HYDROCHEMICAL RESPONSE OF ACID MINE DRAINAGE TO THE STORM EVENT AND METAL LOADING IN EX-MAMUT COPPERMINE

FEONA ISIDORE

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Signature

1. SUPERVISOR
Prof. Madya Dr. Kawi Bidin

2. CO-SUPERVISOR

Prof. Dr. Mohd. Harun Abdullah

DECLARATION

I hereby declare that the material in this thesis is my own except for quotations, excerpts, equations, summaries and references, which have been duly acknowledge.

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PS2010-8047

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ABSTRACT

The purpose of this study is to determine the dissolved metal status during low flow and its behaviour during the storm event. This study also estimates the dissolved metal removal and Metal loading from the Mamut ex-coppermine. Continuous water discharge measurement was recorded from March 2010 to March 2011 while water samples were taken from July 2010 until June 2012 using water level sensor and data logger. Water samples and discharge measurement was taken in seven sampling stations. Surface water samples were collected manually once a month and more regularly during storm event. Storm event samples were collected in December 2012. Six elements (Cu, Al, Fe, Mn, Zn, SO_4) were analysed for the water samples using ICP-OES and Sulfaver 4 method (Hach). The water results for dissolved metals were then used in metal loading analysis in Mamut coppermine. Mass balance method was used to estimate the removal of metals in the temporary settling pond (TSP) from dilution process. The average concentration of sulphate in Mamut is 676.5 mg/L. The trends of dissolved metals during lowflow in Mamut is as follows Al > Fe > Cu > Mn > Zn and there are three hysteresis pattern had been identified during the storm event. The removal of metals in TSP spillway is Fe (86%), Cu (39%), Al (32%), Zn (6%), Mn (2.5%). This is an indication that different behaviour of dissolved metals observed to tolerate dilution process. The metal loadings estimated for the discharge from mine pit (Station M6) are Fe (364.2 - 555.6 kg/day), Al (1209 - 1453.8 kg/day), Cu (142.8 - 231.6 kg/day), Zn (76.13 - 86.54 kg/day), Mn (350.4 - 459.8 kg/day). Loads of dissolved metal reduced substantially in Station M7 due to the dilution and metal attenuation.

ABSTRAK

TINDAKBALAS HIDROKIMIA SALIRAN LOMBONG BERASID TERHADAP HUJAN DAN MUATAN LOGAM DI BEKAS LOMBONG MAMUT

Tujuan kajian ini adalah untuk menentukan status logam terlarut semasa luahan air rendah dan tindakan logam terlarut semasa hujan. Kajian ini juga menganggarkan penyingkiran logam terlarut dan muatan logam daripada bekas lombong Mamut. Pengukuran bacaan luahan secara berterusan telah dijalankan pada bulan Mac 2010 hingga Mac 2011 menggunakan sensor aras air dan pencatat data. Sampel air dan ukuran luahan diambil di tujuh stesen persampelan. Sampel-sampel air diambil sebulan sekali dan persampelan dilakukan dengan lebih kerap semasa hujan. Enam elemen (Cu, Al, Fe, Mn, Zn, SO_4*) telah dianalisis menggunakan ICP-OES dan kaedah Sulfaver 4 (Hach) untuk sampel-sampel air tersebut. Hasil analisa air kemudiannya digunakan dalam analisis muatan logam di bekas lombong Mamut. Kaedah imbangan jisim digunakan untuk menganggarkan penyingkiran logam dalam Kolam Enap Sementara (TSP) daripada proses pembauran. Purata kepekatan Sulfat di Mamut adalah 676.5 mg/L. Kecenderungan logam semasa luahan air rendah di Mamut adalah Al> Fe> Cu> Mn> Zn dan tiga pola histeresis dikenalpasti semasa hujan. Penyingkiran logam selepas melalui TSP adalah Fe (86%), Cu (39%), Al (32%), Zn (6%), Mn (2.5%). Ini menunjukan tindakan logam berbeza untuk bertindak balas dengan proses pembauran. Muatan logam dari luahan tasik (stesen M6) ialah Fe (364.2-555.6 Kg/day), Al (1209-1453.8 Kg/day), Cu (142.8-231.6 Kg/day), Zn (76.13-86.54 Kg/day), dan Mn (350.4-459.8 Kg/day) dan berkurang setelah melalui TSP disebabkan pembauran dan atenuasi logam.*

