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

STELLA HO YEN LING

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

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

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

Saya **STELLA HO YEN LING**, Sesi pengambilan **2009/2010**, mengaku membenarkan tesis doctor falsafah ini disimpan di Perpustakaan Universiti Malaysia Sabah dengan syarat-syarat kegunaan seperti berikut:

1. Tesis ini adalah hak milik Universiti Malaysia Sabah
2. Perpustakaan Universiti Malaysia Sabah dibenarkan membuat Salinan untuk tujuan pengajian sahaja
3. Perpustakaan dibenarkan membuatkan Salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. Sila tandakan (/):

[ ]	SULIT	(Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA 1972)
[ ]	TERHAD	(Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan
[/]	TIDAK TERHAD	

Disahkan Oleh,

STELLA HO YEN LING
PS2009-8247

(Tandatangan Pustakawan)

Tarikh: 28 Julai 2017

(Prof. Dr. Marcus Jopony)
Penyelia

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.

28th July 2017

STELLA HO YEN LING
PS2009-8247

CERTIFICATION

NAME	:	**STELLA HO YEN LING**
MATRIC NO.	:	**PS2009-8247**
TITLE	:	**EFFECT OF NEUTRALIZATION ON pH AND HEAVY METALS CONTENT OF ACID MINE DRAINAGES**
DEGREE	:	**DOCTOR OF PHILOSOPHY (INDUSTRIAL CHEMISTRY)**
VIVA DATE	:	**11^{th} May 2017**

CERTIFIED BY;

1. **SUPERVISOR** Signature
(Prof. Dr. Marcus Jopony)

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
7TH 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 Fe^{3+} and 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 Fe^{3+} and/or 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 Fe^{3+} and/or 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 µS/cm), total acidity (316-807 mg $CaCO_3$/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 Fe^{3+} and/or 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 Al^{3+} requires about 2X more alkalinity for this purpose compared with Fe^{3+}. When calcareous sandstone was used as the alkaline material, the presence of 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 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 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 Fe^{3+} and 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.

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 akues 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 µS/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 memperlahankan 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.

TABLE OF CONTENTS

		Page
TITLE		i
DECLARATION		ii
CERTIFICATION		iii
ACKNOWLEDGEMENT		iv
ABSTRACT		v
ABSTRAK		vii
LIST OF TABLES		xiii
LIST OF FIGURES		xiv
LIST OF ABBREVIATIONS AND SYMBOLS		xix
LIST OF APPENDICES		xxii
CHAPTER	**1 : INTRODUCTION**	1
1.1	Acid mine drainage and Environment	1
1.2	Acid Mine Drainage Treatment	1
1.3	Mamut Copper Mine	4
1.4	Rationale of study	5
1.5	Objectives of Study	7
1.6	Scope of Study	8
1.7	Outline of Thesis	8
CHAPTER	**2 : LITERATURE REVIEW**	9
2.1	Acid Mine Drainage (AMD)	9
	2.1.1 Formation of AMD	9
	2.1.2 Characteristics of AMD	11
	2.1.3 Impacts of AMD on receiving water	11
2.2	Acidity of AMD	16
	2.2.1 Total acidity	16
	2.2.2 Mineral acidity	17
2.3	AMD Treatment Method	20
2.4	Alkaline Treatment	24
	2.4.1 Materials used	24
	2.4.2 Effect of alkaline treatment	26
	a. Increase in pH	26
	b. Metal removal	32
2.5	Factors affecting Alkaline Treatment	33

2.5.1 Type of material 33
2.5.2 Amount of alkaline material 35
2.5.3 Particle size of alkaline material 37
2.5.4 The presence of Fe^{3+} and/or Al^{3+} 38
2.5.5 Concentration of dissolved Fe and/or Al 40
2.5.6 Characteristics of AMDs 41
2.5.7 Effect of coating or armoring 41

