dissolved metals. This is possibly associated with the alkaline materials existing in the areas, such as carbonate minerals, aluminum hydroxide and ferric oxyhydroxide minerals, and aluminosilicate minerals [11-14]. This kind of mine drainage is also required to remove the dissolved heavy metals [15]. It has been reported that the mine drainage of pH 7.5 may also leach arsenite and arsenate from mine wastes and tailings associated with gold mining operation at the Giant Mine site [16,17], causing great public concern because of arsenic's carcinogenic and toxic properties.

$$4\ FeS_2 + 15\ O_2 + 2\ H_2O \rightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2SO_4 \qquad (1)$$

$$MS + 2\ Fe^{3+} \rightarrow M^{2+} + S + 2\ Fe^{2+} \qquad (2)$$

(M = Pb, Cu, Zn and Cd)

ARD is an environmental problem of international scale. Various investigations have been carried out at ARD sites. Subsequent technologies have been developed for the predication, prevention and treatment of ARD. Several lab-scale procedures established, such as lab static method [18,19] and dynamic tests [20,21] are intended respectively for predicating whether a sample of rock or soil will be acid producing after exposure to weathering, and assessing the potential for acid generation and metal leaching under field flow conditions. A variety of computer models have been developed. Geochemical speciation mass-transfer models are used to interpret water chemistry associated with underground mine workings [22-24]. Numerous reactive solute-transport models are developed to simulate sulfide oxidation and transport of its products through mine wastes at site conditions [25-27]. The biotic-ligand model is utilized to predict the metal toxicity related to site-specific differences in waters [28,29].

To prevent ARD generation from iron sulfides oxidation, a common method to build a barrier composed of oxygen-consuming materials [30-34], such as wood wastes or plant polyphenol as antioxidant [35], with water is used. Thus, the influx of O_2 into the underlying sulfide minerals is impeded. Harrington [36] patented a technology to cover the rock heap with soil and vegetation so that ARD is prevented indefinitely by displacing oxygen in rock heap. Many patented technologies have been developed using various formulated materials to encapsulate sulfide minerals, such as the pretreatment of sulfide rocks with a source of manganate ions to form a layer of MnO_2, thereby, reducing ARD [37-39]. Price [40,41] claimed the method for eliminating acid generation in sulfide bearing material with an alkaline mixture of CaO and surfactant. Chugh [42] patented a method using coal processing wastes with neutralization and stabilization properties, which can be filled as a barrier material in abandoned mines. Gould [43] *et al.* employed corrosion inhibitor (2-mercapto-1-methylimidazole) and anti-microbial agent (1,3,4-thiadiazole) for inhibiting the ARD formation.

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1874-4788/09 $100.00+.00

Besides, some synthetic materials [44-46], such as polyethylene, concrete and asphalt [47], were used as a sealing layer to prevent ingress of both oxygen and water [48]. Tri-ethylenetetramine or diethylenetriamine was used either individually or in combination with potassium amyl xanthate, which could provide effective coating for sulfide minerals [49]. Consequently, not only the oxidation of sulfide minerals with O_2 was prevented, but also the bacterial growth was inhibited during ARD formation. However, attempts to prevent oxygen and water from contacting sulfide minerals have only been partially successful. Accordingly, the ARD occurrence could be delayed rather than completely stopped. Hence, ARD treatment is often necessary to prevent the pollution nearby watercourses with heavy metals and acidity.

The technologies of ARD treatment can be classified into four main types: chemical precipitation process, passive treatment, biological system, and adsorption method. It is very important for the design engineer to select an appropriate technology for a particular application, as the dissolved metal chemistry is different for each contaminated ARD site. This review has concentrated on the recent patented technologies in the treatment of ARD including non-acidic mine drainage. They present new ideas and first hand information of new discoveries that must be beneficial to the technology development of ARD treatment.

2. CHEMICAL TREATMENT

Chemical treatment of ARD is the most applicable technique including neutralization of acidity and precipitation of metal ions. Chemical precipitation of heavy metals has long been used as the primary method of treating wastewater in industry. There are several precipitation methods for heavy metal removal, including hydroxide precipitation, sulfide precipitation, carbonate precipitation, sodium borohydride (SBH) treatment and dithiocarbamate precipitation. In the process, colloidal metal-precipitates are further coagulated, flocculated, settled, clarified, or filtered out of solution as sludge, leaving a lower concentration of metals and inorganics in the effluent.

2.1. Hydroxide Precipitation

Metal removal such as hydroxide precipitates is a well-established, simple and relatively inexpensive technology. The common hydroxide precipitating agents include caustic soda, hydrated lime and magnesium hydroxide. Sasowsky *et al.* [50] taught the process using a lithic material to neutralize the acidity of ARD and to precipite dissolved metals out of water. Lime neutralization causing metals hydroxides precipitation from ARD is the most common method, owing to lime is low cost, pump-ability and efficiency to neutralize acidity, and well-proven in industry for metal removal to meet the specified limits of effluent. Table **1** shows the pH values related to metal hydroxides preci-pitation and dissolution.

Iwinski [51] disclosed an improved process for metal removal. Prior to neutralization with lime, a ferric/polymer/-metal complex is formed by adding anionic polymer, ferric chloride sequentially. Followed by addition of lime and flocculent, the hydroxylated complex forms high density sludge through flocculation and coagulation. Thus far, many technical skills have been developed. For example, various polymers with the chelating properties [52] were applied for metal recovery from water or from slurries. Hernandez *et al.* [53] taught a method using a combination of metal-coordinating compound and a sorbent for efficient metal removal from water. Loewenthal *et al.* [54] described a method using magnetite combined with ferrous oxidation to promote metals precipitation from water.

Based on the concept of “waste-treat-waste”, many technologies have been developed for water treatment. McConchie *et al.* [55,56] patented a material composed of treated bauxite refinery residues (commonly known as “red mud”) for acidic neutralization and metal removal of wastewater. Bevan [57] described a process using sapropel, a clay-like material, to remove heavy metals (Al, Cd, Pb, Cu, Ni, Cr, Hg and Zn) from water. Raskin [58] invented a polyphenolic derivative chelating agent for metal removal, which was derived from the treatment of lignin in acidic solution at elevated temperature followed by oxidative degradation.

Recently, Zhuang [59-63] developed the technology utilizing lignosulfonate, waste byproducts of wood sulfite pulping process, to bind the dissolved metals with its oxygen-containing functional groups such as phenolic, carboxyl, sulfonyl, alcoholic and enolic structures as shown in Fig. (**1**). Thus, lignosulfonate combining with metals as tiny stable colloids dispersed in ARD. As a result, lime can be protected from developing an external coating on surface due to the precipitation of dissolved metals while raising pH of acidic wastewater. This protection favors dissociation of hydrated lime and save the consumption of lime.

However, the lime neutralization process generates large amounts of metal-hydroxide sludge. The stability of hydroxide sludge must be considered prior to disposal due to hydroxide precipitates tend to dissociate if the solution of pH is changed. Besides, gypsum precipitation frequently causes the scale problem in the lime process when treating ARD with high sulfate levels. Gypsum scaling on the surface of facilities could seriously affect the system performance. Gypsum coating on the lime particles makes lime more difficult to dissociate hydroxides causing an additional addition of lime to generate excess amounts of sludge. To these deficiencies of lime process, accordingly, many technologies have been developed to provide advanced solutions.

To reduce sludge volume, various HDS (high density sludge) processes have been developed, which represent current conventional technology for ARD treatment. The key feather of all HDS-type lime treatment processes is the addition of lime to recycled sludge in a lime/sludge mix tank at the head of the system. The addition of lime to the sludge assists the process by converting the sludge to a dense, granular, free-draining material with a relatively low viscosity [64].

