

**EFFECT OF NEUTRALIZATION ON pH AND  
HEAVY METALS CONTENT OF ACID MINE  
DRAINAGES**

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**THESIS SUBMITTED IN FULFILLMENT FOR  
THE DEGREE OF DOCTOR OF PHILOSOPHY**

**FACULTY OF SCIENCE AND NATURAL  
RESOURCES  
UNIVERSITI MALAYSIA SABAH  
2017**

**UNIVERSITI MALAYSIA SABAH**

**BORANG PENGESAHAN STATUS TESIS**

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CONTENT OF ACID MINE DRAINAGES**

IJAZAH: **DOCTOR OF PHILOSOPHY (INDUSTRIAL CHEMISTRY)**

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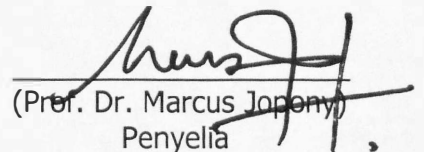
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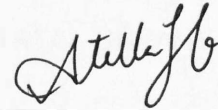


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## DECLARATION

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

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## CERTIFICATION

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**CERTIFIED BY;**

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A handwritten signature in black ink, appearing to read 'Marcus Jopony', is written over the UMS logo.

## ACKNOWLEDGEMENT

First and foremost, I would like to express my sincere gratitude to my supervisor, Professor Dr. Marcus Jopony for his tireless efforts in giving valuable advice, motivation, guidance, support and help throughout this project and over the course of the Doctorate programme. Additionally, I wish to acknowledge the support of the Ministry of Science, Technology and Innovation, Malaysia (MOSTI) for providing research funding of MYBRAIN-MyPhD, I am greatly indebted.

Mr. Sani Gorudin, assistant science officer, is thanked for helping with the fieldwork. Many thanks too, to Lab assistants Mr. Reycheidi and Mr. Yusry Jasli, for assisting for ICP-OES analyses.

To my peers, Mr. Morius Bantas, Ms. Fenny Angella Modi, Mr. EB Johnson Gubod, and Ms. Joyce Primus, I owed them for their invaluable discussions, useful ideas, constructive criticisms and encouragement throughout the writing of this thesis.

The kind help from other members and personnel at the Analytical Lab is very much appreciated. Many thanks to all my supportive friends for their endless co-operation and help whenever I need them. I am also very grateful to all who are not mention but have help in making this research project a successful one. Finally, not forgetting my sincere thanks to the Faculty of Science and Natural Resources for providing the amenities enabling this research project to be carried out successfully.

Last but not least, I could not have completed this thesis without the undivided support and encouragement from my mum, dad and my brothers. My utmost appreciation to my family-Thank you.

Stella Ho Yen Ling  
7<sup>TH</sup> November 2016

## ABSTRACT

Alkaline materials are used for treatment of acidic water, including acid mine drainage (AMD), primarily to increase its pH. The efficacy of this treatment, however, depends on several factors. In this study, the significance of dissolved metals, in particular  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , in neutralization efficiency was the main focus of investigation. In the case of AMD, the dissolved metals can also be represented by the parameter total acidity. Batch neutralization experiments using two alkaline materials, namely NaOH and calcareous sandstone, were carried out involving acidic aqueous solutions, without and with the presence of  $\text{Fe}^{3+}$  and/or  $\text{Al}^{3+}$  at concentration range 2mg/L-100 mg/L, as well as seven AMD samples collected from Mamut, Ranau. The physico-chemical characteristics of these AMD samples were analyzed according to APHA Standard Methods. The neutralization process was also studied at different dosage of calcareous sandstone and under the condition where this material is repeatedly exposed to acidic aqueous solutions in the presence of  $\text{Fe}^{3+}$  and/or  $\text{Al}^{3+}$  as well as to selected AMD samples. The principal parameter monitored and measured in these experiments was solution pH. Additionally, the effect of neutralization using both alkaline materials on dissolved metals concentration of selected AMD samples was also investigated. The final concentration of Fe, Al, Cu, Zn and Mn in solution was determined using ICP-OES. The results showed that the AMDs from Mamut, Ranau have varying pH (2.77-3.36), TDS (741-1485 mg/L), EC (1489-2975  $\mu\text{S}/\text{cm}$ ), total acidity (316-807 mg  $\text{CaCO}_3/\text{L}$ ), sulfate (649-2148 mg/L), and concentration of Fe (0.34-8.93 mg/L), Al (35.59-111.24 mg/L), Mn (6.82-30.88 mg/L), Cu (3.60-26.99 mg/L) and Zn (1.77-9.10 mg/L). The total acidity of the samples was positively correlated ( $R^2=0.968$ ) with dissolved Al concentration. During neutralization of aqueous acidic solutions with NaOH, increasing concentration of  $\text{Fe}^{3+}$  and/or  $\text{Al}^{3+}$  in solution resulted in increasing amount of base required to increase the pH to 7.0. At the same metal concentration (mg/L), the presence of  $\text{Al}^{3+}$  requires about 2X more alkalinity for this purpose compared with  $\text{Fe}^{3+}$ . When calcareous sandstone was used as the alkaline material, the presence of  $\text{Al}^{3+}$  in solution slowed down the rate of increase in pH particularly at high concentration. Such effect was not evident in the presence of  $\text{Fe}^{3+}$ . When AMD samples were used, the amount of alkalinity (NaOH) required to increase the pH to 7.0 increased with increase in dissolved Al concentration as well as total acidity of the AMD. When calcareous sandstone was used as the alkaline material, the rate of increase in pH was slow and vary between AMDs. The pH attained after 8 hours neutralization is dependent ( $R^2=0.9415$ ) on the total acidity whereby the value decreased with increase in total acidity of AMD. The effectiveness of calcareous sandstone in the neutralization process increased with dosage in the order 1.0 g > 0.5 g > 0.1 g, while at a fixed dosage (0.5g) decreased rapidly during successive 24h neutralization cycles when involving aqueous acidic solution with high concentration of  $\text{Al}^{3+}$  as well as AMD samples with high total acidity. Meanwhile, neutralization of AMD using NaOH resulted in effective removal of heavy metal from solution. This removal was pH dependent and occurred sequentially starting from Fe (pH~4.0) followed by Al (pH~5.0), Cu (pH~7.0), Zn (pH~8.0) and Mn (pH~10.0). This removal also produced precipitates of which the amount increased with increased in pH attained as well as with increase in total acidity of AMD. By contrast, the effectiveness of neutralization using calcareous sandstone in removing heavy metals from solution decreased with increased in

