Remediation and Mitigation Measures for Slowing Down the Decomposition of Black Shale at Batu Gajah, Perak

by

Aminur Rashid Bin Mohd Shariai 8498

Dissertation submitted in partial fulfilment of the requirements for the Bachelor of Engineering (Hons) (Chemical Engineering)

JUNE 2010

Universiti Teknologi PETRONAS Bandar Seri Iskandar 31750 Tronoh Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Remediation and Mitigation Measures for Slowing Down the Decomposition of Black Shale at Batu Gajah, Perak

by

Aminur Rashid Bin Mohd Shariai

8498

A project dissertation submitted to the Chemical Engineering Programme Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the BACHELOR OF ENGINEERING (Hons) (CHEMICAL ENGINEERING)

Approved by,

(AP Askury Abdul Kadir)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

June 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Aminur Rashid Hin Mohd Shariai

ABSTRACT

Pyrite, as well as being most important member of the disulfide group, is most abundant sulphide mineral in the earth and has been extensively studied. Once exposed to water and oxygen thru construction, mining and mineral processing operation, it could lead to chemical and biochemical oxidation with production of highly acidic, heavy metal leachates, which refer to acid rock drainage (ARD). This problem will lead to the biggest environmental pollution including underground water source, land and flora and fauna. This study is to find the way to treat the ARD problem by using organic material without harm the environment and cost is cheap. From the experiment, shown that the pH of the water after the reaction took part is very acidic and contains several hazardous heavy metal that are can give bad impact to human and environment. Calcium carbonate together with softwood and hardwood is used to prevent the ARD happen. These findings of the project will lead to solve the ARD problem and introducing the prototype to further research.

KEYWORDS: pyrite; pollution; acid rock drainage; organic material; calcium carbonate

ACKNOWLEDGEMENTS

I am expressing my thankfulness and gratitude to Associate Professor Askury Abdul Kadir, Final Year Project Supervisor for her guidance, support and advice and also for giving me continuous and unlimited motivation.

I would also like to sincerely thank to Dr. Suhaimi Mahadzir Final Year Project Chairman, Coordinator and Committees of January 2010 Chemical Engineering Department for their guidance and contributions.

Finally, I would like to express my thanks to Universiti Teknologi Petronas Information Resource Center and Chemical Engineering Department for much valuable knowledge shared.

TABLE OF CONTENTS

CERTIFICATION		•	•	•	•	•	•	ii
ABSTRACT .	•	•	•	•			•	iv
ACKNOWLEDGEN	MENT	•		•	•	•	٠	v
CHAPTER 1:	INTR	ODU	CTION	Ι.	•	•	•	1
	1.1			l of Stud	ly.	-	•	1
	1.2	Prob	lem Sta	atement	•	•		2
	1.3	Obje	ctives			•	•	4
	1.4	Scop	e of W	ork	•	•	•	4
CHAPTER 2:	LITE	RATU	J RE R I	EVIEW	•	•	•	5
	2.1	Theo	ory	•		•	•	5
	2.2	The	Root C	ause of '	The Pro	blem		6
	2.3	Acid	Rock I	Drainage	e Treatr	nent Tec	hniques	s 9
CHAPTER 3:	METI	HOD	DLOG	Υ.				10
	3.1	Over	all Proi	ject Met	hodolos	zv.		10
	3.2			nalysis i				14
	3.3			or the Pi				16
	3.4					Material	•	18
CHAPTER 4:	RESU	LTS	AND D	ISCUS	SION			17
	4.1	Black	k Shale	Reactiv	itv	•		17
	4.2			f Acid F		ainage	•	18
	4.3			l Analys			-	25
	4.4		bility S	-			•	27
	4.5				ion In I	Real Cas	e	28
CHAPTER 5:	CONC	CLUS	ION A	ND RE(COMM	[ENDA]	ΓΙΟΝ	31
	5.1		lusion	•	•	•	•	31
	5.2		mmend	lations	•	•	•	32
REFERENCES	•			•	•		•	33

LIST OF FIGURES

Figure 1	The Effects of the Black shale. The Plants Died Due to Acidic Conditions	2
Figure 2	The Place Turned to Yellow colour due to the Iron (III) ions	3
Figure 3	Location of the study	7
Figure 4	Image of the Thiobacillus. Ferrooxidans	9
Figure 5	Overall Methodology for This Project	13
Figure 6	Procedures to Perform Atomics Absorption Spectrometry	14
Figure 7	Steps to perform PH reading from the water	15
Figure 8	Design for Organic cover combining with Limestone	17
Figure 9	Example of the container to be the study site for experiment	18
Figure 10	Combining the design of organic layer with black shale in the basin	18
Figure 11	Reactivity of Black Shale in Natural Reaction	21
Figure 12	Water Changed From Colourless to Yellow Colour	23
Figure 13	pH Value for Treatment of the Problem	23
Figure 14	Black Shale Reactivity Before and After Treatment	24
Figure 15	Level of the Heavy Metals in the Water	26
Figure 16	Comparison Cost between Organic Method and Concrete Method	27
Figure 17	Example of the Coir Geotextiles	29
Figure 18	Example of installation the method	29

LIST OF TABLES

Table 1	Chemicals commonly used in the treatment of acid rock drainage	16
Table 2	pH Value for water Discharged from Black Shale	20
Table 3	pH Value for Water Discharged from Black shale	23
Table 4	Average Heavy Metal Contained in the Water	25

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Along the new way to Batu Gajah from Tronoh, Perak there was having some environment issue at the left and right of the new road. Due to the construction of the new road, the black shale which is one kind of the rock is exposing to the atmosphere when the hill is excavate to construct the road.

According to the Sci-Tech Dictionary (2009), the black shale is a dark mud rock rich in organic carbon. Black shales are typically very fine-grained and contain pyrite, phosphate, and abnormally large amounts of heavy metals. They commonly display excellent fissility and well-preserved planktonic and nektonic faunas and plant debris. Benthic fossils are rare or absent. Some black shales are sources of hydrocarbons.

