

SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

ACID MINE DRAINAGE TREATMENT WITH ZEOLITE AND RED GYPSUM AT
TASIK PUTERI, DUNGUN, TERENGGANU

BY

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Dissertation submitted in partial fulfilment of the requirements for the degree of Bachelor
of Engineering with Honors (Mineral Resources Engineering)

Universiti Sains Malaysia

June 2017

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Acid Mine Drainage Treatment with Zeolite and Red Gypsum at Tasik Puteri, Dungun, Terengganu". 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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ACKNOWLEDGEMENTS

I would like to express my gratitude to the following people who without them, this work would have been impossible to achieve.

First of all, I would like to thank for my supervisor DATO' PROF. DR. IR. ERIC K. H. GOH for his support and guidance throughout this research. I have learned and gained first hand experience to be on site and work on something real. All the thanks to tremendous effort shown by research officers, lab assistant and technician in helping me finishing my study on acid mine drainage. Personally, thanks to the late Dr Syamsul Kamal Bin Sulaiman, En. Syahrir, En. Hasnizam, En. Syed, En. Sharul, En. Anuar, Cik Uma dan Puan Haslina.

Then, I would like to thanks Pusat Penyelidikan Mineral (PPM) allowing me to use the equipment or machine in the laboratory to make this final year project of mine a success. In addition, I would like to express my utmost gratitude to the technicians who helped me to conduct the machine although they are busy or away on duty. Besides that, I also would like to thank all lecturers who had indirectly helped me in becoming who I am today. Without your teachings, this project might not be conducted so smoothly. Thank you all for the involvement and your patience in me.

Last but not least, all the love to my family and friends that always supporting me on every decision and steps.

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KAEDAH RAWATAN SISA SALIRAN LOMBONG BERASID MENGGUNAKAN ZEOLITE DAN GYPSUM MERAH DI TASIK PUTERI, DUNGUN, TERRENGANU.

ABSTRAK

Sisa saliran lombong berasid (AMD) adalah salah satu isu yg dihadapi oleh lombong-lombong di seluruh dunia. Ianya disebabkan oleh kesan AMD terhadap kesihatan dan persekitaran. Sebab utama ialah, AMD merosakkan tanah, kehidupan air, tumbuh-tumbuhan dan juga adalah punca hujan asid. Ia akan menjadi punca kemusnahan ekonomi dan perkembangan orang tempatan. Walaupun kapur mampu meneutralkan AMD, namun kesan reaksi eksotermik antara air dan kapur akan merosakkan system ekologi tasik. Kajian ini menunjukkan keputusan eksperimen yang dikendalikan di Tasik Puteri, Dungun, Terengganu to menggunakan zeolite dan gypsum merah sebagai alternatif untuk merawat sumber air yang terkesan dengan AMD. Sampel air di ambil dari Tasik Puteri. Eksperimen dijalankan di dalam makmal menggunakan kaedah ujian kolom. Sebuah meter-pelbagai digunakan untuk mencari dan mengumpul data AMD sebelum dan selepas eksperimen. Tambahan juga, ujian ICP-AES turut di jalankan terhadap sample air AMD sebelum dan selepas eskperimen. Zeolite dan gypsum merah disiasat menggunakan XRF untuk mencari bukti aktiviti penyerapan mineral dan mengkaji elemen yang hadir dalam zeolite dan gypsum merah sebelum dan selepas digunakn untuk merawat AMD. Rawatan AMD menggunakan zeolite menunjukkan hasil yang positif dari segi nilai pH, namun gagal untuk meneutralkan salah satu logam berat yang hadir dalam AMD. Manakala gypsum merah tidak mampu untuk menunjukkan apa-apa kesan terhadap sampel AMD.

**ACID MINE DRAINAGE TREATMENT WITH ZEOLITE AND RED GYPSUM AT
TASIK PUTERI, DUNGUN, TERENGGANU**

ABSTRACT

Acid mine drainage is one of the main issue faced by mines worldwide. This is due to the health effects and environmental problem it may bring to its' surrounding. The most particular reason is that it affect soil, aquatic life, plantations and can also cause acid rain. This will severely affect local's economy and livelihood. While hydrated lime can neutralize the acid mine drainage to national water quality standard, exothermic reaction of lime when reacted with water can harm the lake ecological system. This thesis present the result of study conducted in Tasik Puteri, Dungun, Terrenganu to test zeolite and red gypsum to be used as alternative to treat AMD affected water source. Water sample are taken from Tasik Puteri with in-situ data. Experiment are conducted in lab using column test. A multimeter are used to collect data on AMD sample before and after column test. Plus, ICP-AES test also conducted on AMD sample before and after column test. Zeolite and red gypsum are studied with XRF to investigate their absorbent properties and analyse their elements. National water quality standard are used to compare the result from the column test. AMD treatment with zeolites are show promising result on pH value, but failed to neutralize one of the heavy metal present in the AMD sample. While, red gypsum unable to critically affect the AMD sample.

CHAPTER 1

INTRODUCTION

1.1 Background

Iron Mining is prosperous in Bukit Besi, Pahang around 1927 to 1970. The high quality and concentration of ore in Bukit Besi making it one of the sought after industry in Terengganu. Iron mining has always been the key to the economic sector in Terengganu. Massive iron deposit allowed it to be mine continuously from 1927-1970. This activity developed the town to what it is now.