Demópoulos *et al.* [65] patented a HDS process that comprises multiple stages of lime treatment process illustrated in Fig. (**2**). This process requires the pH to be adjusted in a series of small increments. Through a course of multiple reaction tanks, the retention time of sludge in the process is

Table 1. The pH Relation to Metal Hydroxides Precipitation and Dissolution

pH		**Precipitation of Metal Hydroxides**	
Complete Precipitation	**Start Dissolution**	**Formula**	**K_{sp}**
1.0	13	$Sn(OH)_3$	
1.2		$Ce(OH)_4$	
2.0 – 2.2		$Tl(OH)_3$	1.68×10^{-44}
2.5		$TiO(OH)_2$	
3.8		$ZrO(OH)_2$	
4.5 – 5.0		$Fe(OH)_3$	4.00×10^{-38}
4.7	10	$Sn(OH)_2$	5.45×10^{-27}
5.0		$Hg(OH)_2 \leftrightarrow HgO + H_2O$	3.6×10^{-26}
5.5 – 6.0	7.8	$Al(OH)_3$	4.60×10^{-33}
6.5	12	$Cr(OH)_3$	6.3×10^{-31}
7.0 – 7.5		$Be(OH)_2$	6.92×10^{-22}
7.5 – 8.0		$Cu(OH)_2$	2.20×10^{-20}
8.3 – 8.5	10.5	$Zn(OH)_2$	1.20×10^{-17}
8.5 – 8.7	10	$Pb(OH)_2$	*
9.0 – 9.2		$Ni(OH)_2$	5.48×10^{-16}
9.2	14	$Co(OH)_2$	5.92×10^{-15}
9.2 – 9.5	13.5	$Fe(OH)_2$	8.00×10^{-16}
9.4 – 9.7		$Cd(OH)_2$	2.50×10^{-14}
9.5		Rare-earth	**
9.8 – 10.2	14	$Mn(OH)_2$	2.00×10^{-13}
10.5 – 11		$Mg(OH)_2$	1.80×10^{-11}
12.4		$Ca(OH)_2$	5.50×10^{-6}

*Forming base salt precipitates, such as Pb(OH)Cl, prior to hydroxide precipitation.

**Wood SA, Samson IM. The aqueous geochemistry of gallium, germanium, indium and scandium. Ore Geol Rev 2006; 28: 57-102.

greatly increased, which favors the growth for heavy metal hydroxide crystals at lower super-saturation, leading to produce a dense precipitate having superior handling and disposal properties.

Zhuang *et al*. [66,67] devised a two-stage process using recycled acidic and basic sludges to treat ARD containing high levels of heavy metals, see Fig. (**3**). In stage I, ARD is partially neutralized to pH 4-5 with a mixture of lime and recycled basic sludge to generate acidic sludge. The acidic sludge is then separated for disposal as non-hazardous wastes as classified by US EPA's Toxicity Characteristic Leaching Procedure (TCLP) testing. In stage II, the pH of water is further raised to 9-10 with lime neutralization, in the presence of lignosulfonates (Ligsorb^{TM}). Aeration, followed by adding small amounts of recycled acidic sludge, or its mixture with ferrous solution, or injection of ferric solution decreases the pH of water to 8.5-9.5. Thus, metals are removed from water as a basic sludge mainly consisting of metal hydroxides, which is entirely recycled to stage I. Then, unstable metal components are leached into the water. The remaining solids change into acidic sludge composed of metal complexes with a low TCLP leachability at pH 5. This recycling allows the neutralization potential of basic sludge to be completely utilized. The separation of acidic sludge from the system not only can minimize lime scale formation but also avoid consuming additional lime to increase wastes. The application of lignosulfonates provides lubrication, which pro-motes the smooth flow of both liquid and solid wastes to inhibit scale-forming in the system. This two-stage process can produce a stable sludge at pH ≥ 5 and a high

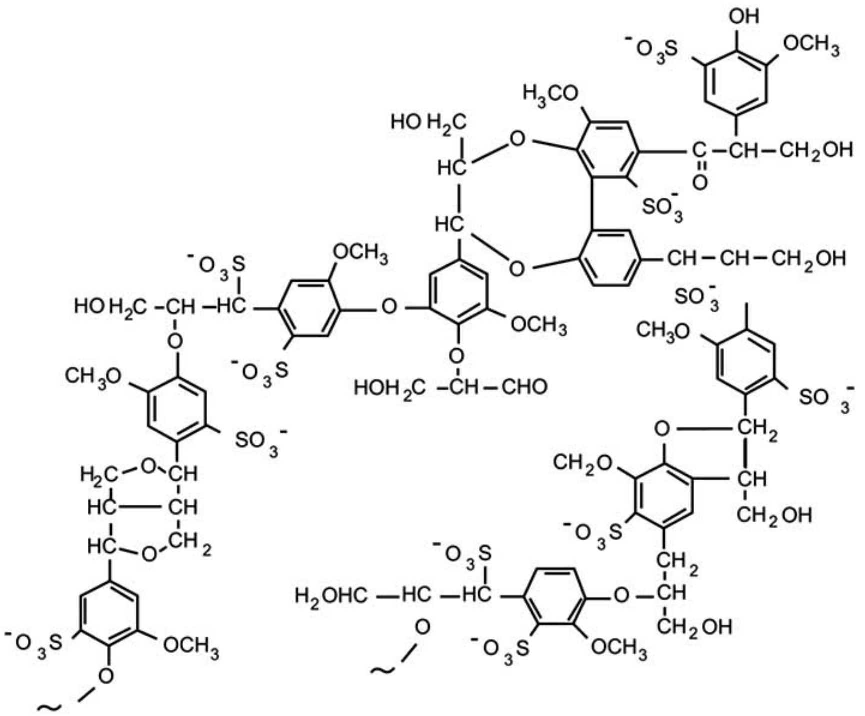

Fig. (1). Proposed structure for a section of lignosulfonate.

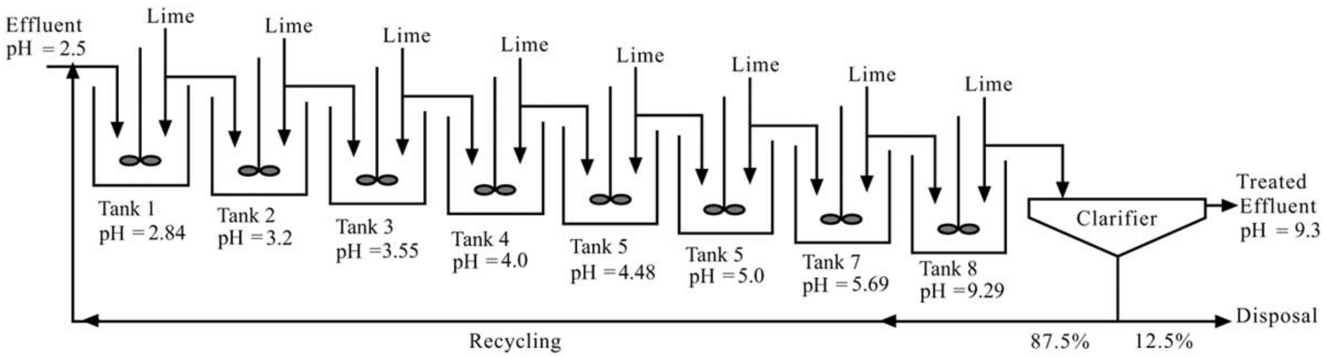

Fig. (2). A multiple stage for lime treatment.

quality effluent in addition to saving > 32% of total chemical costs, and reducing > 20% of sludge amounts in comparison with the conventional lime neutralization process.

The techniques of recycling sludge [64-67] have been well employed in the process for ARD treatment to reduce sludge volume, improve sludge stability, and save chemical cost. However, the application of recycling sludge must be linked with the geochemistry at individual site. For As-contaminated water treatment, the quality of effluent and the stability of sludge become very important factors for concerning in addition to chemical cost. According to the study of As-chemistry, Zhuang *et al*. [17] proposed a two-stage As-contaminated water treatment with Fe(II) and aeration, see Fig. (**4**). In stage I, Fe(II) is added into As-contaminated water at a Fe/As mole ratio of 1.5-2.5. At a pH level of 6.5-7.5 maintained by hydrated lime, Fe(II) is oxidized to Fe(III) with aeration. Thus, the dissolved arsenic can be reduced by Fe(III) co-precipitation from initial 72 mgL^{-1} to < 2 mgL^{-1}. The generated sludge is then separated from water and entirely recycled to the second tank of stage II. In the first tank of stage II, the water is further treated with the same amount of Fe(II) as that used in stage I in the presence of lignosulfonates and aeration. The air-oxidation of Fe(II) to Fe(III) is complete at a pH level of 7.0-8.0. The water output from the first tank is transferred to the second tank in which mixing under aeration with the sludge recycled from stage I. Accordingly, the dissolved arsenic in effluent is down to < 0.1 mgL^{-1}. This two-stage process can save > 50% of total chemical costs, and reduce > 50% of sludge amounts to compare with the conventional Fe(III)/lime treatment process.

