SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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EFFECT OF pH AND CONTACT TIME ON THE ADSORPTION OF HEAVY METALS IN ACID MINE DRAINAGE USING HYDRATED LIME

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Effect Of pH And Contact Time on the Adsorption of Heavy Metals in Acid Mine Drainage Using Hydrated Lime ". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title for any other examining body or university.

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ABSTRAK

Saliran lombong berasid (AMD) adalah salah satu kejadian paling bermasalah yang boleh menyebabkan kemusnahan alam sekitar, ekosistem, kesihatan manusia, dan boleh memudaratkan keadaan air di kawasan tersebut. Masalah utama dengan AMD adalah kandungan logam berat di dalamnya dan jika diabaikan mungkin memberi ancaman besar kepada kesihatan manusia. Sejak kebelakangan hari ini, banyak penyelidikan telah dilakukan untuk merawat saliran lombong berasid tetapi kurang diketahui ramai bagaimana pH dan masa bahan penyerap mempengaruhi kepekatan logam berat. Kajian ini membentangkan hasil kajian yang dijalankan di Pengkalan Hulu, Perak di mana sampel air saliran lombong berasid sebenar diambil untuk dirawat. Kajian ini juga bertujuan untuk menganalisis sifat sampel air AMD dan komposisi media penyerap serta untuk mengenal pasti pH optimum dan masa untuk rawatan sampel saliran lombong berasid menggunakan kapur terhidrat sebagai bahan penyerap. Kajian menunjukkan bahawa masa yang lebih lama diperlukan untuk peratusan tertinggi penyerapan logam berat. Walau bagaimanapun, pH berbeza diperlukan untuk setiap logam berat mencapai tahap penyerapan maksimum. Projek ini penting untuk mematuhi piawaian yang ditetapkan dalam Peraturan Pembangunan Mineral (Efluen) 2016 untuk mengekalkan kualiti alam sekitar.

THE EFFECT OF pH AND CONTACT TIME ON THE ADSORPTION OF HEAVY METALS IN ACID MINE DRAINAGE BY USING HYDRATED LIME

ABSTRACT

Acid mine drainage (AMD) is one of the most problematic occurrence that can cause environmental degradation to the ecosystems, human health, and may devastate the water security in the area. The major problem with AMD is the content of heavy metals in it and if neglected may pose a major threat to the human health. Since today, many research was done to treating the acid mine drainage but less is known on how the pH and contact time of adsorbent material affects the heavy metals concentration. This study present the results of a study conducted in Pengkalan Hulu, Perak where real acid mine drainage water sample is taken to be treated. This study also aims to analyze the characteristic of AMD water sample and composition of adsorbent media as well as to observe the optimum pH and contact time for treatment of acid mine drainage sample using hydrated lime as the adsorbent material. The study shows that longer contact time is needed for the highest percentage of adsorption of heavy metals. However, pH varies for each of the heavy metals to be adsorbed at maximum. This project is significant to comply with the standard set in Mineral Development (Effluent) Regulations 2016 to sustain the environmental quality.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND RESEARCH

Klian Intan, Perak is a small town located between the north of Pengkalan Hulu and south of Gerik town. It is well known for the tin mining industry which is mainly operated by Rahman Hydraulic Tin Sdn. Bhd.(RHT). The company has been mining tin for more than over 100 years ago. There are also some other companies which are operating by further processing mine tailings from RHT namely Binary Reliance and Nalidah Tin Mine. These activities have developed the town to what it is now.

Mining and smelter industries have been one of the major industries in our country which have an immense contribution to the country's economic wealth. Many of the operating mines are focussing on the minerals namely gold, copper, coal, tin and some other economic ores. Despite all the benefits that the mining industries had provided, a common problem faced by the industries worldwide is acid mine drainage(AMD).

AMD is a consequential environmental problem which may affect the health of the human and and poses a threat to the surrounding ecology. This is due to the effluent generated by the mining industries may contain toxic substances and traces of heavy metals if not properly treated. The pH of the water from AMD is also extremely acidic and may be as low as 2. These problems cause severe problems to the other parts of locals economy such as tourism, fishing and farming.

The occurrence of AMD does not only apply to abandoned mines but to operating mines as well. AMD pollutes the nearby streams if discharged without appropriate treatment and the pollutant from AMD can persist for a long time even after the mining activities have stopped(Control, An and Mine, 2006).Thus, the management and every workers in the industry have to be well equipped with the knowledge and be made aware with the issue.