Despite being a significance economy wellspring to the locals and country, there were always been discord between the mines and the surrounding communities. The communities mainly because of the acid mine drainage that are released or seep from the mine into the network of rivers around the mine. These problems cause severe problems to the other parts of locals economy such as, tourism, fishing and farming.

More than 4 decades of iron mining causes irreversible damage to water network around Bukit Besi. Primitive technology and outdated regulations also helped causes acid mine drainage to the lake and rivers. Acutely low pH river water that are filled with heavy metals can also cause severe health damage to human and farm animals.

The Department of Environment (DOE) has been conducting monitoring of river since 1978, primarily to establish baselines and to detect water quality changes in river water quality and has since been extended to identifying of pollution sources as well. A total of 1,064 manual stations located within 143 river basins through out Malaysia.

Water quality data were used to determine the water quality status whether in clean, slightly polluted or polluted category and to classify the rivers in Class I, II, III, IV or V based on Water Quality Index (WQI) and Interim National Water Quality Standards for Malaysia (INWQS) every year. Water Quality Index (WQI) is computed based on 6 main parameters that is biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammoniacal nitrogen (NH₃N), pH, dissolved oxygen (DO), and suspended solids (SS).

Parameter	Unit	Class					
		I	IIA	IIB	#III	IV	V
Temperature	°C	-	Normal± 2	-	Normal± 2	-	-
pH	-	6.5 – 8.5	6.0 – 9.0	6.0 – 9.0	5.0 – 9.0	5.0 – 9.0	-
Conductivity	¹ µmhos/cm	1000	1000	-	-	6000	-
Colour	TCU	15	150	150	-	-	-
DO	mg/L	7	5 – 7	5 – 7	3 – 5	<3	<1
BOD	mg/L	1	3	3	6	12	>12
COD	mg/L	10	25	25	50	100	>100
Oil & Grease (mineral)	µg/L	Natural Level	40; N	40; N	N	-	-
Oil & Grease (emulsified edible)	µg/L		7000; N	7000; N	N	-	-
Total Dissolved Solids	mg/L	500	1000	-	-	4000	-
Total Suspended Solids	mg/L	25	50	50	150	300	300
Turbidity	NTU	5	50	50	-	-	-
Ammoniacal Nitrogen	mg/L	0.1	0.3	0.3	0.9	2.7	>2.7
Floatables	-	N	N	N	-	-	-
Odour	-	N	N	N	-	-	-
Salinity	%	0.5	1	-	-	2	-
Taste	-	N	N	N	-	-	-
Feacal Coliform	² counts /100mL	10	100	400	5000 (20000) ^a	5000 (20000) ^a	-
Total Coliform	² counts /100mL	100	5000	5000	50000	50000	>50000
Hardness	mg/L	Natural Level	250	250	-	-	Levels Above IV
K	mg/L		-	-	-	-	
F	mg/L		1.5	1.5	10	1	
NO ₃	mg/L		7	7	-	5	
P	mg/L		0.2	0.2	0.1	-	
S	mg/L		0.05	0.05	- (0.001)	-	
Cd	mg/L		0.01	0.01	0.01* (0.001)	0.01	
Cu	mg/L		0.02	0.02	-	0.2	
Fe	mg/L		1	1	1	1 (leaf); 5 (others)	
Pb	mg/L		0.05	0.05	0.02* (0.01)	5	
Mn	mg/L		0.1	0.1	0.1	0.2	
Ni	mg/L		0.05	0.05	0.9*	0.2	

Table 1.1 shows National Water Quality Standard (EQR 2006)

Class I represents water bodies of excellent quality. Standards are set for the conservation of natural environment in its undisturbed state. Water bodies such as those in the national park areas, fountainheads, and in high land and undisturbed areas come under this category where strictly no discharge of any kind is permitted. Water bodies in this category meet the most stringent requirements for human health and aquatic life protection.

Class II represents water bodies of good quality. Most existing raw water supply sources come under this category. In practice, no body contact activity is allowed in this water for the prevention of probable human pathogens. There is a need to introduce another class for water bodies not used for water supply but of similar quality, which may be referred to as Class IIA. The determination of Class IIB standards is based on criteria for recreational use and protection of sensitive aquatic species.

Class III is defined with the primary objective of protecting common and moderately tolerant aquatic species of economic value. Water under classification may be used for water supply with extensive and advanced treatment. This class of water is also defined to suit livestock drinking needs.

Class IV defines water quality required for major agricultural irrigation activities, which may not cover minor applications to sensitive crops.

Class V represents other wastes, which do not meet any of those above uses.

The national water quality standard and the classifications are used when writing environmental reports, either government agencies or private companies. However, this

table can only be used for classification of water in Malaysia. The table cannot be applied to the data of another country. This is because of difference in soil type, climate, local mineral and metallic content, plants and also animals.

The table are to make sure that waters released from mines, quarries or any developed are safe to be consumed and not causes health issues. Furthermore, the water also important to that of environment so that we can build a sustainable tomorrow.