The geochemistry for individual site is often different causing each ARD is unique. Interactions among various metals also influence the degree to which metals precipitate. That is why the efficiency of performance could be varied for each ARD when conducting the same water treatment process. Especially, when treating ARD with high levels of Al and Mn, it is often difficult to remove Al and Mn

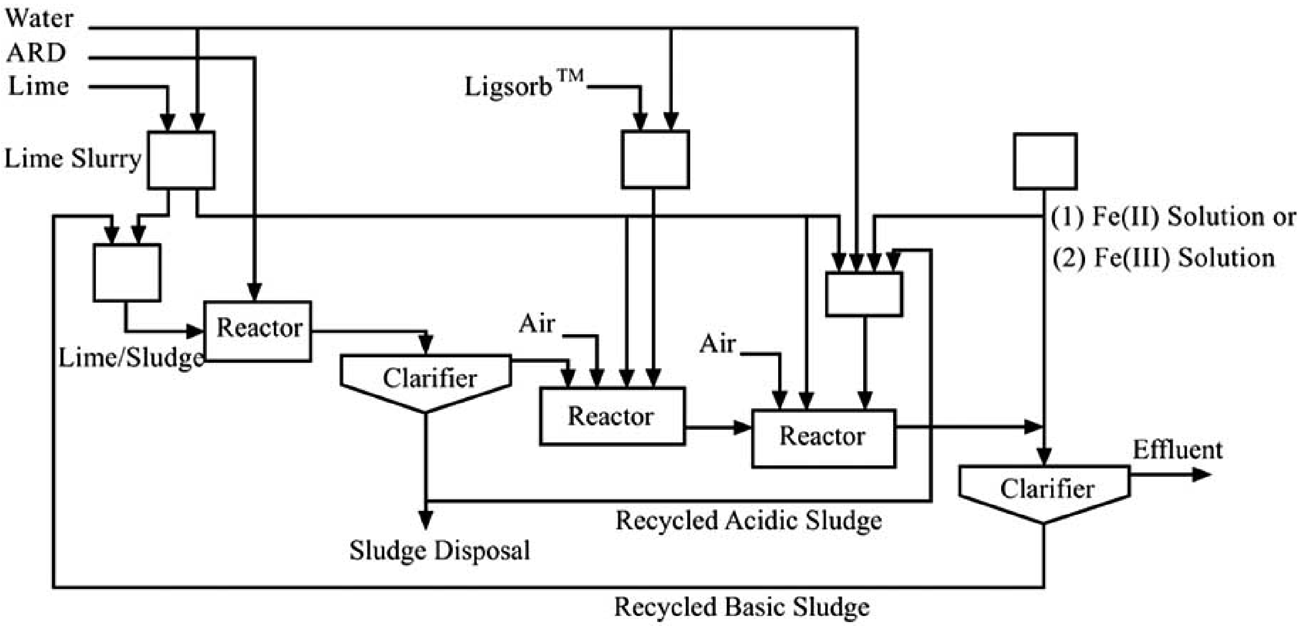

Fig. (3). The two-stage treatment process configuration.

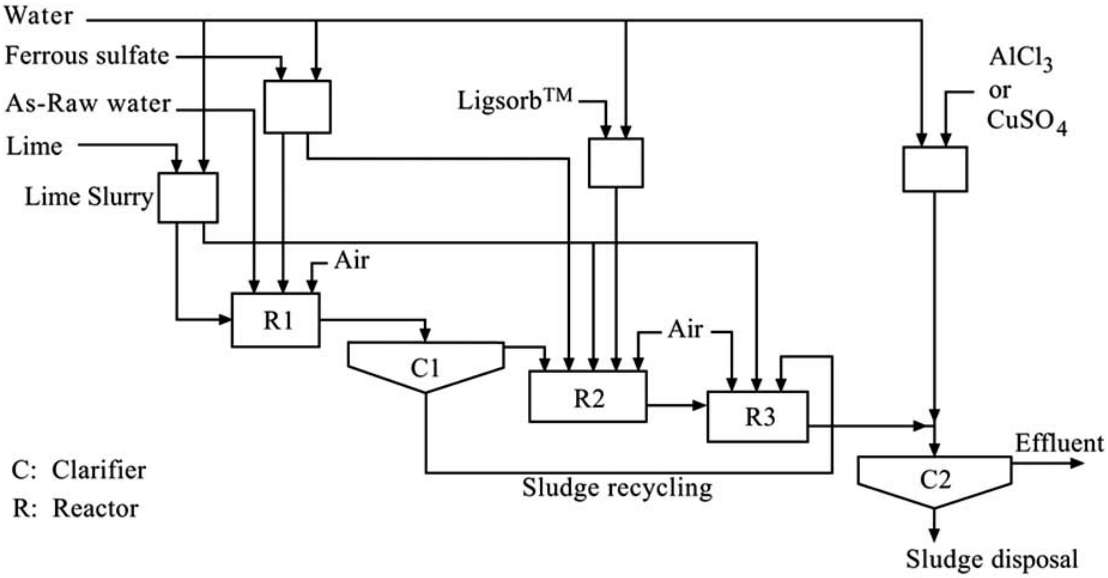

Fig. (4). The two-stage process configuration for As-treatment.

simultaneously by adjusting pH only, owing to their different behaviors of dissolution *vs.* pH (Table **1**). $Al(OH)_3$ precipitates at pH 5.5 - 6.0 and starts dissolution at pH 7.8. Mn will generally precipitate at pH > 9. Hence, it requires new techniques for simultaneous removal of Al and Mn. Otherwise, it could add additional facility to remove Al and Mn separately at two different pH levels [68].

Lichtner *et al.* [69] taught a method to install a reverse osmosis unit for further filtration of effluent from the process of neutralization and clarification. Following microfiltration, the quality of water is characterized by reduced sulfate, Si, Ca, Al, Fe, Mg, and Mn levels in addition to noticeable reduction of total dissolved solids.

Based on the data analysis for ARD containing higher levels of iron and magnesium, Zhuang [70] interestingly found that Al and Mn can be removed simultaneously at pH about 8.5-9.0. For example, when the iron concentration in the ARD is greater than five times the Mn content, Mn may be removed by iron co-precipitation at pH about 8.5. This is associated with the known iron co-precipitation properties. Besides, in the cases of using $Mg(OH)_2$ (or dolomitic lime, $Ca(OH)_2$-MgO) instead of $Ca(OH)_2$ to neutralize ARD, Al can be removed by Mg co-precipitation at pH about 8.5. This concept is further confirmed by the lab tests [68] to show that adding water-soluble $MgCl_2$ salt to increase Mg level in the ARD sample results to Mg co-precipitation with Al when pH is adjusted to about 8.5. It could exhibit an affinity is present between Al and Mg.

2.2. Other Precipitation Techniques

Dissolved heavy metals can be removed from wastewater by other precipitation methods including sulfide precipitation, carbonate precipitation, sodium borohydride (SBH) treatment and dithiocarbamate precipitation. However, each precipitation method usually involves hydroxide precipitation due to most heavy-metals can form hydroxide precipitates at pH ≥ 6 (Table **1**).

2.2.1. Sulfide Precipitation

Sulfide precipitations could be occurred over a broad pH range as shown in Fig. (**5**). Owing to the solubility for metal-sulfides (Table **2**) is much lower than metal-hydroxides' (Table **1**), it requires a low level of sulfide in water to precipitate heavy metal as sulfides to attain a high degree of metal removal than the hydroxide precipitation. So, this method is feasible for selective metal removal and recovery. Generally, sulfide precipitation is conducted at near neutral conditions pH 8-9 by adding soluble Na_2S or NaHS into water. Alternatively, relatively water-soluble FeS is introduced into water to dissociate low levels of sulfide, leading to precipitate Cu, Zn and Pb as insoluble sulfides.

However, excess soluble sulfide in the treated effluent may cause taste and odor problem in addition to the potential problem of evolving toxic H_2S gas. Accordingly, Klock *et al*. [71] disclosed a modified sulfide process to remove heavy metals, particularly Cu and Zn from water with no detectable sulfide. Following addition of soluble sulfide, a soluble ferrous salt is added into water under aeration. Finally, the sludge is separate from the water, which comprises iron sulfide, iron oxide, iron hydroxide and metal sulfides, leading to produce a clean effluent with very low metal concentrations (< 100 μg/L) and no detectable sulfide.

