

**ACTIVE NEUTRALISATION AND
AMELIORATION OF ACID MINE DRAINAGE
WITH FLY ASH**

DAMINI SURENDER



SUBMITTED IN FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE
IN THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WESTERN CAPE

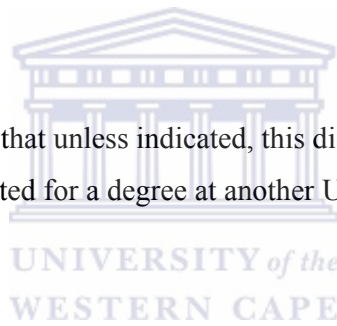
SUPERVISOR: Dr L PETRIK

NOV 2009

Final Copy

DECLARATION BY CANDIDATE

I, Damini Surender, declare that unless indicated, this dissertation is my own and that it has not been submitted for a degree at another University or Institution



.....
D Surender

Nov 2009

ACTIVE NEUTRALISATION AND AMELIORATION OF ACID MINE DRAINAGE WITH FLY ASH

Damini Surender

KEYWORDS

Fly ash

Acid mine Drainage

Limestone

Active Neutralisation

Treatment

Feasibility

Circum-neutral

Adsorption

Precipitation

pH



ABSTRACT

Due to the constraints being placed on water resources and a drive for major industries to recycle waste water, improved and cheaper water treatment technologies are being investigated. During mining, pyrite (FeS_2), a mineral naturally occurring in the earth's structure, becomes oxidised when exposed to oxygen and water, resulting in the release of hydrogen ions, sulphate ions and metal cations. Coal mining operations, located in one of the largest coalfields in the country, in Mpumalanga province, is a major contributor to the generation of acid mine drainage (AMD) and is estimated to produce 360 Ml/d after closure of the entire Mpumalanga Coalfields. Commonly applied chemically treatment processes for AMD involve the use of limestone to neutralise the AMD, however elevated sulphate concentrations persist in the neutralised water. Membrane and ion exchange technology are more successful in attenuating sulphate in AMD; however, they are often complex and have exorbitant capital and operating costs.

Universally, fly ash has been applied for the treatment of AMD primarily in passive treatment systems. Passive treatment technologies require little or no operation and maintenance e.g. constructed wetlands and anoxic limestone drains. However, with specific reference to AMD treatment, passive treatment systems require long retention times and greater space as well as provide uncertain treatment efficiencies. Recent research has demonstrated the potential to apply fly ash in active treatment systems for AMD treatment and amelioration. Active treatment technologies make use of some chemical addition or advanced technology e.g. membrane technologies and ion exchange resins. Whilst active treatment technologies are often more expensive than passive treatment systems, active treatment occurs at a faster rate and treatment efficiencies are more controllable and effective. This study investigated the potential of fly ash to actively neutralise and ameliorate or improve the quality of AMD at beaker and large scale with special attention given to sulphate attenuation. The results of the investigation were compared to data of state-of-the-art treatment technologies, obtained from literature. These included chemical treatment, membrane treatment, ion exchange and biological treatment systems. A comparative study was conducted

to ascertain the feasibility of fly ash versus the commonly used limestone treatment technology.

Fly ash and AMD samples were characterised by standard analytical methods for selection of the test materials. Active treatment by means of mixing fly ash with AMD in beakers and a large tank at pre-determined ratios have shown that fly ash is capable of neutralising AMD and increasing the pH beyond neutral values, which optimises the removal of heavy metals and ions. The trend was: the more fly ash added the quicker was the reaction time and higher the pH values achieved. Iron was reduced by as much 99 % in beaker scale experiments via $\text{Fe}(\text{OH})_3$ precipitation at pH values >4.0 . A 99 % decrease in aluminium concentration was observed which was attributed to the precipitation of primarily gibbsite and various other mineral phases at pH values >5.5 . As the pH increases, sulphate is adsorbed via $\text{Fe}(\text{OH})_3$ and gypsum precipitation at elevated pH. Sulphate attenuation with fly ash was excellent, achieving 98 % attenuation with beaker scale experiments and 1:1 fly ash:AMD ratio. Sulphate attenuation with fly ash was comparable to membrane and ion exchange systems and exceeded the performance of limestone treatment.

Except for the larger volumes of fly ash needed to neutralise the AMD, fly ash proved to be a feasible and cost efficient alternative to limestone treatment. Fly ash produced competing results to limestone concerning acidity removal and sulphate attenuation. The comparison highlighted the advantages of utilising fly ash in comparison to limestone and demonstrated its cost effectiveness.

The results of this study have shown that fly ash could be successfully applied for the neutralisation of acid mine drainage (AMD) and effectively attenuate the sulphate load in the treated water. The critical parameters to this technology are the variations of chemical composition and mineralogy of fly ash, which could influence the pH, contact time of the neutralisation reaction, and the same is true if the AMD quality varies.

ACKNOWLEDGMENTS

The author gratefully acknowledges the following:

- Dr Leslie Petrik, for her guidance, support and endless encouragement.
- Annabelle Ellendt and Olivier Etchers for their assistance with the XRF & XRD analysis as well as Dr Ravi Vadapalli for his assistance with the experimental work.
- Averil Abbott for her administrative assistance.
- Mr G Gericke for the knowledge he imparted onto me, the opportunities granted and his on-going guidance.
- Eskom Resources and Strategy for their financial support.
- My family, for their support and patience.



DEDICATION

To my family, Vinesh, Arya, Raeya and mum.



TABLE OF CONTENTS

DECLARATION BY CANDIDATE	ii
KEYWORDS	iii
ABSTRACT	iv
ACKNOWLEDGMENTS	vi
DEDICATION	vii
ACRONYMS AND ABBREVIATIONS	xv
CHAPTER 1	1
INTRODUCTION	1
1.1 MOTIVATION FOR APPLICATION OF FLY ASH FOR AMD NEUTRALISATION AND AMELIORATION.....	5
1.2 PROBLEM STATEMENT AND RESEARCH QUESTIONS	8
1.3 OBJECTIVES OF STUDY	8
1.3.1 APPROACH	9
1.4 STUDY AREA	9
1.5 OUTLINE OF THIS THESIS.....	11
CHAPTER 2	13
LITERATURE REVIEW: COMPARISON OF AMD/SULPHATE TREATMENT PROCESSES.....	13
2.1 INTRODUCTION	13
2.2 CHEMICAL TREATMENT	14
2.2.1 Lime and Limestone	14
2.2.2 Savmin Process	17
2.3 MEMBRANE SYSTEMS	21
2.3.1 Reverse Osmosis.....	21
2.3.2 Electro-dialysis Reversal (EDR).....	27
2.4 ION EXCHANGE	30
2.4.1 GYP-CIX	30
2.4.2 Metal Precipitation and Ion Exchange (GYP-CIX).....	32
2.5 BIOLOGICAL SULPHATE REMOVAL.....	34
2.4.1 Bioreactors	35
2.4.2 Constructed Wetlands	37
2.5 SUMMARY OF COMPARISON	39
CHAPTER 3	43
EXPERIMENTAL METHODOLOGY.....	43
3.1 SAMPLING AND STORAGE METHODS.....	43
3.1.1 Fly Ash.....	43
3.1.2 Acid Mine Drainage.....	43
3.1.3 Post neutralisation liquid and solid samples	43
3.2 EXPERIMENTAL METHODS.....	44
3.2.1 Beaker scale neutralisation tests	44
3.2.2 Large scale neutralisation tests	44
3.2.3 Comparison of limestone versus fly ash treatment of AMD	44
3.3 ANALYTICAL METHODS	45

3.3.1	pH determination	45
3.3.2	Electrical conductivity (EC) measurements.....	46
3.3.3	Acidity measurements.....	46
3.3.4	Percentage CaCO ₃ in neutralising material (fly ash and limestone).....	47
3.3.5	Alkalinity measurement.....	48
3.3.6	Loss on ignition (LOI).....	49
3.3.7	Inductively Coupled Plasma (ICP) Optical Emission Spectroscopy for metal analysis.....	49
3.3.8	Ion chromatography for ion analysis	50
3.3.9	Particle size analysis	51
3.3.10	X-Ray Fluorescence (XRF) Spectrometry	52
3.3.11	Computer Controlled Scanning Electron Microscopy (CCSEM)	53
3.4	COMPARISON OF LIMESTONE AND FLY ASH FOR NEUTRALISATION OF AMD WITH HIGH SULPHATE CONCENTRATION	54
3.4.1	Experimental Protocol	54
CHAPTER 4		56
CHARACTERISATION AND SELECTION OF FLY ASH AND AMD FOR NEUTRALISATION EXPERIMENTS		56
4.1	DETERMINATION OF AMOUNT OF CAO IN FLY ASH, LIME AND LIMESTONE.....	56
4.2	X-RAY FLOURESCENCE (XRF) SPECTROMETRY ANALYSIS	59
4.3	SCANNING ELECTRON MICROSCOPY (SEM) ANALYSIS	60
4.4	PARTICLE SIZE ANALYSIS	64
4.5	SUMMARY OF FLY ASH CHARACTERISATION.....	65
4.6	CHEMICAL COMPOSITION OF AMD.....	67
CHAPTER 5		70
BEAKER AND LARGE SCALE NEUTRALISATION EXPERIMENTS.....		70
5.1	BEAKER SCALE NEUTRALISATION EXPERIMENTS WITH SKOONGESIG AMD.....	70
5.1.1	Results of beaker scale experiments with Skoongesig AMD.....	71
5.1.2	Summary of beaker scale neutralisation experiments.....	80
5.2	LARGE SCALE NEUTRALISATION EXPERIMENTS	80
5.2.1	Large scale mixer design	81
5.2.2	Large scale neutralisation experiments of 1:3 to 1:10 Arnot fly ash:Skoongesig AMD ratios	82
5.2.3	Large scale neutralisation experiments at 1:6 fly ash:AMD ratio with varying agitation rates.....	84
5.2.4	Large scale neutralisation experiments at 1:6 fly ash:AMD ratio	88
5.2.5	Large scale neutralisation experiments at 1:6 ratio with Arnot fly ash and Toeseep AMD.....	90
5.2.6	Morphology of solids by scanning electron microscopy	93
5.2.7	Summary of large scale neutralisation experiments	95
CHAPTER 6		96
FEASIBILITY STUDY OF FLY ASH VERSUS LIMESTONE TREATMENT OF AMD		96

6.1	INTRODUCTION	96
6.2	BACKGROUND	96
	6.2.1 Limestone Neutralisation	96
	6.2.2 Fly ash as an alternative to limestone neutralisation	98
6.3	COMPARISON OF LIMESTONE AND FLY ASH FOR NEUTRALISATION OF AMD WITH HIGH SULPHATE CONCENTRATION	100
	6.3.1 Experimental Results of Chemical Characteristics of Neutralising Material, Neutralisation Reaction and Treated AMD	100
	6.3.2 Discussion of results obtained for the comparison of limestone versus fly ash neutralisation of Toeseep AMD	117
6.4	CURRENT LIMESTONE PRACTICE	122
6.5	ADVANTAGES OF SUBSTITUTING LIMESTONE WITH FLY ASH FOR AMD NEUTRALISATION.....	124
CHAPTER 7		126
TREATMENT OF CIRCUM-NEUTRAL MINE WATER		126
7.1	INTRODUCTION	126
7.3	SUMMARY FLY ASH TREATMENT OF CIRCUM-NEUTRAL WATER	131
CHAPTER 8		133
DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS.....		133
8.1	INTRODUCTION	133
8.2	BEAKER AND LARGE SCALE NEUTRALISATION EXPERIMENTS.....	134
8.3	FEASIBILITY STUDY OF FLY ASH VERSUS LIMESTONE TREATMENT OF AMD	135
8.4	TREATMENT OF CIRCUM-NEUTRAL MINE WATER WITH FLY ASH	136
8.5	RECOMMENDATIONS.....	136
8.6	SIGNIFICANCE OF THE STUDY.....	137
CHAPTER 9		139
REFERENCES		139
APPENDIX A:..... DETERMINATION OF ALKALINITY OF WATER ELECTROMETRIC TITRATION		147
APPENDIX B:..... DETERMINATION OF ANIONS IN WATER BY ION CHROMATOGRAPHY WITH CONDUCTIVITY MEASUREMENTS: CHROMATOGRAPHIC METHOD		150
APPENDIX C:.. METAL ANALYSIS OF RAW, POTABLE AND WASTE WATER BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP)		156

LIST OF FIGURES

Figure 1.1:	Map detailing the location of the power plants (Arnot, Hendrina, Kriel and Duvha) and coal mine (Landau) that provided the samples for this study.....	10
Figure 2.1:	Schematic illustration of CaCO ₃ handling and dosing system on full scale incorporated with the limestone neutralisation, gypsum crystallisation and CaCO ₃ precipitation system at Navigation pilot plant.....	15
Figure 2.2:	Savmin process applied at Stilfontein gold mine (Sibilski, 2001).....	17
Figure 2.3:	TRO Plant Design applied at the Sasol, Secunda desalination plant...	23
Figure 2.4:	Process Flow Diagram of Emalahleni mine water treatment project (Water Sewage & Effluent, 2006)	25
Figure 2.5:	Principle of Electro-dialysis.....	27
Figure 2.6:	Simplified GYP-CIX process flow diagram for treatment of mine water (Schoeman <i>et al.</i> 2001)	31
Figure 2.7:	Flow sheet of the metal precipitation process for a gold mine water treatment project	33
Figure 2.8:	Schematic diagram of anaerobic reactor for treatment of sulphate rich mine water.....	36
Figure 5.1:	Stirrer unit for bench scale neutralisation experiments.....	71
Figure 5.2:	Variation in pH and EC for different ratios of fly ash:AMD in beaker scale neutralisations experiments with Skoongesig AMD and Arnot fly ash	72
Figure 5.3:	Effect of fly ash neutralisation on iron attenuation at varying pH endpoints and fly ash:AMD ratios.	74
Figure 5.4:	Effect of fly ash neutralisation on sulphate attenuation at varying pH endpoints and fly ash:AMD ratios	75
Figure 5.5:	Effect of fly ash neutralisation on aluminium attenuation at varying pH endpoints and fly ash:AMD ratios	77
Figure 5.6:	Neutralisation of Landau AMD with Arnot fly ash (Long Term) – 1:1, 1:2 and 1:3 ratios.....	78
Figure 5.7:	Neutralisation of Landau AMD with Arnot fly ash (Long Term) – 1:5, 1:10 and 1:20 ratios.....	79
Figure 5.8:	Large scale mixer with 250 L tank capacity and turbulator/aeration unit.	81
Figure 5.9:	Agitation achieved with large rig.....	82
Figure 5.10:	Variation in pH and EC for different ratios of fly ash:AMD in large scale neutralisations experiments with Skoongesig AMD and Arnot fly ash	83
Figure 5.11:	Effect of varying agitation rates on the pH of a 1:6 Arnot fly ash:Skoongesig AMD neutralisation ratio	85
Figure 5.12:	Iron reduction with pH variation: neutralisation of 1:6 fly ash:AMD	86
Figure 5.13:	Sulphate reduction with pH variation: neutralisation of 1:6 fly ash:AMD.....	86
Figure 5.14:	Aluminium reduction with pH variation: neutralisation of 1:6 fly ash:AMD.....	87
Figure 5.15:	Neutralisation experiments at 1:6 fly ash:AMD ratio with extended reaction time.....	88
Figure 5.16:	Neutralisation experiments at 1:6 ratio with extended reaction time ..	90

Figure 5.17:	Iron attenuation with pH variation: neutralisation of Toeseep AMD with Arnot fly ash at 1:6 ratio	91
Figure 5.18:	Aluminium attenuation with pH variation: neutralisation of Toeseep AMD with Arnot fly ash at 1:6 ratio.....	91
Figure 5.19:	Sulphate attenuation with pH variation: neutralisation of Toeseep AMD with Arnot fly ash at 1:6 ratio.....	92
Figure 5.20:	Iron-oxide rimming aluminosilicate particle as observed by CCSEM analysis.....	94
Figure 6.1:	Limestone mixing and dosing plant (Greben <i>et al.</i> , 2004)	97
Figure 7.1:	Effect of Arnot and Duvha fly ash treatment on sulphate concentration in circum-neutral mine water	129
Figure 7.2:	Effect of Hendrina fly ash treatment on sulphate concentration in circum-neutral mine water	129
Figure 7.3:	Effect of fly ash treatment on iron concentration in circum-neutral mine water at pH 9	130
Figure 7.4:	Effect of Hendrina fly ash treatment on iron concentration in circum-neutral mine water at pH 9.....	130