The water that has been affected by acid mine drainage must be treated in order to prevent any further problems strating in the river or streams and to aid in reversing any effects that might occur when the AMD polluted water enter the water system. Nowadays there are systems that are installed in the affected areas to manage the drainage that comes into the water flow. These systems are classified into two system where they are either treat with chemicals which is known as active treatment or by using natural and biological processes which is also known as passive treatment.

Many studies has been conducted with respect to the AMD and although many treatment and prevention measures has been taken, this problem still arise and most likely will affect the next generation as well. As time passes, more and more attention is given to this aspect and various regulations has been made in order to keep the ecosystem balance.

Organizations such as the Department of Environment(DOE) and Mineral and Geocience Department(JMG) has been conducting monitoring on water quality in the industries to ensure that the effluent generated are of safe specifications. The industries especially mining and quarries must abide the Mineral and Development Act 1994 under the Mineral Development (Effluent) Regulations 2016 for safe discharge of the effluent.

Effluent means any liquid waste produced by any exploration, mining or processing of mineral activities. Several parameters and limit of the effluent have been set and must not exceed the limit (Regulation 4). The *Table 1.1* below shows the parameters and limits involved.

SCHEDULE

[*Regulation 4*]

Table 1.1: Parameters and limit of effluent

Item [1]	Parameter [2]	Limit [3]	[4]	Unit [5]
1	Aluminium	10.0	15.0	mg/L
2	Arsenic	0.05	0.1	mg/L
3	Barium	1.0	2.0	mg/L
4	BOD_5[1] at 20°C	20	50	mg/L
5	Boron	1.0	4.0	mg/L
6	Cadmium	0.01	0.02	mg/L
7	Chromium, Hexavalent	0.05	0.05	mg/L
8	Chromium, Trivalent	0.20	1.0	mg/L
9	Free Cyanide	0.1	0.8	mg/L
10	Cyanide (WAD)[2]	0.5	0.8	mg/L
11	Fluoride	2.0	5.0	mg/L
12	Formaldehyde	1.0	2.0	mg/L
13	Free Chlorine	1.0	2.0	mg/L
14	Iron	1.0	5.0	mg/L
15	Lead	0.10	0.5	mg/L
16	Mercury	0.005	0.05	mg/L
17	Oil and Grease	1.0	10.0	mg/L
18	pH value	6.0 to 9.0	5.5 to 9.0	mg/L
19	Phenol	0.001	1.0	mg/L
20	Selenium	0.02	0.5	mg/L
21	Silver	0.1	1.0	mg/L

22	Sulphide	0.50	0.50	mg/L
23	Suspended solids	50	100	mg/L
24	Temperature	40	40	°C
25	Zinc	2.0	2.0	mg/L
26	Copper	0.20	1.0	mg/L
27	Manganese	0.20	1.0	mg/L
28	Nickel	0.20	1.0	mg/L
29	Tin	0.20	1.0	mg/L
30	Ammoniacal Nitrogen	10	20	mg/L

Notes :

1. BOD_5 = Biochemical Oxygen Demand
2. WAD = Weak Acid Dissociable

From the Mineral Development (Effluent) Regulations 2016, these regulations shall not apply to mining activities or mineral exploration activities carried out offshore. It can be observed that there are two columns of limits, [3] and [4] which has been stated that no person shall discharge any effluent containing parameters specified in column [2] of the Schedule where the effluent contain parameters exceeding the limits specified in column [3].

The discharged effluent may exceed column [3] provided that the parameter of the effluent do not exceed column [4] of the Schedule for some certain cases. However, the license holder must apply to the Director General for permission. The Director General has full authority to approve or reject the application from the license holder. Failure to follow the regulations may result in fining or imprisonment.

Thus, the license holder or company carries a huge responsibily and must ensure the effluent disposed comply with the provisions of the Regulations. Therefore, to make certain that the effluent is safe, one must monitor closely by taking samples of the effluent and analysing the concentration of the parameters of the effluent within certain period. A proper record of the sampling and analysis of the discharged effluent must be kept and maintained.

The company should also provide relevant training on monitoring of effluent parameters including sampling and analysis to appropriate personnel. For conducting this research, the Mineral Development (Effluent) Regulations 2016 has been used as reference for guidance and directory.