1.2 PROBLEM STATEMENT

Study of the acid mine drainage always shows that the problems came from an area on development or in severe cases in mining activities. Taking into account the severe effects that acid mine drainage can bring to human health, properties and environment. Thus making it a necessity for a further study in this arena for making the surrounding a safer place.

A small studies carried out nowadays on acid mine drainage. Plus, the studies are mostly conducted decades ago. Those studies has found out that lime has the best result in recovering the pH and heavy metal content in acid mine drainage. Thus causes a halt in further studies using other type of minerals that newly created or by-products.

There are only a needle in a haystack of published studies on treatment of acid mine drainage focused on Malaysia. One of it is by Anuar Othman, Azli Sulaiman and Shamsul Kamal Sulaiman. It is a study to find a suitable quantity of carbide lime which is a waste from acetylene gas process to be used for acid mine drainage treatment. The experiment from the study concluded that carbide lime suitable to be used to treat acid mine drainage. Thus making it not impossible for another kind of mineral or by-products to be used as AMD treatment.

Sustainability of the Bukit Besi is important to the environment and locals. Rehabilitation of the water source in Bukit Besi to recover former state of nature as best as it could before further developments. Steps must be taken to to bring Tasik Puteri, Bukit Besi to it's former glory.

1.3 Objectives

This study aims to achieve several studies.

1. To evaluate the quality of water source nearby the abandoned mine
2. To evaluate effectiveness of AMD treatment using zeolite and red gypsum.
3. To validate the data and make an assessment whether the minerals used for AMD treatment are applicable.

1.4 Scope of Study

This research involved a thorough study to carried out at Tasik Puteri, Bukit Besi, Pahang. The data was sampled within the Tasik Puteri, specifically, in the vicinity of the dam. On site, while taking the sample, we also took the in-situ data which present. The in-situ data is consists of temperature, pH, dissolved oxygen (DO), total suspended solids (TSS), turbidity and conductivity. These are the top parameters to know the quality of the water on site almost immediately, especially pH of the water. Example, the water taken in a river has a pH value of 2, it immediately tagged as a polluted river.

The studies mainly focused on treating the pH and the heavy metal content of the sample. Using zeolite and red gypsum, which are high in calcium content which can increase the pH value back into a national water quality standard class I. The absorption value of zeolite and red gypsum plays an important role in diminishing the heavy metal content of the water.

Thus freeing the water from mobile metal ion, making the water more safe and environmental friendly.

From 27th February until 3rd March 2017, data was collected using a mobile insitu data reader, which are used to read DO, turbidity, and total suspended solids. Another machine is a mobile pH reader which can also read the temperature of the water. The sample that are going to be test with inductive coupled plasma are filtered using 4.5 μ and acidify until a pH of 2 and stored below 4°C. This is to ensure the sample for inductive coupled plasma test are not polluted or damaged.

1.5 Thesis Outline

This thesis is organized into five main chapters:

Chapter 1 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 covers in detail the existing literature on AMD relating to it's 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 presents the overall flow of this study and experiments conducted, information about the location, equipment, and methodology of the experimental work.

Chapter 4 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 summarizes and draw conclusions for this study and its' objective.

CHAPTER 2

LITERATURE REVIEW

2.1 Acid Mine Drainage

2.1.1 Definition of Acid Mine Drainage (AMD)

Acid mine drainage is discharge of acidic liquid from metal or coal mines. The acid liquid occurred during and after mining process. The process exposes sulphides to water and air, together they react to form sulfuric acid. 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, as happened in Bukit Besi.