LIST OF ABBREVIATION

AMD	Acid Mine Drainage
As	Arsenic
Cd	Cadmium
Pb	Lead
Fe	Iron
Al	Aluminium
Cu	Copper
Zn	Zinc
Mn	Manganese
TSP	Temporary Settling Pond
APHA	American Public Health Association
ICP- OES	Inductively Coupled Plasma- Optical Emission Spectrometry
AAS	Atomic Absorption Spectrometry

LIST OF APPENDIXES

LIST OF FIGURES

LIST OF SYMBOL

mg/L	Milligram per litre
m^3/s	Cubic metre per second
min	Minute
t	Metric tonne
Kg	Kilogram
%	Percentage
Q	Discharge

LIST OF TABLES

TABLE OF CONTENTS

CHAPTER 3: METHODOLOGY

CHAPTER 4: RESULTS AND DISCUSSION

CHAPTER 5: CONCLUSION AND SUGGESTIONS

CHAPTER 1

INTRODUCTION

1.1 Background of study

Mining activity is an extraction of useful minerals from earth and usually with economic value. In the 20th century, mineral mining such as copper and aluminum played an important role in economic growth but the production of minerals had reduced over time either due to mineral depletion or reduction in production capacity. Most countries have stringent regulations on mining activities to minimise the environmental impact and to avoid adverse impact on human health. However, the law and regulation itself is not sufficient to prevent mining problems from occurring. Scientific studies help us to better understand post mining problems in order to mitigate the existing problems and to prevent further damage to the environment.

Surface mining is considered as one of the most profitable methods in the mining industry. The mining product can be accessed quickly and easily using the surface mining method. Mamut ex-coppermine is an example of surface mining in Malaysia. Mamut ex-coppermine is now facing some environmental problems after its mining activity ceased in 1999. When mining activity was active in Mamut, the water accumulated in the mine pit was pumped for the excavation of minerals. The maintenance of the mine pit had since stopped as the mining activity had ceased in 1999. Therefore, the water in the mine pit had accumulated overtime turning it into a pit lake. Unfortunately, the area is not suitable for recreational use and there had been some reports that the discharge from the ex-mine area had resulted in some problems such as infertile crops in nearby rivers that were affected by the Acid Mine Drainage (AMD) from the Mamut ex-coppermine (Bibi Noorarlijannah Mohamed Ali, Mohamed Harun Abdullah dan Lin Chin Yik 2010; Mohamed Harun Abdullah, Bibi Noorarlijannah Mohamed Ali, Lin Chin Yik 2008). The discharge from the mine pit is not the only source of AMD but the tailings, dumpsites and some exposed areas also contributed to the AMD production.

AMD affected rivers are capable of transporting large amount of heavy metals that can reach human environment through the contamination of downstream rivers or water reservoirs. Contaminated water can easily allow heavy metals to enter the food chain. Metals accumulate in vegetation or the body of the consumer after it is consumed and prolong exposure to the metals build up a high level of concentration. High concentration of heavy metals can lead to adverse health effects such as joint problem, liver problem and nerve problem. Apart from that, heavy metals can also enter groundwater through hydrologic processes and contaminate drinking water source. Heavy metals such as arsenic (As), cadmium (Cd) and lead (Pb) have been reported to cause adverse health effects (Frau *et al.*, 2009). In addition to the problems above, soil fertility, aquatic and terrestrial life ecology and local vegetation will also be affected.

AMD is acidic water that contains a high concentration of dissolved metals through the leaching of sulphide minerals. Highly water soluble salts available in the area will affect the soluble metal content in the AMD. Iron speciation of yellow precipitation is because of the less soluble iron hydroxysulphate and iron oxyhydroxides (Herbert, 2006). The most common sulphide minerals involved in the chemical reaction are pyrite, marcasite, phyrrhotite, and chalcopyrite. These minerals will go through processes such as oxidation, hydrolysis, neutralisation and evaporation to form new iron-rich material (ferric hydroxides) called AMD precipitates. The final product of these minerals is iron oxyhydroxide. Sulphate-rich minerals can form intermediary materials which involve clay, phosphates, hydrated salts and etc. Apart from that, these minerals will also go through a process to become crystalline structures. Poor crystalline structures of minerals will produce less soluble minerals called iron (III) hydroxide minerals which are different from efflorescene minerals that are highly soluble in water. Efflorescence minerals are more susceptible to dissolve during rainfall. The highly soluble characteristic increases the mobility of toxic materials (e.g. heavy metals) to the environment because it will release heavy metal and acidity during reaction with water (Valente and Gomes, 2009). The second process of efflourescene and iron (III) hydroxide will form encrustation which will form a thick crust overtime. The oxidation of Pyrite and other sulphide minerals produces sulfuric acid which is the dominant process in heavy metal mobility and speciation (Kovacs, Dubbin and Tamas 2006).