1.2 PROBLEM STATEMENT

Acid mine drainage produced in the tin mining area has the potential to cause environmental degradation to ecosystems, human health and threatens the water security of the area. Study of the acid mine drainage always shows that the problems came from an area on development or in severe cases in mining activities.

As the area is very well known for its mining activities for more than 100 years and still operating till today, some environmental problems may have rise. In the past, environmental issue may not be of a big deal and given less attention but if late preventive measures is to be taken then the obstacle at hand will be very huge.

The major problem with AMD is the content of heavy metals in it and if neglected may be a major threat to human health. One of the method to remove heavy metals from water is by controlling its pH. Various studies has been conducted and it has shown that lime neutralisation remains by far the most widely applied method.

Lime treatment essentially consists in bringing the pH of the AMD to a point where the metals of concern are insoluble. These metals therefore precipitate to form minuscule particles(Aubé and Zinck, 2003). The principle of lime neutralisation lies in the insolubility of heavy metals in alkaline conditions.

This project focussed on the removal of heavy metals in acid mine drainage and hydrated lime is used as the neutralisation agent. It was also conducted to observe the efficiency of using hydrated lime for treating acid mine drainage. It was to observe the insolubility of heavy metals at different pH value. Thus, this can be used to determine what is the optimum pH of water to be maintained to prevent the dissolution of heavy metals ion.

1.3 OBJECTIVES

i) To analyze the characteristic of AMD water sample and composition of adsorbent media.

ii) To observe the optimum pH and contact time for treatment of acid mine drainage sample using hydrated lime.

1.4 SCOPE OF STUDY

The observation was made at Pengkalan Hulu, Perak where it is situated near to a tin mine and agricultural activities. More specifically, the samples were taken near a tin tailing processing facility on 28 February 2018 based on the recommendation by an environmental officer from Rahman Hydraulic Tin Sdn. Bhd.

On site, while taking the sample, we also took the in-situ data which present. The in-situ data consisted of the temperature and pH. The initial pH recorded was pH 2 and it was immediately classified as an AMD polluted area. However, the acid mine drainage occurs in stagnant water and does not flow out into rivers or stream.

Nevertheless, acid mine drainage still occurred in the area and may affect the surrounding plantation and soils. The treatment media which is hydrated lime is provided by Rahman Hydraulic Tin Sdn. Bhd. The parameters studied were the pH and concentration of heavy metals present specifically aluminium(Al), copper(Cu), nickel(Ni), iron(Fe), lead(Pb), zinc(Zn) and arsenic(As).

1.5 THESIS OUTLINE

This thesis had been organized into five main chapters:

- **Chapter 1: Introduction,** this chapter introduces briefly the coverage of the thesis, including the overview of the research background, problem statement, objectives and scope of this research work.

- **Chapter 2: Literature Review,** covers in detail the existing literature on AMD relating to its nature, classification, sources, effects and regulations. Information on the equipment and measurement techniques and measurement techniques, as well as treatment methods that are available and applicable in the industry arena.

- **Chapter 3: Research Methodology,** presents the overall flow of this study and experiments conducted, information about the location, equipment, and methodology of the experimental work.

- **Chapter 4: Results and Discussion,** presents and discusses results from the data and result tabulated. Explain the importance of findings and acknowledge any mistake or limitation in experiment.

- **Chapter 5: Conclusions and Recommendations,** summarizes the finding of the research and makes recommendations based on it.

CHAPTER 2

LITERATURE REVIEW

2.1 ACID MINE DRAINAGE FORMATION

Acid mine drainage remains one of the most problematic occurrence to the water system as it can devastate rivers, streams, and aquatic life for hundreds, thousands of future years. This acid can further damage the water network by dissolving heavy metals from surrounding rocks during movement or seepage. The pH changes and high heavy metal content severely affect surrounding flora and fauna.