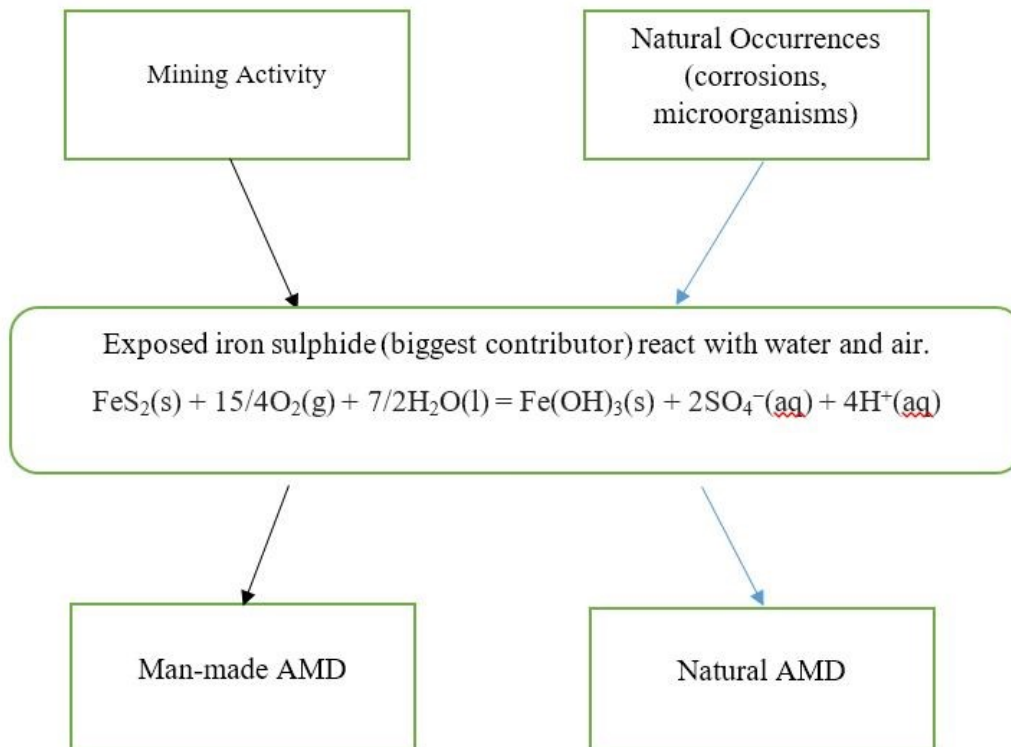


Figure 2.1 Shows a process of how AMD happened.

The presence of acid mine drainage has the potential, and under certain conditions has actually devastated 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 sulphide minerals, reflecting rock or sediment environments generally high in sulphur content and low or devoid of free molecular oxygen. Once exposed to water and air during mining, pyrite and other iron sulphide rocks release sulphuric acid in the presence of extremely acidophilic microorganisms. These complex interactions occur in microbial communities of autotrophic and heterotrophic bacteria and archaea which catalyse iron and sulphur oxidation, determining the release rates of metals and sulphur to the environment as acid mine drainage (Baker and Banfield, 2003). Even eukaryotic life forms (fungi and yeasts, protozoans, microalgae, and rotifera) may be part of microbial communities present in low-pH environments. Although the primary aerobic iron- and sulphur-oxidizing bacteria have been studied for decades, more recently, DNA analysis and genetic studies have identified some archaea, and even a few eukaryotes, to be present in the microbial community in the extremely low-pH acid mine drainage environments studied (Baker and Banfield, 2003). The ecology and biodiversity of acid mine and rock drainage microbial communities have been well documented by Baker et al. (2004, 2009) and Rawlings and Johnson (2002, 2007).

Once the sulphuric acid is created, the pyrite dissolves in drainage water, releasing associated metals and metalloids such as aluminium or arsenic into the surrounding environment. Wherever iron sulphides are exposed, such conditions can occur: open pits, underground excavations, leach pads, and tailing and waste rock piles.

Contaminated water flowing from abandoned coal mines is one of the most significant contributors to water pollution in former and current coal-producing areas. Acid mine drainage can have severe impacts on aquatic resources, can stunt terrestrial plant growth and harm wetlands, can contaminate groundwater, can raise water treatment costs, and can damage

concrete and metal structures. In the Appalachian Mountains of the eastern United States alone, more than 7500 miles of streams are affected. The Pennsylvania Fish and Boat Commission estimates that the economic losses on fisheries and recreational uses are approximately \$67 million annually. While most modern coal-mining operations must meet strict environmental regulations concerning mining techniques and treatment practices, there are thousands of abandoned mine sites in the United States.

Treatment of a single site can result in the restoration of several miles of affected streams. For example, acid runoff from the Summitville mine in Colorado, a designated federal Superfund site, killed all biological life in a 17-mile stretch of the Alamosa River. Acid and metals in runoff from the mining of molybdenum at the Questa mine in New Mexico adversely affected biological life along 8 miles of the Red River. The effect on the environment can be severe. Streams and surface water bodies with a pH of 4.0 or lower can be devastating to fish, animals, and plant life. Once started, the process becomes very difficult to stop and can occur indefinitely, requiring mitigation and water treatment long after mining ends—in perpetuity. Along with countless other mines throughout the world featuring serious long-term environmental impacts, acid drainage at the Golden Sunlight mine is estimated to continue for thousands of years.

Common iron sulphide minerals, primarily pyrite (FeS_2), but also marcasite (FeS_2), arsenopyrite (FeAsS), and chalcopyrite (CuFeS_2), are exposed to the oxygen in the atmosphere during mining, excavation, or through natural erosion processes, and the compounds react with oxygen and water to form sulphate, resulting in acid drainage. This acidity results from the action of extremely acidophilic bacteria, which generate their energy by oxidizing ferrous iron [Fe(II) or Fe^{2+}] to ferric iron [Fe(III) or Fe^{3+}] using oxygen for cellular respiration. The ferric

iron, in turn, dissolves the pyrite to produce soluble ferrous iron and sulphate. The ferrous iron is then available for oxidation by the aerobic acidophilic microbes, which scavenge dissolved oxygen in the pore space or water column. This biogeochemical cycle continues until the iron sulphide mineral (e.g., pyrite) is dissolved.

Due to the exothermic nature of the oxidation process, removing the oxygen from the pore spaces of sulphur-rich waste rock piles can minimize the chance for oxidation and combustion.

The hot exothermic reactions produce sulphuric acid-rich solutions which contain high concentrations of metals, frequently iron, aluminium, arsenic, lead, copper, cadmium, manganese, and zinc. Although this reaction can occur abiotically, it appears that most of the oxidation of sulphide minerals on Earth over the past more than 2 billion years since oxygen has been present in the atmosphere has occurred as a result of aerobic microbial-catalyzed processes on the reaction surfaces of iron sulphide minerals in the presence of atmospheric oxygen and water.