This black shale can cause the acid rock drainage (ARD). Acid rock drainage is produced when sulphide-bearing rocks and mine waste minerals such as pyrite (FeS₂) and pyrrhotite (Fe_{1-x}S) are exposed to water and atmospheric oxygen (Keith 1992). The mixture may react via chemical and/or biological oxidation processes to form sulphuric acid which, together other metal hydroxides and heavy metal products can contaminate soils and pollute surface and ground water resources. Increased soil and water acidity and heavy metal contamination has very serious and damaging environmental ramifications for flora and fauna.

1.2 PROBLEM STATEMENT

Acid Rock Drainage is low pH ground and surface waters generated by the oxidation of the sulfide minerals to produce sulphuric acid. The process occurs naturally, but it can be caused or made worse by exposes sulphide-bearing rocks to air. Poor environmental practices can cause ARD. The major problem with ARD is that acidic waters dissolve metals, which in certain quantities are harmful to aquatic life and humans.

If the rock at the site contains sulfide minerals such as pyrite (FeS₂), then it could generate ARD when exposed to oxygen and water. The sulphur will react with oxygen with the help of bacteria (Thiobacillus ferroxidans) to form sulfuric acid. When the rock oxidizes, they change colour to rusty brown, and the waters will show a drop in pH. From the figure 1, all the green stuff at the site will be died due to the acidic soil.

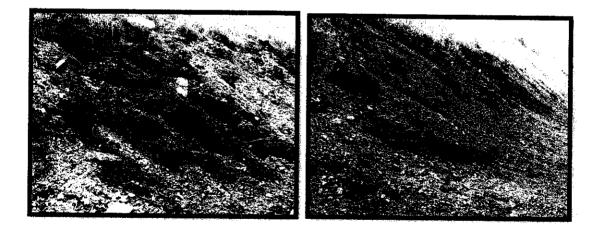


Figure 1: The Effects of the Black shale. The Plants Died Due to Acidic Conditions.

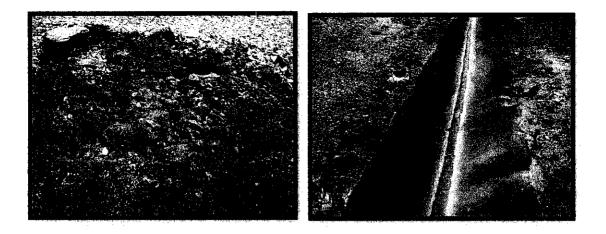


Figure 2: The Place Turned to Yellow colour due to the Iron (III) ions.

The figure 2 above is taken from the study area at new road to Batu Gajah, Perak. The ARD is become seriously problems to that area. The figure 1, shown the black shale that containing pyrite that expose to the atmosphere due to excavate the hill for the construction of the new road. Figure 2 the effect of the ARD that containing acid and the iron that had been changing from iron (II) to iron (III).

The grass at the surrounding black shale had been died due to the acidic environment that had been release by the black shale.

1.3 OBJECTIVE AND SCOPE OF THE STUDY

1.3.1 Objective

The objectives of this study are:

- 1. To analyze the chemical contain in the black shale and the effects expose to the environment.
- 2. To identify the mechanisms for controlling the oxidation of black shale.
- 3. To plan the remedial actions again the problem.

All the objective will be study at the along the new road to Batu Gajah, Perak.

1.3.2 Scope of work.

The scope of study for this project is to study the effects from the black shale to the environment and the remedial and mitigate action to prevent the problem. The analysis of the black shale roles to the problem is needed to perform by Atomic Absorption Spectrometry. Once all the properties that should be considered are been determined, they will be an experiment to prevent the problem by using organic material. Finally, the experiment result will be analyzed and the value added of the experiment will be conducted.

CHAPTER 2

LITERITURE REVIEW

2.1 THEORY

Acid rock drainage formation is recognized as a complicated process. Furthermore, the actual ARD formation reactions are not only chemical in nature but also involve some biological or biochemical influences, which add to the complexity of the process. There have been various studies on the mechanism of ARD formation. The reactions describe and present in 3 stages (Kleinmenn al. 1993).

Stage 1 involves the relatively slow chemical or biochemical oxidation of pyrite and other sulfide minerals near-neutral pH according to Eqn (1).

$$2FeS_2(s) + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO^{2-} + 4H^+(1)$$

This initial step might be catalyzed by acidophilic microorganisms, such as *Thiobacillus ferrooxidans*, through direct contact with sulfide minerals. As acid begins to accumulate around the minerals as indicated in Eqn (1), the process enters stage 2.

In stage 2, ferrous iron is oxidized to ferric iron (Eqn 2), which precipitates as ferric hydroxide (Eqn 3) and releases more acidity.

$$4Fe^{2+} + 4H^{+} + O_2 \rightarrow 4Fe^{3+} + 2H_2O (2)$$
$$Fe^{3+} + 3H_2O \rightarrow Fe (OH)_3(s) + 3H^{+} (3)$$

As the pH falls even further, below about 3.5, some ferric iron remains in solution to oxidize additional pyrite directly according to Eqn (4).

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

In stage 3, the associated acidophilic bacteria rapidly catalyzes the process by oxidizing more ferrous iron to ferric iron (Eqn 5) and the overall rate of acid production is increased by several orders of magnitude. This stage will produces large quantities of acids associated with the release of heavy metals into solution. At this stage, acid rock drainage becomes a problem.

$$Fe^{2^+} + O_2 (aq) \rightarrow Fe^{3^+} (5)$$

 $Fe^{3^+} + FeS_2(s) \rightarrow Fe^{2^+} + SO^{4^+} (6)$

2.2 THE ROOT CAUSE OF THE PROBLEM

From the past years study, the acid rock drainage (ARD) is one of the biggest issues for environment throughout the last decade. The study had been conducted regarding this big issue and found that there are several factors that could lead this problem happen. The three major factors are oxygen from atmosphere, water from rain or underground source and last factor is the rock in this case, the black shale. When the three elements are meeting the formation of the acid rock drainage could be happen and the process is natural.