Due to instability of metal sulfides especially in oxidizing environment, the metal sulfide rich sludge with loose structure can not be disposed directly to the environment. Some anti-oxidation agents or oxygen-consuming materials, such as iron filings, might be suitable to stabilize the metal sulfides sludges. For example, the mercury sulfide sludge

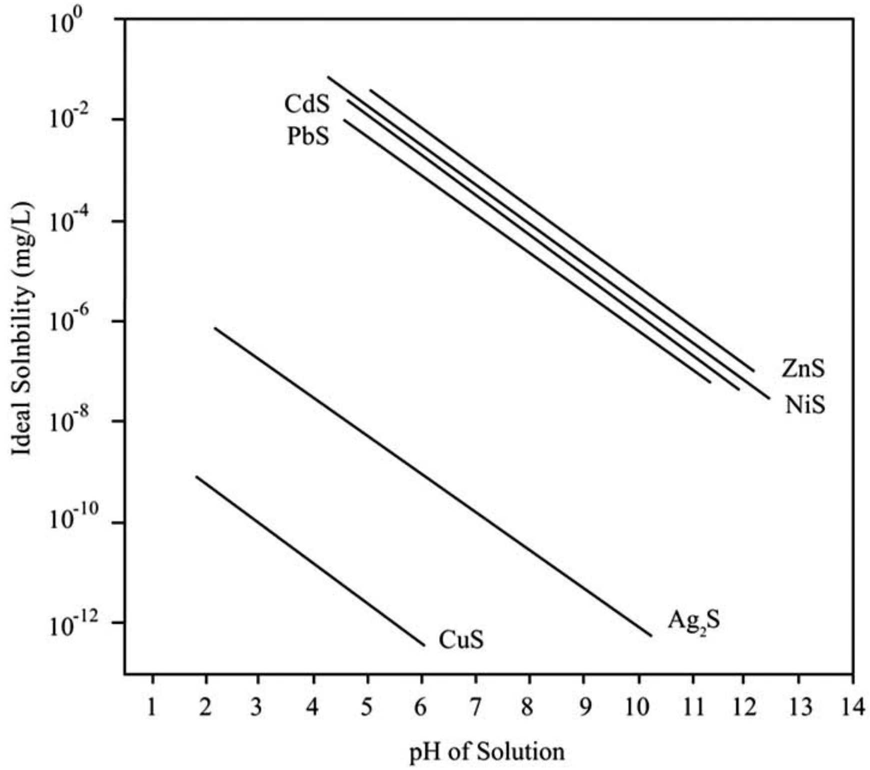

Fig. (5). Solubility of metal sulfides *vs*. pH.

Table 2. Solubility Product Constants for Metal Sulfides

Formula	K_{sp} (25°C)	Formula	K_{sp} (25°C)	Formula	K_{sp} (25°C)
CdS	1×10^{-27}	FeS	8×10^{-19}	NiS, beta	1.3×10^{-25}
CoS, alpha	5×10^{-22}	MnS, pink	3×10^{-11}	PbS	3×10^{-28}
CoS, beta	3×10^{-26}	MnS, green	3×10^{-14}	ZnS, alpha	2×10^{-25}
CuS	8×10^{-37}	NiS, alpha	4×10^{-20}	ZnS, beta	3×10^{-23}

could slowly become leachable that could be associated with the oxidation conversion of sulfide to sulfate. After mixing with iron filings, the mercury sulfide sludge was then stabilized and passed the US EPA's TCLP threshold as non-hazardous wastes [72]. The stabilization roles of iron may include (i) natural oxidation of iron to Fe(II) and Fe(III) to protect sulfide from oxidation, (ii) reduction of heavy metals to element metals by iron and Fe(II), (iii) metal-adsorption of iron, Fe(II) and Fe(III).

2.2.2. Carbonate Precipitation

Carbonate precipitation is an effective method alternative to hydroxide precipitation, which can operate at a lower pH range of 6-9. The prices for carbonate precipitating agents, such as soda ash (Na_2CO_3), sodium bicarbonate ($NaHCO_3$) and calcium carbonate ($CaCO_3$), are competitive in relation to hydroxide precipitating agents. But, carbonate reactions take longer time, and have the potential for evolving carbon dioxide. The produced sludge is gelatinous and difficult to settle.

Watten [73] developed a process for carbon dioxide pretreatment and accelerated limestone dissolution for treatment of acidic water as shown in Fig. (**6**). This method includes charging the effluent with carbon dioxide, intermittently fluidizing and expanding at least one pulsed limestone bed with the charged effluent, treating the charged effluent with limestone in the bed for about 4 to 8 minutes, displacing the lime-stone treated effluent with untreated charged effluent, stripping excess carbon dioxide from the effluent after treatment in the limestone bed, and discharging the limestone treated effluent. This process decrease limestone bed sensitivity to limestone armoring by the intermittent fluidizing of the limestone beds and raising the pH of the treated effluent to ≥ 5.

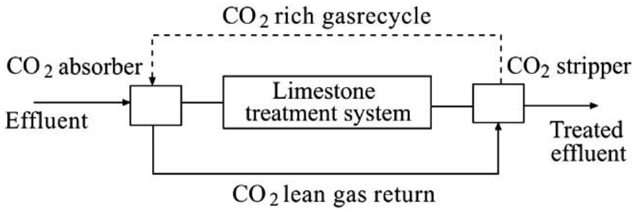

Fig. (6). Schematic diagram for limestone ($CaCO_3$) treatment system

In a case study [74] on limestone neutralization of As-rich effluent from a gold mine, the results show that limestone can effectively neutralize arsenic rich acid water instead of lime neutralization. The cost for limestone treatment is 45.8% less than that of lime. The acidity can be reduced from 33.5 to 0.06 gL^{-1} as $CaCO_3$. In addition, there are no differences in the TCLP characteristics of the resultant sludge when water is treated with lime or with limestone. As a result, sludge from the limestone treatment process can be disposed of on a non-hazardous landfill site.

2.2.3. SBH ($NaBH_4$) Treatment and Dithiocarbamate Precipitation

SBH is often employed to selectively reduce dissolved metals for metal recovery. Alexander *et al.* [75] disclosed a sequential two-step chemical precipitation process, whereby the dissolved metal content is treated by SBH reduction to selectively recover Ni at pH 7-11, followed by sodium dithiocarbamate precipitation to remove remaining dissolved metals. Accordingly, the amount of metal-bearing sludge produced is minimal, resulting in significant reduction in hazardous waste disposal costs.

Water soluble sodium dithiocarbamate Fig. (**7**) can use its one or two sulfur atoms such as a uni-dentate or bi-dentate ligand to complex metals as insoluble ionic metal colloids. As a result, it achieves a high degree of metal rem-oval, and produces sludge with improved dewatering properties. Kreisler [76] was granted a patent which relates a process using water-soluble dithiocarbamate or its derivatives with neutralization agent (NaOH) to form metal ion complexes, followed by addition of $CaCl_2/FeCl_3$ and a flocculating agent to promote the metals complexes growth and precipitation in the form of sludge. After de-watering and drying, the recovered metal powder is either sold as a commodity or is further converted to metal ingots for sale to primary smelters.

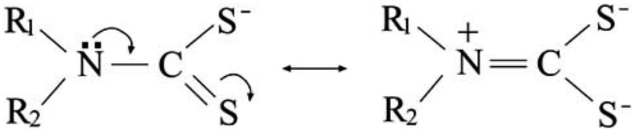

Fig. (7). Proposed resonance structures for dithiocarbamate.

Salmen *et al*. [77] patented a method using a water-soluble polymer containing dithiocarbamate functionalities, which are able to chelate metals to form larger insoluble species at pH 6 to 10. After that, these insoluble metals species and abrasive solids can be removed simultaneously by a micro-filter to produce a clean effluent.