total acidity of AMD. Overall, the significant presence of dissolved metals in particular at high concentration of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  can reduce the effectiveness of neutralization treatment, either using alkaline solution (NaOH) or alkaline generating material (calcareous sandstone), in increasing pH. Consequently, this can reduce the effectiveness of the treatment in removing heavy metals from AMD. Therefore, besides the initial pH, another parameter that need to be considered during treatment of AMD by alkaline materials is the total acidity of the AMD.



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## ABSTRAK

### **KESAN PENEUTRALAN KE ATAS pH DAN KANDUNGAN LOGAM BERAT SALIRAN ASID LOMBONG (SAL)**

Bahan-bahan alkali adalah digunakan untuk rawatan air berasid, termasuk asid saliran lombong (SAL) untuk meningkatkan pH. Keberkesanan rawatan ini, walau bagaimanapun, bergantung kepada beberapa faktor. Dalam kajian ini, pengaruh logam terlarut, khususnya  $Fe^{3+}$  dan  $Al^{3+}$  terhadap efisiensi peneutralan adalah tumpuan utama. Dalam kes SAL, logam terlarut juga boleh diwakili oleh parameter jumlah keasidan. Eksperimen peneutralan batch menggunakan dua bahan alkali iaitu NaOH dan batu pasir berkapur, telah dijalankan melibatkan larutan akueus berasid, tanpa dan dengan kehadiran  $Fe^{3+}$  dan/atau  $Al^{3+}$  pada julat kepekatan 2 mg/L-100 mg/L, dan juga tujuh sampel SAL yang diperolehi dari Mamut, Ranau. Ciri-ciri fiziko-kimia sampel SAL dianalisis mengikut Kaedah Piawai APHA. Proses peneutralan juga dikaji pada dos batu pasir berkapur yang berbeza dan di bawah keadaan di mana bahan ini berulang kali didedahkan kepada larutan akueus berasid dengan and tanpa kehadiran  $Fe^{3+}$  dan/atau  $Al^{3+}$  serta dengan sampel SAL yang terpilih. Parameter utama yang dipantau dan diukur dalam eksperimen ini adalah pH. Selain itu, kesan peneutralan menggunakan kedua-dua bahan-bahan alkali ini terhadap kepekatan logam dalam sampel SAL terpilih juga dikaji. Kepekatan akhir Fe, Al, Cu, Zn dan Mn dalam larutan ditentukan menggunakan ICP-OES. Hasil kajian menunjukkan bahawa sampel SAL dari Mamut, Ranau mempunyai pH (2.77-3.36), TDS (741-1485 mg/L), EC (1489-2975  $\mu$ S/cm), jumlah keasidan (316-807 mg  $CaCO_3$ /L), sulfat (649-2148 mg/L), dan kepekatan Fe (0.34-8.93 mg/L), Al (35.59-111.24 mg/L), Mn (6.82-30.88 mg/L), Cu (3.60-26.99 mg/L) dan Zn (1.77-9.10 mg/L) yang berbeza-beza. Jumlah keasidan SAL didapati berkorelasi secara positif ( $R^2 = 0.968$ ) dengan kepekatan Al terlarut. Semasa peneutralan larutan akueus berasid dengan NaOH, peningkatan kepekatan  $Fe^{3+}$  dan/atau  $Al^{3+}$  dalam larutan menyebabkan peningkatan jumlah bes yang diperlukan untuk menaikkan pH kepada 7.0. Pada kepekatan yang sama (mg/L) bagi logam, kehadiran  $Al^{3+}$  memerlukan sekitar 2X lebih bes untuk tujuan ini, berbanding  $Fe^{3+}$ . Apabila