2.2.1 Black Shale

The black shale is a dark mud rock rich in organic carbon. Black shale are typically very fine-grained and contain pyrite, phosphate, and abnormally large amounts of heavy metals (Sci-Tech Dictionary 2009). They commonly display excellent fissility and well-preserved plank tonic and nektonic faunas and plant debris. Benthic fossils are rare or absent. Some black shale's are sources of hydrocarbons.

Pyrite (FeS_2) that is available at the black shale is the major element that can be directed to the formation of the ARD. Pyrite is containing iron and sulfur mineral, when it

exposed to the atmosphere it could be formation the change of the iron. The process happened when The oxidation of the sulfide to sulfate soluble the ferrous iron (iron(II)), which is next oxidized to be ferric iron (iron(III)). When this happened, it will flow the yellow liquid which is iron (III) from the rock to the environment that was containing acid to the environment.

2.2.2 Oxygen

The oxidation process of the pyrite happens when the rock is exposing to the atmosphere. In this case, the construction of the new road at Batu Gajah, had cut of the hill to give the new road being construct at the middle of the hill. Before the construction, the black shale remain at the underground of the hill, the excavation process for construction new road exposed the rock to the atmosphere. As mention early, the process occur in natural, so the acid drainage formation will be happen without any prevention action taken early.

2.2.3 Water

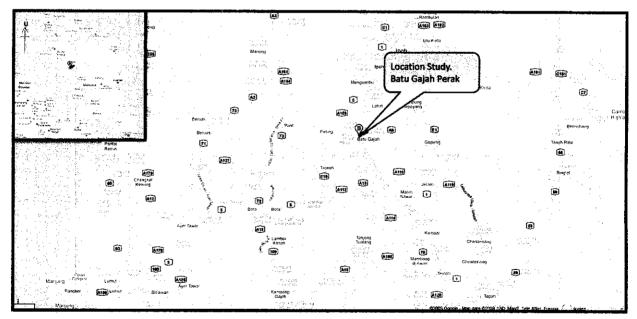


Figure 3: Location of the study (Google map, 2009)

Batu Gajah is situated at $+4^{\circ}$ 27' 43.65" latitude and $+101^{\circ}$ 2' 0.55" longitude and the climate is equatorial. The climate is characterized by fairly high but uniform temperatures (ranging from 23° to 31° C /73° to 88° F throughout the year), high humidity, and copious rainfall (averaging about 250 cm/100 in annually). So the water is very available at this area.

2.2.4 Bacteria role.

The specific role of acidophilic chemoautotrophic bacteria in pyrite oxidation thru the research is become controversy matter. Some of the researcher did not agreed with the study regarding the pyrite oxidation to ARD formation. Since it is isolation in 1947, *T. ferrooxidans* has been regarded as a possible agent in the problem of ARD formation.

Since oxidation of FeS_2 may proceed slowly by chemical routes, it had been suggested that microorganisms are not important to ARD formations. Their role has been suggested as direct catalyst that alters the overall the chemical reaction rates or as specific catalyst agent which alters the rate of intermediate reaction. It is suggested that the microorganism remove electron from the surface pyritic iron to start reaction and/or catalyst sulfur oxidation or they simply increase iron(III) concentration.

2.2.4.1 Bacteria profile

Thiobacillus are colorless, rod-shaped, Gram-negative bacteria with polar flagella. They possess an iron oxidize, which allows them to metabolize metal ions such as ferrous iron (Baker RA.1970):

 $Fe^{2+} + 1/2 O_2 + 2H^+ --> Fe^{3+} + H_2O(7)$

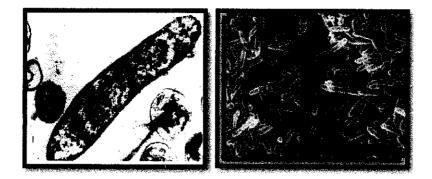


Figure 4: Image of the Thiobacillus. ferrooxidans (Sci-Tech Encyclopaedi, 2009)

Thiobacillus are strictly aerobic bacteria as shown in figure 4. All species are respiratory organisms. *Thiobacillus* are obligate autotrophic organisms, meaning they require inorganic molecules as an electron donor and inorganic carbon (such as carbon dioxide) as a source. They obtain nutrients by oxidizing iron and sulfur with O2. *Thiobacillus* do not form spores; they are Gram-negative Proteobacteria. Their life cycle is typical of bacteria, with reproduction by cell fission.(Nosa & Ben Oni,2007)

2.3 ACID ROCK DRAINAGE TREATMENT TECHNIQUES

2.31 Active Treatment

Active treatment, or treatment using an added chemical, is the most reliable and effective treatment technique. A system consists of an alkaline chemical added to an acidic release that flows into a series of settling ponds to allow for the precipitation of dissolved metals, before the discharge is released into nature. The disadvantages of this technique are the material costs and the maintenance and operational costs, along with the possibility of the environment exposed to dangerous chemicals.

There are six main chemicals that are used in ARD treatment. Limestone (calcium carbonate - CaCO₃), hydrated lime (calcium hydroxide - Ca(OH)₂), pebble quicklime

(calcium oxide - CaO), soda ash (sodium carbonate - Na_2CO_3), caustic soda (sodium hydroxide - NaOH), and ammonia (anhydrous ammonia - NH_3).