Acid mine drainage (AMD) is harmful because it can occur indefinitely, long after mining has ended. The new generation will be the one that will be impacted the most if no or little attention is given to this issue. The presence of acid mine drainage has the capability, and under certain circumstances had destroyed rivers, streams, and aquatic life for a very long time. Mineral resources such as coal, and metal ores such as gold, silver, and copper, are often rich in sulfide minerals, reflecting rock or sediment environments generally high in sulphur content and low or devoid of free molecular oxygen

Acid mine drainage is formed when sulfide minerals especially pyrite or iron disulphide (FeS_2) undergone oxidation (Jennings *et al.*, 2008). This is a naturally occurring phenomenon which will happen when these minerals are exposed to air and water. This problem has been faced all around the world as a result of natural occurrence as well as disturbances to the land by human activities such as highway construction and mining activities. Thus, resulting the exposure of the sulfide minerals to the surface.

For instance, mine tailings and waste rocks will have a greater surface area due to their smaller grain size, are more susceptible to generating AMD. Since massive amount of sulfide minerals are quickly exposed during mining operations, the surrounding conditions cannot immediately lessen the lowering down of pH. In low pH values, some common elements such as Cu, Zn, Al, Fe and Mn will drastically increase.(Jennings *et al.*, 2008)

In a study conducted by (Skousen, Sexstone and Ziemkiewicz, 2000), the metal content and concentration of AMD depends on the quantity and type of mineral present in the water body. The water quality discharged from backfills of surface mines or underground mines relies on the minerals themselves either acid producing (sulfides) or alkaline (carbonate) minerals which are contained in the disturbed rocks.

The AMD water discharged usually have the characteristics as follows; low pH, high specific conductivity, high concentrations of iron, aluminium and manganese, and low concentrations of toxic heavy metals (Akcil and Koldas, 2006). AMD has become a serious problem due most treatment technologies available are insufficient or quite expensive resulting the AMD left untreated.(Diz, 1997).

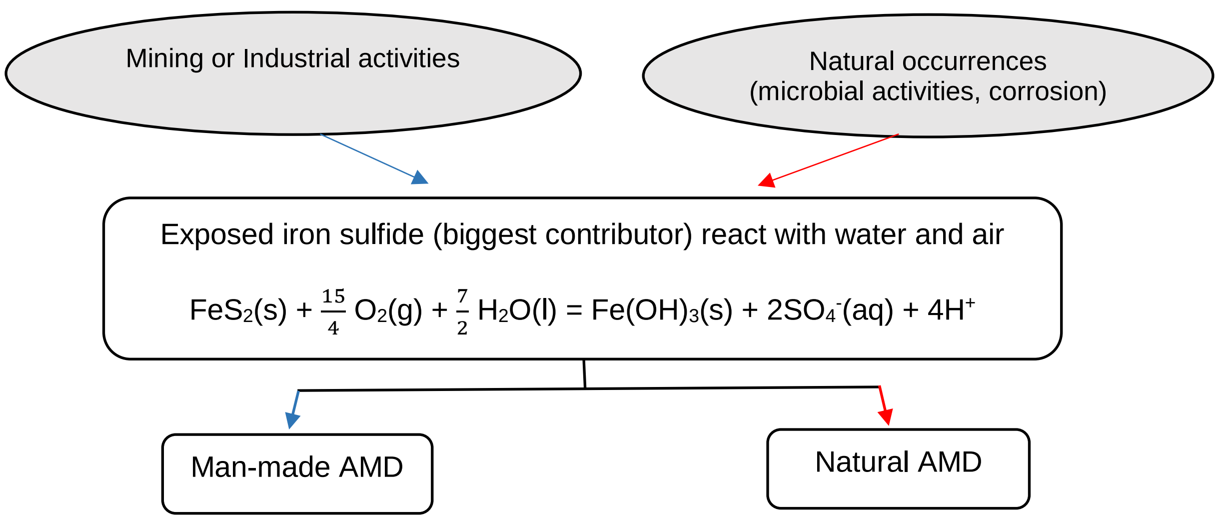

Figure 2.1: Overview of the chemistry of the AMD

The acid generation primary ingredients are as follows:

1) Sulfide-bearing minerals
2) Water or humid atmosphere
3) An oxidant (oxygen from the atmosphere)

The detailed chemical reaction from the *Figure 2.1* above reaction of acid mine drainage are shown below. The atmospheric oxygen will tend to oxidize pyrite to produce sulphuric acid and ferrous iron (Fe^{2+}) according to equation (1).

$$FeS_2 + \frac{7}{2} O_2 + H_2O \rightarrow Fe_2O + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + \frac{1}{4} O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2} H_2O \quad (2)$$

For equation (2), the reaction will occur when the surrounding environment is sufficiently oxidizing. It depends on several factors like the O_2 concentration, pH and bacterial activity.