batu pasir berkapur digunakan sebagai bahan alkali, kehadiran  $Al^{3+}$  dalam larutan memperlambatkan kadar kenaikan pH terutamanya pada kepekatan yang tinggi. Kesan ini tidak ketara apabila  $Fe^{3+}$  yang hadir. Apabila sampel SAL digunakan, jumlah alkaliniti (NaOH) yang diperlukan untuk menaikkan pH kepada 7.0 meningkat dengan peningkatan kepekatan Al dan juga jumlah keasidan. Apabila batu pasir berkapur digunakan sebagai bahan alkali, kadar peningkatan pH adalah perlahan dan berbeza antara SAL. Nilai pH yang dicapai selepas 8 jam peneutralan bergantung ( $R^2=0.9415$ ) kepada jumlah keasidan di mana nilainya menurun dengan peningkatan jumlah keasidan. Keberkesanan batu pasir berkapur dalam proses peneutralan meningkat dengan peningkatan dos mengikut urutan 1.0 g > 0.5 g > 0.1 g, manakala pada dos yang tetap (0.5g), ianya menurun dengan cepat semasa kitaran 24j peneutralan berturut-turut dengan larutan akueus berasid dengan kepekatan  $Al^{3+}$  tinggi serta dengan sampel SAL dengan jumlah keasidan yang tinggi. Sementara itu, peneutralan SAL menggunakan NaOH menyebabkan penyingkiran yang efektif terhadap logam berat dalam larutan. Penyingkiran ini bergantung kepada pH dan berlaku secara berturutan bermula dari Fe (pH~4.0) diikuti oleh Al (pH~5.0), Cu (pH~7.0), Zn (pH~8.0) dan Mn (pH~10.0).



*Penyingkiran ini, walau bagaimanapun, menghasilkan mendakan yang amaunnya meningkat dengan peningkatan pH dan jumlah keasidan SAL. Sebaliknya, keberkesanan peneutralan menggunakan batu pasir berkapur dalam penyingkiran logam berat menurun dengan peningkatan jumlah keasidan SAL. Secara keseluruhannya, kehadiran logam terlarut khususnya  $Fe^{3+}$  and  $Al^{3+}$  pada kepekatan yang tinggi boleh mengurangkan keberkesanan rawatan peneutralan, sama ada menggunakan larutan alkali (NaOH) atau bahan beralkali (batu pasir berkapur), dalam meningkatkan pH serta mengurangkan kepekatan logam dalam SAL. Dengan itu, selain pH, satu parameter lain yang wajar diberi pertimbangan semasa rawatan SAL oleh bahan beralkali ialah jumlah keasidan SAL.*



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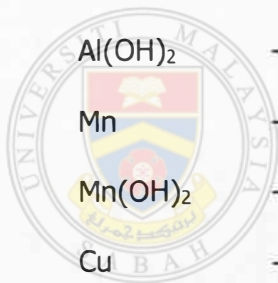
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mL	-	milliliter
L	-	Litre
N	-	Normality
mg/L	-	milligram per liter
mg CaCO <sub>3</sub> /L	-	milligram calcium carbonate per liter
nm	-	nanometer
μS/cm	-	microsiemens per centimeter
Fe	-	Iron
Al	-	Aluminium
Fe <sup>3+</sup>	-	Ion Iron (III)
Al <sup>3+</sup>	-	Ion Aluminium (III)
Al(OH) <sub>2</sub>	-	Aluminium hydroxides
Mn	-	Manganese
Mn(OH) <sub>2</sub>	-	Manganese hydroxides
Cu	-	Copper
Cu(OH) <sub>2</sub>	-	Copper hydroxides
Zn	-	Zinc
Zn(OH) <sub>2</sub>	-	Zinc hydroxides
Cd	-	Cadmium
Cr	-	Chromium
TDS	-	Total dissolved solids
SO <sub>4</sub> <sup>2-</sup>	-	sulfate
CO <sub>3</sub> <sup>2-</sup>	-	Carbonate
HCO <sub>3</sub> <sup>-</sup>	-	Bicarbonate
H <sub>2</sub> CO <sub>3</sub>	-	Carbonic acid