2.3.2 Passive Treatment

Passive treatment systems do not require chemical inputs, instead they use naturally occurring chemical and biological processes. They do require more time and a larger amount of area and provide a less certain treatment efficiency. Passive treatment systems also have a limited life and will require rejuvenation or reconstruction after the materials have been completely used. However, they do have considerably reduced costs and need for maintenance, and are not as harsh to the environmental surroundings. There are several types of passive treatment systems, and are chosen based on this parameters:

- 1) Water chemistry what is the dissolved oxygen concentration in the water, the dissolved iron and aluminum concentrations, is the water net acidic or net alkaline, and the pH.
- 2) Flow rate accurate flow data is needed to properly size the system including readings of extreme high and low flow volume.
- Local topography of the area is there enough area for the construction of the system and is there a sufficient gradient to create flow or pressure.

The types of passive treatments are:

- Constructed Wetlands (aerobic and anaerobic)
- Anoxic Limestone Drains (ALD)
- Successive Alkalinity Producing Systems (SAPS) or Vertical Flow Ponds (VFP)
- Open Limestone Channels

2.3.3 Mitigation

Passive treatments are sometimes limited by the area available for the system construction or the chemistry of the water is not favorable to a particular system design. Therefore, sometimes relatively creative, treatment options are needed to treat an acidic discharge. One option for treatment is the injection of an alkaline material directly into the soil of acidic rock. The goal is to chemically affect the water by adding significant quantities of alkalinity that should neutralize the acidity, increase the pH, and allow any metal species to precipitate out of the water. Usually the alkaline material is a byproduct of coal combustion. These ashes contain large amounts of caustic alkalinity due to calcium compounds already found in the coal or to the addition of alkaline materials associated with air pollution control processes (Canty and Everett, 2006).

Another option for increasing alkalinity in an acidic fill area is to cover the surface with a layer of limestone. The goal is to allow water to generate enough alkalinity before infiltration through the acidic material. Due to the faster rate of acid production versus the rate of alkaline production, it is important to line the surface with enough limestone so that water flows more through the alkaline material than the acidic material (Caruccio and Geidel, 1996), which is difficult to do if there is a large quantity of acidic material.

2.3.4 Elimination

Both oxygen and water are necessary in order for the oxidation process to be initiated, and therefore, elimination of one or both of these components will also be effective in the prevention of acidic drainage. A method to achieve the goal of reducing oxygen or water influx is horizontal wells to remove groundwater and construction of some sort of cover system over the waste material to prevent surface water infiltration. In this case, the final cover must be designed and constructed to:

- 1) Provide long-term minimization of migration of liquids through the closed fill,
- 2) function with minimum maintenance
- 3) Promote drainage and minimize erosion or abrasion of the cover (Gagne and Choi, 2001). There are many different types and designs of caps that are used on landfills, hazardous wastes sites, and mining waste piles but emphasis should be on the selection of materials which are readily available, technologically feasible to construct, and have assurance of long-term stability. This review will briefly look at five types of covers:
 - a) Natural soil,
 - b) Compacted clay
 - c) Geomembranes,
 - d) Geosynthetic clay liners,
 - e) Capping with asphalt, concrete, or shotcrete.

CHAPTER 3

METHODOLOGY

3.1 OVERALL PROJECT METHODOLOGY.

This project will consist two parts to be done. The first part is the experiment to investigate the reactivity of the black shale and the process to treat the problem. The second part is the analysis of the heavy metal contains in the water. For this stage, the atomic absorption spectrometry is used to determine the heavy metal in the water. Below is the overall methodology for this project.

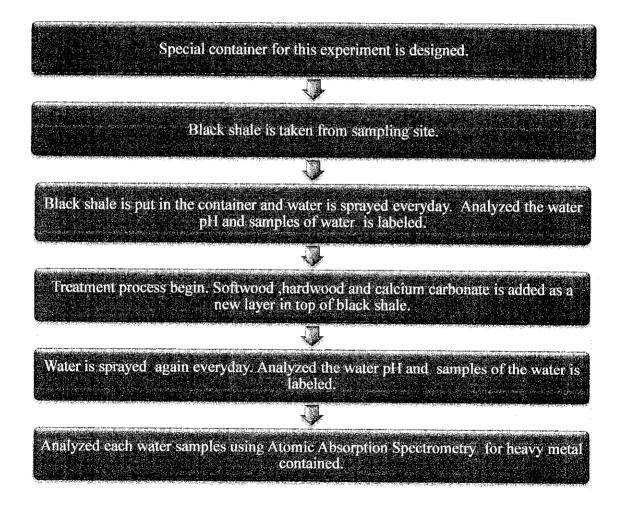


Figure 5: Overall Methodology for This Project.

3.2 CHEMICAL ANALYSIS FOR WATER AROUND THE STUDY SITE

3.2.1 Heavy metal composition.

In order to determine the rate of the pollution of acid rock drainage, the experiment using atomic absorption spectrometry need to perform. The objective of this experiment is to know the heavy metals those are contained in the water. By using the experiment, we can know the level of heavy metals that can pollute the soil and also the water source when the water is going to the river or lake nearby.

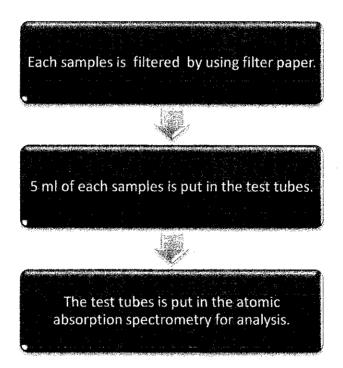


Figure 6: Procedures to Perform Atomics Absorption Spectrometry

3.2.2 PH measurement during the experiment.

When the experiment is performing, the rate of the PH can easily be determined. The water from the black shale can easily be gathering using the hole that is available from the container of the rock. So the water from the holes can easily be measured using PH device to determine the PH. This step need to be performed everyday and continuously.