As discussed by (Akcil and Koldas, 2006), at pH values between 2.3 - 3.5, ferric iron will precipitate as $Fe(OH)_3$ and will leave a little amount Fe^{3+} and at the same time lowering the pH of the water. The reaction is shown in equation (3).

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3\ solid} + 3H^+ \quad (3)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} 2SO_4^{2-} + 16H^+ \quad (4)$$

From equation (2) and (3), any Fe3+ that do not precipitate may be used to oxidize additional pyrite according to equation (4).

Based on these simplified basic reactions, acid generation that produces iron which will precipitate as $Fe(OH)_3$ may be portrayed by the combination of equation (1) to (3). This can be shown in equation (5).

$$FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \quad (5)$$

Therefore, for a stable ferric iron that is used to oxidize additional pyrite is shown in equation (6).

$$FeS_2 + \frac{15}{8}O_2 + \frac{13}{2}Fe^{3+} + \frac{17}{4}H_2O \rightarrow \frac{15}{2}Fe^{2+} + 2SO_4^{2-} + \frac{17}{2}H^+ \quad (6)$$

The hydrous ferric hydroxide, $Fe(OH)_3$ will form a layer which nothing around the area can grow. This red-orange to ochre-yellow sludge is known as "yellow-boy". The *Figure 2.2* below shows the formation of "yellow-boy".

Figure 2.2: The formation of ferric hydroxide,$Fe(OH)_3$ or also known as "yellowboy"

The primary factors that determine the rate of acid generation are:

a) pH

b) Temperature

c) Oxygen content of the gas phase, if saturation is less than 100%

d) Oxygen concentration in the water phase

e) Degree of saturation with water

f) Chemical activity of Fe^{3+}

g) Surface area of exposed metal sulfide

h) Chemical activation energy required to initiate acid generation

i) Bacterial activity.

The rate of acid generation is mainly governed by the chemical, biological and physical factors. The presence of bacteria also enhances the rate of acid generation as they play an important role in the oxidation pyrite. One of the bacteria is *Acidithiobaccillus ferrooxidans* and for it to flourish, certain conditions are favorable. If the conditions are not favorable it will result in minimal acid generation. For instance, a ferrooxidans will be most active in water with pH less than 3.2 (Akcil and Koldas, 2006).

This formation of acid mine drainage is quite complicated since factors like microbial activities, temperature (weather and seasonal conditions), availability of oxygen and type of mineral deposits vary from place to place, thus influencing the quality (pH and metals content) and amount of AMD produced.

2.2 EFFECTS OF ACID MINE DRAINAGE

Acid mine drainage contains very high levels of heavy metals and very high acidity. These heavy metals pose a serious threat when this toxic mixture flows into groundwater, streams and rivers to human health, animals and ecological systems it gives rise to several environmental problems and toxic to aquatic organisms and also destroys ecosystems.

As summarized by (Mansour, 2014), heavy metals are naturally occurring elements in the Earth's crust and due to human activities causes the release of these heavy metals into the environment excessively. Moreover, these heavy metals cannot be deteriorated or destroyed and can simply enter the human body through the food chains either food, water or air.

Some of the known heavy metals are such as mercury, cadmium, lead, chromium, and arsenic. A human population living near an industrial site which utilizes these common heavy metals which have been improperly disposed have a higher risk of exposure and health impact. Subsistence lifestyle have a higher tendency to be affected due to the hunting and gathering activities (Griswold and Ph, 2009).

Some of the health effects caused by heavy metals from the acid mine drainage are explained below(Mansour, 2014)(Griswold and Ph, 2009):

i) Arsenic

Arsenic is odorless and tasteless. Inorganic carcinogen is known carcinogenic substance and can cause cancer of the skin, lung and liver. Lower exposure of arsenic can cause nausea and vomiting, decreased production of red and white blood cells, abnormal heart rhythm, damage to blood vessels and a sensation of "pins and needles" in hand and feet. Arsenic ingestion at too high levels may result in death.

ii) Cadmium

Cadmium upon low-level exposure are chronic obstructive pulmonary disease and emphysema and renal tubular disease. There may also be effects on the cardiovascular and skeletal systems. Ingesting very high levels of cadmium severely irritates the stomach, leading to vomiting and diarrhea.