LIST OF TABLES

Table 1.1:	Classification of fly ash (ASTM C618, 2003).....	4
Table 2.1:	List of AMD treatment processes Error! Bookmark not defined.	
Table 2.2:	Water qualities of the feed and treated water of the integrated lime/limestone process (Geldenhuis <i>et al.</i> , 2001).....	16
Table 2.3:	Incoming and outgoing concentrations of mine water treated by Savmin process at Stilfontein compared to discharge quality water (Sibiliski, 2001).....	19
Table 2.4:	Incoming and outgoing concentrations of mine water treated by Savmin process at Stilfontein compared to potable quality water (Sibiliski, 2001).....	20
Table 2.5:	Incoming and outgoing concentrations of mine water treated by Savmin process at Stilfontein compared to high quality industrial water (Sibiliski, 2001).....	20
Table 2.6:	Water quality from Secunda TRO plant at different treatment stages (du Plessis & Swartz, 1992).....	24
Table 2.7:	Design feed and treated water qualities of the Emalahleni mine water treatment plant	26
Table 2.8:	Results from a 1.6 L/s EDR pilot plant for treating brackish water (INAP Report 2003).....	27
Table 2.9:	Results of the treated mine water by the metal precipitation process applied at a gold mine in South Africa (Feng <i>et al.</i> , 2000).....	34
Table 2.10:	Summary of comparison of chemical treatment processes.....	40
Table 2.11:	Summary of comparison of membrane treatment processes	41
Table 2.12:	Summary of comparison of ion exchange treatment processes	41
Table 2.13:	Summary of comparison of biological sulphate removal treatment processes	42
Table 4.1:	Percent CaO of Arnot power plant ash	57
Table 4.2:	Percent CaO of Kriel power plant ash	57
Table 4.3:	Percent CaO of Hendrina power plant ash.....	58
Table 4.4:	Percent CaO of Limestone	58
Table 4.5:	Percent CaO of Lime	58
Table 4.6:	XRF data of fly ash samples	59
Table 4.7:	Volume percent phase proportions	61
Table 4.8:	Fly ash classification and phase nomenclature	62
Table 4.9:	Calculated CaO	64
Table 4.10:	Particle size distribution of fly ash.....	65
Table 4.11:	Estimated distance between power plants and AMD sites	66
Table 4.12:	Chemical Composition of Skoongesig AMD	67
Table 4.13:	Chemical Composition of Toeseep AMD.....	68
Table 5.1:	Comparison of treatment technologies for sulphate attenuation.....	76
Table 5.2:	Loss on ignition (LOI) of Arnot fly ash.....	89
Table 5.3:	Volume-% fly ash phase distribution of fly ash and 96 hour solid residue sample from 1:6 Arnot fly ash:Toeseep AMD neutralisation reaction.....	93
Table 6.1:	Determination of acidity and sulphate concentration of Toeseep AMD	101
Table 6.2:	Determination of CaCO ₃ content of limestone used at Navigation Plant	102

Table 6.3:	Limestone neutralisation reaction data and % solid and water content results	104
Table 6.4:	Acidity and sulphate concentration of treated AMD from the limestone neutralisation reaction.....	105
Table 6.5:	Arnot fly ash neutralisation reaction data and % solid and water content results (1:7 ratio)	106
Table 6.6:	Acidity and sulphate concentration of treated AMD from the Arnot fly ash neutralisation reaction (1:7 ratio)	107
Table 6.7:	Arnot fly ash neutralisation reaction data and % solid and water content results (1:4 ratio)	108
Table 6.8:	Acidity and sulphate concentration of treated AMD from the Arnot fly ash neutralisation reaction (1:4 ratio)	109
Table 6.9:	Hendrina fly ash neutralisation reaction data and % solid and water content results (1:7 ratio)	110
Table 6.10:	Acidity and sulphate concentration of treated AMD from the Hendrina fly ash neutralisation reaction (1:7 ratio)	111
Table 6.11:	Hendrina fly ash neutralisation reaction data and % solid and water content results (1:4 ratio)	112
Table 6.12:	Acidity and sulphate concentration of treated AMD from the Hendrina fly ash neutralisation reaction (1:4 ratio)	113
Table 6.13:	Kriel fly ash neutralisation reaction data and % solid and water content results (1:7 ratio).....	114
Table 6.14:	Acidity and sulphate concentration of treated AMD from the Kriel fly ash neutralisation reaction (1:7 ratio)	115
Table 6.15:	Kriel fly ash neutralisation reaction data and % solid and water content results (1:4 ratio)	116
Table 6.16:	Acidity and sulphate concentration of treated AMD from the Kriel fly ash neutralisation reaction (1:4 ratio)	117
Table 6.17:	Comparison of limestone and FLY ASH treatments of high sulphate AMD	118
Table 7.1:	Chemical composition of circum-neutral mine water from Middleburg mine.....	127
Table 7.2:	Selected ratios for treatment of circum-neutral mine water with Arnot and Duvha and Hendrina fly ash.....	128

ACRONYMS AND ABBREVIATIONS

AMD	Acid mine drainage
ALD	Anoxic limestone drains
COD	Chemical oxygen demand
EC	Electrical conductivity
ED	Electro-dialysis
EDR	Electro-dialysis reversal
HDS	High density separation
ICP	Inductively coupled plasma spectroscopy
IC	Ion chromatography
LOI	Loss on ignition
NA	Not available
NaOH	Sodium hydroxide
OLC	Open limestone channels
RO	Reverse osmosis
SEM	Scanning electron microscopy
TDS	Total dissolved solids
TRO	Tubular reverse osmosis
XRF	X-ray fluorescence spectroscopy
g	Gram
K	Kelvin
kg/m ³	Kilograms per cubic meter
l	litres
m ³ /h	Cubic meter per hour
ml	Millilitre
min	Minute
mg/l	Milligrams per litre
mS/cm	Millisiemens per centimetre
MI/d	Megalitres per day
N	Normality
NTU	Nephelometric turbidity unit
R/kg	Rand per kilogram

R/m³

Rand per cubic meter



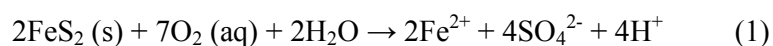
CHAPTER 1

INTRODUCTION

Increased concern has been raised with regards to the limited water supply available for major industries, drinking water and other activities such as irrigation for agriculture. Further, the detrimental environmental impacts associated with discharge of contaminated water into water resources has seen authorities the world over, implementing more stringent guidelines that govern this practice.

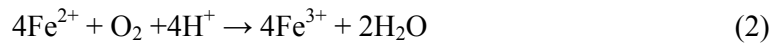
The mining industry is a major contributor to the generation of toxic waste streams e.g. acid mine drainage (AMD) that could lead to long-term impairment of the water resources and biodiversity. The coal mining industry is closely associated with the power industry. South Africa's coal fired power plants are located in the Mpumalanga Highveld region where the major coal reserves are found. Coal mining in South Africa is estimated to produce 200 Ml of acid mine drainage (AMD) per day in the Pretoria-Witwatersrand-Vereeniging (PWV) area alone (Maree *et al.*, 1996), while electricity production resulted in approximately 36 million tons (Eskom, 2008) of coal ash being produced in 2008 of which only 7 % was recycled in the cement industry, the remainder was disposed into ash dams or dumps. A large number of collieries in South Africa are linked to power plants where these two waste streams, acid mine drainage and fly ash, have the capacity to neutralise each other and provide an opportunity for co-disposal.

AMD is produced when pyrite (FeS_2), a mineral naturally occurring in the earth's structure, becomes oxidised when exposed to oxygen and water, resulting in the release of hydrogen ions, sulphate ions and metal cations (equation1) (Akcil and Koldas, 2006).



The oxidation process occurs in undisturbed rock but at a slow rate and the surrounding water usually has some buffering capacity. Mining activities lead to greater exposure of these pyrite bearing rocks to oxygen and water, resulting in excess acid generation beyond the water's natural buffering capabilities.

Oxidation of the ferrous (Fe^{2+}) to the ferric (Fe^{3+}) occurs when sufficient oxygen dissolves in the water or if the water is exposed to sufficient atmospheric oxygen.



At low pH, between 2.3 and 2.5, ferric iron can either precipitate as $\text{Fe}(\text{OH})_3$ (equation 3) (Akcil and Koldas, 2006) or react directly with pyrite to produce more ferrous iron and acidity (equation 4).



Equations (2) and (3) are perpetuated if more ferrous iron is produced and sufficient dissolved oxygen is present resulting in greater acidity.

The acidic medium generated allows for the acidophilic bacteria (e.g. *Thiobacillus ferrooxidans*) to establish themselves. This bacterium can catalyse the oxidation of ferrous iron, further accelerating the chemical reactions. Recently, another microbe namely *Ferroplasma acidarmanus* was discovered to also play a significant role in the production of acidity (Edwards *et al.*, 2000).

The exceptionally high concentrations of sulphate present in some AMD sources present a challenge to treat. Metals and ions that are naturally occurring dissolve from the bedrock because of the weathering process over time. The dissolution process is accelerated under acidic conditions. Over time the concentrations reach toxic levels. Discharge of AMD into water resources could have deleterious effects on the aquatic environment and drinking water supplies. Stricter controls and laws are being imposed by environmental authorities with regard to wastewater discharge

practices the world over. AMD treatment is thus crucial. A host of AMD treatment processes exist, with on-going development of new, improved and cost effective technologies. The industries have realised that treatment and reuse could lead to legal and financial benefits.

Fly ash is the material remaining when coal is combusted in fossil driven power plants generating electricity. Fly ash is that fraction of waste that enters the flue gas stream and is collected by bag house precipitators or other emission control devices (Adriano *et al.*, 1980). This waste is usually disposed of as a slurry to a waste dam site. Fly ash is considered to be a ferro-alumino silicate material made up of glass spheres (Fisher and Natusch, 1979) of very small particle size (20 – 80 μm) (Carlson and Adriano, 1993; Mattigod *et al.*, 1990) and high surface areas (Summers *et al.*, 1983). The lime occurring on the surface of the glass spherules originates from the decarbonation of limestone and/or dolomite impurities in the coal and leads to the fly ash being alkaline (Warren and Dudas, 1984). The chemical constituents of fly ash depend mainly on the chemical composition of the coal. However, fly ashes that are produced from the same source and which have very similar chemical composition can have significantly different ash mineralogy depending on the coal combustion technology applied. The amount of crystalline material versus glassy phase material depends largely on the combustion and glassification process used at a power plant. The minerals present in the coal dictates the elemental composition of the fly ash. However, the boiler design and operation dictate the mineralogy and crystallinity of the ash.

The total metals content for a specific fly ash source depends on the composition of the coal. The metal leaching potential of the ash depends on the total metals content is also influenced by the crystallinity of the fly ash. The crystallinity of the fly ash would determine whether the metals are incorporated within the glasseous phase or within the crystalline compounds. The metals in the glasseous phase are expected to leach at much lower rate than that from the crystalline phase. The classification of fly ashes is shown in Table 1.1.

Table 1.1: Classification of fly ash (ASTM C618, 2003)

	Class F	Class C
Silicon dioxide (SiO ₂) plus aluminium oxide (Al ₂ O ₃) plus iron oxide (Fe ₂ O ₃), min, %	70	50
Sulphur trioxide (SO ₃), max, %	5.0	5.0
Moisture Content, max, %	3.0	3.0
Loss on ignition, max, %	6.0	6.0

Class F fly ash is produced from burning anthracite or bituminous coals and has siliceous or siliceous and aluminous material. Class C fly ash is produced from lignite and sub-bituminous coals and usually contains significant amounts of lime.

South African fly ashes are produced from bituminous coals. The major non-crystalline component is glass while the major mineral components are mullite quartz, ferrite, spinel and lime with minor amounts of hematite and portlandite.

The alkalinity of South African fly ash may not be as high as that of lime and limestone, however its availability in large quantities offers a cost effective alternative for neutralising acidic mine drainage and sulphate removal. In addition, the primarily coal-based production of electricity produces in excess of 20 Mt fly ash per annum of which only a small percentage is utilised, thus providing an abundance of fly ash for application in alternative processes. O'Brien, (2000) have conducted work which exploits the alkaline nature of fly ash. Their studies have demonstrated the potential to neutralise AMD by co-disposing fly ash or aqueous extracts of the ash with AMD. This process has resulted in reduced concentration of heavy metals, which precipitate at higher pH values. Precipitation of aluminosilicates and iron compounds occurred at a pH of 10. Direct mixing of AMD and fly ash to a predetermined pH enhanced the formation of zeolites, gypsum and soil components. These secondary aluminosilicate and and/or aluminocalcium sulphate (ettringitic) or ferrihydrite precipitates have the capacity for mutual beneficiation of water quality in the neutralised AMD and fly ash. Such materials when precipitated may also be of value in low-cost attenuation of toxic metallic waste streams (O'Brien, 2000). The successful treatment of AMD with fly

ash would be mutually beneficial for AMD and fly ash neutralisation and utilisation respectively.

1.1 MOTIVATION FOR APPLICATION OF FLY ASH FOR AMD NEUTRALISATION AND AMELIORATION

Use of fly ash for soil amelioration has been limited as fly ash contains only small amounts of beneficial nutrients, has an undesirable pH and often contains potentially toxic trace elements such as As, B, Ba, Cd, Cr, Pb, Hg, Mo and Se. Further, appropriate handling and disposal of fly ash remains a serious problem.

The use of fly ash to prevent or treat AMD generation in abandoned coalmines has been the subject of several experiments with mixed success. Minimum work has been conducted on active neutralisation of AMD with fly ash.

Due to their alkaline nature, fly ashes are often used in surface mine reclamation to neutralise acidity and reduce hydraulic conductivity (K_{sat}) of disturbed mines. In addition to the excess alkalinity contained in the fly ashes, fly ashes are enriched with many trace metals, which could possibly leach into nearby water sources. However, the water pollution potential is much lower because of the stability of most heavy metals at high pH values.

Ash filling in the coalmines aimed at AMD neutralisation and to maximise coal extraction has been investigated for several decades. The first ash filling operation undertaken in South Africa began in 1963 at the Koornfontein Colliery in the Witbank coalfield in an attempt to stabilise pillars associated with mining. Hydraulic ash filling prevented further major collapses. Additional ash filling operations conducted at the Springfield colliery in 1973 and 1979 proved successful. More recent ash filling investigations conducted by the CSIR indicated that the major benefits include increased coal extraction, stabilised pillar strength, reduced surface subsidence and the treatment of AMD (Ilgner, 2000).

The buffering capacity of fly ash was further demonstrated by Twardowska, (1990), by examination of samples obtained from a mine spoils which contained layers of fly ash on the spoil tip. Water percolation through the tip was reduced, acidity neutralised and sulphate, TDS and heavy metal loads reduced through the formation of stable heavy metal compounds and the reduction of acid generation due to exclusion of atmospheric oxygen transport to the iron sulphide minerals.

Van den Berg *et al.*, (2001) investigated the in-situ neutralisation of Matla, Hendrina and Duvha fly ash at Rietspruit, Optimum and Middleburg colliery. The objective of their investigation was to establish possible scenarios for the utilisation of fly ash for coal mining rehabilitation and predict the long-term chemical behaviour and environmental impact of such systems. They found that the calcium oxide in the fly ash could neutralize some of the acid in the acidic waters. Their report indicated that the addition of fly ash below the final decanting level introduces a high risk of metal leaching due to acidification of the mine water. Over time, applying the ash as a cover will minimise rainwater and oxygen ingress thus improving water quality. However, they found that the alkalinity released from the ash cover is insufficient to neutralise acid production in the spoil below. Application of fly ash leachate could improve water quality by raising the pH and precipitation of gypsum and heavy metals but this requires the fresh ash water to be injected through boreholes into the spoil to ensure maximum efficiency.