1.2 The importance of study

This study discusses the importance of the dilution process in the hydrochemistry of AMD. Currently, hydrological studies on Mamut are lacking and the behavior of AMD is poorly understood. Previous studies in Mamut focused on the AMD during low flow. This study helps us to understand the hydrochemistry of AMD in different weather conditions.

The water quality of AMD differs during high flow and low flow due to the dilution process. In high flow, the water is slightly better in quality than in low flow. Although the stream water looks dirtier with turbid water during high flow, the dilution process helps to reduce pollutant concentration in the water. Analytical result of water quality in different discharge fluctuation determined that the level of water quality improved from natural dilution. However, a discharge value with analytical result cannot represent the whole catchment area because a big catchment area is made up of many smaller catchment areas with different levels of pollution. The study in Mamut will be helpful to future researchers as a guide to determine the best treatment required in Mamut.

1.3 Objectives

There is a lack of hydrochemistry studies conducted in the Mamut ex-coppermine which involves input water and output water of the ex-mining pit lake. Most studies focused on the water quality of the AMD or the affected river. This study takes into account the effects of hydrology factors on the water quality. The objectives of this study are:

1) to determine the status of selected metals in Mamut ex-coppermine during low flow and storm event

2) to determine the hysteresis pattern of AMD during storm event

3) to estimate the heavy metal removal in Temporary Settling Pond

4) to estimate selected metal load in Mamut ex-coppermine

1.4 Background of Study Area

1.4.1 Geographical Setting

Mamut ex-coppermine, situated in between coordinate 5°57′- 5°58′ N and 115°59′-116°01′ E, is the first open cast coppermine in Malaysia. The area is located at an altitude of 1400m a.s.l. and 68 km direct distance east of Kota Kinabalu. The diameter of the pit lake is approximately 1200 m and the depth is approximately 150 m. The approximate volume of water retain in the pit lake is 23,433,406 m^3. The ex-coppermine is situated adjacent to the Bukit Hampunan Forest Reserve Class I which was recently gazetted in 2009 (Mohd Azizli k., 1995, Osborne and Chappel, 2009; Chung, Chew, Majapun and Nilus 2013).

1.4.2 Hydrological Setting

According to Fera Cleophas (2012), the mean of monthly rain received in the area is 359.43 mm and the estimated yearly rainfall received is 4313.19 mm based on data collected in 2010 and 2011 (Figure 1.1). There is no specific pattern in rainfall season and the annual precipitation varies from year to year. The monthly mean of evaporation in the lake is 106.82 mm. The daily temperature ranges from 20°C to 36°C with a mean humidity of 70% to 90% (Mohamed Harun Abdullah et al., 2008).