iii) Chromium

Chromium compounds bind to soil and unseeingly to migrate into groundwater however, they are terribly persistent in sediments in water. Chromium (VI) compounds are toxins and known human carcinogens, whereas Chromium (III) is an essential nutrient. When chromium intake is excessive through breathing this can cause irritation in the lining of nose, nose cancers. Long term exposure can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation.

iv) Lead

Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system.

v) Mercury

Metallic mercury is an allergen, which may cause contact eczema, and mercury from amalgam fillings may give rise to oral lichen. Short-term exposure to high levels of metallic mercury vapors may cause lung damage, nausea, vomiting, diarrhea, increases in blood pressure or heart rate, skin rashes, and eye irritation.

vi) Lead

Lead can affect every organ and system in the body. Long-term exposure of adults can result in decreased performance in some tests that measure functions of the nervous system. Exposure to high lead levels can severely damage the brain and kidneys and ultimately cause death. Miscarriage may happen if pregnant women receive high exposure of lead. On the other hand, for men excessive lead may harm organ that produce sperms.

vii) Zinc

Zinc is a nutrient that is necessary for the body and its deficiency may cause severe health effect. Excessive exposure to zinc is relatively uncommon and occurs only at very high levels. Zinc may affect the human lives when freshly formed fumes of zinc are inhaled and known to cause metal fume fever.

viii) Nickel

Human exposure may occur through inhalation, ingestion, and dermal contact. Deposition, absorption, and elimination of nickel particles within the tract for the most part rely on the particle size and concentration of nickel. The speed of dermal absorption depends on the speed of penetration within the epidermis that differs for various types of nickel. A study conducted by (McCoy and Kenney, 1992) hypothesized that nickel damages DNA through reactive oxygen species.

ix) Copper

Copper is an essential nutritional element to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Copper toxicity occurs in the form of nausea, vomiting and diarrhea (Pizarro *et al.*, 1999). Ingestion of large amounts of copper salts may produce hepatic necrosis and death. Excessive accumulation of copper in the liver, brain, kidneys, and cornea manifests into Wilson's disease.

x) Iron

Acute iron poisoning is common in some animals such as dogs, cats and many other animals (Mansour, 2014). Iron is also a leading cause of unintentional poisoning deaths in children less than 6 years-old. No system in the body have the mechanism for excreting iron, thus toxicity depends on the iron already present in the body.

Heavy metals are toxic to human health and they also represent a threat to the environment due to their tendency to accumulate in different environmental components. Heavy metals pollution has been recorded to have occurred for a very long time. It has been reported that the first evidence of palaeopollution discovered in an archaeological cave of the Iberian Peninsula. The research was done through geochemical analyses of the heavy metals. It was discovered that heavy metal pollution happened since the Early-Middle Paleolithic (Monge *et al.*, 2015).

In South Africa, there are a lot of abandoned mines which includes gold, copper and coal. In the country, the abandoned mines are controlled by an act which is the Water Amendment Act 58 of 1997 which functions to protect the water quality and to control the discharge by the industries. Before the act was implemented, many mines were abandoned without any measures to prevent the pollution that might arise which are commonly acid mine drainage (Naidoo, 2017).

Contaminated water flowing from abandoned coal mines is among the foremost vital contributors to pollution in former and current coal-producing areas. Acid mine drainage will give severe impact on aquatic resource, stunt terrestrial plant growth and damage wetlands, contaminates groundwater and might corrode concrete and metal structures. Serious acid mine drainage cases will be harder to treat thus increasing the cost of water treatment. The Canadian mining industry identified acid mine drainage as one of the greatest environmental liability and to clean up the acid generating mines would require a cost of between $2 billion and $5 billion (Jennings et al. 2008, p 4).

In the Appalachian Mountains of the eastern United States alone, more than 7500 miles of streams are affected. The Pennsylvania Fish and Boat Commission appraises approximately $67 million annually on the losses on fisheries and recreational uses. Even though there exist a strict environmental regulation regarding mining techniques that should be met, there are still numerous abandoned mine sites in the United States. In some other cases, hard rock mines in the western USA (Idaho and Colorado) seems to have given rise to water quality problems (Naidoo, 2017). According to the statistics from the US Forestry service, it was estimated about 8000 to 16000 km of streams in the USA had been affected by acid mine drainage. The major cause of it is from the active and inactive mines and waste rock piles.