Long term column leaching studies of co-disposed fly ash and mine spoil was conducted by Steward *et al.*, (1997) over a four year period. An important finding was that a balance must exist between the alkalinity of the fly ash and the acidity of the mine spoil. The fly ash, with sufficient neutralisation potential, was capable of maintaining neutral pH levels with minimal metal leachate occurring.

Extensive laboratory investigations into the ability of fly ash to behave as a barrier to the flow of AMD and possible AMD treatment were performed by Reynolds, (2004). This initial investigation made use of perspex columns packed with ash from Kendal power plant at 1.5, 1.0, 0.5 and 0.25 m depths. AMD from Middleburg mine was gravity fed through the columns and analysed daily for pH, conductivity, sulphates and heavy metals. The analysis frequency was reduced to weekly after only slight

variations were detected and terminated when the pH of the solution exiting the columns dropped to below 8.5. After day 1, the AMD seepage with an initial pH of 2.88 increased to pH >12 for all columns except the 0.25 m which increased to pH 12 on day 3. The pH of the shorter columns decreased rapidly thereafter and a plateau was reached at a pH of 8.0 and 273 days. The electrical conductivity (EC) increased rapidly in all columns in the initial days and it was suspected that the solubilisation of the elements in the ash during contact with the AMD lead to this. Thereafter, the EC steadily decreased and stabilised after 44 days. The sulphate (SO_4^{2-}) concentration initially decreased from 3654 mg/l to between 1000 and 2000 mg/l for all columns. This was attributed to the formation of calcium sulphate (CaSO_4) on reaction with fly ash. The longer two columns showed a further decrease to ~ 200 mg/l SO_4^{2-} before steadily increasing and stabilising at ~ 2000 mg/l SO_4^{2-} . The other columns displayed a smaller decrease in sulphate and a similar stabilisation concentration. The heavy metal concentrations generally decreased with Be, Cd, Co, Pb and Ni being lower than detection limits. The ash removed from the columns after completion had hardened due to the pozzolanic effect, this being the desired barrier effect. Sectional mineralogical analysis of the columns indicated that gypsum (CaSO_4) did actually form at the top of the columns. Only slight variations were detected from the original fly ash and the column except for a decrease in the calcium content.

Reynolds (2006) performed further investigations, using fly ash from different power plants namely Matla and Duvha power plants. This investigation displayed similar trends as with the Kendal ash. The major difference here was that the column containing the Matla ash completely restricted AMD flow by around 30 days and the pH remained at 10. This was attributed to the smaller particle size of Matla ash as compared to the other ash samples.

Neutralisation studies were conducted by O' Brien, (2000) using simulated AMD and fresh fly ash from two different sources i.e. Arnot power plant and Sasol, a petroleum company. During this study, it was noted that higher lime concentration in the Arnot fly ash enhanced its neutralisation potential compared to the Sasol ash with a higher mullite concentration. Rapid pH adjustment occurred within the first 30 minutes of the neutralisation reaction. Ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}26\text{H}_2\text{O}$), which could play

a significant role in the removal of trace contaminants, precipitated between pH 12-10.3.

1.2 PROBLEM STATEMENT AND RESEARCH QUESTIONS

Treatment of AMD with fly ash exists primarily as passive treatment methods, however neutralisation and treatment of AMD is often insufficient, with high concentrations of metals and ions remaining after neutralisation. Passive treatment technologies require little or no operation and maintenance e.g. constructed wetlands and anoxic limestone drains. However, with specific reference to AMD treatment, passive treatment systems require long retention times and greater space as well as provide uncertain treatment efficiencies. Further, the treatment process can be costly especially when additional treatment is required for metal and ion attenuation. Recent research has demonstrated the potential to apply fly ash in active treatment systems for AMD treatment and amelioration. Active treatment technologies make use of some chemical addition or advanced technology e.g. membrane technologies and ion exchange resins. Whilst active treatment technologies are often more expensive than passive treatment systems, active treatment occurs at a faster rate and treatment efficiencies are more controllable and effective. Based on the aforementioned problem and numerous research investigations, the following questions were raised:

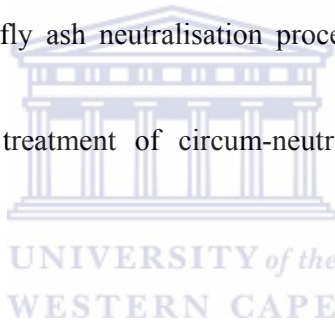
- Does fly ash provide a feasible alternate for active AMD neutralisation and amelioration, specifically sulphate attenuation?
- How does fly ash compare to existing AMD treatment technologies?
- Does fly ash have the potential to treat circum-neutral mine waters?

1.3 OBJECTIVES OF STUDY

This study was initiated due to concerns raised with regards to the environmental impact of both fly ash disposal and AMD production. More importantly, conventionally applied AMD chemical treatment methods e.g. limestone, are not very effective in the reduction of sulphate, which can be present in significant concentrations. The mutual beneficiation associated with the application of fly ash

for AMD treatment and prevention has demonstrated potential for large scale active neutralisation of AMD. The objectives of this thesis are thus to:

- Demonstrate the active neutralisation of AMD with fly ash at beaker and large scale.
- Investigate the sulphate reducing capability of fly ash in AMD. The required sulphate concentrations will be dependant upon the intended use by the mine after pre-treatment. The three general categories are potable water quality, high quality industrial water and water for discharge. The South African National Standard, SANS 241:2006, specifies the limits for contaminants for the potable water applications where sulphate concentrations <400 mg/l are allowed. However, for purposes of this investigation, sulphate concentrations are compared to those achieved with state-of-the-art treatment technologies since a specific application after pre-treatment was not identified.
- Compare the active fly ash neutralisation process with the commonly used limestone treatment.
- Investigate fly ash treatment of circum-neutral water aimed at sulphate attenuation.



1.3.1 APPROACH

The protocol applied in meeting the objectives of this study was to actively neutralise AMD using fly ash, from selected coal mining and power plant sites, at both beaker and large scale. Standard analytical procedures were applied for the analysis of the liquid and solid portions. The feasibility study was conducted by comparing the performance of limestone versus fly ash to actively treat the AMD in beaker experiments.

1.4 STUDY AREA

This study was initially aimed at a site specific study using fly ash from the Arnot power plant to neutralise AMD emanating from Arnot colliery. Due to drought conditions, AMD was not abundantly available to conduct the necessary experiments.

Therefore, AMD that was sufficiently acidic, containing significantly high concentrations of sulphate and emanating from a colliery that was situated in close proximity to various power plants was selected. Fly ash samples from various power plants, including Arnot, Hendrina and Kriel were characterised and based on certain critical criteria, a single source was selected. Arnot fly ash and two different qualities of AMD emanating from Landau colliery namely Skoongesig and Toeseep AMD were selected for the experimental aspect of this study. The Skoongesig AMD results from underground seepage. Toeseep AMD results from the seepage of water from the coal discard dump which is then stored in the toe dam. The difference in the two AMD samples was a difference in sulphate concentration. The Skoongesig AMD sample contained sulphates in the region of 5000 mg/l whilst the Toeseep AMD contained sulphates in excess of 20000 mg/l. These samples were expected to provide for a good comparative study between fly ash and alternate AMD treatment processes, as well as an indication of the sulphate attenuation potential of Arnot fly ash. Treatment of circum-neutral mine water was tested with AMD emanating from Middleburg mine in the Mpumalanga, Witbank region and fly ash from Arnot, Duvha and Hendrina power plants. The locations of power plants are shown in Figure 1.1.

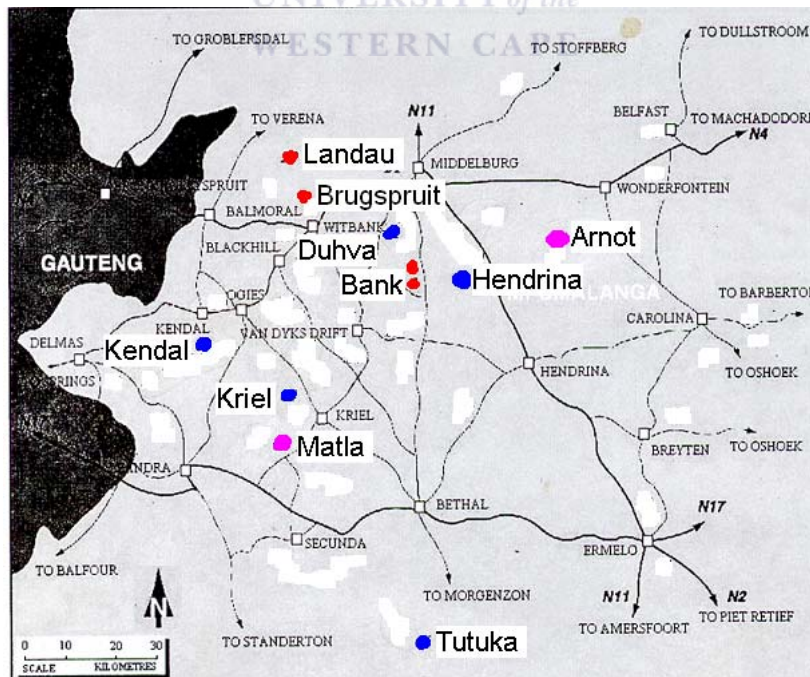


Figure 1.1: Map detailing the location of the power plants (Arnot, Hendrina, Kriel and Duvha) and coal mine (Landau) that provided the samples for this study.

1.5 OUTLINE OF THIS THESIS

The remainder of the thesis is divided into the following chapters:

Chapter 2: Literature Review

A review of some existing AMD treatment technologies, with emphasis on sulphate reduction is presented. A comparison of the existing technologies concludes the chapter.

Chapter 3: Experimental Methodology

A description of the sampling, experimental and analytical methods applied in this study is presented.

Chapter 4: Characterisation and selection of AMD and fly ash for neutralisation experiments.

The analysis of fly ash and AMD, which determined their suitability for the experimental work, are presented. The rationale behind their selection is also explained.

Chapter 5: Beaker and large scale neutralisation experiments at various fly ash:AMD ratios.

Results of neutralisation experiments conducted at both beaker and large scale are discussed. The results of the sulphate concentrations are compared to the results of the alternate treatment technologies presented in chapter 2.

Chapter 6: Feasibility study of fly ash treatment versus limestone treatment of AMD.

The feasibility of applying fly ash for AMD treatment is presented by means of a comparative study between fly ash and the conventionally applied limestone treatment. Results are tabulated to compare the neutralisation potential and sulphate reducing capabilities of both materials.

Chapter 7: Treatment of circum-neutral mine water

Beaker scale experiments were conducted to determine the effectiveness of fly ash to treat circum-neutral mine water, primarily focusing on sulphate attenuation.

Chapter 8: Conclusions and Recommendations

Conclusions are drawn from the data obtained in chapters 5, 6 and 7. Recommendations for further investigations are proposed.



CHAPTER 2

LITERATURE REVIEW: COMPARISON OF AMD/SULPHATE TREATMENT PROCESSES

2.1 INTRODUCTION

Most AMD treatment technologies concentrate primarily on the acid neutralising and toxic metal removal aspect. More recently, attention is being drawn to the elevated concentration of sulphate in mine waters. Whilst sulphate is not generally associated with any toxic effects, its presence at concentrations tend to exceed the limits for either domestic use, industrial use or discharge purposes. Industries engaged in water treatment practices are now paying particular attention to sulphate concentrations and the capability of the various technologies to reduce these concentrations. South Africa, in particular, has made significant progress in AMD neutralisation and sulphate treatment. This would be apt in view of the broad mining activities, ranging from gold to coal and the generation of acidic waters at these mines.

The various treatment processes can be broadly categorised as follows:

- Chemical treatment.
- Membrane treatment.
- Ion exchange treatment.
- Biological sulphate treatment.

This list is not comprehensive but covers a range of various processes that are available for AMD treatment. These range from simple chemical treatment options, which include limestone/lime and the Savmin process to the more complex membrane and ion exchange systems (Table 2.1).

Table 2.1: List of AMD treatment processes

Chemical treatment	Membrane systems	Ion exchange	Biological sulphate removal
Limestone/lime	Reverse osmosis	GYP-CIX	Bioreactors
Savmin process	Electro-dialysis reversal (EDR)		Constructed Wetlands

The remainder of this chapter reviews the various treatment processes under the above categories.

2.2 CHEMICAL TREATMENT

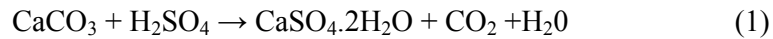
2.2.1 Lime and Limestone

Traditionally, limestone is used for the neutralisation and sulphate removal of acidic mine waters through gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) precipitation. The solubility product of gypsum limits sulphate attenuation. Recently, an integrated limestone/lime process was developed, capable of reducing sulphate concentrations to less than 1500 mg/l. The process was applied at pilot scale ($10 \text{ m}^3/\text{day}$) to mine water emanating from the Navigation coalmine near Witbank in South Africa (Geldenhuis et al., 2001). The quality of this particular mine water is very acidic (pH 2.1) and high in sulphate, calcium and magnesium. Using the integrated limestone/lime process, AMD was firstly neutralised with limestone (CaCO_3) with a resulting decrease in acidity and increase in pH. The presence of dissolved Ca^{2+} lead to CaSO_4 precipitation (Geldenhuis et al., 2001) thereby reducing the sulphate load. Sulphate removal was maximised by raising the pH to >12 with lime ($\text{Ca}(\text{OH})_2$) resulting in $\text{Mg}(\text{OH})_2$ precipitation and gypsum crystallisation.

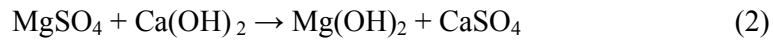
A unique CaCO_3 handling and dosing system, with a capacity of 10 MI/d was designed and implemented in the first stage of the Navigation coalmine water treatment process. This consisted of an inclined (7°) concrete slab onto which the CaCO_3 powder was slurried with a water jet and collected in a slurry tank through

gravity flow. The treatment process consisted of three stages as illustrated in Figure 2.1.

Stage 1: Limestone neutralisation to raise the pH to 7. CO₂ was produced at this stage with gypsum precipitation (equation 1) (Geldenhuis et al., 2001).



Stage 2: Lime treatment to raise the pH to 12 for Mg(OH)₂ precipitation and gypsum crystallisation (equation 2) (Geldenhuis et al., 2001).



Stage 3: Adjustment of the pH with CO₂ recovered from stage 1 and CaCO₃ precipitation.

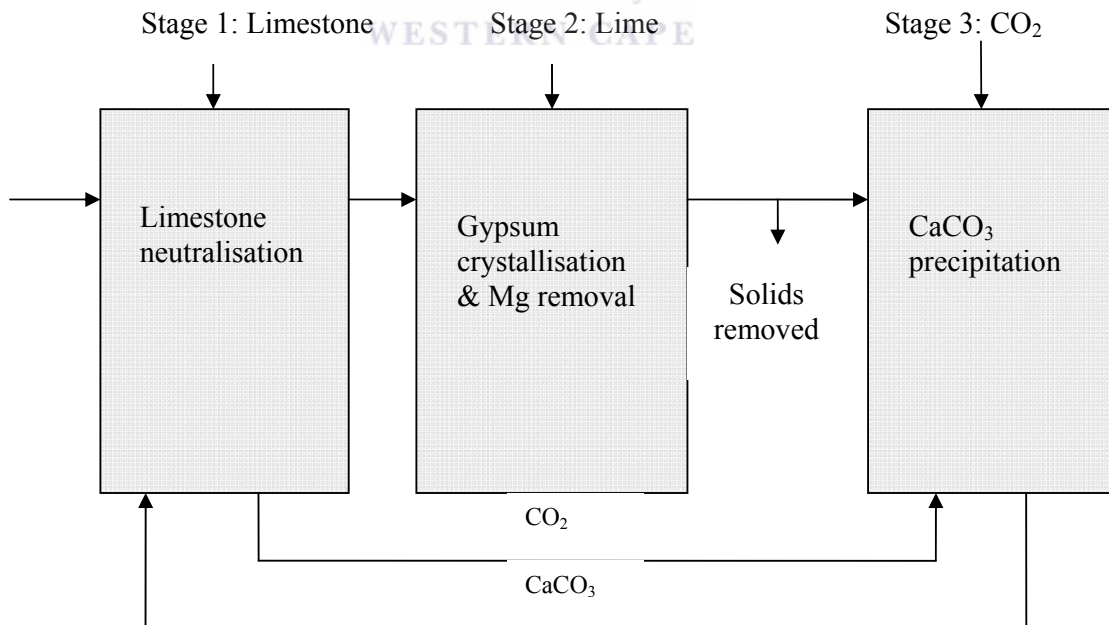
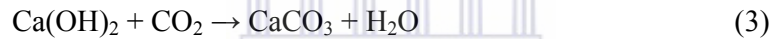


Figure 2.1: Schematic illustration of integrated limestone/lime treatment process at Navigation pilot plant (Geldenhuis et al., 2001).