2.3. Sludge Stability and Treatment

Sludge produced from chemical treatment process should be evaluated under the local regulations. In the United States, the generated sludge should pass the US EPA's TCLP threshold as non-hazardous wastes. The TCLP test uses a dilute acetic acid either in de-ionized water (TCLP fluid 2) or in de-ionized water with a sodium hydroxide buffer (TCLP fluid 1) depending on the alkalinity of waste solids. This is an extracting procedure to determine whether the waste solids would be classified as a hazardous waste when discarded. For example, the sludge from the HDS process comprises high levels of metal hydroxides tending to dissociate metals at lower level of pH, which could not pass TCLP threshold. Hence, it is required to convert unstable sludge to a more chemically stable form by a proper stabilization method.

Owing to the low solubility of phosphates for most heavy metals, phosphate is often used as an important component in many patented metal-stabilizers. A combination of phosphate with adsorbent (SiO_2 and Al_2O_3 and Fe_2O_3) plays the main function for metal stabilization in Slattery *et al.* [78] patented formulation. Bhat [79] claimed another formulation using sulfonated calcium aluminum magnesium phosphate alone or in combination with reducing agents magnesium sulfite and/or hydroboracite to stabilize heavy metals like Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Hg, Mo, Ni, Se, Ag, Tl, V and Zn. Pal *et al.* [80] invented a process for chemical fixation of radio-active Pb compounds present in waste solids. This is a two-step treatment of mixing with $CaSO_4$ and a phosphate agent sequentially to produce a substantially insoluble lead composition.

Forrester [81-83] further developed several formulations of metal-stabilizer mainly comprising precipitants (phosphate and sulfide), flocculants (ferric sulfate and alum), adsorbents (activated alumina and carbon), and solidifying materials (Portland cement and cement kiln dust). According to his method of in-line stabilization using these components into the waste stream, the dissolved heavy metals are complexed to the stabilizing agents during waste production. Thus, the leachability of heavy metals from the processed solid waste is reduced.

Fix *et al.* [84] invented a process for stabilizing heavy metals in ash, by which an aqueous slurry of ash is adjusted to pH < 5.0 in the presence of ferric sulfate followed by a sequential treatment with organic sulfur compound (thiocarbamate, thiocarbonate or trimercaptotriazine), $Mg(OH)_2$, humic and fulvic acids, phosphoric acid. Finally, the pH of waste is adjusted with lime to $\geq$ 9. This process involves the co-treatment of the waste with both an organic-S chelating agent, $Mg(OH)_2$, humic/fulvic acids, and phosphoric acid.

Jones *et al.* [85] disclosed a method to mix the solid waste with asphalt and tall oil pitch in water resulting in an emulsion. The leachable metals are chemically immobilized by a thin organic film. Thus, the processed wastes having improved structural properties are utilized as engineered fill such as road base material.

Vyshkina *et al.* [86] taught a method for treating heavy metal contaminated soils, particularly Cr(VI) contaminated soils, which comprises of a two-stage washing process. In the first stage, soil is washed at pH 9-12 with a flocculant (anionic polyacrylamide co-polymer). Then, the soil sludge from the first washing stage is optionally washed at pH 2.5-3.0 with an addition of a reducing agent ($Na_2S_2O_5$) to reduce Cr(VI) to Cr(III). Finally, the lime slurry is added to bring the pH to 9.0 and to form insoluble $Cr(OH)_3$. The final non-toxic stable solid material is usable for backfilling, road construction subbase, and landfill.

Zhuang [59-61] patented the formulation of metalstabilizer (Ligmet^{TM}) comprising lignosulfonates, Fe(II)/Fe(III), Al(III), $CaSO_4$, Mg(II), etc., and combinations. It has shown a great capability of immobilizing many heavy metals, such as As, Hg, Cu, Ni, Mn, Zn, in solid wastes [87-89]. Lignosulfonate, waste by-product of the wood sulfite pulping process, is composed of polymeric phenol structures with an abundance of oxygen-containing functional groups, such as phenolic, carboxyl, sulfonyl, alcoholic and enolic structures, which enable lignosulfonate not only to have a high binding affinity for metals but also to be effective in stabilizing Cu-tailings in seawater against oxidation [90]. The Ligmet^{TM} stabilizer can be produced in-line of treating waters. Consequently, the dissolved metals in water are removed by combination with the components of Ligmet^{TM}, and separated from water as a stable sludge. Hence, adding excess components of Ligmet^{TM} to water enables to improve the quality of treated water, and also increases the metal-adsorption capability of the sludge. This kind of sludge which showed an improved stability even at low pH 5 [67], is usable to immobilize leachable metals in solid wastes [90].

3. ADSORPTION METHOD

Adsorption technology as an effective method has been commonly employed for metals removal from waters. Comparing with chemical treatment to precipitate metals out of water, the adsorption system requires much less maintenance, furthermore, the cost for facility, operation and chemicals can be greatly reduced. In some cases, it could provide a method to extract and retain valuable metals [91, 92] from wastewaters for reuse. One of the key adsorption technologies is to develop new adsorbents having significant metal adsorption capability, great metal adsorption rate and mechanical strength for specific applications.

Lu *et al.* [93] developed a cellulose derivative phosphoric ester, 2,3-dihydroxypropyl cellulose or 3-(2,3-dihydroxy-propoxy)-2-hydroxypropyl cellulose. Its phosphoric group possesses the metal adsorption characteristics. Hence, the phosphoric ester of cellulose exhibits high metal adsorption performance and great metal adsorption rate. In addition, it can be formed into a variety of shapes with high mechanical strength. Thus, it has an excellent processability for heavy metals removal from waters within a wide pH range, and can be readily reutilized.

Okada *et al.* [94] taught a method to make a bi-functional adsorbent composed of chelate adsorbent fibers, which is able to adsorb metals in water at acidic conditions. Synthetic polymer (polypropylene, polyethylene or polyester) or natural polymer fibers are used as the substrate for preparing chelate adsorbent fibers of a phosphonic acid type, a sulfonic acid type, or a complex thereof. According to the radiation of the polymer substrate, the graft polymerization is performed with two reactive monomers, one having a phosphonic acid group and the other having a sulfonic acid group. Its Pb-adsorption capacity at pH $\leq$ 2 was more than twice that of the commercial chelate resin and a monofunctional fiber. Furthermore, it showed a satisfactory Fe(III)-adsorption behavior at more than 100 times faster flow rate. Hiroyuki *et al.* [95] created another type of fiber based metal adsorbent with amidoxime groups as chelating functional groups.

Soane *et al.* [96] successfully made synthetic polymer complements having various functional groups on the surfaces to trap targets, such as heavy metals, etc. They comprise many kinds of monomers containing a variety of functional groups, such as alcohols, carboxylic acids, amides, amines, phosphates, sulfonates, aromatics, and saccharides, and diverse cross-linking groups. Numerous functional groups of these adsorbents enable to trap biological molecules.

Ion exchange resins are adsorbents that effectively remove specific anions or cations from many types of waters. Marshall *et al.* [97] disclosed a process for the production of dual-functional ion exchange resins from lignocellulosic agricultural material, which possess enhanced adsorption properties with respect to the uptake of both anions and cations. The process involves the lignocellulosic material, which is anionized with citric acid to create a negative surface charge, and cationized with dimethyloldihydroxy-ethylene urea and choline chloride to create a positive charge. Thus, the produced dual-functional products have a range of adsorption efficiencies for both cations (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Cr^{3+}, Hg^{2+}, Al^{3+}, Co^{2+}, Sn^{2+}, Sn^{4+}, Ca^{2+} and Mg^{2+}) and anions (CrO_4^{-2}, AsO_4^{-3}, SeO_4^{-2}) in waters.

Many efforts have been made to develop new adsorbents comprising natural materials instead of synthetic materials. Benjamin *et al.* [98] developed an absorbent with sand or olivine as support material that is coated with iron oxide. Thus, the adsorbent can be used to remove metal contaminants and natural organic matter from water. Sanjay *et al.* [99] described a method of preparing a humic based adsorbent for removal of organics, cations and anions from contaminated water. Anderson *et al.* [100] invented a novel absorbent comprising a hydrated cementitious material, that is, formed cement. The cementitious materials can be used for heavy metals removal, which have significant economic advantages over ion exchange resins.