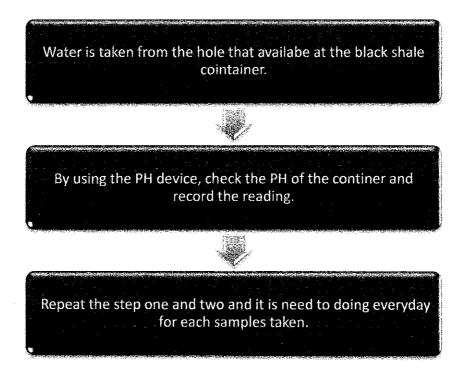


Figure 7: Steps to perform PH reading from the water.

3.3 TREATMENT FOR THE PROBLEM

3.3.1 Limestone

Generally there was not having specific guideline available at the journal and article to perform the experiment to treat the problem. From the reading, the command treatment method is neutralization with alkaline material. The technique is to neutralize the acidic environment to the neutral environment by adding the alkaline material. Limestone is the command material to treat the ARD. The typical reactions involved in limestone neutralization of acid mine effluent are:

$$CaCO_{3}(s) + 2H^{+} \rightarrow Ca^{2+} + H_{2}O + CO_{2} (8)$$
$$CaCO_{3}(s) + SO^{4+} + 2H^{+} \rightarrow CaSO_{4}(s) + H_{2}O + CO_{2} (9)$$

Other reactions include:

$$CaCO_{3}(s) + SO_{2-}+ 2H^{+} + H2O \rightarrow CaSO_{4}\cdot 2H_{2}O(s) + CO_{2} (10)$$

$$3CaCO_{3}(s) + Fe^{3+} + 3H + \rightarrow 3Ca^{2+} + Fe(OH)_{3}(s) + 3CO_{2} (11)$$

$$3CaCO_{3}(s) + Al^{3+} + 3H + \rightarrow 3Ca^{2+} + Al(OH)_{3}(s) + 3CO_{2} (12)$$

Furthermore, the rate of the neutralization reaction was observed to decrease dramatically with increasing pH, so that limestone is not very useful above pH of 5. So, a fresh limestone surface must continually be presented to the acidic drainage for neutralization to occur.

Material	Cliencel composition	Cost per Kanole of OH-appiratent (2005 USS)		
Limestone	CaCO3	0.99		
Hydrated lime	Ca(OH)2	3.80		
Ammonia	NH3	8.00		
Soda ash	Na2CO3	21.20		
Caustic soda	NaOH	31.30		

Table 1: Chemicals commonly used in the treatment of acid rock drainage. (Nosa & Ben Oni, 2007)

The analysis from the table 1 shown that cost of limestone is the cheapest compared to another alkaline material. So by using the cheapest cost and little bit modification of the method and the way to performance the experiment, it will give more valuable method to application the treatment from the study.

3.3.2 Organic Material.

Organic material such as wood can give most economical solution to treat the problem. The wood can be differentiating to the two categories which is hard wood and small wood. Both materials can easily get or collect from the nearby waste saw mill. The idea is simple. The black shale will be covered by 2 meter of softwood and hardwood with overplanted grass on the top of the cover. The cover can prevent the black shale from expose to the water and air. The organic cover can easily decompose with the soil. Some modification can be done by combining the limestone and this organic cover.

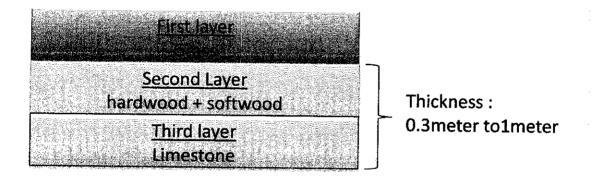


Figure 8: Design for Organic cover combining with Limestone.

The design is consist of three layers. Each layer has their owns specific job. For the first layer which is the top part of the design, the grass will cover the soil and prevent the soil from slide from the hill. Second layer is function to prevent the black shale from exposed water and oxygen and the third layer will treat the acidic environment to neutral environment.

3.4 EXPERIMENT USING ORGANIC MATERIAL

The Experiment can be conducted in the lab. The sample of the black shale is taken from the study area and put in the specially design container using Perspex. The container is the study case for this experiment. Before that, make sure drill holes at the bottom of the container to collect the water from the black shale to measure for pH.



Figure 9: Example of the container to be the study site for experiment

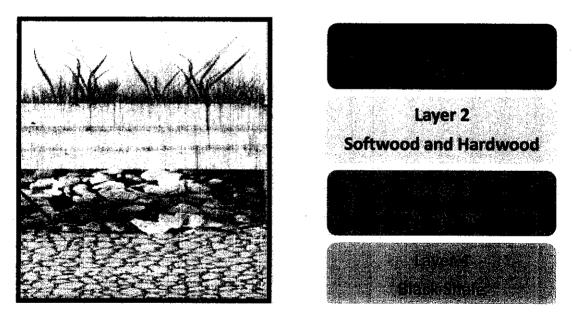


Figure 10: Combining the design of organic layer with black shale in the basin.

From the figure 9, show the design of the layer for the experiment to treat the problem. The layer one to layer three is the design of organic cover to prevent the formation of the ARD. This will prevent the rock to expose to the environment and it will limit the oxygen and water to meet the rock directly. Whereas, the layer four and five to be put in into the plastic basin. This experiment will be done in University Teknologi PETRONAS laboratory at block 5. To create the real environment, the water spray will be used. Spraying the water will be done once a day and the amount of water will be like the average rain fall in Malaysia.

CHAPTER 4

RESULT AND DISCUSSION

4.1. BLACK SHALE REACTIVITY.

This experiments is consist of two part. First part is to monitor and investigate the reactivity of the black shale when it is exposed to the environment. For this part, the pH is measured from the released water from the container and monitors anything changing in sample and the water. The water is sprayed by using 1 liter distilled water in consistent time. During the experiment, the water will be sprayed at 10 to 11 o'clock in the morning. The result of the pH reading is presented in table below.