The result of the treatment process is presented in Table 2.2 by comparison of the feed water with each treatment stage.

Table 2.2: Water qualities of the feed and treated water of the integrated lime/limestone process (Geldenhuys *et al.*, 2001)

	Acid Feed Water	Treated Water		
		CaCO ₃	Ca(OH) ₂	CO ₂
pH	2.10	7.68	12.26	8.50
SO ₄ (mg/l)	3000	1900	1094	1219
Ca (mg/l)	420	636	829	542
Mg (mg l)	160	147	0	3.03
Na (mg/l)	41	40	47	46.80
Mn (mg/l)	17	13	0	0.01
Cl (mg/l)	16	17	-	-
Alkalinity (mg/l)	-3000	100	940	50

When the pH was raised to >12 with lime, it was found that the sulphate was further reduced from 1900 to 1094 mg/ l at Navigation. Improved sulphate removal was achieved when magnesium was removed by Mg(OH)₂ precipitation at the high pH as this lead to further gypsum precipitation (equation 2). The increase in sulphate observed in the third stage (Figure 2.1) was attributed to the dissolution of gypsum washed out from the second stage. However, there existed a limitation to sulphate removal, as the final sulphate concentration did not meet the requirements for discharge (500 mg/ l). As can be seen from Table 2.2, the acidity decreased and an increase in buffer capacity stabilised the pH of the water. The increase in calcium concentration was attributed to the dissolution of lime from stage 2.

A sludge waste product containing a mixture of gypsum and magnesium hydroxide is produced by this process. The sludge that settles down after treatment is pumped to a lined hazardous waste storage area. The density of the sludge, which was not provided in literature, if high, could create problems for pumping and removal. Storage costs per annum are estimated to be high for scale up. The sludge has a very high water content thereby reducing water recovery.

2.2.2 Savmin Process

The Savmin process utilises several successive precipitation reactions to treat acid mine drainage. This process was applied at pilot scale at the Stilfontein gold mine (Anglogold) in South Africa (Sibiliski, 2001). 30 ML of mine water was being pumped daily and discharged into the nearby Koekemoerspruit. The process flow and various stages specific to this plant are shown in Figure 2.2.

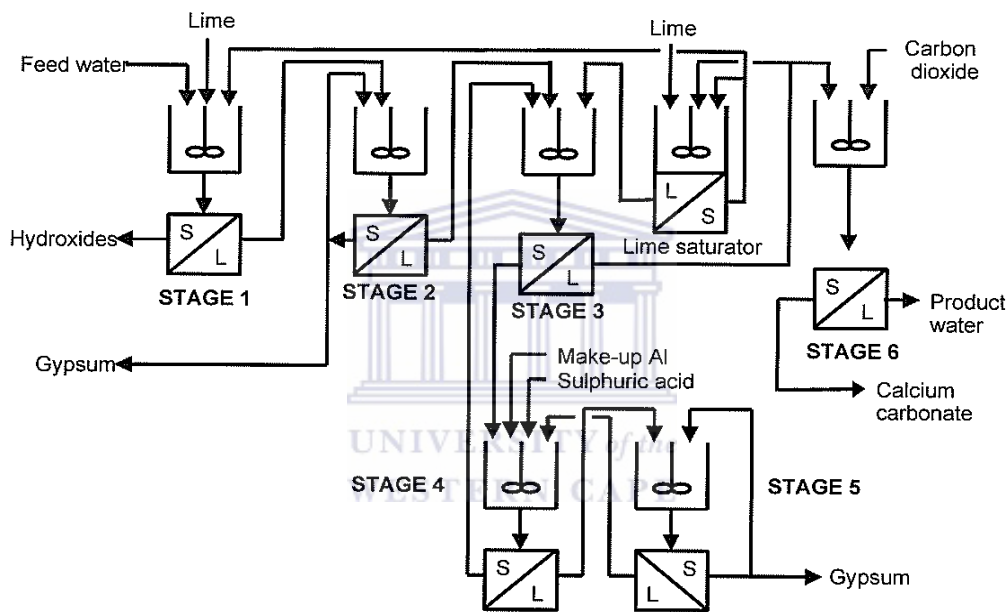
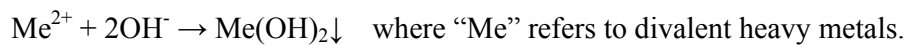


Figure 2.2: Savmin process applied at Stilfontein gold mine (Sibiliski, 2001)

Stage 1: Precipitation of heavy metals and magnesium

Lime was added to raise the pH of the feed water to pH 12.0-12.3 where heavy metals and magnesium were precipitated as hydroxides (Sibiliski, 2001).

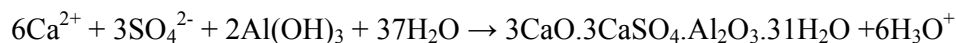


Stage 2: Gypsum de-supersaturation

The solution from stage 1 was contacted with gypsum seed crystals where gypsum precipitated from the supersaturated solution and filtered out. Some of the precipitated gypsum is returned to Stage 2 mixing tank to provide the seed crystals required for rapid crystallisation of the dissolved calcium sulphate.

Stage 3: Ettringite precipitation

Aluminium hydroxide which was regenerated and recovered from stage 4 was added to effect calcium and sulphate removal via ettringite (a calcium aluminium sulphate mineral) precipitation according to the following equation (Sibiliski, 2001):



Additional lime was introduced at this stage to control the final pH at 11.8.

Stage 4 & 5: Aluminium hydroxide recycling

Aluminium hydroxide from stage 3 was recycled by decomposing the above ettringite slurry with sulphuric acid at pH 6.5 in gypsum-saturated water. The calcium and sulphate remained in solution as supersaturated calcium sulphate by controlling the liquid-to-solid ratio of the solution. The aluminium hydroxide was recovered by thickening/filtration and recycled to stage 3. The supersaturated gypsum solution was contacted with seed crystals to precipitate and remove gypsum. The remaining solution is recycled.

Stage 6: Carbonation

The pH of the solution from stage 3 was lowered with carbon dioxide to precipitate calcium carbonate which is removed by filtration.

The precipitation reactions in the treatment process are performed in conventional stirred tank reactors at ambient temperature and pressure.

The water quality obtained with the Savmin process at Stilfontein gold mine are compared with respect to discharge, potable and high quality industrial water

standards are listed in the Tables 2.3-2.5. The target water quality for individual applications are obtained from the South African National Standards.

Table 2.3: Incoming and outgoing concentrations of mine water treated by Savmin process at Stilfontein compared to discharge quality water (Sibiliski, 2001)

Element	Incoming	Outgoing	% Removal	Target Quality
Sulphate, mg/l	682	359	47	500
Calcium, mg/l	196	142	28	300
Aluminium, mg/l	<1	<1	0	20
Sodium, mg/l	142	138	3	115
Chloride, mg/l	61	62	-2	140
Magnesium, mg/l	83	<1	>99	NA
Potassium, mg/l	8	11.1	-39	NA

The dissimilarity in incoming water quality was due to the difference in sampling periods and times. The incoming and outgoing water quality data listed in Table 2.3 consists of an average of one month's data. Data presented in Table 2.4 also consists of a monthly average, but sampled over a different period to that presented in Table 2.3. The data used for comparison to high quality industrial water, was sampled over a shorter period (~5 days).

Table 2.4: Incoming and outgoing concentrations of mine water treated by Savmin process at Stilfontein compared to potable quality water (Sibiliski, 2001)

Element	Incoming	Outgoing	% Removal	Target Quality
Sulphate, mg/l	685	167	76	200
Calcium, mg/l	192	113	41	150
Aluminium, mg/l	<1	<1	0	0.5
Sodium, mg/l	144	143	1	200
Chloride, mg/l	62	63	1	200
Magnesium, mg/l	83	<1	>99	50
Potassium, mg/l	9	11	-39	100

Table 2.5: Incoming and outgoing concentrations of mine water treated by Savmin process at Stilfontein compared to high quality industrial water (Sibiliski, 2001)

Element	Incoming	Outgoing	% Removal	Target Quality
Sulphate, mg/l	649	69	89	50
Calcium, mg/l	162	91	44	50
Aluminium, mg/l	<1	<1	0	NA
Sodium, mg/l	144	145	-1	40
Chloride, mg/l	66	65	2	NA
Magnesium, mg/l	83	<1	>99	NA
Potassium, mg/l	9.4	10	-6	NA

From the data tabulated in Tables 2.3 – 2.5, it can be concluded that the discharge and potable water quality were achieved whereas the target water quality for industrial purposes were not.

Metal hydroxide, calcium sulphate and calcium carbonate sludge was produced. These differed depending on the target water quality. The metal hydroxide sludge varied from 0.98 to 1.18 kg/m³ water, whereas the gypsum varied from 0.67 to 2.10 kg/m³ water (Sibiliski, 2001). Whilst the high-grade gypsum and calcium carbonate

could be used in various other industrial applications, the metal hydroxide sludge has to be disposed of in an environmentally acceptable manner.

2.3 MEMBRANE SYSTEMS

2.3.1 Reverse Osmosis

Reverse osmosis (RO) is a pressure driven process that forces a solvent from a region of high solute concentration through a semi permeable membrane to a region of low solute concentration by applying a pressure in excess of the osmotic pressure. The basic components of a membrane system consist of the membranes, pressure vessels that house the membranes coupled with the structure which cohere the configuration such as high pressure pumps and pre/post treatment of the plant (Aptel and Buckley, 1996).

Pre-treatment via filtration and chemical treatment of the feed water is necessary to prevent fouling of the RO membrane by suspended solids, mineral precipitation or microbial growth. The accumulation of material on the membrane surface makes them highly susceptible to fouling and subsequent loss of production capacity (Ridgway and Flemming, 1996).

The pressure of the high pressure pump is dependent on the quality of the feed water. For example, sea water with a high salt content requires 40 – 70 bar pressure whilst fresh water varies between 2 – 17 bar (Buckley and Hurt, 1996). The RO membrane permits the passage of water molecules but is a barrier to most of the dissolved solids in the water. The membrane assembly consists of a pressure vessel and a membrane capable of withstanding a high pressure gradient. Its design is such that only water is allowed to pass through while preventing the passage of solutes e.g. salts. Membrane configurations vary, with the two most common configurations being spiral-wound and hollow-fibre (Taylor and Jacobs, 1996).

The desalinated water from RO systems is usually very corrosive and is conditioned to protect downstream pipelines and storages prior to distribution. This post-

treatment involves adjusting the pH, alkalinity and hardness (Taylor and Jacobs, 1996).

The life of RO membranes is largely affected by mechanical failure and fouling. The development of low pressure membranes and improved pre-treatment methods have improved the efficiency of the membrane and reduced operational costs (Taylor and Jacobs, 1996). Treatment of sulphate enriched effluents by reverse osmosis results in the production of brine as the waste product. Depending on the composition and quantities produced, brine disposal and/or treatment have proved to be complex, costly to treat and an even greater environmental threat than the mine water. Irrespective, reverse osmosis finds many applications in drinking water purification, water and wastewater purification, desalination etc. These systems can remove up to 90-95 % of all total dissolved solids (TDS).

Sasol Secunda

Sasol Secunda, a petrochemical company in South Africa, utilises a technology that produces synthetic fuels and chemicals from low-grade coal. Sasol Mining is responsible for the supply of coal to the synthetic fuels and chemical plants in South Africa. There are two regional coal mining operations: The Sigma Colliery and the Secunda Collieries. The coal mining operations have resulted in large volumes of mine water being generated, which are characterised by high TDS and sulphate concentrations (du Plessis and Swartz, 1992; INAP Report 2003). Environmental policy dictates that water of this quality cannot be discharged into water resources without proper treatment. A Tubular Reverse Osmosis (TRO) pilot plant was investigated by Sasol Secunda for desalination. The schematic of the TRO plant design is shown in Figure 2.3.

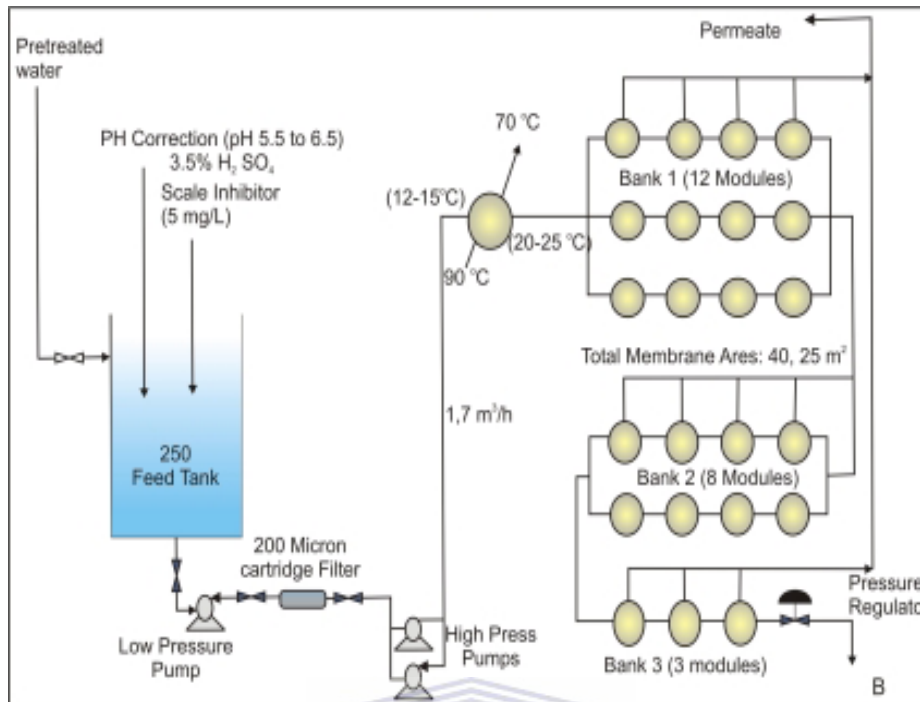


Figure 2.3: TRO Plant Design applied at the Sasol, Secunda desalination plant

Due to the high suspended solid concentration (174 mg/l), the raw mine water had to be pre-treated to reduce the suspended solids as well as eliminate bacteria to inhibit scaling and minimise hydrolysis of the membranes. This involved a combination of chemicals (FeCl_3) and filtration (du Plessis & Swartz, 1992). Sulphuric acid was then used to adjust the pH between 5.5 and 6.5 to minimise hydrolysis of the membranes. A scale inhibitor (Flocon) was added to the pre-treated water to inhibit scaling. The feed water was supplied to the module banks via a series of pumps at a flow rate of $1.7 \text{ m}^3/\text{h}$. A heat exchanger regulated the temperature of the feed to the modules. Water recovery was controlled by continuous adjustment of the system pressure using a pressure regulator between 30-40 bars (du Plessis & Swartz, 1992).