Early treatment of a single can actually make a difference and can result in the restoration of affected streams. For instance, an acid runoff from the Summitville in Colorado had destroyed all the biological life over a 17-mile distance of the Alamosa River. Acid metals from the runoff of the Questa mine which mined molybdenum in New Mexico had negatively affected biological life along 8 miles of the Red River. Streams or surface waters with pH below 4.0 can be overwhelming to fish and other aquatic life. Preventive measure should be taken as when the problem starts it will be very difficult for mitigation and treatment even after mining activities has ended.

Another research by (Jaffe *et al.*, 1995) which described about the Tuy River which is located in the north-central Venezuela. The river has also been contaminated due to the effluent of active agricultural and industrial activities from a city, Caracas which have about 4 million inhabitants living in the area. On top of that, the waste water only undergoes minor water treatment.

In Bolivia, intensive mining activities has seriously damaged the natural resources which affect the local agriculture. Acid mine drainage which contained traces of heavy metals are released into the streams. This is a potential hazard to the villagers as the water stream is used to irrigate the farm produce. Consumption of the produce may harm both humans and animals (Garrido *et al.*, 2009).

Acid mine drainage generation has been closely related with the presence of bacteria. The most common studied pyrite oxidizing bacterium is *T.ferrooxidan* (Garrido *et al.*, 2009). From the study conducted, it was observed that *T.ferrooxidan* can oxidize both elemental sulfur and sulfide to sulfuric acid according to the equation below:

$$S + 1.5O2 + H2O \rightarrow H2SO4 \qquad (1)$$

$$S2- + 2O2- + 2H+ \rightarrow H2SO4 \qquad (2)$$

Generally, the mechanisms of pyrite oxidation are divided into two classes which are direct metabolic reactions and indirect metabolic reactions. Direct metabolic reaction will require the physical contact between bacteria particles while no physical contact is not needed for indirect metabolic reactions.

2.3 ACID MINE DRAINAGE TREATMENT

There are various types of treatment for acid mine drainage which can be divided into two types of systems known as active or passive treatment. The choice for the type of treatment is crucial to ensure that acid mine drainage can be treated successfully. There are some factors to be considered before choosing either one of the type of system. For example, if an acid mine drainage exceeds specific threshold, more neutralizing agent would be required for the water treatment. Therefore, an active treatment system would be a more suitable choice(Trumm, 2010).

2.3.1 ACTIVE TREATMENT SYSTEM

An active treatment system involves the addition of chemicals to increase the pH and precipitates the metals. Several chemicals can be used to counter acid mine drainage but involves the installation of machineries to insert the chemicals into the water. Active treatment can be a very effective treatment mechanism but a the appropriate chemicals to be used are determined through a site by site basis (Kirby, 2014).

To achieve the discharge limits within a short span, the practice of adding neutralizing agent and metal precipitating chemicals is very common (Roy Chowdhury, Sarkar and Datta, 2015). A wide range of chemical agents such as limestone ($CaCO_3$), hydrated lime ($Ca(OH)_2$), caustic soda ($NaOH$), soda ash (Na_2CO_3), calcium oxide (CaO), anhydrous ammonia (NH_3), magnesium oxide (MgO) and magnesium hydroxide ($Mg(OH)_2$) are being used during the active treatment of AMD water around the world.

i) Limestone

For the usage of limestone in active water treatment, it requires silo or hopper with mechanical feed screw to dispense the powder. Mixing will be needed for the powder therefore, a batching tank will be required to mix the powder with water.(Trumm, 2010). Limestone is most suitable when the area is not too acidic and only contains a few metals. It is not suitable for extreme conditions because limestone is not very soluble and can develop a covering preventing any from getting into the water. (Kirby, 2014) stated that an issue face when using limestone is that limestone can develop armor when in contact with mine drainage that contains aluminium and iron(III) which reduces its ability to treat the water.

ii) Hydrated lime

It is known as the most popular used chemical throughout the world. Hydrated lime is most suitable when dealing with mine drainage areas that has high acidity and high flow rate (Kirby, 2014). It has a very high efficiency and most metals can be precipitated. As it is widely available and have low cost making it a favorable choice chemical worldwide. Some of the drawbacks are regarding health issues and without proper maintenance will cause plugged dispensing and complete failure (Trumm, 2010). Using hydrated lime will require a mixing plant on site to deliver it to the affected water.