CHAPTER 3 : METHODOLOGY 42
3.1 Water Samples 42
3.1.1 Acidic aqueous samples 42
3.1.2 Acidic aqueous samples containing dissolved metals Fe and/or Al 42
a. Acidic aqueous sample containing dissolved Fe 43
b. Acidic aqueous sample containing dissolved Al 43
c. Acidic aqueous sample containing dissolved Fe and Al 43
3.1.3 Acid mine drainage (AMD) samples 44
3.2 Determination of Physico-chemical Characteristics 48
3.2.1 pH 48
3.2.2 Conductivity and Total Dissolved Solids 49
3.2.3 Total acidity 49
3.2.4 Sulfate 49
a. Preparation of sulfate calibration curve 49
b. Analysis of sample 50
3.2.5 Dissolved metals (Fe, Al, Mn, Cu, and Zn) 50
a. Operating condition of ICP-OES 50
b. Preparation of standard solutions 51
c. Preparation of calibration curve 51
d. Analysis of sample 51
3.3 Neutralization Experiments 51
3.3.1 Alkaline materials used 51
a. NaOH 51
b. Calcareous sandstone 52
3.3.2 Neutralization with NaOH 54
3.3.3 Neutralization with calcareous sandstone 54
3.4 Effect of alkaline material dosage on Neutralization 55
3.5 Effect of Repeated Exposure on neutralization efficiency

of calcareous sandstone 56
3.6 Effect of neutralization on metal concentration of AMD 57
3.6.1 Alkaline solution (NaOH) 57
3.6.2 Alkaline generating material (calcareous sandstone) 57

CHAPTER 4 : RESULTS AND DISCUSSION 59
4.1 Physico-chemical Characteristics and Heavy metal content of AMD Samples 59
4.2 Interaction Between Acidic Aqueous solutions and NaOH 64
4.2.1 Interaction in the absence of dissolved metal in solution 64
4.2.2 Interaction in the presence of Fe^{3+} 64
4.2.3 Interaction in the presence of Al^{3+} 68
4.2.4 Interaction in the presence of Fe^{3+} and Al^{3+} 70
4.3 Interaction Between Acidic Aqueous solutions and Alkaline Generating Material 73
4.3.1 Interaction of acidic aqueous solution with calcareous sandstone 73
4.3.2 Interaction in the presence of Fe^{3+} 74
4.3.3 Interaction in the presence of Al^{3+} 79
4.3.4 Interaction in the presence of Fe^{3+} and Al^{3+} 81
4.3.5 Effect of alkaline material dosage on neutralization 83
4.4 Effect of Alkaline Treatment (Neutralization) on pH of AMDs 88
4.4.1 Neutralization of AMD using alkaline solution, NaOH 88
4.4.2 Neutralization of AMD using alkaline generating Material 93
4.4.3 Effect of calcareous sandstone dosage on neutralization of AMD 96
4.5 Effect of repeated exposure of calcareous sandstone to Acidic aqueous solutions 99
4.5.1 Acidic aqueous solutions containing dissolved Fe^{3+} and/or Al^{3+} 99
4.5.2 AMD samples (AMD1, AMD4, and AMD6) 105
4.6 Effect of neutralization on dissolved metals (Fe, Al, Mn, Cu and Zn) concentration in AMD 110
4.6.1 Neutralization of AMD using alkaline solution, NaOH 110
4.6.2 Neutralization of AMD using alkaline generating,

material, Calcareous sandstone 122
4.7 Comparison of effectiveness of alkaline materials (NaOH and calcareous sandstone) in the treatment of AMD 127
4.7.1 Neutralization efficiency 127
4.7.2 Metal removal efficiency 128

CHAPTER 5 : CONCLUSION 130
REFERENCES 133
APPENDICES 146

LIST OF TABLES

			Page
Table 2.1	:	Oxidation reactions of other sulfide minerals commonly found in mine waste dumps	10
Table 2.2	:	Characteristics of mine waters from various locations	13
Table 2.3	:	Biological effects of metals on fish and human's health	15
Table 2.4	:	Acidity values of mine waters reported in selected studies	17
Table 2.5	:	Ionic Potentials of selected metal ions	19
Table 2.6	:	Various Methods of AMD treatments	23
Table 2.7	:	Typical alkaline materials used in AMD treatment	24
Table 2.8	:	Typical alkaline generating materials used in treating AMD	25
Table 2.9	:	Various types of alkaline minerals	30
Table 2.10	:	Solubility products of various carbonate minerals	31
Table 2.11	:	pH range for the formation of metal hydroxides	33
Table 3.1	:	Types of aqueous acidic samples investigated in this study	44
Table 3.2	:	GPS location and description of AMD samples	48
Table 3.3	:	ICP-OES operating condition	50
Table 3.4	:	Chemical composition of calcareous sandstone	53
Table 4.1	:	Values of pH, E_C, TDS, Total Acidity and sulfate of AMD samples	60
Table 4.2	:	Dissolved metals concentration according to AMD samples	61