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$H^+$	-	proton
$OH^-$	-	Hydroxide
$CaCO_3$	-	Calcium carbonate
$H_2SO_4$	-	Sulphuric acid
$HCl$	-	Hydrochloric acid
$NaOH$	-	Sodium hydroxide
$H_2O_2$	-	Hydrogen peroxide



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# CHAPTER 1

## INTRODUCTION

### 1.1 Acid mine drainage and Environment

Acid Mine Drainage (AMD) is synonymous with base metals and coal mining activities. Typically, AMD is characterized by low (acidic) pH, high acidity, and high concentration of dissolved heavy metals (Singh, 1987; Gray, 1997; Nordstrom *et al.*, 2000; Bell *et al.*, 2001). Many rivers or streams in ex-mining areas worldwide are known to be affected by AMD pollution (Banks *et al.*, 1997; Gray, 1997; Lottermoser, 2010). Continuous inputs of AMD into nearby streams and/or rivers can adversely affect water quality, including acidic pH and elevated concentrations of heavy metals (Singh, 1987; Gray, 1997; Nordstrom *et al.*, 2000; Bell *et al.*, 2001). Subsequent precipitation of heavy metals can increase the suspended solid load besides blanketing the bottom sediment (Stoertz *et al.*, 2002; Levings *et al.*, 2005). These characteristics will lead to the destruction of the aquatic habitat, which can be evident several kilometres downstream of mine area (Sengupta, 1993; Allan, 1995; Evangelou and Seta, 1999).

### 1.2 Acid mine Drainage Treatment

Due to the adverse impacts arising from AMD, it is important that AMD produced at a mine area undergoes proper and effective treatment prior to final discharge into the surrounding aquatic environment. A number of treatment techniques are available including neutralization (Sengupta, 1993; Cravotta and Trahan, 1999; Potgieter-Vermaak *et al.*, 2006), adsorption (Mohan and Singh, 2002; Hughes and Gray, 2013; Falayi and Ntuli, 2014), ion-exchange (Feng *et al.*, 2000; Prasad and Kumar, 2015), oxidation-reduction (Younger *et al.*, 2002), biological treatment (Hallberg and Johnson, 2005), membrane filtration (Barton, 1978) and electrolysis (Park *et al.*, 2015). Among these, the most commonly used

is neutralization (or alkaline treatment) where alkaline materials are used to increase the pH of the AMD to a desired value. Additionally, this process will lead to reduction of dissolved concentration of heavy metals (Singh and Rawat, 1985; Skousen *et al.*, 2000; Cravotta and Trahan, 1999; Kalin, 2004).

The efficacy of neutralization treatment is however dependent on several factors including the type of alkaline material, the amount used, particle size, contact time and AMD characteristics (Barton, 1978; Evangelou, 1995; Sengupta, 1993; Skousen *et al.*, 2000; Bernier, 2005). A conventional alkaline material such as sodium hydroxide (NaOH) or caustic soda is more effective due to its high solubility than non-conventional materials, such as limestone, which are lower in solubility (Sengupta, 1993; Evangelou, 1995; Skousen *et al.*, 2000; Kalin *et al.*, 2006). In the case of non-conventional alkaline materials, the efficiency is higher for smaller particle sizes (Barton and Vanathanam, 1976).

Besides the nature of the alkaline material used, another critical factor in AMD treatment is the characteristics of the AMD being treated. Based on its pH value, there may be little variation between AMD samples, but based on total acidity values, there can be significant variation between samples (Singh, 1987; Chon and Hwang, 2000; Younger, 2001; España *et al.*, 2005). AMD can also vary in heavy metal content, which is an important parameter associated with total acidity (Chon and Hwang, 2000; Kirby and Cravotta, 2005). The significance of AMD characteristics in neutralization treatment, however, has mainly been demonstrated using aqueous acid solutions or synthetic AMD (Barton and Vatanatham, 1976; Volpicelli *et al.*, 1981; Maree *et al.*, 1992; Du Plessis and Maree, 1994; Maree and Du Plessis, 1994) while very limited work was done using real AMD samples (Maree and Du Plessis, 1994). Acidic aqueous solutions or synthetic AMD can only partially represent the actual characteristic of real AMD samples, but nevertheless the information obtained can serve as the fundamental basis in designing an effective treatment of AMD.

In general, the purpose of neutralization treatment is to increase the pH of an acidic solution from an initial value (e.g. pH~3.0) to a much higher value (e.g.