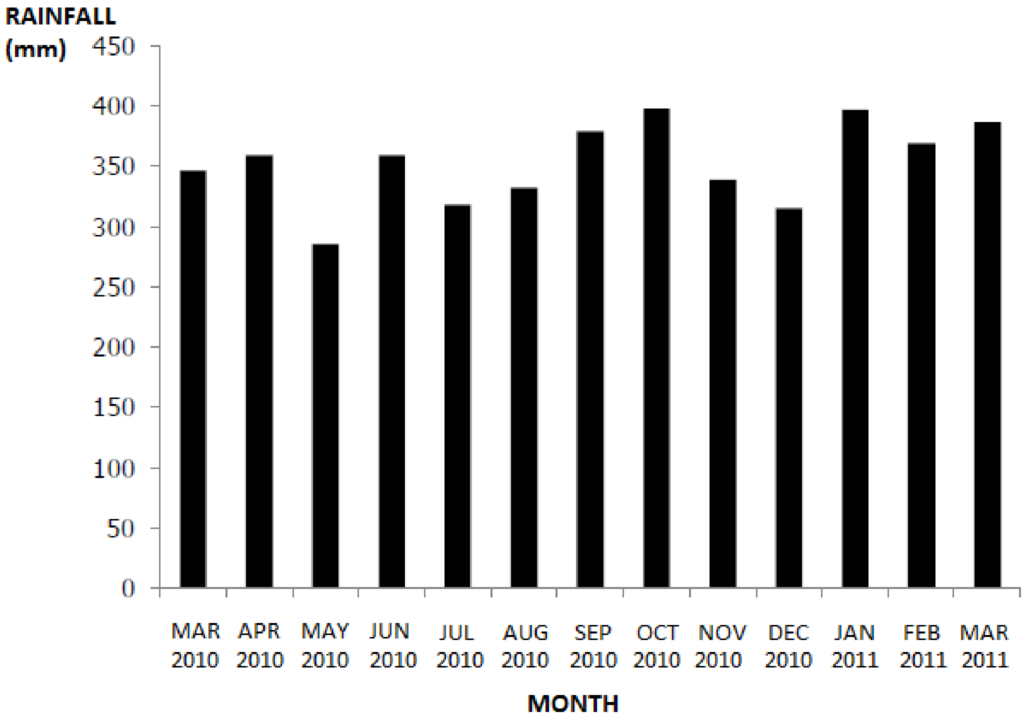

Figure 1.1: Rainfall tabulation in ex-Mamut Coppermine from March 2010- March 2011.

Source : Fera Cleophas, 2012: 55

There are two lakes in the study area (Figure 1.2) which was made when the mining activity was still active. The lakes will be referred to as Pit Lake and Temporary Settling Pond (TSP) in this study. The Pit Lake is larger in volume and size compared to the TSP. The Pit Lake receives water mainly from rainfall and drainage directed to the pit lake. There are eight drainage directed to the pit lake. The water from the pit lake is directed by drainage to the TSP before being discharged to the river. The TSP is a mixing point of AMD from the Pit Lake and water from the Ulu Mamut River. The main river for the mine is Lohan river which flows southeast to east, Bambangan river which flows to the south, and Mamut river which flows to the east (Mohd Azizli, 1995).