LIST OF FIGURES

		Page
Figure 1.1 :	A general map of Mamut Copper Mine (MCM)	6
Figure 1.2 :	An aerial view of Mamut Copper Mine (MCM)	7
Figure 2.1 :	Acidity compositions in various AMD samples	20
Figure 2.2 :	Relationship between acidity of AMD with dissolved Fe^{3+}	21
Figure 2.3 :	Relationship between acidity of AMD with dissolved Al^{3+}	21
Figure 2.4 :	Calculated versus measured acidity of AMD samples	22
Figure 2.5 :	Titration curve of a strong acid and strong base	26
Figure 2.6 :	Titration curve obtained from titration of AMD sample with NaOH	28
Figure 2.7 :	pH increase during alkaline treatment using different oxides, hydroxides and carbonates	32
Figure 2.8 :	Neutralization of AMD using limestone from different sources	35
Figure 2.9 :	Effect of neutralization on pH of acidic Fe aqueous solution (250 mg/L) at different amount of olivine	36
Figure 2.10 :	Interaction of AMD at different dolomite and limestone solid solution ratio (g/L)	36
Figure 2.11 :	Interaction of AMD and olivine of different water/rock ratio (W/R)	37
Figure 2.12 :	Effect of limestone size on neutralization reaction of acid sulfuric solution	38
Figure 2.13 :	Effect of metal ions on neutralization rate of acid sulfuric solution using limestone	39
Figure 2.14 :	Effect of different initial concentration of Fe^{3+} on neutralization using olivine	40
Figure 3.1 :	Location map of Mamut Copper Mine area	45
Figure 3.2 :	AMD sampling sites at the mine area	46

Figure 3.3 : Calcareous sandstone sampling site at stone quarry, Kudat 52

Figure 3.4 : Particle size (1-2mm) of Calcareous Sandstone 53

Figure 3.5 : X-ray diffraction (XRD) pattern of the calcareous sandstone used in this study [A = aragonite; C= calcite; D= dolomite; Q = quartz] 53

Figure 4.1 : Relationship between pH and total acidity of AMDs 60

Figure 4.2 : Relationship between total acidity and dissolved Fe of AMDs 62

Figure 4.3 : Relationship between total acidity and dissolved Al of AMDs 63

Figure 4.4 : Relationship between total acidity and dissolved Fe and Al of AMDs 63

Figure 4.5 : Titration graph of an acidic aqueous solution and NaOH 65

Figure 4.6 : Titration graphs of acidic aqueous solutions of different Fe^{3+} concentrations 67

Figure 4.7 : Effect of Fe^{3+} concentration on the amount of base required to increase pH of an acidic aqueous solution to pH 7.0 (Initial pH = 3.0) 68

Figure 4.8 : Titration graphs of acidic aqueous solutions of different Al^{3+} concentrations 71

Figure 4.9 : Effect of Al^{3+} concentration on the amount of base required for neutralization of acidic aqueous solution to pH 7.0 (Initial pH = 3.0) 72

Figure 4.10 : The amount of base required for neutralization to pH 7.0 of acidic aqueous solution at different Fe^{3+} and Al^{3+} concentrations 72

Figure 4.11 : Titration graphs of acidic aqueous solution of different Fe^{3+} and Al^{3+} concentrations 75

Figure 4.12 : Effect of Fe^{3+} and Al^{3+} concentration on the amount of base required for neutralization of an acidic aqueous solution to pH 7.0 (Initial pH = 3.0) 76

Figure 4.13 : Amount of base required for neutralization to pH 7.0 of acidic aqueous solution at various Fe^{3+} and/or Al^{3+} concentrations 76

Figure 4.14 : pH change during interaction of acid aqueous solution with calcareous sandstone. The solid solution ratio used was 1:100 77

Figure 4.15 : pH change during interaction of acid aqueous solutions containing Fe^{3+} at different concentrations with calcareous sandstone. The solid solution ratio used was 1:100 78