1	8/2/2010	2.34
2	9/2/2010	1.69
3	10/2/2010	2.15
4	11/2/2010	2.01
5	12/2/2010	1.96
6	15/2/2011	2.14
7	16/2/2011	1.78
8	17/2/2011	2.07
9	18/2/2011	1.93
10	19/2/2011	2.21
11	22/2/2011	2.05
12	23/2/2011	1.92
13	24/2/2011	2.13
14	25/2/2011	1.92
15	1/3/2011	2.08
16	2/3/2011	1.99
17	3/3/2011	1.84

Table 2: pH Value for water Discharged from Black Shale

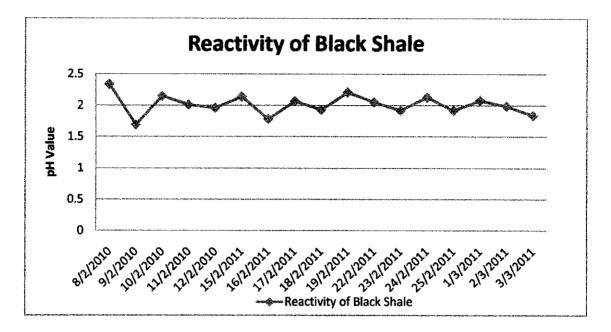


Figure 11: Reactivity of Black Shale in Natural Reaction

From figure11, it can be seen that the reaction of the black shale is very fast. When the black shale is exposed to the atmosphere, the natural reaction occurred straight away and give the water discharged pH is in acidic solution. The pH value is around 1.5 to 2.5 and the trend is fluctuation and not stable. From the literature review, it confirmed that this reaction involved bacteria that helping the reaction to be acidic. This is maybe the reason why the trend from the graph is fluctuating.

From the figure 12, the water discharged from the black shale is yellow in colour. From the equation, the water is undergoing the chemical reaction which is the hydroxide ion from water will be react with iron(III) ion and turned to iron(III) hydroxide .

$$Fe^{3+} + 3H2O \rightarrow Fe (OH)_3 (s) + 3H^+ (13)$$

It confirmed from the study that the acid rock drainage was occurred with introduce oxygen and water. Thus, this problem can be directly affected the environment in after it is exposed to atmosphere. This problem can be seriously dangerous to environment if the problem not be prevented.

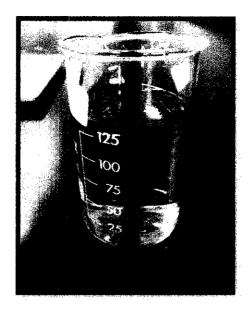


Figure 12: The Water Changed From Colourless to Yellow Colour.

4.2 TREATMENT OF ACID ROCK DRAINAGE.

This treatment is combining with two types of treatments technique which is active and limitation. For active treatment, calcium carbonate is chosen for treat this problem. Calcium carbonate is added onto black shale as second layer whereas the softwood and hardwood from limitation technique is put onto black shale after calcium carbonate as third layer.

		an a
1	4/3/2011	6.77
2	5/3/2011	7.36
3	8/3/2011	7.89
4	9/3/2011	8.29
5	10/3/2011	8.1
6	11/3/2011	7.53
7	12/3/2011	7.91
8	15/3/2011	8.28
9	16/3/2011	8.17
10	17/3/2011	7.46
11	18/3/2011	7.95
12	19/3/2011	7.65
13	22/3/2011	7.87
14	23/3/2011	7.91
15	25/3/2011	8.16
16	26/3/2011	8.24
17	29/3/2011	7.38

Table 3: pH Value for Water Discharged from Black shale

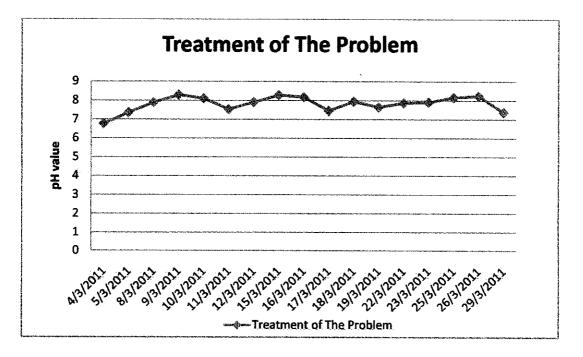


Figure 13: pH Value for Treatment of the Problem.

From figure 13, it can be seen the reactivity of the reaction is in the neutral phase. The pH value is around 7.0 to 8.5. After the treatment had been performed, the pH is increased drastically from 2 to 7. This is due to the softwood and hardwood is functioned to prevent the oxygen from exposed to the black shale directly whereas the calcium carbonate is used to neutralize the acidic solution if the reaction is occurred because the hardwood and softwood is cannot to prevent the black shale 100% from oxygen.

From the experiment, the trend projected from the data obtained also fluctuate and not constant. This is due to the extra alkaline which is not reacted with acid solution but the pH value still in the range and safe for the environment.

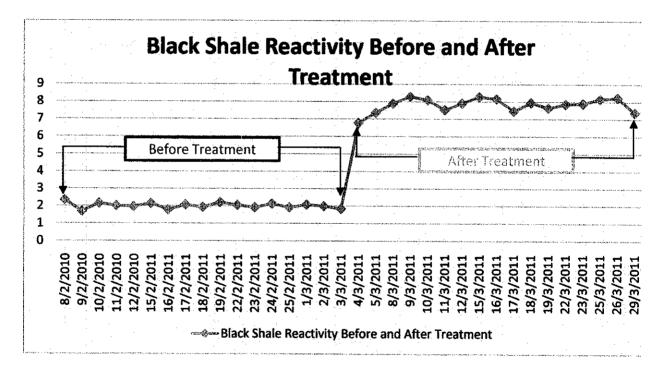


Figure 14: Black Shale Reactivity Before and After Treatment

From figure 14, it shown that the reactivity of the black shale before and after treatment is moved from acidic condition to neutral condition. Before the treatment took part, the pH of the water is about pH 2. After the data is like more consistent, the treatment of the problem is begun. The pH of the water is increase to pH 7 which is in neutral condition. From the figure, is shown that the problem can be solved directly through this method. The water that released to from the black shale is neutral.