iii) Caustic soda

Caustic soda is can raise the pH very efficiently and is heavier than water and can also be applied to ponds. Caustic soda is stored as a liquid in tank, dispense through metering pump or valve and feeder hose near top of pond or water inlet. It is easier to be handled because no mixing is required but is very costly. It is however poses some health and safety issues and the sludge has very poor settling rates. The water may also be toxicated by sodium(Trumm, 2010).

iv) Soda ash

The usage of soda ash gives very little control on how much is added and when, however it is only used in areas which has very little problems of acid mine drainage. It utilizes a small system that delivers soda ash briquettes periodically to the water(Kirby, 2014). This is supported by (Skousen et al, 1996). Unfortunately, the usage of soda ash causes poor settling rates and prone to sodium toxicity.

v) Quicklime or calcium oxide

The usage of quicklime has high efficiency and will cause most of the metals to precipitate. It is very cheap and readily available. For using quicklime, a silo or hopper with mechanical feed screw to dispense powder or water wheel feeder with 1 tonne storage bin with no power required. Quicklime will require slaking and a mixing tank to mix the powder with water. The reagent saturation may reduce the efficiency and armoring of pebbles may occur. Apart from the health and safety issues the quicklime must be watertight or it will hydrate and form calcium hydroxide(Trumm, 2010).

vi) Anhydrous ammonia

It comes in a compressed form and stored as liquid in a tank. The gas will be injected near the bottom of the pond or at the water inlet of the pond. It can immediately increase the pH of the water and no mixing is needed. Nevertheless, the operators must be aware of how much ammonia is added into the water system because in excess in can severely affect the stream. Its usage must be decided based on a site by site basis to see whether it is appropriate to be applied.

vii) Magnesium oxide or hydroxide

This chemical is rarely used as it is not widely available. It has a high efficiency and produce less sludge. It is also can be bought at a low cost. This chemical also needs mixing as it is in powder form. Therefore, a silo or hopper with mechanical feed screw is used to dispense the powder. Some hazard may arise to the health and safety while handling the chemical. It is also less preferable as it has lower reaction rate than calcium hydroxide(Trumm, 2010).

2.3.2 PASSIVE TREATMENT SYSTEM

Passive treatment system can be defined as any technologies that utilizes the chemical and biological process that occur in nature for the treatment of contaminated water. Passive treatment was considered to be an ideal system due to their expected lower cost of construction, operation and maintenance and able to operate and remote locations with minimal supervision(Stankovi, 2012). Passive treatment systems differ from active treatment systems where the active systems need the use of power, more hazardous chemicals are used and are more expensive. Passive systems involve the use of sulfate reducing bacteria or limestone and are sometimes known as “wetlands” or “bioreactors” (Ford, 2003).

Passive treatment systems for acid mine drainage use the chemical, biological and physical removal processes that occur naturally in the environment to modify the influent characteristics and amend any associated environmental impacts (Stankovi, 2012). The major processes include:

- Chemical processes: oxidation, reduction, coagulation, adsorption, absorption, hydrolysis, precipitation;
- Physical processes: gravity, aeration, dilution;
- Biological processes: biosorption, biomineralization, bioreduction, alkalinity generation.

The types of treatment system may only utilize on of the type or sometimes more than one system is selected and constructed in sequence. However, its suitability is still dependent on the site characteristics and other criteria(Taylor, Pape and Murphy, 2005).

i) Aerobic wetlands

Aerobic wetlands are chosen to treat acid mine waters that are net alkaline(Stankovi, 2012). This is because the reaction that occurs within them is the oxidation of ferrous iron and subsequent hydrolysis of the ferric iron is produced. The mine drainage will flow horizontally through the pond and over substrate. It is suitable to be used for treating water samples with pH more than 5.5 (Trumm, 2010). The *Figure 2.3* below shows the schematic diagram of the aerobic wetlands.

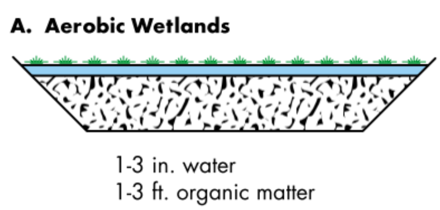

Figure 2.3: Schematic diagram of an aerobic wetland