Owing to no formation of sludge during the treatment, there is no need for adsorption process to handle sludge. Therefore, the adsorption process is capable of efficiently providing simplified procedures and simple small-sized facilities at a high treatment rate. Yasunori *et al.* [101] patented a treatment system involving two adsorption devices, which are filled with ferrous adsorbent for heavy metals removal, and equipped with circulation, concentration and discharge facilities. Berezutskiy [102] induced a porous adsorbent (carbon, silica, alumina, etc.) impregnated with oxidation catalyst (metal, metal oxide, or a bimetallic combination). This kind of catalyst adsorbent could have advantages to improve the process for the removal of metals, metal oxides or salts selectively from the wastewaters.

4. BIOLOGICAL SYSTEM

Biological technologies have emerged as an alternative approach to ARD treatment. Biological system, employing micro-organisms to treat metal-contaminated wastewaters, provides a compact and cost-effective solution. Recently, many new technologies, involving biosorption, biological oxidation and reduction, have been patented in application for heavy metals removal from waters.

4.1. Biosorption

Biosorption refers here to reversible physico-chemical mechanisms of binding metal ions to a part of biomass (living or nonliving). In brief, ion exchange and complexation can be pointed out as the most prevalent mechanisms for the biosorption of most heavy metals. Here, biomass is merely regarded as an assemblage of various biopolymers containing diverse functional groups, such as carboxyl, hydroxyl, sulfate, phosphate and amino groups, which play significant roles in combination with dissolved metals onto biomass. The strong metal-binding ability of biomass has attracted much attention in the fields of metal remediation. Unlike conventional organic and inorganic adsorbents, biosorption employs inexhaustible, inexpensive, and non-hazardous materials that exhibit significant specificity for the target metal contaminants, thus generating low volumes of non-hazardous waste. The waste from the biosorption process could be easily disposed of by incineration.

Macaskie [103] developed a bioreactor containing an immobilized phosphatase-producing microorganism, which was cultivated within a culture medium of an organic phosphorus source, for removal of actinide or other metals from aqueous solution. It is effective to remove a target metal having an insoluble phosphate (e.g. actinide, etc.), by passing the solution through the bioreactor. To avoid the fast metal-saturation of the biomass, when treating water containing relatively high levels of metals (e.g., 50-100 mgL^{-1} Cu), Tadic *et al.* [104,105] devised a pre-treatment comprising chemical precipitation, solvent extraction or membrane-filtration to reduce the load of metals to the treatable levels of biosorption. Following the pre-treatment, the biosorption process can be continuously performed by operating 1-3 fixed bioreactors, which packing material has been colonized with microorganisms as a bio-film formed with the capability of binding metals.

4.2. Biological Oxidation and Reduction

Through diverse metabolism courses, microorganisms may enable to oxidize dissolved metals to insoluble metal hydroxides and carbonates, which are readily separated from water. For example, removal of dissolved ferrous and manganese is feasible by biological oxidation to form precipitates of insoluble MnO_2 and $Fe(OH)_3$. Perriello [106] disclosed the bio-technologies used for oxidizing heavy metals, such as As, Ag, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Tl and Zn, with hydrocarbon-utilizing bacteria. The high solubility of butane is a particularly suitable hydrocarbon to stimulate the growth of bacteria, which may oxidize iron and other metals leading to metal-precipitates out of water.

It has become an important application for biological sulfate reduction to sulfide [107] instead of directly using soluble chemicals Na_2S and NaHS (**2.2.1 Sulfide Precipitation**) to precipitate dissolved metals as insoluble sulfides out of water. This bio-reduction process can remove dissolved metals, recovery marketable metals [108] and reduce sulfate in the wastewater. Noah *et al.* [109] devised a bioreactor system, which is composed of a series of sub-units referred to as bioreactor modules. Thus, the bioreactor system can be subdivided into smaller units for conveniently transported to waste site where they are combined to form bioreactor system of any size. The wastewater is under controlled to flow at a vertical direction in each bioreactor module. The reactor fill comprises a sulfate reducing bacteria to generate sulfide for metal removal from ARD as insoluble metal sulfides.

Owing to the precipitated metals are often co-mingled, the precipitates for metal-sulfides have little commercial value and usually treated as a waste material. Burckle *et al.* [110] claimed the technologies of controlling the data on pH, pS and Eh at each of multiple-stages, consequently, metals are recovered from ARD in forms with commercial values (Table **3**). Therefore, it is important to control the sulfide production rate of microorganisms based on demand.

Table 3. Summary of the Operating Conditions and Results for the Batch Reactor System

Metal in ARD	Sequential Stage	Operation Conditions	Metal	
			Recovery (%)	Purity (%)
Cu 223 mgL^{-1}	Stage 1, CuS	t = 10°C pH = influent pH of ARD pS = 10-15 Eh = -100 to -120 mV	99.7	98.4
Fe(III) 150 mgL^{-1}	Stage 2, $Fe(OH)_3$	t = 25°C pH = 4.5 pS < 2 Nitrogen gas sparged	96.4	90.6
Zn 630 mgL^{-1}	Stage 3, ZnS	t = 25°C pH = 4.5 pS = 10-15 Eh = -100 to -120 mV	98.1	97.4
Al 293 mgL^{-1}	Stage 4, $Al(OH)_3$	t = 25°C pH = 6.0 pS = 10-15 Nitrogen gas sparged	99.3	90.2
Fe(II) 514 mgL^{-1}	Stage 5, FeS	t = 25°C pH = 6.0 pS = 5-8 Eh = -180 to -200 mV	98.6	99.1
Mn 223 mgL^{-1}	Stage 6, MnS	t = 25°C pH = 8.0 pS = 10-15 Eh = -100 to -120 mV	99.1	99.3

To control sulfide production by bacteria, Truex *et al.* [111] invented a process used to make a bioreactor produce sulfide “on-demand”. Thus, the production of sulfide can be matched to its use as a metal-sulfide precipitation agent, and avoid to generate excess of toxic H_2S gas. Consequently, the process cost can be reduced in addition to increase the process safety. The critical feature of this technology is to carefully control and rapidly adjust pH within a bioreactor affecting a quick change in the distribution H_2S and HS^- as shown in Fig. (**8**), which prompts effects on the metabolism of sulfate-reducing bacteria (SRB).

SRB are inhibited by H_2S and not by HS^-. At pH < 7, the dominant species H_2S can inhibit SRB that becomes the primary mechanism leading to halt the production of sulfides. At pH > 7, more HS^- is present in solution than H_2S, and then SRB may resume the production of sulfides. Accordingly, through the pH quick adjustment by introducing acids and bases, the activity of SRB can be readily controlled. As a result, the rate of SRB producing sulfides can meet the demand.

Biological reduction of sulfate to sulfide has been further applied to the remediation of solid wastes. Bartlett [112] taught a method for in situ anaerobic bioremediation of metal contaminated solid waste media. The method uses an emulsion of organic nutrient in water to disengage inside the solid waste media. Thus, the dispersed organic nutrient is attached to the media where it is accessible for microbial redox reactions at anaerobic conditions. Accordingly, metal sulfate is biologically reduced to insoluble metal sulfide, which is stable in an anoxic environment.

4.3. Bioreactor Structures

Two basic types of bioreactors, aerator and anaerator, can perform biological oxidation and reduction respectively. Many applications of bioreactors are continuously increased in wastewater treatment (**4.2. Biological Oxidation and Reduction**). Recently, many new technologies have been applied in the area of bioreactor structures with specified functions. Han [113] employed sponge tubular biological carriers in the bioreactor to increase the overall micro-organism concentration. Thus, the capacity of biological treatment is greatly strengthened. Langhans *et al.* [114] devised a method to control top scum problems in a bio-reactor when treating a suspension. A portion of the suspension is suctioned off from the bioreactor, which is used as a fluid to pass into the area of the suspension fill level. The top scum floating on the surface of the suspension is forced into rotary flow. Thus, the top scum and foam particles accumulating around the periphery of the tank have