The results of the TRO treatment are tabulated in Table 2.6. The table presents a comparison of feed water quality at various stages in the treatment process and the product water quality

Table 2.6: Water quality from Secunda TRO plant at different treatment stages (du Plessis & Swartz, 1992)

	Raw mine water	Clarifier effluent	RO feed	RO concentrate	RO product
Sulphate, mg/l	2200	2150	2125	>3000	14
Sodium, mg/l	917	914	920	2222	26
Chloride, mg/l	220	305	313	754	26
Calcium, mg/l	176	176	176	452	2.0
Flouride, mg/l	3.0	3.5	3.0	6.0	1.1
Iron, mg/l	0.3	0.3	0.3	0.7	0.1
pH	8.4	7.1	7.1	6.8	6.3
TDS, mg/l	3.959	3.919	4.092	8.720	104
TSS, mg/l	174	76	47	347	<10
COD, mg/l	70	45	40	900	<2
Turbidity	9.0	6.0	0.9-1.5	9.0	0.9

The concentration of suspended solids in the mine water was reduced during pre-treatment via flocculation and filtration. TRO treatment reduced the sulphate concentration by 99%, in addition to a significant reduction in the monovalent and divalent ions. Fouling of the membranes was not irreversible and these required cleaning every 350 hrs.

Whilst the TRO treatment process was successful in improving the overall quality of the mine water, operating costs associated with cleaning and replacing of membranes were found to be high depending on the feed water quality.

Anglo Coal Emalahleni Water Treatment Plant

Anglo Coal has embarked on a mine water treatment project in the Witbank-Middleburg area of Mpumalanga at Emalahleni. The Emalahleni Water Treatment Plant uses a combination of precipitation and membrane desalination technologies to treat AMD from three mine sources to produce 20 ML/d of potable (SABS 241, 1999; Günther *et al.*, 2006). A combination of two processes developed by the Council for Scientific and Industrial Research (CSIR) in South Africa was applied. These were the limestone/lime neutralization and gypsum crystallisation processes, used as pre-treatment of mine water, followed by green sand filters to remove residual manganese from mine water, before being processed through ultrafilters to remove any microorganisms and suspended solids. The final processing step of desalination was performed using reverse osmosis (RO) membranes. The brine (dissolved salts removed from the RO membranes), which is highly oversaturated in gypsum salts was treated with lime to remove the over saturation (Günther *et al.*, 2006). This last cycle was performed a total of three times to increase the water recovery, maximise the solids removal and minimise the volume of brine. The basic process flow diagram is depicted in Figure 2.4.

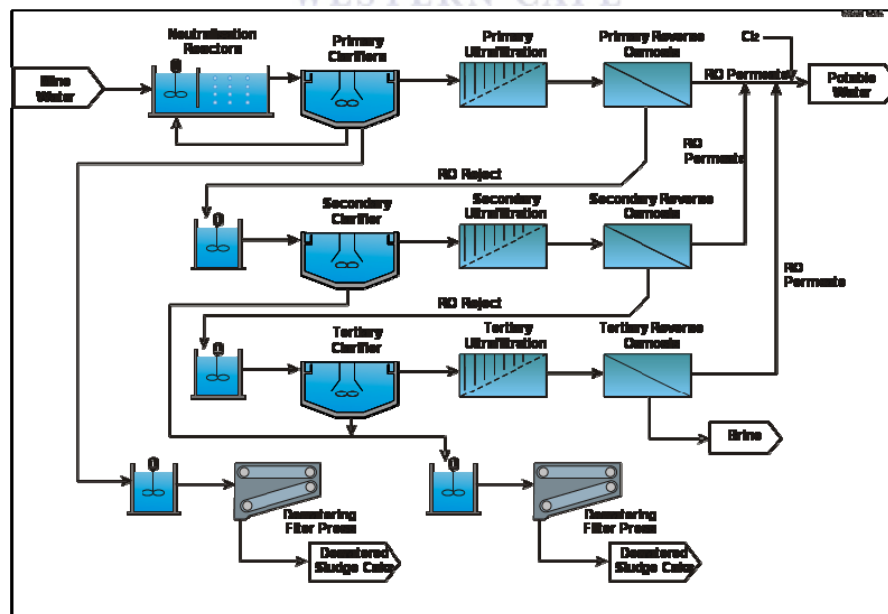


Figure 2.4: Process Flow Diagram of Emalahleni mine water treatment project (Water Sewage & Effluent, 2006)

The plant runs at a 99% recovery rate, and a number of research and development projects have been undertaken to investigate the utilisation of the gypsum and brine by-products of the purification process. Two projects investigating the utilisation of the gypsum waste are:

- conversion into pure by-products like sulphur, limestone and magnesite,
- and creation of building and mining products.

Summarised in Table 2.7 is the design feed water qualities, with corresponding treated water qualities of the Emalahleni mine water treatment plant (Günther *et al.*, 2006). All results are reported relative to the target water quality range for each element as specified by the South African Water Quality Guidelines for Fresh Water, 1995.

Table 2.7: Design feed and treated water qualities of the Emalahleni mine water treatment plant

Water quality parameter	Feed water	Treated water	Class 1 drinking water limit
pH	2.7	6.0 - 9.0	5.0-9.5
Acidity, mg/l as CaCO ₃	1050	0	NA
Electrical Conductivity, mS/m	460	<70	<150
Total dissolved solids, mg/l	4930	<450	<1000
Calcium, mg/l	660	<80	<150
Magnesium, mg/l	230	<30	<70
Sodium, mg/l	130	<100	<200
Potassium, mg/l	13	<25	<50
Sulphate, mg/l	3090	<200	<400
Chloride, mg/l	70	<100	<200
Iron, mg/l	210	<0.01	<200
Manganese, mg/l	35	<0.05	<100
Aluminium, mg/l	40	<0.15	<300

The treated water quality passed drinking water quality requirements with respect to all elements listed in Table 2.7 which were reduced to below the limits prescribed by

the South African National Standard for Class 1 drinking water (SANS 241:2006). Sulphate reduction was very successful but the process is highly complex with many treatment stages.

2.3.2 Electro-dialysis Reversal (EDR)

Electro-dialysis (ED) is an electrochemical separation process in which charged ion selective membranes and an electrical potential difference are used to separate ionic species from an aqueous solution and other uncharged components. Water flows between alternatively placed cation and anion permeable membranes, which are built into a so-called stack. Direct current provides the motive force for ion migration through the membranes and the ions are removed or concentrated in the alternate water passages by means of perm-selective membranes. The cation exchange membrane is negatively charged and is permeable to cations such as sodium (Na^+) and calcium (Ca^{2+}) while being impermeable to anions such as chloride (Cl^-) and sulphate (SO_4^{2-}). Anion exchange membranes behave conversely. This perm-selectivity forms the basis of the electro-dialysis systems. This principle is further illustrated for saline feed water in Figure 2.5 below.

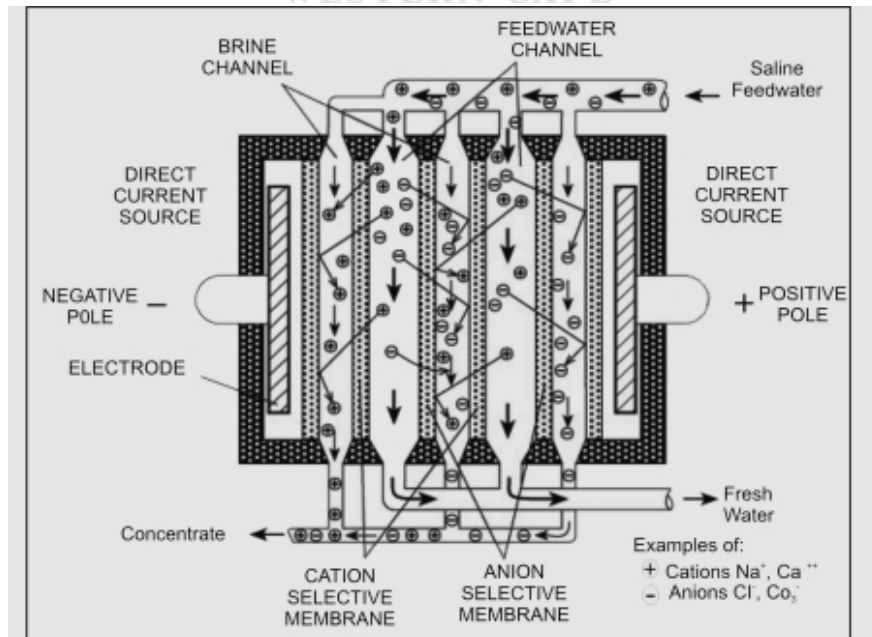


Figure 2.5: Principle of Electro-dialysis

Electro-dialysis reversal (EDR) operates on the same basic principles as the standard ED process. However, in EDR, the polarity of the electrodes is periodically reversed (~ 3 to 4 times per hour) by means of motor operated valves. The fresh water product and wastewater outlets from the membrane stack are interchanged and the ions are transferred in opposite directions across the membrane. The process aids in breaking up and flushing out scale, slime and other deposits from the cells. The product water emerging from the previous brine/concentrate cells is usually discharged to waste for a period of one to two minutes until the desired water quality is restored. The polarity reversal system greatly reduces maintenance time. The capability of EDR to control scale precipitation more effectively than standard ED is a major advantage of this process, especially for applications requiring high water recovery. However, it is a more complicated operation and maintenance requirements necessitate more labour and a greater skill level than those of RO systems. EDR is widely used in desalination of brackish water and to some extent for the production of potable water (Malleville *et al.*, 1996).

An EDR pilot plant was installed and operated for 6 000 hrs on “non-scaling mine water” from a gold mine in the Free State of South Africa, to determine its scaling potential as opposed to waters with a known high scaling potential e.g. sodium chloride type waters. Membranes employed on this plant were characterised as pH resistant, resistant to fouling and impermeable to water under pressure. The data of the pilot plant trials are presented in Table 2.8. The feed water required pre-treatment to remove potential membrane foulants e.g. iron and manganese which had to be removed to concentrations of less than 0.3 mg/l and turbidity to less than 2.5 mg/l (Juby, 1992).

Table 2.8: Data from a 1.6 l/s EDR pilot plant for treating brackish water (Juby, 1992)

	Raw mine water	EDR feed	EDR product	EDR brine
Chloride, mg/l	1750	1750	375	4990
Sodium, mg/l	1400	1400	200	3110
Sulphate, mg/l	74	74	5	340
Calcium, mg/l	10	100	25	400
Total Fe, mg/l	1.0	0.2	0.15	0.4
Total Mn, mg/l	0.6	0.3	0.16	1.1
Barium, mg/l	0.6	0.6	0.3	1.1
pH	6.42	6.42	6.14	5.42
Turbidity, NTU	20	0.91	0.36	0.40
TDS, mg/l	3200	3200	640	9150

Pre-treatment of the raw mine water was necessary to prevent membrane fouling. This involved:

- Oxidation of iron and manganese with potassium permanganate.
- Addition of a flocculent.
- Primary and secondary filtration.
- Addition of a sodium hexametaphosphate anti-scalent to prevent scaling by barium sulphate.

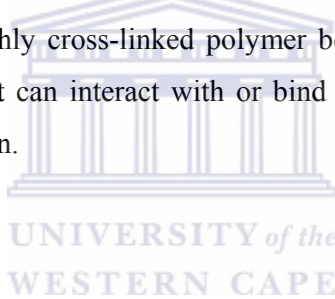
Overall, the EDR plant performed well in the treatment of the “non-scaling” mine water. The dissolved salts, sodium and chloride were significantly reduced. However, extensive pre-treatment of the raw water was a necessity and the associated costs could render the technology unfeasible.

Salt precipitation on membranes limits industrial applications of EDR systems. Numerous investigations have been undertaken to address this problem. Pilat (2003) evaluated the kinetics of precipitation, based on TDS increase, in 1, 10 and 30 days of

operation using styrene-divinyl-benzene membranes with a capacity of 30 l/h (domestic use). High reversal frequencies theoretically improve the desalination. However, with very frequent reversal, water in the paths of desalination becomes mixed with the concentrate and desalination is either incomplete or non-existent. Thus, one cycle was optimised at 30 minutes (Pilat, 2003). The results indicated that whilst reversal almost completely restored the permeability of the membranes, the precipitation increase within one cycle essentially grew. The high efficiency of reversal of these membranes concluded the possibility of application in domestic systems. Industrial systems applied for the desalination of high salt content waters require acid washing of the membranes with or without dismantling.

2.4 ION EXCHANGE

Ion exchange is a science that makes use of ion exchange resins in its applications. Ion exchange resins are highly cross-linked polymer beads containing positively or negatively charged sites that can interact with or bind to an ion of opposite charge from the surrounding solution.



2.4.1 GYP-CIX

The use of ion exchange resins for AMD treatment was previously limited due to the presence of calcium sulphate in neutralised AMD, which resulted in scaling, or fouling of the ion exchange resin thereby affecting its performance. The patented GYP-CIX process (US Patent 5057298), which utilises a counter current fluidised bed ion exchange method and a single fluidised bed bath regenerator, was specifically developed for the desalination of AMD and to overcome the above limitation. This process is unique in that it makes use of low cost sulphuric acid (H_2SO_4) and lime slurry ($Ca(OH)_2$) to regenerate the cation and anions respectively, which produce gypsum as a solid waste product. It is particularly well suited to the removal of dissolved sulphate from water that is close to saturation with gypsum. The GYP-CIX ion exchange process was applied to underground mine water discharged by the Grootvlei mines in South Africa (Schoeman and Steyn, 2001). The process flow schematic of this treatment plant is shown in Figure 2.6.

The cation resin is regenerated with 10 % sulphuric acid solution, seeded with gypsum crystals recirculated from a stirred tank. Since calcium sulphate solubility is low, the gypsum seed crystals act as precipitation nuclei thereby avoiding the formation of supersaturated solutions. Upon completion of resin regeneration, the gypsum is washed out and settled in a clarifier. The washed resin is then conditioned by thorough rinsing with the decationised water and returned to service. The anion resin is regenerated in a similar manner to the cation resin using a 2 % lime solution seeded with gypsum crystals. This process also produces gypsum due to the low solubility of lime. After the gypsum is removed, the anion resin is rinsed with product water and then returned to service.

Continuous precipitation of gypsum during both cation and anion regeneration allows for re-use of the solutions thereby minimising reagent consumption. The GYP-CIX process is best suited to waters with sulphate concentrations below 1500 – 2000 mg/l. At higher sulphate concentrations, liming is a cheaper treatment option (INAP, 2003). The main disadvantage of the GYP-CIX process is the volume of gypsum sludge produced during regeneration of the ion exchange resins.

2.4.2 Metal Precipitation and Ion Exchange (GYP-CIX)

Feng *et al.*, 2000, applied a combination of metal precipitation and ion exchange for the treatment of acid mine water emanating from a gold mine in South Africa at laboratory scale. The metal precipitation process flow is indicated in Figure 2.7.

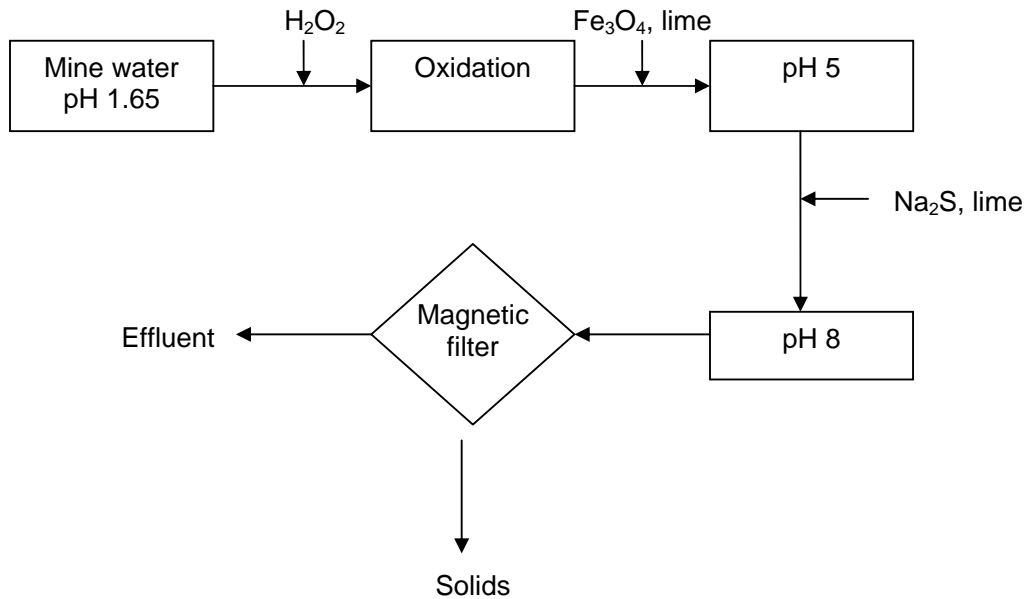


Figure 2.7: Flow sheet of the metal precipitation process for a gold mine water treatment project

Hydrogen peroxide (H_2O_2) was firstly added to the mine water to oxidise the divalent iron and manganese before lime precipitation. The extent of oxidation was determined by the ferric concentration. Thereafter, magnetite (Fe_3O_4) was added at a concentration of 0.5 g/l for magnetic seeding. Lime was also added at this stage to raise the pH to 5, primarily to prevent hydrogen sulphide (H_2S) generation with the addition of sodium sulphide (Na_2S). The pH was increased to pH 8 by further addition of lime where precipitation of metal sulphides and hydroxides occurs. The precipitates are separated via magnetic filters producing separated solids and partially treated mine water. Table 2.9 presents the results of the metal precipitation process applied to water emanating from a gold mine. The results compare the heavy metals, ions and toxic elements in the feed water to the treated water. Toxic element data was not provided by the previous studies mentioned in the literature review, however this does not imply that toxic elements were not present in the waste and treated water.