2.1.2 Factors increasing the Acid Mine Drainage

- I. Type of mineral present : Not all type of sulphide minerals oxidized at the same rate.
- II. Amount of oxygen present : Sulphide minerals oxidized more rapidly where there are more oxygen available. Thus, acid mine drainage often form at a faster rate where the sulphides are exposed to air than buried in soil or water.
- III. Amount of water available : Dissolving oxidized sulphide and reacting to it form more and more acidic water.
- IV. Temperature : pyrite oxidation occurs most quickly at around 30°C.
- V. Microorganism : Some microorganism able to accelerate acid mine drainage.

2.1.3 Effects toward environment and human health.

- I. Forest ecosystem : Acidic deposition has chemically altered the forest soils. The soil now unable to neutralize continuing inputs of strong acids, provide poor living condition for plants and extend recovery time for the soil itself. Acidic deposition also depletes other nutrients cations such as magnesium and potassium from soil and increase accumulation of nitrogen and sulphur in soil.
- II. Tress: Cause the decline of certain species of trees such as red spruce trees and sugar maples. Symptom of tree declining include poor crown condition, reduced tree growth and high level of mortality rate. Acidic deposition from acid mine drainage leached calcium from leaves and needles (foliage) of trees making them affected to winter

injury. It also cause depletion of tree nutrients from soil such as magnesium and calcium, which are important to development of trees.

III. Aquatic ecosystem: acidic deposition causes the water to lower its' pH value making the water more acidic, and increasing dissolved inorganic heavy metals concentrations. Decrease in pH and elevated concentration of inorganic heavy metals have reduced he species diversity and abundance of aquatic life in many streams and lakes. This has inflicted the whole food webs.

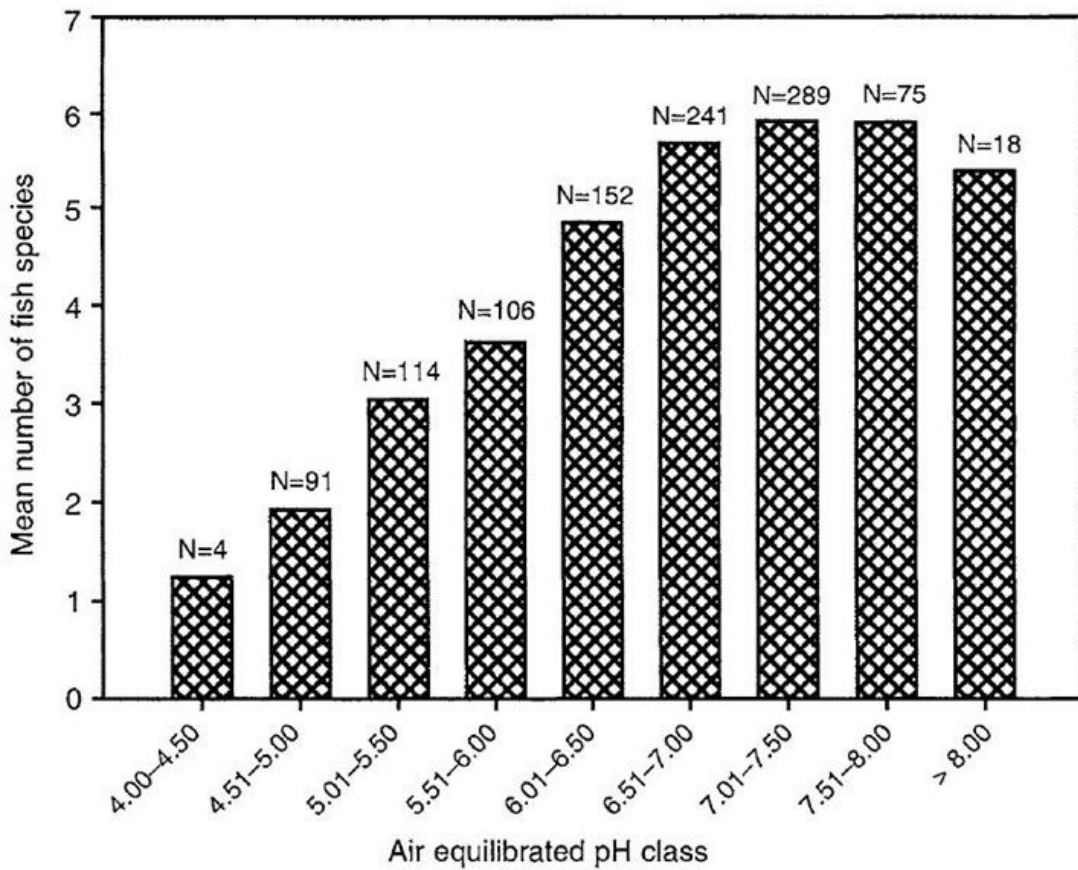


Figure 1.2 The mean number of fish species for Ph classes from 4.0 to 8.0 in lakes in the Adirondack region of New York. N represents the number of lakes in each pH class (Driscoll et all, 2001).

IV. Human Health: The water decreasing pH value causes acidity which surely damage the human organs. Primarily skin, which are exposed more regularly to this kind of pollutant, which subsequently cause eczema, and skin irritation. Sulphur particulate and nitrogen oxide that exist from AMD may also cause asthma and bronchitis if it were to find a way into human body. These heart and lung disease can cause death, if severe.