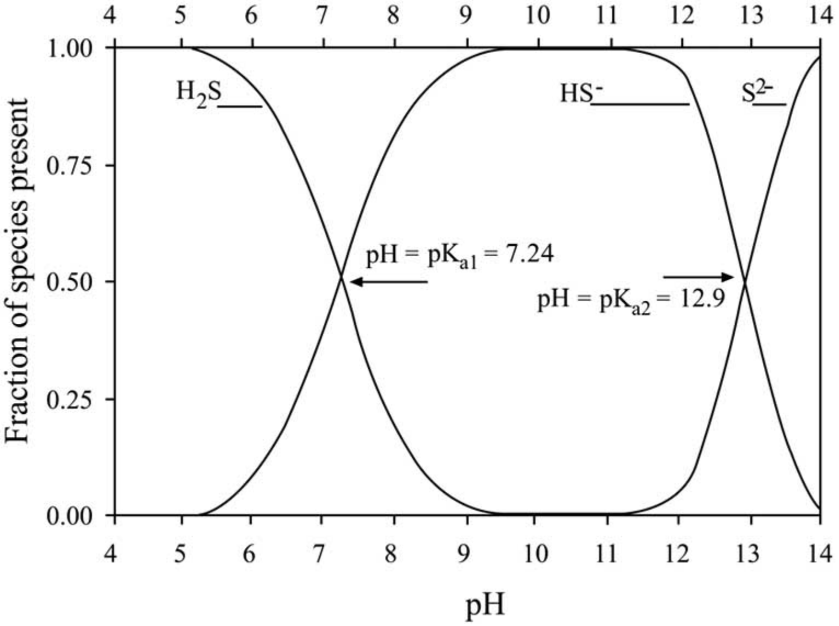

Fig. (8). Composition diagram for H_2S as a function of pH.

the tendency to stick and compact together overtime. Jowett [115] developed an in-pipe biological system for wastewater treatment. In place of the conventional aerobic treatment station, wastewater undergoes aeration and settlement in a treatment-pipe, ensuring a uniform complement of the water treatment. Since the water flow will carry solids along to the outlet, it is unlikely that there will be much build-up of sludge in the treatment pipe.

It has been recognized that oxygen in bio-system may benefit some biological processes while interfering with others. Elefritz *et al.* [116] taught a method of strategic management of oxygen in streams for improving the bio-treatment efficiency. In a bio-system having an anoxic zone, aerobic zone and a separator, the stream with enhanced oxygen level is introduced to the aerobic treatment zone equipped with recycling pump. A source of bio-degradable carbon may be added to reduce the oxygen level in the stream. Then, the stream with a depleted oxygen level is introduced to anoxic zone for further treatment.

The membrane in bioreactor could be clogged by the residual flocculating agent (polyelectrolyte) from the sludge system, which could cause a permanent damage to the performance of membrane even after restoration. Langlais *et al.* [117] disclosed a method of recycling the water originating from the sludge dewatering step as shown in Fig. (**9**) to mix with the biological sludge from the bioreactor. Through the sludge membrane, the polyelectrolyte-free filtrate is recycled to the head of the membrane bioreactor, and the polyelectrolyte-loaded biological sludge is sent to the dewatering step. Thus, the risk of clogging the membrane in bioreactor is completely eliminated.

During the bio-treatment of contaminants, micro-organisms continuously grow within the bio-system. If not properly limited, biomass and precipitate is detrimental to the bio-system performance. The filter could be clogged, causing the bio-system shut-down for restoration. To substantially reduce the production of solid waste in bio-system, Jordan [118] applied an offline treatment vessel in the membrane bioreactor process for carrying out biological sludge digestion in a very low oxygen environment. The fluid from the digestion process is transferred back to the membrane bioreactor. Frisch [119] developed a bioreactor equipped with a lift tube as shown in Fig. (**10**) to control biomass growth. The lift tube has an inlet disposed at the bottom region of the vessel and an outlet disposed at the top region of the vessel. The introduction of air into the liquid supplies oxygen for biological treatment and its upward cavity movement causes currents to be developed in the liquid. Thus, the interaction between solid species with biomass and the interior wall leads to liberate accumulated biomass from its carriers. This liberated biomass will typically rise to the top of the vessel, as its density is less than that of the liquid system. The biomass slurry will be excluded from the bioreactor. Accordingly, the accumulation of biomass and precipitate is inhibited and the growth of biomass is controlled.

Goldsmith [120] devised a bioreactor equipped with a submerged vertically-mounted membrane device. This is a porous ceramic membrane that utilizes one or multiple passageway porous monoliths as a micro-filtration. A gas-sparged feed stock at the bottom of bioreactor provides airlift circulation of the feed stock through the device. As a result, the use of hydrophilic ceramic membrane favors to resist the accumulation of biomass. Haridas *et al.* [121] developed a novel bioreactor referred to as “Reverse Fluidized Loop Reactor” (RFLR), which enables to provide continuous biological treatment of waste water to convert its contaminants to solids for easy separation and removal. The microbes are selected from the group of oxidizing and/or reducing bacteria, such as sulfide or iron oxidizing bacteria, and sulfate reducing bacteria. Under gas-sparging, some dissolved contaminants of the waste water are continuously converted to solids on the surface of microbial film, which is

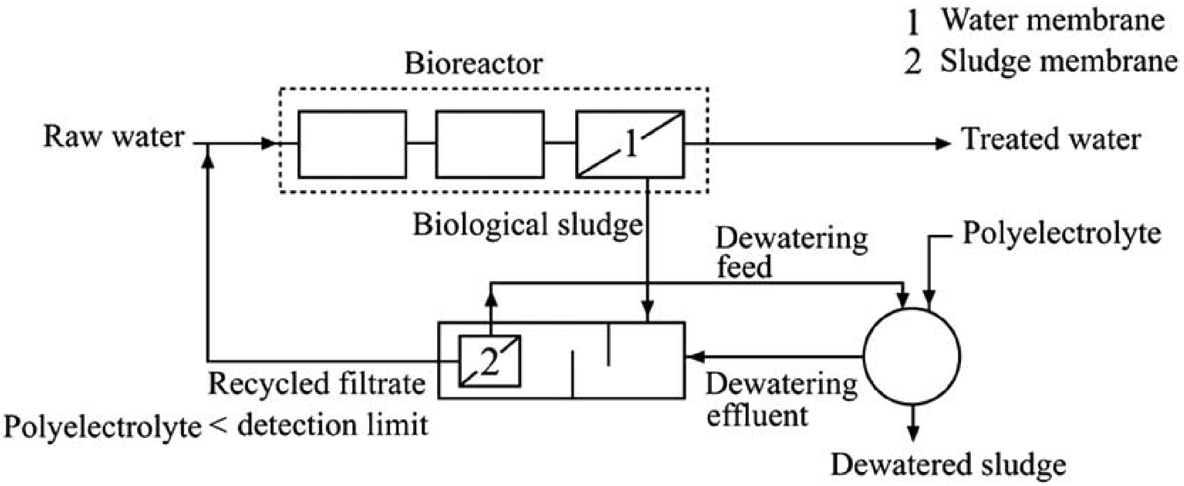

Fig. (9). Schematic diagram for recycling the water from the sludge dewatering step.

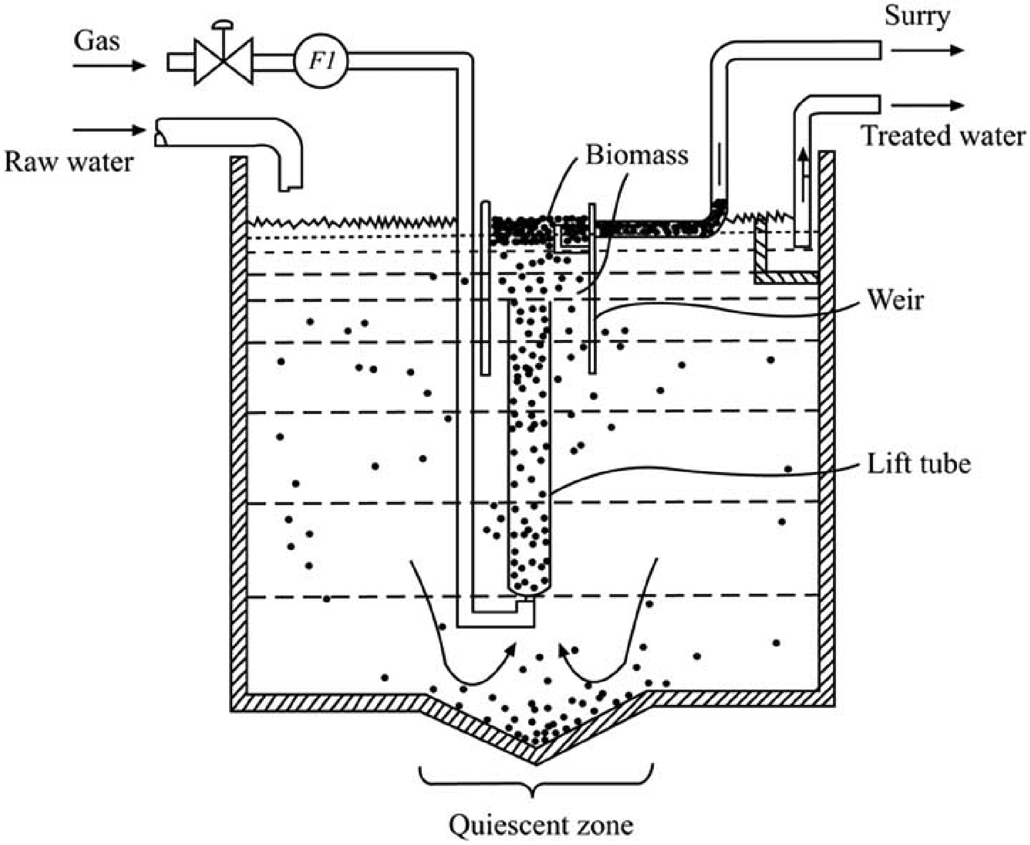

Fig. (10). Diagram for a bioreactor equipped with the lift tube.