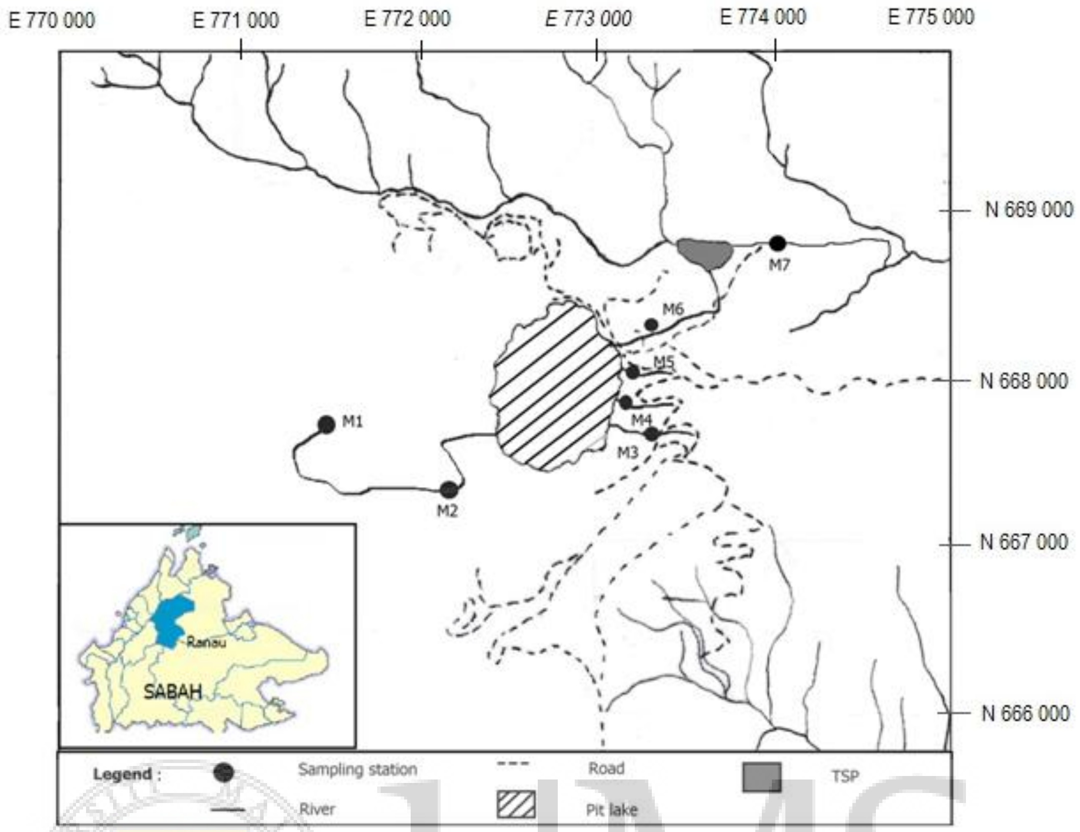

Figure 1.2: Study area in ex-Mamut Coppermine.

1.4.3 Water Quality

The water quality status in Mamut had been affected by mineral oxidation and dissolution which lead to the lowering of pH, high concentration of toxic ions and siltation (Mohamed Harun Abdullah et al., 2009, Bibi Noorarlijannah Mohamed Ali et al., 2011). The AMD discharge from Mamut mine pit to Mamut river has a pH of 2-4. It acidified a large volume of water and added a high concentration of dissolved heavy metals to the Mamut River (Fera Cleophas, 2012, Mohamed Harun Abdullah et al., 2008). The highest element concentration is in the mine pit and TSP while the lowest concentration is in Nasapang river which is not affected by the AMD (Mohd Harun Abdullah et al, 2008). The acidity of the water is subjected to the concentration of dissolved metal in water and the most dominant metals in AMD in Mamut are Fe, Al, Cu, Mn and Zn (Marcus Jopony and Felix Tongkul, 2009).

1.4.3 Geological Setting

Mamut is located within the Crocker range which is in the Northwest-Southeast trending tectonic zone of Sabah. The potash-rich rocks in Mamut such as adamellite are present in the intrusion locally and in the wall rocks. The wall rocks consist of serpentinite and clastic sedimentary rocks (Kosaka and Wakita, 2006; Rosdeano Roslee, Sanudin Tahir, Baba Musta dan S. Abd. Kadir S. Omang 2010). The principal ore minerals in Mamut are chalcopyrite and pyrrhotite including magnetite with minor amounts of gold and silver associated with copper mineralisation. The ore deposits are characterised as low grade. The magmatic sulphides of Mamut are identical to Mt. Kinabalu adamellitic rocks (Mohd Azizli, 1995; Imai, 2000,)

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In a natural environment, the process of rocks being exposed to weathering and releasing minerals is slow (Metesh, 1998). Mining activity exposes a large quantity of readily weatherable surface of rocks in a short period of time thus accelerates the oxidation process (Geller, Klapper and Schultze, 1998). Accelerated oxidation of sulphide bearing rocks will cause more rapid production of sulfuric acid than the natural buffer in the environment could comprehend therefore causing an imbalance in the natural water pH (Geller et al, 1998). The combination of sulfuric acid and dissolved metals caused by current or previous activity at the mine is called AMD. AMD is a common problem in operating and abandoned mines which can lead to the deterioration of water quality, ecology destruction, adverse health condition and poor economy.

2.2 Sulfur Cycle and Acid Mine Drainage

Abandoned surface mines have large volumes of waste and rocks of unknown hydrology (Metesh, 1998). The sulfur cycle (Figure 2.1) plays an important role in mining which is characterised by AMD (Knoller, Fauville, Mayer, Strauch, Friese, and Veizer, 2004). Sulphide minerals and sulfur can be oxidised either by biotic or abiotic processes. The oxidation of sulphide mineral is a major contributor of iron and sulphate in the AMD. Abiotic oxidation of sulphide mineral is when pyrite and marcasite react with water and oxygen to produce sulfuric acid (Geller et al., 1998). Surface and ground water will pick up the sulfuric acid and heavy metals while running through the tailings. Sulphate in soil can be taken up by plants and assimilated to form protein. When the plants die and decay, microorganisms mineralise the sulphur in the proteins into hydrogen sulphide or sulphate. The hydrogen sulphide will combine with metal to form metal sulphide or oxidised into elemental sulphur and sulphur dioxide. Sulfur dioxide in gas form will be released to