2.1.4 Treatment Methods

Lime Neutralization

The most commonly used commercial process for treating acid mine drainage is lime precipitation in a high-density sludge (HDS) process. In this application, a slurry of lime is dispersed into a tank containing acid mine drainage and recycled sludge to increase water pH to about 9. At this pH, most toxic metals become insoluble and precipitate, aided by the presence of recycled sludge. Optionally, air may be introduced in this tank to oxidize iron and manganese and assist in their precipitation. The resulting slurry is directed to a sludge-settling vessel, such as a clarifier. In that vessel, clean water will overflow for release, whereas settled metal precipitates (sludge) will be recycled to the acid mine drainage treatment tank, with a sludge-wasting side stream. A number of variations of this process exist, as dictated by the chemistry of ARD, its volume, and other factors (Zinck, J.M. and Griffith, W.F. 2000). Generally, the products of the HDS process also contain gypsum and unreacted lime, which enhance both its settle-ability and resistance to re-acidification and metal mobilization.

In a less complex and more cheap process, the lime neutralization may involve only a few lime bags, mixing machine and a settling pond. The cheap option are, however less efficient and more suitable for small water flow and less complex AMD.

In another study by Anuar Othman, carbide lime was used. The usage of carbide lime mainly because to repurpose carbide lime from waste of acetylene gas process to be used as neutralisation material for AMD treatment. High calcium content in carbide lime helped increasing the pH value of AMD. Carbide lime also has the capability to reduce certain heavy metals such as cadmium, lead, zinc etc. Water sample in this study are collected active tin mine which have pH around 2.6 until 2.8. Jar test was used in the laboratory to investigate the capability of carbide lime in treating AMD. Result from experiment shows that carbide lime suitable for treating AMD (Anuar et al., 2016).

Calcium Silicate neutralization

By removing the free H^+ ions from the AMD, calcium silicate which are made from processed steel slag can neutralize the acidity in AMD system. As the silicate anion entrapped H^+ ions and thus raising the pH, it also forms monosilicic acid (H_4SiO_4) a neutral solution. The monosilicic acid that remains in the solution play it's roles in correcting the adverse effects of acidic conditions. In the bulk solution, the silicate anion is very active in neutralizing H^+ cations in the soil solution (Ziemkiewicz Paul 2011).

Calcium silicate reacts differently than lime stone when there are presence of heavy metal in the solution. While limestone raises the pH and precipitated the metal hydroxides, in the calcium silicate aggregates, as silicic acid species are absorbed into metal surface, the developed silica layers lead to formation of colloidal complexes with neutral or negative surface charges. The negatively charged colloids give an electrostatic repulsion with each other and the isolated metal colloids are stabilized and remain in dispersed state. Rendering them unable to precipitate.

Ion Exchange

The principle is that an ion exchange resin can remove potentially heavy metals (cationic resins), or chlorides, sulfates and uranyl sulfate complexes (anionic resins) from acid mine drainage. Once the contaminants are adsorbed, the exchange sites on resins must be regenerated, which typically requires acidic and basic reagents and generates a brine that contains the pollutants in a concentrated form (M. Botha, L. Bester, E. Hardwick, 2009).

2.2 Zeolite

2.2.1 Definition of Zeolites

Zeolites are crystalline nanoporous hydrated aluminosilicates in which linked Si, O and Al form a three-dimensional frame work structure. The linkages create surface pores of uniform diameter (2 to 10Å) enclosing regular internal cavities and channel with the discrete size and shape depending on the zeolite species. The cavities contain loosely bound metal cation that can engage in ion-exchange. There infinite possibilities for framework topologies, although in practice there are 40 known in nature, and more than 150 synthetics zeolite have been manufactured (Peter W. Harben 1999).

Table 2.2 Broad Based Categories of Zeolites (Peter W. Harben 1999)

Pore Size	No. of Tetrahedra	Maximum free diameter	Commercial Examples
Large	12	7.5 Å	Mordenite
Medium	10	6.3 Å	ZSM-5, ferrierite
Small	6, 8	4.3 Å	Clinoptilolite, Chabazite

2.2.2 Characteristic of Zeolite

Characteristic of zeolites that are an interest to this project is cation exchange capacity (CEC) and also the calcium content that can increase the AMD pH value. CEC is the ability to exchange cations to other cations on a basis ion selectivity without any change on zeolite matrix.

More on the cation exchange; this property depend on the certain loosely bonded ions in zeolites being exchanged for other ions relatively easily by washing with a strong solution of another ion. Different zeolites have cation preferences which in turn provides for cation selectivity, example, clinoptilolite and chabazite have preference for larger cations: clinoptilolite is Cs> Rb> K> NH₄> Ba> Sr> Na> Ca> Fe> Al> Mg> Li; whereas chabazite prefer Ti> Cs> K> Ag> NH₄> Rb> Li> Ca> Zn> Sr> Ba> Ca> Co> Ni> Cd> Hg> Mg. In most water treatment (AMD) processes the zeolite can be regenerated and reused.