Figure 4.16 : pH change during interaction of acid aqueous solutions containing Al^{3+} at different concentrations with calcareous sandstone. The solid solution ratio used was 1:100 80

Figure 4.17 : pH change during interaction of acid aqueous solutions containing both Fe^{3+} and Al^{3+} at different concentrations with calcareous sandstone. The solid solution ratio used was 1:100 82

Figure 4.18 : pH change during interaction of acidic aqueous solutions containing Fe^{3+} (100 mg/L) with calcareous sandstone at various dosages (0.1 g, 0.5 g and 1.0 g) 84

Figure 4.19 : pH change during interaction of acidic aqueous solutions containing Al^{3+} (100 mg/L) with calcareous sandstone at various dosages (0.1 g, 0.5 g and 1.0 g) 85

Figure 4.20 : pH change during interaction of acidic aqueous solutions containing Fe^{3+} and Al^{3+} (100 mg/L) with calcareous sandstone at various dosages (0.1 g, 0.5 g and 1.0 g) 87

Figure 4.21 : Titration graphs of AMD samples 90

Figure 4.22 : Titration graph of weak acid and strong base 91

Figure 4.23 : Amount of NaOH required for neutralization of AMD samples to pH 7.0 91

Figure 4.24 : Relationship between total acidity and mmoles of base required to increase the pH to 7.0 92

Figure 4.25 : Relationship between concentration of Al and mmoles of base required to increase the pH to pH 7.0 92

Figure 4.26 : Relationship between concentration of Fe and mmoles of base required to increase the pH to 7.0 93

Figure 4.27 : Effect of neutralization using calcareous sandstone on the pH of AMDs at solid solution ratio 1:100 94

Figure 4.28 : Relationship between total acidity and pH attained after 8 hours of neutralization interaction of calcareous sandstone with AMDs 96

Figure 4.29 : Interaction of AMD6 with calcareous sandstone at various dosages (0.1 g, 0.5 g and 1.0 g) 97

Figure 4.30 : pH change in acidic 100 mg/L Fe^{3+} solution during 15 successive neutralization cycles (24 hours/cycle) at solid solution ratio 1:100 100

Figure 4.31 : pH change in acidic 100 mg/L Al^{3+} solution during 12 successive neutralization cycles (24 hours/cycle) at solid solution ratio 1:100 100

Figure 4.32 : pH change in acidic 100 mg/L Fe^{3+} and Al^{3+} solution during 11 successive neutralization cycles (24 hours/cycle) at solid solution ratio 1:100 101

Figure 4.33 : Proportion of acidity in acidic aqueous solution containing 100 mg/L Fe^{3+} during 15 successive neutralization cycles (24 hours/cycle) at solid solution ratio 1:100 103

Figure 4.34 : Proportion of acidity in acidic aqueous solution containing 100 mg/L Al^{3+} during 12 successive neutralization cycles (24 hours/cycle) at solid solution ratio 1:100 103

Figure 4.35 : Proportion of acidity in acidic aqueous solution containing 100 mg/L Fe^{3+} and Al^{3+} during 11 successive neutralization cycles (24 hours/cycle) at solid solution ratio 1:100 104

Figure 4.36 : Schematic diagram of armoring on calcareous sandstone by Fe and/or Al precipitates 104

Figure 4.37 : Armoring on calcareous sandstone 105

Figure 4.38 : pH change in AMD1 during successive neutralization cycles (24 hours/cycle) at solid solution ratio 1:100 107

Figure 4.39 : pH change in AMD4 during successive neutralization cycles (24 hours/cycle) at solid solution ratio 1:100 108

Figure 4.40 : pH change in AMD6 during successive neutralization cycles (24 hours/cycle) at solid solution ratio 1:100 108

Figure 4.41 : Proportion of acidity neutralized in AMD1 during successive neutralization cycles (24 hours/cycle) at solid solution ratio 1:100 109

Figure 4.42 : Proportion of acidity neutralized in AMD4 during successive neutralization cycles (24 hours/cycle) at solid solution ratio 1:100 109

Figure 4.43 : Proportion of acidity neutralized in AMD6 during successive neutralization cycles (24 hours/cycle) at solid solution ratio 1:100 110