attached to the float bed. The gas-sparging forms an upward flow to disturb the float bed, resulting in a separation of the solids from the float bed. Thus, the waste solids can be readily removed.

5. PASSIVE TREATMENT AND OTHERS

ARD treatment can take two basic modes, i.e., active and passive treatment systems. The active treatment systems, such as chemical and biological treatments, often require a constant maintenance of the system, chemical supplies and transport of wastes away from the site. But, passive treatment systems are commonly designed to allow for low or no maintenance, and should be self contained with regards to treatment and wastes.

Passive treatment is generally restricted to use wetland for the remediation of mine drainage. According to the environmental conditions of geochemistry and biology, the wetland may be constructed to a system possessing various functions, including neutralization, metal precipitation and filtration, and bioremediation under aerobic or anaerobic conditions. Thus, the constructed-wetland can utilize its pH-buffering capacity and adsorption properties to neutralize ARD acidity and remove metals as hydroxides and carbonates, or promote biological sulfate reduction by the bacteria naturally occurring in the sediments to precipitate metals as insoluble sulfides.

It is commonly observed that the performance of the constructed-wetland showed favorable response to metals load at rainy seasons but the efficiency for metal removal significantly reduced at dry seasons. This implies the constructed-wetland system could be impacted by the accumulation of heavy metals leading to a poor performance. Hilton *et al*. [122,123] disclosed a passive treatment, referred to as “Hybrid Flow Pond” (HFP), for removing metals as insoluble metal hydroxides from mine drainage. The HFP is an open, pond-like structure utilizing a horizontal or vertical operational flow path through a bed of treatment media. A vertical flush flow path is installed for flushing accumulated solids from the bed. During flushing, the effluent can be collected in a separate pond through an adjustable outlet riser [124] for recovery of the precipitates as a source of valuable metals.

Many other technologies have been applied to the remediation of ARD generation site, such as passivation of iron sulfides materials [125]. Misra *et al.* [126] taught a method for passivating sulfidic iron-containing rock with Mg-based salts and bases to reduce the acid generation potential of rock. Ma *et al*. [127-129] developed a method of using fern plants for wetland vegetation. Thus, metal contaminants can be removed from water and soil via photo-remediation through roots and fronds. The biomass can be harvested and readily disposed of, or can be treated to recover the metal contaminants.

6. CURRENT AND FUTURE DEVELOPMENTS

This paper focused on the ARD treatment reviews more than 85 patents filed mainly since the year 2000. Four main types of ARD treatments, including chemical precipitation process, adsorption method, biological system, passive treatment and others, have been surveyed. Currently, other types of advanced technologies with minor patents for ARD treatment have been developed, such as electrochemical ARD treatment.

Weakly *et al.* [130,131] developed an apparatus and process for metal recovery from water. Under a very high voltage, a very small trickle current charge is created in an electrolytic chamber to enhance adsorption, polarization, ion exchange or agglomerate the dissolved metal. Then, the metal is separated and recovered from water by filtering, adsorbing, exchanging. Johannes [132] invented a method of electrochemical ARD treatment. Under a controllable electrical energy supply, Zn^{2+} cations from the anode are dissolved into water to control the pH value in a range of 6 to 7, causing the formation of the insoluble zinc-hydroxyl-sulfate complex. Then, the metal-contaminant precipitates are removed from the water. Maxwell [133] devised a flow battery system of using ARD as electrolyte for large scale electrical energy storage. The charge is stored in double layer capacitors of flow battery system prior to discharge.

Chemical precipitation is simple, reliable and well proven, which has become the most common process for ARD treatment to compare with other available technologies. Typically, hydroxide precipitation using lime has been widely employed to treat ARD due to effectiveness and low process cost including facility cost, chemical cost, and operation and maintain cost. However, a major disadvantage of the lime process is that large amounts of sludge are generated, which is closely associated with the formation of gypsum scale on lime surface leading to hinder hydroxide liberation of lime. Hydroxide precipitates tend to resoluble when the solution pH is changed that could cause the difficulty for sludge management. Similarly, other (sulfide or carbonate) precipitation methods are facing these challenges too. Hence, the current and future development of chemical precipitation process requires producing less sludge amount, improving sludge stability and reducing process cost in addition to its efficiency. This conception is carried out in the development of patented process [66, 67], that is, a two-stage process for ARD treatment using recycled acidic and basic sludges to produce a stable sludge at $pH \geq 5$ and a high quality effluent in addition to saving > 32% of total chemical costs, and reducing > 20% of sludge amounts in comparison with the conventional lime neutralization process.

Besides, chemical precipitation system can be used as a pre-treatment step [104,105] to block dissolved metals from interfering with subsequent processes. Theodore [134] developed a chemical/biological water treatment process employing the injection of sulfur dioxide for dissolved contaminants removal followed by a biological system treatment to produce water of sufficient quality to meet discharge requirements. The biological treatment could be carried out in a designed lagoon.

Adsorption technology is an effective method of showing many advantages in the application of metal removal, such as much less cost for facility, easy operation and maintenance. Typically, adsorption method is suitable for selectively recovering valuable metals from water. However, the adsorbent could be quickly exhausted while treating water containing high levels of heavy metals. Currently, it may require a chemical pre-treatment to remove dissolved solids and reduce the metal loading to the adsorption column. Therefore, it could require an engineering system designed for automatically refreshing the adsorption column and recovering metals. Then, this would provide a solution for adsorption technology employed to treat ARD with high levels of dissolved metals although such an approach is not yet available.

Biological treatment methods of using microorganisms have become active fields to treat metal contaminated water, such as bio-sorption, bio-oxidation and bio-reduction. However, the biological system is usually unable to completely remove proton and mineral acidity of ARD on its own. In many cases, it still requires lime neutralization at the end. In addition, the bacteria growth needs a good carbon source for metabolism that often leads to a high cost of biological system. The generated metal sulfides-based solids from the biological system are not stable in oxidation environment; owing to insoluble metal sulfide can be slowly converted to soluble metal sulfate by air-oxidation. Hence, the metal sulfide rich sludge should be disposed to an anoxic environment. All of these concerns may receive the solutions from the future development of new bio-technologies.

Passive treatment is usually designed to use the properties of wetland, such as pH-buffering capacity, adsorption properties and natural occurrence of bacteria in the sediments, for the ARD neutralization and dissolved metals removal. The mechanisms for metal removal by constructed wetland include the formation and precipitation of insoluble metal sulfides, hydroxides and carbonates, and metal complexes with organic carbons, and direct uptake by plants. But, the construction of wetland is often highly engineered, requiring much higher maintenance cost for ARD treatment. Additionally, a growing concern is associated with the latent effects of heavy metals accumulation in the soil of wetland. Therefore, an idol model for constructing wetland should be a self sustaining ecosystem over time. Thus, the removed metals would be maintained in an unavailable form in the wetland in all four seasons.

ACKNOWLEDGMENTS

Financial support by NORAM Engineering and Constructors Ltd. (Project No. V0379) is gratefully acknowledged.

CONFLICT OF INTEREST

The author declares no patents are cited, which are in various stages of legal litigation, causing any conflict of interest.

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