Table 2.9: Results of the treated mine water by the metal precipitation process applied at a gold mine in South Africa (Feng *et al.*, 2000)

	Feed	Product		Feed	Product
pH	1.65	8.0	Pb ²⁺ , mg/l	0.349	0.0015
Turbidity	92.9	1.8	Si ²⁺ , mg/l	23.8	0.919
Al ³⁺ , mg/L	249	0.267	Sr ²⁺ , mg/l	1.77	1.06
Ba ²⁺ , mg/L	0.0749	0.0281	Ti ²⁺ , mg/l	3.55	0.005
Ca ²⁺ , mg/L	300	823	Zn ²⁺ , mg/l	10.1	0.0001
Cr ³⁺ , mg/L	4.85	0.0001	Zr ²⁺ , mg/l	0.0919	0.0500
K ⁺ , mg/L	558	556	Cd ²⁺ , mg/l	0.260	0.0018
Na ⁺ , mg/L	345	345	Co ²⁺ , mg/l	1.94	0.005
Cu ²⁺ , mg/L	1.80	0.0020	F ⁻ , mg/l	431	44.0
Fe*, mg/L	942	0.214	Cl ⁻ , mg/l	954	478
Mg ²⁺ , mg/L	359	348	Br ⁻ , mg/l	280	258
Mn*, mg/L	113	0.0899	SO ₄ ²⁻ , mg/l	6305	3353
Ni ²⁺ , mg/L	5.75	0.0441	PO ₄ ³⁻ , mg/l	337	0.0005

* Total concentration

As can be seen from the data in Table 2.9, dissolved metals could be precipitated by the addition of lime and sodium sulphide. Calcium, magnesium, sodium, potassium, sulphate, fluoride, chloride and bromide concentrations were still high and could not be reduced by precipitation alone. Since the turbidity was within limits (< 4 NTU) for treatment by ion exchange, anion and cation resins were used to decrease the salinity of the effluent. The ion exchange process applied was very similar to the GYP-CIX process with slight differences in the regeneration of the resins. All the cation (calcium, magnesium, sodium and potassium) concentrations were reduced to <3 mg/l following the cation exchange process (Feng *et al.*, 2000). The anions were reduced by >90 % following the anion exchange process (Feng *et al.*, 2000).

2.5 BIOLOGICAL SULPHATE REMOVAL

Biological removal of sulphate as sulphide or sulphur is possible provided that a suitable carbon and energy source e.g. ethanol is available. The sulphate is reduced to

sulphide which is undesirable and thus is removed from the treated effluent by precipitation as metal sulphides. Excess sulphide can be oxidised to elemental sulphur in an aerobic reactor for further removal. Alkalinity is also generated, which allows for neutralisation of the acid water. Biological sulphate removal is applied in various wastewater treatment technologies. These include:

- Bioreactors,
- Constructed wetlands,
- Alkalinity producing systems and
- Permeable reactive barriers (PRB).

2.4.1 Bioreactors

Maree *et al.*, (2001) demonstrated that sulphate rich mine water could be treated biologically on a 400 m³/day plant. The process was supplied with a mixture of ethanol and sugar as the carbon and energy source. The plant process included an anaerobic stage for sulphate reduction to sulphide, a H₂S stripping stage, conversion of H₂S to elemental sulphur or gypsum via CO₂ addition, and an aerobic stage for removal of residual chemical oxygen demand (COD) and CaCO₃ precipitation. The schematic of the anaerobic reactor is shown in Figure 2.8.

Feed water from a CaCO₃ treatment stage was supplied to the bioreactor at a rate of 8 to 16 m³/h. The reactor was inoculated with 10 m³ anaerobic digester sludge. The H₂S stripping step was fed at 0.3 m³/h. 0 to 0.5 g sugar and 0.25 to 1.5 ml alcohol (75% ethanol & 25% propanol) were added per litre of feed water as the carbon and energy source. 25 mg/l ammonium sulphate and 5 mg/l phosphoric acid were added to maintain the COD:N:P ratio at 100:5:1. 3 mg/l iron(II) was the only trace element added as all trace elements required by sulphate reducing bacteria was present. 25 kg sodium carbonate was added every 24 h to maintain the pH above 7.0. Sodium carbonate addition was terminated once sufficient alkalinity was generated from sulphate reduction (Maree *et al.*, 2001). The contents of the reactor were stirred with a side entry stirrer positioned at the bottom of the reactor tank at 260 rpm.

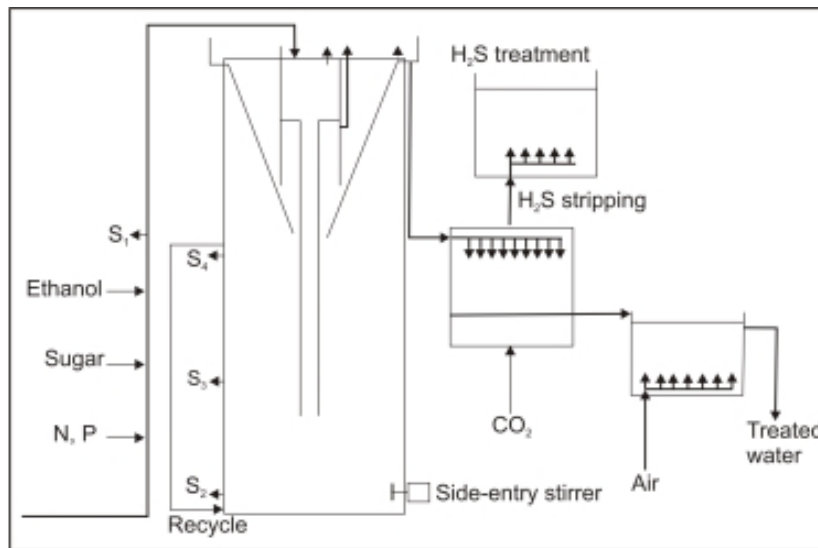


Figure 2.8: Schematic diagram of anaerobic reactor for treatment of sulphate rich mine water (Maree *et al.*, 2001)

Sulphate was consistently reduced from ~ 2000 mg/l to less than 500 mg/l and even to concentrations as low as 200 mg/l when sufficient carbon and energy source was provided. This was accompanied by a stoichiometric-equivalent increase in dissolved sulphide concentration. The sulphide was effectively removed from 364 mg/l to 0 mg/l by passing it through two serial stripping units with the molar ratio of CO₂(g). The sulphate reduction rate in the bioreactor increased to 12 g/l SO₄ per day at a temperature of 20°C and a retention time of 6 hrs. This was expected to improve at higher temperatures (30°C) and throughput (16 m³/h). The alkalinity was found to increase to values as high as 2000 mg/l as CaCO₃. This process has the disadvantage of producing various sludges i.e. gypsum and iron hydroxide sludge (CaCO₃ treatment stage) and calcium carbonate sludge (biological sulphate removal stage).

A 10 MI/d full-scale plant to treat toxic mine water from the Grootvlei gold mine on the Witwatersrand basin in South Africa was commissioned at Ancor Wastewater Treatment works (The Water Wheel & Water Sewage & Effluent, 2006). The process, called the Rhodes BioSURE process utilises primary sewage sludge which acts as a carbon donor to desalinate the water prior to be discharged. 75 MI of

polluted mine water is pumped per day. The water is initially treated at a high density separation (HDS) plant to remove iron and condition the pH levels. It is then pumped two kilometres to the biological sulphate treatment plant at Ancor treatment works. This water is mixed with the primary sewage sludge in a mixing tank. The material is then split to eight biological sulphate reducing reactor or bioreactors. The sulphide rich overflow water is pumped to another tank where iron slurry from the HDS process is added and mixed. This is further split into four reactors for sulphide removal. The treated overflow water contains reduced sulphate and sulphide concentrations. Biofilters are applied to removal the chemical oxygen demand (COD) and ammonia before final release. The process claims to remove heavy metals and radioactive elements, destruct pathogens, provide a robust biotechnological solution and have low capital and operational costs.

2.4.2 Constructed Wetlands

Exorbitant sums of money are spent each year on treating acid drainage with alkaline chemicals e.g. hydrated lime, sodium hydroxide, sodium carbonate or ammonia. However, active chemical treatment of AMD to remove metals and acidity is often an expensive, long term liability. Alternative techniques have been developed called passive treatment systems that do not require continuous chemical inputs and take advantage of naturally occurring chemical and biological processes to condition contaminated mine waters. The primary passive technologies include constructed wetlands; anoxic limestone drains (ALD), limestone ponds and open limestone channels (OLC). Although many passive systems have realised successful short term implementation in the field and have substantially reduced water treatment costs, passive systems require long retention times and greater space, provide less certain treatment efficiency and are subject to failure in the long term (Skousen *et al.*, 2000).

Constructed wetlands utilise soil- and water-borne microbes associated with wetland plants to remove dissolved metals from mine drainage. Metal retention within the wetlands occur via 1) formation and precipitation of metal hydroxides, 2) formation of metal sulphides, 3) organic complexation reactions, 4) exchange with other cations on negatively charged sites, and 5) direct uptake by living plants. Other mechanisms

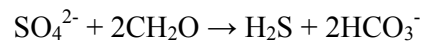
include neutralisation by carbonates, attachment to substrate materials, adsorption and exchange of metals onto algal mats, and microbial dissimilatory reduction of iron hydroxides and sulphate (Skousen *et al.*, 2000). Constructed wetlands are characterised between “aerobic” and “anaerobic” wetlands.

Aerobic wetlands are generally used to collect water and provide a residence time to promote metal oxidation and hydrolysis. This causes precipitation and physical retention of iron, aluminium and manganese hydroxides. The effectiveness of this system is dependent on dissolved metal and oxygen content, pH and net alkalinity of the mine water, presence of active microbial biomass and water retention time within the wetland. Since pH influences the solubility of metal hydroxide precipitates and the kinetics of metal oxidation and hydrolysis, this factor as well as the acidity/alkalinity of the water is particularly important. The water usually has a net alkalinity. Plants are included in these systems to add some organic matter which aids in ensuring a more uniform flow and thus a more effective wetland.

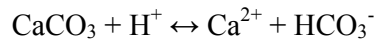
Analysis of results from various sites employing constructed wetlands indicates that this technology works well for moderate pH waters but was less successful for waters with a net acidity (Skousen *et al.*, 2000). An example is the Rougeux 1 site in Pennsylvania, where the AMD has a pH of 2.9, 445 mg/l acidity, 45 mg/l Fe, 70 mg/l Mn and 24 mg/l Al. After treatment through a two-celled aerobic wetland, the pH only increased to 3.2, the acidity decreased 43%, and Fe decreased 50%, Mn by 17 % and Al by 83 %. Whilst there was some improvement in the water quality, the wetland effluent did not conform to effluent limits (Skousen *et al.*, 2000).

Anaerobic wetlands promote metal oxidation and hydrolysis in aerobic surface layers, but also rely on subsurface chemical and microbial reduction reactions to precipitate metals and neutralise acid. Water passes through the wetland which contains organic rich substrates and may contain a layer of limestone either at the bottom or mixed among the organic matter for treatment purposes. Wetland plants are also transplanted into the organic substrate. These systems are applied when the water to be treated is highly acidic. Alkalinity is imparted to the water before dissolved metals precipitate. Alkalinity can be generated in one of two ways. *Desulfovibrio* and *desulfotomaculum* bacteria can utilise the organic substrate as a carbon source and

sulphate as an electron acceptor for growth. The bacterial conversion of sulphate to hydrogen sulphide results in the bicarbonate alkalinity being produced:

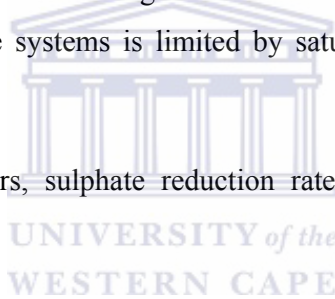


Limestone present within the wetland is another source of alkalinity:



Treatment mechanisms are enhanced in anaerobic wetlands as compared to aerobic wetlands, including the formation and precipitation of metal sulphides, metal exchange and complexation reactions, microbially generated alkalinity and continuous formation of carbonate alkalinity due to limestone dissolution under anoxic conditions. Since these systems produce alkalinity, they can be used to treat poor quality, low pH, high Fe and high dissolved oxygen AMD. However, the adsorption capacity of these systems is limited by saturation of the exchange sites (Skousen *et al.*, 2000).

In comparison to bioreactors, sulphate reduction rates in wetlands are very low (INAP, 2003).



2.5 SUMMARY OF COMPARISON

The tables that follow compare the individual technology within the various treatment processes.

The lime/limestone process was limited in its sulphate removal capabilities, whilst the Savmin process could reduce sulphate to very low concentrations (Table 2.10). Both processes are capable of removing trace metals. The lime/limestone process is inexpensive and thus provides a useful option for pre-treatment purposes. In comparison, the Savmin is a more expensive process (INAP, 2003).

Table 2.10: Summary of comparison of chemical treatment processes

	Lime/Limestone	Savmin
Pre-treatment	No	No
Feed water (SO₄²⁻)	3000 mg/l	649 mg/l
Product water (SO₄²⁻)	1219 mg/l	69 mg/l
Brine production	No	No
Sludge production	Low	High
Maintenance	Low	Low
Advantages	Trace metals removed	Greater sulphate reduction
	Lower cost	Trace metals removed
Disadvantages	Limited sulphate removal.	Sludge produced
	Sludge produced	

Whilst both the RO and EDR processes are capable of producing a high quality of treated water, the production of brine poses further environmental and financial challenges (Table 2.11). This form of treatment has high capital and operating costs due to scaling and membrane fouling (INAP, 2003). As such, they are not suitable for the treatment of scaling mine waters.

Table 2.11: Summary of comparison of membrane treatment processes

	TRO	EDR
Pre-treatment	Yes	Yes
Feed water (SO₄²⁻)	2200 mg/l	74 mg/l
Product water (SO₄²⁻)	14 mg/l	5 mg/l
Brine production	Yes	Yes
Sludge production	Low	Low
Maintenance	High	High
Advantages	Produce water of drinking water quality	Produce water of drinking water quality
Disadvantages	Problems due to scaling Membrane fouling – short life	Problems due to scaling Membrane fouling – short life

Table 2.12: Summary of comparison of ion exchange treatment processes

	GYP-CIX & Metal precipitation
Pre-treatment	No
Feed water (SO₄²⁻)	6305 mg/l
Product water (SO₄²⁻)	50 mg/l
Brine production	Yes
Sludge production	Low
Maintenance	Moderate
Advantages	Produce water of drinking water quality
Disadvantages	Gypsum sludge produced

GYP-CIX is capable of treating scaling mine waters and producing high quality treated water. The main disadvantage of the GYP-CIX process is the volume of gypsum sludge produced during regeneration of the ion exchange resins.