4.3 HEAVY METAL ANALYSIS.

Each samples of the water from black shale is undergoing the heavy metal analysis by using atomic absorption spectrometry. This analysis is to determine the heavy metal level that contaminated the water and it can be the hazardous problems to human, animals and plant. The data is presented in the table below.

Sample	kon (mg/D)	Mangamene (mgA)	Alumintum (mg/l)	Magnesium (mg/L)	Romeine (ngl)
1	2.4	13.3	26.5	1.5	4.1
2	0.4	2.9	9.6	1.4	2.3
3	0.2	2.2	8.7	1.3	1.1
4	1.8	1.9	6.4	1	3.2
5	0.9	3.5	5.8	1.9	3.2
6	3.5	4.4	10.8	2.3	1.7
7	4.4	1.8	6.7	2.1	2.1
8	1.8	1.8	6.8	1.3	0.6
9	1.6	1.6	2.3	1.8	1.1
10	1.5	1.5	5.2	1.4	1.7
11	0.8	1.6	4.1	1.1	0.7
12	1.1	1.2	5	2.8	2.8
13	1.3	1.5	6.8	2.1	1.3
14	1.2	1.1	2.2	1.4	1.5
15	0.9	10.4	6.1	1.6	1.6
16	0.8	0.7	3.1	1.2	1.2
17	1.1	1.1	5	1.3	0.7
Average (mg/L)	1.51	3.09	7.12	1.62	1.82

Table 4: Average Heavy Metal Contained in the Water.

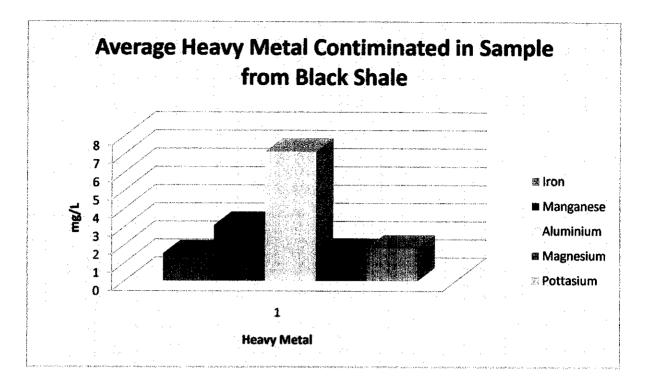


Figure 15: Level of the Heavy Metals in the Water

The aluminum is the most higher heavy metal contained in the samples of the water and followed by manganese, potassium, magnesium and iron. Black shale is contained a lot of heavy metal and can be dissolved by the water.

The heavy metal can be the hazardous to the human, aquatic life and vegetation. According to National Water Quality Standard For Malaysia, the limit amount of heavy metal contained in the water are aluminum 0.06 mg/L, iron 0.3 mg/L, manganese 0.1 mg/L potassium 0.4 mg/L and magnesium 0.3 mg/L. The ph level should be at 6.5 to 8.5. Over than this limits, the water is not suitable for aquatic life, agriculture and not safe for drinking.

4.4 FEASIBLE STUDY

In Malaysia, the problem ARD is being solved by using concrete. This is because the concrete is gave the best solution to solve the problem and do not having maintenance in the future, but for this type of the method is very costly. Meanwhile, if this organic method is being used the cost can be saved compare to the concrete method.

The price of the concrete $1m^3$ in Malaysia is RM 207.50 whereas by using this method the cost for same case, $1m^3$ is RM 4.51.

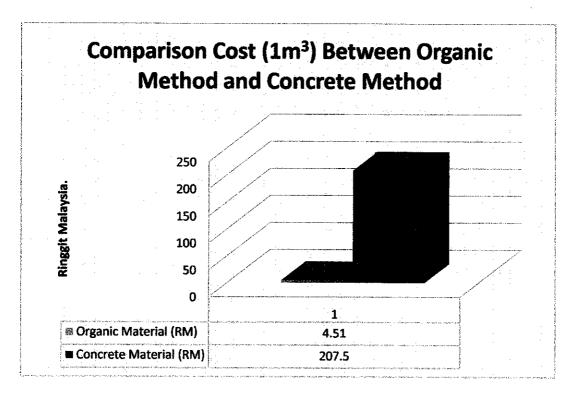


Figure 16: Comparison Cost between Organic Method and Concrete Method

From figure 16, it is shown that the organic method is can saved 46 times compared to concrete method. The materials to perform this kind of the treatment are easy to get in Malaysia. To construct treatment for $1m^3$ area, only 45 kg softwood and hardwood needed and 0.1 kg of Calcium Carbonate (*(Nosa & Ben Oni, 2007)*.

4.5 DESIGNS FOR INSTALLATION IN REAL CASE ENVIRONMENT

Due to the weather in Malaysia, to put the softwood and hardwood without cover is impossible. The water from the rain can easily cause the hard word and softwood gone from the place. Therefore, the suggestion of installation for this project is proposed.

The purpose of the suggestion method to ensure the softwood and hardwood can stand alone without being disturb by the water from heavy rain and also to stabilized the slope at the area. The geotextiles material is suitable to maintain the hardwood and softwood at the same time the price is cheaper. Geotextiles are permeable textiles used in conjunction with soil, rock, foundation, earth or any geotechnical engineering related material, as an integral part of a man-made project (John, 1987). For this project, the coir geotextiles is being suggested due to the efficiency and proven to prevent soil erosion in this world. Besides that, it was made from organic material from coconut or jute. The advantages of the coir geotextiles are:

- 100% natural and bio-degradable
- Capable of being customized to specific requirements
- High tensile strength of coir protects steep surfaces from heavy flows and debris movement
- High durability permits plant and soil establishment, natural invasion and land stabilization

The price for $1m^2$ coil geotextiles is about RM 0.50-0.80. With the cheaper price and proven quality to prevent the soil erosion so this type of geotextiles is suggested to use for this method of installation. The most important things, this type of geotextiles is 100% natural which mean, it can not to give the side effect to the environment.