In recent studies by T.Motsi, adsorption behaviour of natural zeolite, more precisely clinoptilolite, has been studied to determine its applicability in treating acid mine drainage

containing heavy metals. Test to determine both rate of adsorption and the uptake at equilibrium were performed. The optimum conditions for treatment process were investigated by observing pH levels, presence of competing ions, varying mass of zeolite and thermal modification of zeolite. Selectivity sequence of absorption of heavy metal can be given as $Fe^{3+} > Zn^{2+} > Cu^{2+} > Mn^{2+}$. Preliminary tests using AMD from Wheal Jane Mine, UK, shows that this absorption characteristic of zeolite has great potential as an alternative low cost material for AMD treatment (T. Motsi et al., 2009).

2.2.3 Quality and Specifications of Zeolite

For quality and specifications, an importance difference between natural and synthetic zeolite is that natural zeolites may contain impurities and be non-uniform whereas synthetic zeolites are purity specialty chemical manufactured to exact specifications on a consistent basis. Sophisticated uses such as molecular sieve and catalyst are served by synthetic zeolites, natural zeolites are best suited with less demanding uses such as adsorption and ion-exchange in aquaculture, liquid carries and pet litter.

2.2.4 Health and Safety of Zeolite

Health and safety. Under section 5(a) [2] of the Toxic Substance Control Act (TCSA), the US EPA issued a final rule in 1991 that persons who intended to manufacturer, import or process erionite fibre for any use must notify EPA at least 90 days before beginning that activity. The EPA classified fibrous erionite as a Category B1 or probable human carcinogen. Mordenite also a fibrous mineral, but to date has no record of carcinogenic problems. IARC now classifies crystalline silica Class 1, known carcinogen so that, for example, industrial mineral and chemical containing 0.1% or more crystalline silica are regulated by OSHA's Hazard Communication Standard in the USA, that is a worker right to know regulation requiring worker training, product labelling, as well as MSDS describing carcinogenic hazard.

Thus, unless processing can reduce crystalline silica content to less than 0.1%, zeolites will come under the regulations similar to US OSHA Hazard Communication Standards.

2.3 Gypsum

2.3.1 Background

Gypsum has been used since earliest recorded history. Chinese, Assyrians, and Greeks used gypsum for artistic work, in carvings and decorations. It was used as a mortar in the Cheops pyramid and the entire pyramid was sheathed in solid sheets of alabaster, which is a massive, granular variety of gypsum.

In the 18th century, gypsum was used as a soil conditioner in Western Europe. Gypsum was discovered in New York in 1792, Virginia (1835), Michigan (1840), Ohio (1850), Iowa (1872), Colorado (1875), and California in (1875). In 1885, a commercial method of retarding the setting of gypsum plaster was developed. This revolutionized the gypsum industry by permitting the use of plaster in construction.

The development of prefabricated lath and wallboard against revolutionized the gypsum industry. In 1973, 67 percent of the gypsum marketed as prefabricated products.

2.3.2 Definition of Gypsum

Gypsum is a naturally occurring mineral, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with 79 percent calcium sulfate and 21 percent water. The clear, crystalline heterogeneity is called selenite. The massive, granular heterogeneity is called alabaster. The fibrous heterogeneity is called satin spar. Gypsite is a mixture of clay and gypsum crystals.

Anhydrite is naturally occurring mineral, CaSO_4 , with no water of crystallization. When gypsum is calcined at higher temperatures, it is converted to anhydrite.

Calcined gypsum $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$, is a manufactured product produced by partial calcination of gypsum. It has been called “plaster of paris”. In the presence of water, it sets quickly and returns to gypsum.

By-product of gypsum is a chemical product of a manufacturing process such as manufacture of phosphoric acid.

Keene’s cement is completely calcined gypsum with ni water of crystallization.

2.3.3 Geology of gypsum

Gypsum deposits may be originated in any geological era, but they are most common in the Permian. They are frequently found in association with the source rocks of petroleum. Most gypsum deposits occur as large lenticular stratified bodies that formed by precipitation from saline waters. Deposits usually contain both gypsum and anhydrite.

The chemistry of the deposition of gypsum in evaporate basins is uncertain. It is difficult to account for the tremendous thickness of salt free gypsum beds. Seawater hold only 0.13 percent of CaSO_4 . To account for a bed of gypsum 30.48 meters thick, a column of seawater 75.64 kilometres deep would be completely evaporated. Also for complete evaporation, a bed of salt 1 kilometres thick will overlies the gypsum beds.

2.3.4 Red Gypsum

'Red' gypsum as it is commonly known, because of the red colour imparted by the iron from ilmenite (FeTiO_3) ores, is a waste product from an industrial process in the production of titanium dioxide (TiO_2). Titanium is extracted from ilmenite by sulfuric acid digestion and the

spent acid is neutralized with calcium carbonate to produce the waste product gypsum. It is estimated that this sole industry in Malaysia produces 400 000 tonnes of this material annually. Normally, this waste product is disposed off in landfills or left as stacks close to the titanium dioxide plant.

Land application has been proposed as a disposal option for red gypsum; however, there is some concern that heavy metals found in this waste product may be taken up by plants, or pollute surface water or leach into the groundwater. But, the present of calcium content in red gypsum may be used to treat acidity of the AMD. By increasing the pH of the acidic acid mine drainage, by certain pH, it may also retained heavy metals. The retained heavy metals that are trapped in soil then will form sedimentation at the bottom of river or lake, will be removed by excavators.