Table 2.13: Summary of comparison of biological sulphate removal treatment processes

	Bioreactor	Constructed Wetlands
Pre-treatment	Yes	Yes
Feed water (SO₄²⁻)	2000 mg/l	-
Product water (SO₄²⁻)	<200 mg/l	-
Brine production	No	No
Sludge Production	Low	No
Maintenance	Moderate	Low
Advantages	Trace metals are removed H ₂ S and CO ₂ can be recycled	Trace metals are removed
Disadvantages	Gypsum sludge produced Costs for carbon and energy source	Limited sulphate reduction

Bioreactors are effective in removing sulphate whereas constructed wetlands are very poor in reducing sulphate. Bioreactors produce sludge i.e. gypsum and iron hydroxide sludge (CaCO₃ treatment stage) and calcium carbonate sludge (biological sulphate removal stage) which require disposal. Both processes are effective in removing trace metals. The costs associated with the biological sulphate removal processes claim to be lower than all the others mentioned here.

In general, the technologies that are most efficient in reducing sulphate e.g. membrane and ion exchange processes are often associated with exorbitant capital and/or operating costs. The fly ash treatment of AMD being developed in this study aims at providing a cost effective alternative to lime/limestone treatment options with efficient sulphate reduction.

CHAPTER 3

EXPERIMENTAL METHODOLOGY

This chapter describes the methods applied for the sampling, experimental and analysis conducted in this study.

3.1 SAMPLING AND STORAGE METHODS

3.1.1 Fly Ash

Fresh fly ash was collected directly from hoppers in bulk at Arnot power plant into plastic bags. Samples were extracted from the bulk samples for both the laboratory and large scale experiments. The samples were sealed in the plastic bags and labelled with the date, unit number and power plant identity. The fly ash was delivered directly to the laboratory and stored in a cool dark area, in the absence of any other material to avoid contamination.

3.1.2 Acid Mine Drainage

Bulk AMD was sampled from dams at Landau colliery, Navigation plant in high density 10 l polyethylene (HDPE) containers. The containers were sealed and refrigerated at $\pm 4^{\circ}\text{C}$. The AMD was allowed to reach room temperature and samples were extracted from the bulk containers for the neutralisation experiments.

3.1.3 Post neutralisation liquid and solid samples

The liquid and solid samples collected after neutralization experiments were separated by firstly allowing the solid component to settle and then filtration through a Whatman No 1 filter paper. The liquid samples were stored in glass Schott bottles under refrigeration at $\pm 4^{\circ}\text{C}$. Multi-element analysis was performed using Inductively

Coupled Plasma Spectroscopy (ICP) and ion analysis by Ion Chromatography (IC). The solid samples were stored in sealed plastic bags.

3.2 EXPERIMENTAL METHODS

3.2.1 Beaker scale neutralisation tests

In the beaker scale neutralisation experiments, a fixed volume of AMD was continuously stirred by means of an overhead stirrer in 500 ml beakers and a known mass of fly ash was added at pre-determined FA:AMD ratios. Electrical conductivity (EC) and pH measurements were recorded routinely in-situ until the pH stabilised. The solid and liquid portions were separated and analysed.

3.2.2 Large scale neutralisation tests

In order to perform large scale neutralisation experiments, a 250 l capacity tank with an agitator was designed and constructed for this specific application. A fixed volume of AMD, 200 l, was stirred continuously and a known mass of fly ash was added at pre-determined ratios. The pH and EC measurements were recorded routinely, until the pH stabilised. The stirrer was then switched off and the solid was allowed to settle in the tank. Once all the solids had settled, this was removed from the base of the mixing tank in the form of a sludge into large trays. The moisture was driven off by drying in large ovens at $\pm 105^{\circ}\text{C}$. The dried solid was then stored in dark, sealed plastic bags. The liquid sample was also collected from the base of the mixing tank. Smaller volumes were extracted for multi-element and ion analysis. These were filtered through a Whatman No 1 filter paper and then stored under refrigeration.

3.2.3 Comparison of limestone versus fly ash treatment of AMD

Fly ash from three different South African power plants namely, Arnot, Hendrina and Kriel, was sampled and beaker scale neutralisation experiments conducted with AMD from Landau colliery. The AMD in use had a very low pH and significantly high

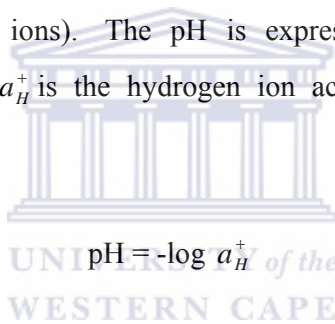
sulphate concentration, thereby providing a possible worst case scenario. All comparison experiments were conducted at beaker scale. The pH, acidity and sulphate concentration of the AMD was compared before and after neutralisation. The cost comparison accounted for material and transportation costs.

3.3 ANALYTICAL METHODS

3.3.1 pH determination

Principle

The pH is a measure of the activity of protons in aqueous solutions, to differ between the acidity and alkalinity of that solution. The amount of hydrogen ions (H⁺) causes a liquid to be acidic (high concentration of hydrogen ions) or alkaline (low concentration of hydrogen ions). The pH is expressed mathematically by the following equation where a_H^+ is the hydrogen ion activity of the solution being measured is:



Measurements are carried out using a pH meter consisting of a measuring and reference electrode. The measuring electrode delivers a varying voltage (potential) and the reference electrode delivers a constant voltage to the meter. The potential generated at the junction site of the measuring portion is due to the free hydrogen ions present in solution. This potential is proportional to the pH of the solution.

Method

A Hanna HI 991301 portable combination pH/EC/TDS/Temperature meter was used for the pH measurements. Calibration of the meter was performed with buffer solutions at pH 4.01 and pH 7.01 prior to sample measurements. A quality control sample of known pH (pH 6.99) was intermittently read to confirm the stability and accuracy of the pH meter.

3.3.2 Electrical conductivity (EC) measurements

Principle

Electrical conductivity is a measure of a sample's ability to conduct an electric current. The sensor simply consists of two metal electrodes that protrude into the water. A constant voltage (V) is applied across the electrodes. An electrical current (I) flows through the water due to this voltage and is proportional to the concentration of dissolved ions in the water - the more ions, the more conductive the water resulting in a higher electrical current which is measured electronically. EC is the reciprocal of electrical resistivity and has the SI unit of Siemens per meter (S/m). Since the electrical current flow (I) is temperature dependent, the EC values refer a standard value at 25°C

Method

A Hanna HI 991301 portable combination pH/EC/TDS/Temperature meter was used for the EC measurements. The EC meter was calibrated before use with a standard solution of 12.88 mS/cm. A quality control sample of known EC (141.3 mS/cm) was intermittently read to confirm the stability and accuracy of the EC meter during an experiment.

3.3.3 Acidity measurements

Principle

Acidity is defined as the quantitative capacity of a water sample to neutralise a strong base to a selected pH. Acidity is the net effect of the presence of several constituents, including dissolved carbon dioxide, dissolved multivalent metal ions, strong mineral acids and weak organic acids. Titrating an acidic sample with a base to a pH of 8.3 measures the phenolphthalein acidity or total acidity. Total acidity measures the neutralising effects of essentially all the acid species present, both strong and weak.

Method

Acidity was measured according to standard methods (APHA, 1985) by titrating a fixed volume of sample with 0.1 N NaOH to pH 8.3. The acidity was calculated by the following formula:

$$\text{Acidity (mg/l CaCO}_3) = \frac{T \times N \times 1000}{V}$$

Where T = ml NaOH titrant used,

N = normality of NaOH, (gram equivalent/l),

V = volume of sample (ml).

3.3.4 Percentage CaCO₃ in neutralising material (fly ash and limestone)

Principle

The rationale for determining the percentage CaCO₃ is that the total CaO content must be quantified and not just the alkalinity as this plays a major role in the neutralisation of the acid mine waters. The method employed was provided courtesy of Dr Jannie Maree previously of the Council of Scientific and Industrial Research (CSIR) in South Africa (2006).

Method

25 g of the fly ash was stirred in 100 ml HCl for 5 minutes. The solution was then filtered and 5 ml of the filtrate was titrated with 0.1 NaOH to a pH 7. The percentage CaCO₃ was calculated using the following equation.

$$\% \text{ CaCO}_3 = \frac{\text{MM of CaO} * [((\text{vol HCl} \times \text{N HCl})/1000) * (\text{vol sample}/100) - (\text{vol NaOH}) * (\text{N NaOH}/1000)]}{[(\text{mass fly ash} * \text{vol sample})/100]} * 100$$

Where

MM = molar mass

vol = volume, ml

N = normality

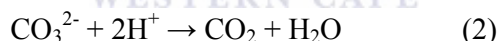
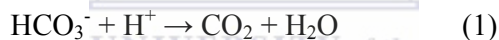
Mass = gram (g)

Due to the higher CaO content of limestone, a smaller mass of 2.5 g was used and the formula adjusted accordingly.

3.3.5 Alkalinity measurement

Principle

Alkalinity is a measure of the ability of a solution to neutralise an acid to the equivalence point of carbonate or bicarbonate. Alkalinity is the stoichiometric sum of the bases in solution and expressed in meq/l (milli equivalent per litre). Alkalinity can be measured by titrating a sample with a strong acid until the buffering capacity of all relevant ions above the pH of bicarbonate or carbonate is consumed (equation 1 and 2). This point is functionally set to pH 4.5. At this point, all the bases of interest have been protonated to the zero level species; hence they no longer cause alkalinity.



Method

Alkalinity was determined using the ISO 17025 accredited method (Eskom Method 304: Appendix A), which was based on standard methods (APHA, 1998). The sample was titrated with standardised 0.02 N HNO₃ to an endpoint of 4.5 with a Metrohm 702 SM Titrino autotitrator. The endpoint is determined electrometrically with automatic calculation of the alkalinity. A sodium carbonate quality control sample was analysed with the samples to ensure accuracy of the measurement.

3.3.6 Loss on ignition (LOI)

Loss on ignition (LOI) is a gravimetric measurement of combustible matter loss during prolonged air oxidation of ashes at high temperatures.

Method

The samples are firstly milled in a Spectro Mill for ten minutes to $<75\ \mu\text{m}$ and then dried at 100°C for 1 hour. Thereafter approximately 2 g of sample is heated in a furnace between $900 - 1000^\circ\text{C}$. The sample is allowed to cool down in a dessicator before it is weighed.

3.3.7 Inductively Coupled Plasma (ICP) Optical Emission Spectroscopy for metal analysis

Principle

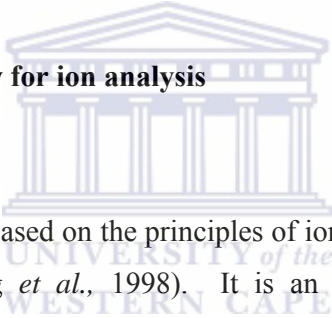
Inductively Coupled Plasma (ICP) spectrometry is a technique for elemental analysis which is applicable to most elements over a wide range of concentrations (Skoog *et al.*, 1998). The sample, which must be in a liquid form, is pumped (usually with a peristaltic pump) into a nebulizer, where it is converted into a fine aerosol with argon gas. The fine droplets of the aerosol, which represent only 1 - 2% of the sample, are separated from larger droplets using a spray chamber. The fine aerosol then emerges from the exit tube of the spray chamber and is transported into the plasma torch via a sample injector. This ionizes the gas and, when seeded with a source of electrons from a high-voltage spark, forms a very high temperature plasma discharge ($\sim 10,000\ \text{K}$) at the open end of the tube. In ICP-OES, the plasma, usually oriented vertically, is used to generate photons of light by the excitation of electrons of a ground-state atom to a higher energy level. When the electrons “fall” back to ground state, wavelength-specific photons are emitted that are characteristic of the element of interest (Skoog *et al.*, 1998)

Method

Elemental analysis, (in particular iron and aluminium) was performed using an ISO 17025 accredited method (Eskom Method 412: Appendix C). The ICP in use was the Perkin Elmer Optima 5300 DV ICP which was calibrated and samples were diluted with demineralised water for elements that read outside of the calibration range. The Optima 5300 DV ICP was fitted with a glass concentric nebuliser and HF-resistant spray chamber. The detector in use was a segmented-array charge-coupled detector (SCD). Samples were nebulised and transported as an aerosol to the plasma torch, where excitation occurred. Characteristic atomic-line emission spectra were produced by radio frequency inductively coupled plasma (ICP) and the intensity of the lines were monitored by means of a charge injection device. Background correction was applied to compensate for variable background contribution to the determination of the elements.

3.3.8 Ion chromatography for ion analysis

Principle



Ion chromatography (IC) is based on the principles of ion exchange via functionalised ion exchange resins (Skoog *et al.*, 1998). It is an analytical technique for the separation and determination of ionic solutes in water in general. IC can be classified as a liquid chromatographic method, in which a liquid permeates through a porous solid stationary phase and elutes the solutes into a flow-through detector. The stationary phase is usually in the form of small-diameter (5-10 μm) uniform particles, packed into a cylindrical column. The column is constructed from rigid material (such as stainless steel or plastic) and is generally 5-30 cm long and the internal diameter is in the range of 4-9 mm. A high pressure pump is required to force the mobile phase through the column at typical flow rates of 1-2 ml/min. The sample to be separated is introduced into the mobile phase by injection device, manual or automatic, prior to the column. The detector usually contains low volume cell through which the mobile phase passes carrying the sample components (Skoog *et al.*, 1998).

Method

Ion analysis, in particular sulphate, was performed using an ISO 17025 accredited method (Eskom Method 307: Appendix B). The IC in use was the Dionex ICS 1500 IC which was calibrated as per method 307 and samples were diluted with demineralised water for elements that read outside of the calibration range. This IC instrument makes use of a conductivity detector and anion exchange column with carbonate-bicarbonate eluent. The sample was injected into a stream of carbonate-bicarbonate eluant and passed through a series of ion exchangers. The anions of interest are separated on the basis of their relative affinities for a low capacity, strongly basic anion exchanger. The separated anions are directed onto a strongly acidic cation exchanger (suppressor column) where they are converted to their highly conductive acid form and the carbonate-bicarbonate eluant is converted to weakly conductive carbonic acid. The separated anions in their acid form are measured by conductivity. They are identified on the basis of retention time as compared to standards.

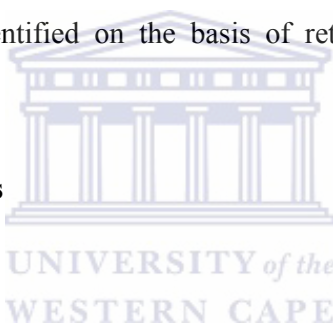
3.3.9 Particle size analysis

Principle

The particle size of the samples was determined by a laser diffraction technique. The laser diffraction technique is based on the fact that the diffraction angle of a light source is inversely proportional to particle size (Kippax, supplier info). In laser diffraction particle size analysis, a representative cloud or ‘ensemble’ of particles passes through a broadened beam of laser light that scatters the incident light onto a Fourier lens. This lens focuses the scattered light onto a detector array and, using an inversion algorithm, a particle size distribution is inferred from the collected diffracted light data. Sizing particles using this technique depends upon accurate, reproducible, high resolution light scatter measurements to ensure full characterisation of the sample.

Method

The instrument in use was the Malvern Mastersizer with a 300 mm lens. The sample was dispersed in demineralised water and introduced into the instrument via the sample cell. The sample cell provides a means of exposing particles to the laser by

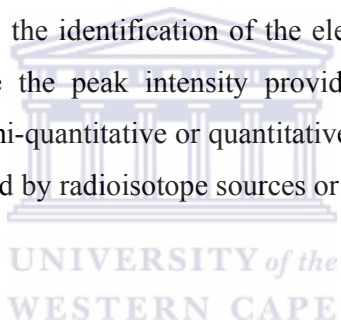


circulating them passed the beam. The laser acts as a source of coherent intense light of fixed wavelength.