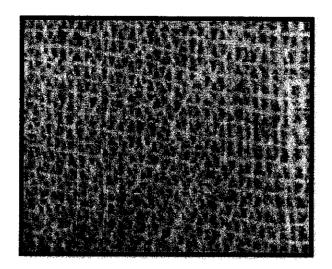


Figure 17: Example of the Coir Geotextiles

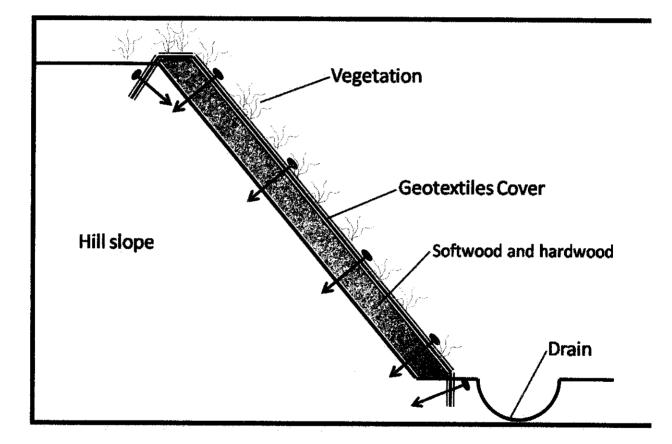


Figure 18: Example of installation the method

From the figure 18, it can be seen that the proposed design to install the organic method to prevent the ARD by using coir geotextiles material. This kind of the material can

ensure the softwood and hardwood is stabled with the hill slope for the long period thus the problem of ARD can be prevented. The coir geotextile is piled with the concrete steel to make sure the hardwood and softwood is strong enough together with the hill slope. The grass is planting on the top of the geotextiles to make the slope is more strong and prevent the soil erosion in future.

CHAPTER 5

CONCLUSION

5.1 CONCLUSION

The objective to control the oxidation of black shale and analyzed the chemical contained into black shale was achieved. Once black shale is exposed to the environment, the natural reaction is straightly occurred and the reaction going so fast. It was prove that 3 elements is needed in other to reaction occurred which is oxygen, water and black shale itself.

After the reaction took part, the water is very acidic which is in pH 2 and the colour of the water from colourless turned to yellow colour which contained iron (III) ion. The combination between organic material and calcium carbonate prove that the problem can be treated and it is cost efficient. The pH of the water after the treatment process was neutral and saves for the environment.

Analysis using atomic absorption spectrometry proved that the water contained hazardous heavy metal. Aluminum is the higher value of heavy metals contained in the water and followed by manganese, potassium, magnesium and iron which is these heavy metals are dangerous to human, aquatic life and vegetation.

It can be concluded as this experiment succeeded to find the method to treat the acid rock drainage and this method is very cheap and give better result. The reaction of this black shale is very fast and the condition of the water was very acidic, which can be a big problem to the environment if this problem did not treat early.

5.2 RECOMMENDATION

Several things can be done in order to improve the project:

- Make sure all the equipment is well calibrated and maintenances are done frequently. Therefore errors could be avoided.
- The duration of the experiment need to be longer for investigating the reaction of the calcium carbonate.
- Real case experiment need to be performed to ensure the result from the experiment is same because for the experiment the amount of the water is set to be constant throughout this experiment whereas the real case amount of rain fall is different for each day.
- The rain water should be used for this experiment to get the accurate result because this experiment is used distill water.
- Try other alkali materials for this experiment, so that it can be compared for the best material for this treatment.

REFERENCES

- Amer M. Burgan, Che Aziz Ali, Sanudin Hj Tahir 2006. Chemical Composition of the Tertiary Black Shales of West Sabah, East Malaysia. Chin.J. Geochem
- Baker RA, Wilshire AG. In Microbiological Factor in Acid Minie Drainage Formation. Wat. Pullut. Control Res, Series no 14010 DKN 11/70, SME: Washington DC, 1970a
- Canty, G.A., J.W. Everett. 2006. Alkaline injection technology: Field demonstration. Fuel 85:2545-2554.
- Caruccio, F.T., Geidel, G. 1996. Limestone additions to affect changes in loading to remediate acid mine drainage. National Meeting of the American Society for Surface Mining and Reclamation, Knoxville, TN.
- Colmer AR Hinkle ME. The Role of Microorganisms in Acid Mine Drainage: A Preliminary Report Science Magazine 1947
- Environmental Resources Management August 2003. Acid Rock Drainage Management. www.ecm.cm (25th August 2009)
- Gagne, Dennis P., Choi, Yoon-Jean. 2005. Technical Memorandum: Alternative Cap Design Guidance Proposed for Unlined, Hazardous Waste Landfills in the EPA Region. <u>http://www.epa.gov/ne/superfund/resource/C524.pdf</u> (27th ferbruary 2010)
- Jordan D. Smoke. Preliminary Design of A Treatment System to Remediate Acid Rock Drainage Into Jonathan RunCase Western Reserve University, 2005.

Keith Richert. 1992. Acid Rock Drainage, Science of Mining. Westview Secondary, Maple Bridge. BC

Kleinmann RLP, Erickson PM. 1993. Control of Acid Drainage from Coal Refuse Using Anionic Surfactants. U.S. Bereou of Mines Washington, DC Report

- K. Temple and AR colmer, 1951. The autotrophic oxidation of iron by a new bacterium: Thiobacillus ferrooxidans, Journal of Bacteriology
- Nosa O. Egiebor & Ben Oni, Curtin 2007. Asia Pacific Journal of Chemical engineering. Acid Rock Drainage Formation and treatment: a review. Wiley Interscience
- Sci-Tech Encyclopaedia http://www.answers.com/topic/black-shale (30th august 2009)