Figure 4.44 : Changes in Fe, Al, Mn, Cu and Zn concentration with increasing pH for AMD1 113

Figure 4.45 : Changes in Fe, Al, Mn, Cu and Zn concentration with increasing pH for AMD4 114

Figure 4.46 : Changes in Fe, Al, Mn, Cu and Zn concentration with increasing pH for AMD6 115

Figure 4.47 : Metal removal (Fe, Al, Mn, Cu and Zn) as a function of pH for AMD1 116

Figure 4.48 : Metal removal (Fe, Al, Mn, Cu and Zn) as a function of pH for AMD4 116

Figure 4.49 : Metal removal (Fe, Al, Mn, Cu and Zn) as a function of pH for AMD6 117

Figure 4.50 : Weight of precipitate as a function of pH for AMD1, AMD4 and AMD6 118

Figure 4.51 : Relationship between weight of precipitates formed and total acidity of AMDs 118

Figure 4.52 : Precipitates formed from AMD1 at various pH values 119

Figure 4.53 : Precipitates formed from AMD4 at various pH values 120

Figure 4.54 : Precipitates formed from AMD6 at various pH values 121

Figure 4.55 : Changes in Fe, Al, Mn, Cu and Zn concentration with time for AMD1 during interaction with calcareous sandstone 123

Figure 4.56 : Metal removal (Fe, Al, Mn, Cu and Zn) for AMD1 after 24 hours of interaction with calcareous sandstone 125

Figure 4.57 : Metal removal (Fe, Al, Mn, Cu and Zn) for AMD4 after 24 hours of interaction with calcareous sandstone 126

Figure 4.58 : Metal removal (Fe, Al, Mn, Cu and Zn) for AMD6 after 24 hours of interaction with calcareous sandstone 126

Figure 4.59 : Aluminium precipitates formed in Sg. Poring 127

mL	-	milliliter
L	-	Litre
N	-	Normality
mg/L	-	milligram per liter
mg $CaCO_3$/L	-	milligram calcium carbonate per liter
nm	-	nanometer
µS/cm	-	microsiemens per centimeter
Fe	-	Iron
Al	-	Aluminium
Fe^{3+}	-	Ion Iron (III)
Al^{3+}	-	Ion Aluminium (III)
$Al(OH)_2$	-	Aluminium hydroxides
Mn	-	Manganese
$Mn(OH)_2$	-	Manganese hydroxides
Cu	-	Copper
$Cu(OH)_2$	-	Copper hydroxides
Zn	-	Zinc
$Zn(OH)_2$	-	Zinc hydroxides
Cd	-	Cadmium
Cr	-	Chromium
TDS	-	Total dissolved solids
SO_4^{2-}	-	sulfate
CO_3^{2-}	-	Carbonate
HCO_3^-	-	Bicarbonate
H_2CO_3	-	Carbonic acid

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

LIST OF APPENDICES

		Page
APPENDIX A	Standard Solutions Preparation	146
APPENDIX B	Preparation of metal stock solution	147
APPENDIX C	Data for total acidity calculation	148
APPENDIX D	Preparation of solutions for determination of sulfate concentration	149
APPENDIX E	Data for sulfate concentration	150
APPENDIX F	Preparation of metal solutions (ICP-OES)	151
APPENDIX G	Calibration graphs in WINLAB for Fe, Al, Mn, Cu and Zn	152
APPENDIX H	pH, EC, TDS, Total acidity and dissolved metals data for AMD	153
APPENDIX I	Number of moles of NaOH used in AMD potentionmetric titration to reach pH 7.0	155
APPENDIX J	Interaction between Acidic Aqueous Solution and NaOH	156
APPENDIX K	Interaction between Acidic Aqueous Solution and Alkaline Generating Material	165
APPENDIX L	Calcareous sandstone dosages	171
APPENDIX M	Effect of Alkaline treatment (Neutralization) on pH of AMDs	174
APPENDIX N	Repeated Exposure Test	186
APPENDIX O	Effect of neutralization on metals (Fe, Al, Mn, Cu and Zn) concentration in AMD1, AMD4 and AMD6	189
APPENDIX P	Metal removal (Fe, Al, Mn, Cu and Zn) for AMD1, AMD4 and AMD6 after 24 hours of interaction with calcareous sandstone	191

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; Españа *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.