2.4 Induced Coupled Plasma Atomic Emission Spectroscopy

2.4.1 Definition of ICP-AES

Induced Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. It is a flame technique with a

flame temperature in a range from 6000 to 10000 K. The intensity of this emission is indicative of the concentration of the element within the sample.

2.4.2 Process of ICP-AES

ICP-AES is an emission spectrophotometric technique, exploiting the fact that excited electrons emit energy at a given wavelength as they return to ground state after excitation by high temperature argon plasma. The fundamental characteristic of this process is that each element emits energy at specific wavelengths peculiar to its atomic character. The energy transfer for electrons when they fall back to ground state is unique to each element as it depends upon the electronic configuration of the orbital. The energy transfer is inversely proportional to the wavelength of electromagnetic radiation.

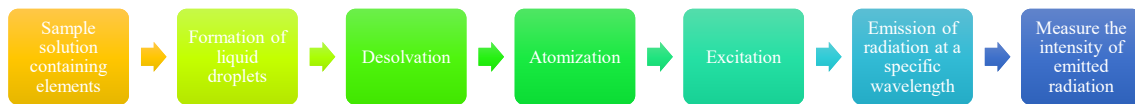


Figure 2.3 Working principle of ICP-AES in order.

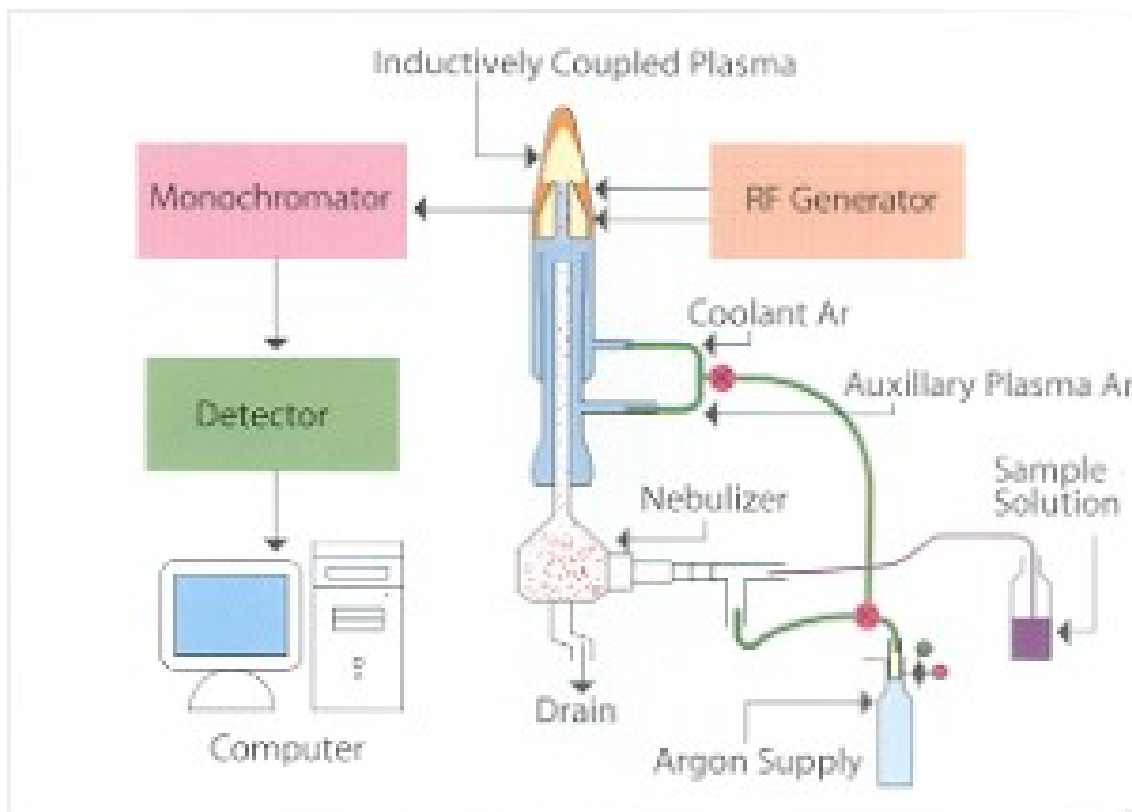


Figure 2.2 ICP-AES diagram

First of all, sample solution will be pump into the nebulizer using peristaltic pump. By using a process known as peristalsis, the pump move the solution through tubing by utilizing series of rollers. This to ensure a fixed flow rate of the solution into nebulizer not dependent on viscosity and surface tension.

The nebulizer are a machine that converts liquid into aerosol droplets. In this diagram, the nebulizer uses compressed argon to break up the solution into aerosol particles.

The solution moved into spray chamber. A chamber placed between nebulizer and torch. This chamber functioning as a tool to remove large droplets from the aerosol. This allowing only aerosol droplets with about 10 micro meters or smaller to pass to plasma. Secondly, the chamber also used to smooth out pulses that occur during nebulization due to peristalsis pumping of solution.