3.3.10 X-Ray Fluorescence (XRF) Spectrometry

Principle

X-ray fluorescence analysis is a method that uses the characteristic X-ray (fluorescent X-ray) that is generated when X-ray is irradiated on a substance (Skoog *et al.*, 1998). The principle of the techniques is explained further. An inner shell electron is excited by an incident photon in the X-ray region. During the de-excitation process, an electron moves from a higher energy level to fill the vacancy. The energy difference between the two shells appears as an X-ray, emitted by the atom. The X-ray spectrum acquired during the above process reveals a number of characteristic peaks. The energy of the peaks leads to the identification of the elements present in the sample (qualitative analysis), while the peak intensity provides the relevant or absolute elemental concentration (semi-quantitative or quantitative analysis). The irradiation of a sample is usually performed by radioisotope sources or the more commonly used X-ray tubes.



Method

A Phillips 1404 XRF Wavelength Dispersive Spectrometer equipped with an array of 6 analyzing crystals, namely: LIF200, LIF220, LIF420, PE, TLAP and PX1 and fitted with an Rh X-ray tube target were used. The detectors were a gas-flow proportional counter, scintillation detector or a combination of the two. A vacuum was used as the medium of analyses to avoid interaction of X-rays with air particles. The gas-flow proportional counter uses P10 gas, which is a mixture of 90% Argon and 10% Methane. Major elements were analysed on a fused glass bead at 50 kV and 50 mA tube-operating conditions. Approximately 0.3 g of sample was mixed with flux in a platinum crucible and then heated at 1000 °C until the melt was complete. The melt was then poured onto a carbon disc where they were pressed to produce a flat disc. This disc was then analysed by XRF. Matrix effects in the samples were corrected for by applying theoretical alpha factors and measured line overlap factors to the raw intensities measured.

3.3.11 Computer Controlled Scanning Electron Microscopy (CCSEM)

Principle

SEM analysis permits the observation of materials in macro and submicron ranges, providing information about the composition and morphology of individual mineral grains. This analytical technique is capable of generating three dimensional images for analysis of topographic features. When used in conjunction with EDS, elemental analysis can be performed on microscopic sections of the sample. A SEM generates high energy electrons and focuses them on a specimen. Electrons are speeded up in a vacuum until their wavelength is extremely short, only one hundred-thousandth that of white light. Beams of these fast moving electrons are focused on a sample and are absorbed or scattered by the specimen and electronically processed into an image. EDS utilises x-rays that are emitted from the specimen when bombarded by the electron beam to identify the elemental composition of the specimen. The EDS x-ray detector measures the number of emitted x-rays versus their energy. The energy of the x-ray is characteristic of the element from which the x-ray was emitted. A spectrum of energy versus relative counts of the detected x-rays is obtained and evaluated for qualitative and quantitative determinations of the elements present.

Method

Fly ash and solid residues from the neutralisation of AMD with fly ash pulverised and mixed with iodinated epoxy resin and allowed to cure for 12 hours. Iodinated epoxy resin allows differentiation any char from organic (carbon rich) particles in the fly ash. The cured samples were then polished and the polished sections coated with carbon to ensure good sample conductivity and image quality. The samples were analysed by a computer controlled CAMSCAN CS44 scanning electron microscopy (CCSEM) with an energy dispersive x-ray detector.

3.4 COMPARISON OF LIMESTONE AND FLY ASH FOR NEUTRALISATION OF AMD WITH HIGH SULPHATE CONCENTRATION

3.4.1 Experimental Protocol

A cost estimate based on using limestone and fly ash was developed. The treatment of a worst case AMD with sulphate concentration of 17 100 mg/l using limestone and fly ash was compared in a simulated study to obtain a circum neutral pH. In addition to Arnot fly ash, two other fly ashes from different power plants were also tested namely Kriel and Hendrina fly ash. For purposes of the comparison, certain chemical characteristics of the neutralising material, the neutralisation reactions and treated AMD and were required. These chemical characteristics included the following:

- Acidity and pH of the AMD and treated AMD
- Total alkalinity of the neutralising material
- Quantity of neutralising material
- Sulphate concentration of the untreated and treated AMD
- Reaction time to reach neutralisation
- Water and solid content of sludge recovered from the neutralisation reaction

The following procedures were employed extracting the required information:

- a) The acidity of the Toeseep AMD was determined employing a standard method described in **Chapter 3, Section 3.3**. A new batch of Toeseep AMD was sampled for experiments conducted in **Chapter 6**, the chemical composition and pH of which is different from the Toeseep AMD utilised in **Chapter 4**. The variation in chemical composition of the AMD could be attributed to process conditions and weathering affects.
- b) The CaCO_3 content of the limestone and fly ash samples were determined by the method and calculated as described in **Chapter 3, Section 3.3**.
- c) Thereafter, neutralisation experiments were conducted at beaker scale, using 500 ml of AMD and different volumes of limestone and fly ash at pre-determined ratios. The volume of fly ash is expressed as kg/m^3 of AMD. An

additional experiment with Kriel fly ash was run for an extended reaction time.

- d) When the pH stabilised, the reaction was terminated and the mixture was allowed to settle. Once all the solids had settled, the liquid and solid portions were separated. A portion of the solid fraction was filtered with a Whatman filter paper. The filtered portion was then weighed and dried in an oven at 105°C until a constant dry weight was obtained. This was used to determine the % water content and solids in the sludge.
- e) The acidity of the neutralised AMD, termed process water, was determined by titration with standardised NaOH to a pH endpoint of 8.30 as described in **Chapter 3, Section 3.3.**
- f) The sulphate concentrations of the neutralised AMD were determined by ion chromatography **Chapter 3, Section 3.3.**

The cost comparison was conducted by initially obtaining costs (Table 6.1) for purchasing the material utilised e.g. limestone, flocculants etc, in the neutralisation reaction and costs for transport of the material from the suppliers. The neutralisation cost, expressed as R/m³ of AMD (Table 6.1), was calculated taking into the account the price of neutralising material, with and without transportation costs, and volume of material utilised. The cost of acidity removal, expressed as R/kg as CaCO₃ (Table 6.1), was calculated taking into account the cost of neutralisation and final acidity of the neutralised water. Sulphate removal costs, expressed as R/kg (Table 6.1), were calculated in a similar manner, taking into account the cost of neutralisation and final sulphate concentrations. The experimental data is presented in the tables below and the comparison in Table 6.1

CHAPTER 4

CHARACTERISATION AND SELECTION OF FLY ASH AND AMD FOR NEUTRALISATION EXPERIMENTS

Chapter 1 highlighted numerous applications of fly ash for AMD treatment and prevention. The applications ranged from the in-situ application of fly ash on mine spoils and ash filling, column leaching studies and co-disposal of fly ash and AMD. Most applications resulted in neutralisation of the AMD with some metal and sulphate reduction, by direct contact with fly ash. **Chapter 2** detailed various technologies applied for AMD treatment and more specifically sulphate reduction. The indication was that optimum sulphate reduction was possible, but only with the most expensive of technologies.

Chapter 4 sets out to understand the properties of selected fly ash samples to determine the most effective and cost efficient fly ash for active neutralisation of AMD. This was undertaken by performing chemical, mineralogical and physical analysis of the selected fly ash samples. The analysis methods employed are detailed in **Chapter 3**

4.1 DETERMINATION OF AMOUNT OF CAO IN FLY ASH, LIME AND LIMESTONE

Free CaO in the fly ash is the primary neutralising agent. The percentage CaO content of the three fly ash samples and for comparison with lime and limestone was initially determined by employing the technique recommended by Dr J Maree (Pers. Communication, CSIR, 2006).

Based on the CaO results, the limestone and lime are expected to have a much larger neutralisation capacity compared to the ash. However, it is the CaO available at the

surface of the particles that is involved in the neutralisation process, whilst the residual alkalinity acts as a chemical scrubber for trace elements via precipitation, adsorption and other processes. Further, sulphate removal is minimal when applying lime or limestone for neutralising acidity. The fly ash is expected to further reduce sulphate levels via the formation of gypsum, CaSO_4 at high pH. It is thus prudent to test the neutralising as well as toxic element removal capacity of fly ash. Tables 4.1 to 4.5 compare the amount of CaO present in the fly ash samples, limestone and lime.

Table 4.1: Amount of CaO of Arnot power plant ash

Normality of HCl	1
Normality of NaOH	1.0534
Mass of Arnot ash (g)	25
Volume of HCl (ml)	100
Volume of NaOH (ml)	31.5
Volume of sample (ml)	72.9
Molar mass of CaO	28
Amount of CaO in FA (%)	6.1

Table 4.2: Amount of CaO of Kriel power plant ash

Normality of HCl	1
Normality of NaOH	1.0534
Mass of Kriel ash (g)	25
Volume of HCl (ml)	100
Volume of NaOH (ml)	11.6
Volume of sample (ml)	66
Molar mass of CaO	28
Amount of CaO in FA (%)	9.1

Table 4.3: Amount of CaO of Hendrina power plant ash

Normality of HCl	1
Normality of NaOH	1.0534
Mass of Hendrina ash (g)	25
Volume of HCl (ml)	100
Volume of NaOH (ml)	34.9
Volume of sample (ml)	76
Molar mass of CaO	28
Amount of CaO in FA (%)	5.7

Table 4.4: Amount of CaO of Limestone

Normality of HCl	1
Normality of NaOH	1.0534
Mass of limestone (g)	2.5
Volume of HCl (ml)	100
Volume of NaOH (ml)	48.3
Volume of sample (ml)	95
Molar mass of CaO	50
Amount of CaO in Limestone (%)	93

Table 4.5: Amount of CaO of Lime

Normality of HCl	1
Normality of NaOH	1.0534
Mass of lime (g)	2.5
Volume of HCl (ml)	100
Volume of NaOH (ml)	32.2
Volume of sample (ml)	95
Molar mass of CaO	50
Amount of CaO in lime (%)	72

Determination of the percentage CaO in the three selected fly ash samples revealed that the hierarchy with respect to CaO content was Kriel fly ash which contains the highest amount of CaO, followed by Arnot and the Hendrina fly ash. Limestone and lime had much larger amount of CaO than the fly ash samples.

4.2 X-RAY FLOURESCENCE (XRF) SPECTROMETRY ANALYSIS

Chemical composition of the fly ash samples was determined by XRF analysis as per the method detailed in **Chapter 3**.

Table 4.6: XRF data of fly ash samples

Component	Arnot Fly Ash %	Kriel Fly Ash %	Hendrina Fly Ash %
Silicon (as SiO ₂)	57.3	48.4	57.06
Aluminium (as Al ₂ O ₃)	25.4	27	26.01
Calcium (as CaO)	5.3	10.4	4.6
Sulphur (as SO ₃)	4.1	5.6	2.6
Iron (as Fe ₂ O ₃)	3.3	2.8	3.3
Magnesium (as MgO)	2.1	2.6	1.5
Titanium (as TiO ₂)	1.3	1.6	1.4
Potassium (as K ₂ O)	0.3	0.5	0.6
Phosphorus (as P ₂ O ₅)	0.29	1.04	0.48
Manganese (as MnO)	0.03	0.04	0.03
Sodium (as Na ₂ O)	<0.1	<0.1	<0.1

With reference to Table 1.1 in **Chapter 1**, the fly ash samples analysed here are classified as Class F fly ash. The most abundant phase in a Class F fly ash is the glass that results from the melting of the clays and subsequent exsolution of mullite from the melt. The concentration of the three major phases, SiO₂, Al₂O₃ and Fe₂O₃ do not vary significantly between the different ash sources. The CaO concentrations are also comparative to those determined by titration methods. The component of interest,

CaO in Kriel fly ash is double the concentration that of the Arnot and Hendrina samples. CaO will hydrolyse in water and is subsequently transformed into carbonates, forming the buffering constituents. However, it must be noted that the total CaO content detected by XRF does not distinguish the free lime from that entrapped within the glass matrix. The free lime will dissolve at a much faster rate than that contained within the glass matrix and the rate of dissolution will ultimately influence the extent of neutralisation. To further elucidate, scanning electron microscopy (SEM) analysis was performed on the fly ash samples. The percentage CaO was determined via SEM. Other minor components do not vary significantly amongst the three fly ash samples.

4.3 SCANNING ELECTRON MICROSCOPY (SEM) ANALYSIS

Three fly ash samples were submitted for detailed mineralogical analysis by Computer Controlled Scanning Electron Microscopy (CCSEM). The SEM analysis was conducted by Van Alpen Consultancy according to the method described in section 3.3. The fly ash samples were derived from Arnot, Kriel and Hendrina power plants. The volume percent phase/mineral proportions are summarized in Table 4.7. The phase classification is presented in Table 4.8. Fly ash phase classification is based on the elemental composition of fly ash and the nomenclature is based on the original minerals in the coal particles.

Table 4.7: Volume percent phase proportions of Arnot, Kriel and Hendrina fly ash

Phase	Arnot, %	Kriel, %	Hendrina, %
Anhydrite	0.06	0.15	0.07
Ca-oxide	2.6	5.8	2.0
CaMg-oxide	2.8	3.5	2.1
Kaolinite (aluminosilicate)	46.4	45.0	55.4
Kaolinite(pyrite/carbonate)	2.4	1.4	1.1
Kaolinite(carbonate)	12.2	21.3	6.5
Kaolinite(pyrite)	1.7	0.7	2.0
Kaolinite(CaMg)	1.1	1.0	0.7
Muscovite/illite	0.4	0.6	0.5
Orthoclase	1.2	1.0	1.7
Quartz-glass	5.4	4.0	2.8
Quartz60Kaol40	2.2	1.4	1.5
Quartz80Kaol20	2.3	1.5	1.5
Quartz	16.4	10.1	19.1
Iron-oxide/pyrite	2.1	1.6	2.4
Ti-oxide	0.2	0.1	0.2
Other	0.5	0.8	0.6
Total	100.0	100.0	100.0

Table 4.8: Fly ash classification and phase nomenclature

Fly ash group name	Origin
Anhydrite	Ca-sulphate formed by the reaction of Ca-oxide and sulphur presented in the flue gas.
Ca-oxide	Ca rich-oxide with minor Si, Al, Fe and Mg. Transformation product of extraneous calcite.
CaMg-oxide	CaMg rich-oxide with minor Si, Al, Fe and Mg. Transformation product of extraneous dolomite.
Kaolinite (Aluminosilicate)	Al-Si-O. Transformation product of kaolinite. Includes metakaolinite, silicon spinel and mullite.
Kaolinite(pyrite, carbonate) (Ca-Fe-aluminosilicate glass)	Ca-Fe aluminosilicates glass. Represents the interaction of kaolinite, pyrite and carbonates.
Kaolinite(carbonate) (Ca aluminosilicate glass)	Ca-aluminosilicate glass. Represents the interaction of kaolinite and calcite.
Kaolinite (pyrite) (Fe-aluminosilicate glass)	Fe-aluminosilicate glass. Represents the interaction of kaolinite, pyrite and siderite.
Kaolinite (CaMg) (CaMg-aluminosilicate glass)	CaMg-aluminosilicate glass. Represents the interaction of kaolinite, calcite and dolomite.
Muscovite/Illite (K-aluminosilicate)	K-bearing aluminosilicate with same Al/Si ratio as muscovite/illite
Microcline (K- aluminosilicate)	K-bearing aluminosilicate with same Al/Si ratio as the feldspar, microcline.
Quartz glass	Si-rich glass with minor Al, Ca, Si, Fe and Mg. Represents the interaction of quartz, calcite, dolomite and pyrite.
Quartz60Kao140	Si-Al-O with Si concentrations greater than the expected Si concentration of metakaolinite. Represents mixture of quartz and kaolinite in an

	estimated proportion of $\pm 60:40$.
Quartz 80Kaol20	Si-Al-O with Si concentrations analogous to mixture of quartz and kaolinite in an estimated proportion of $\pm 80:20$.
Quartz	Si-O with trace concentrations of Al and possibly Ca, Mg, Fe and K. Represents the mineral transformation product of quartz.
Iron-oxide/pyrite	Extraneous pyrite transformation product. Includes pyrrhotite, pyrite (not transformed), Fe-S-O phases and Fe-oxide (hematite and magnetite). Represent fly ash particles with varying proportions of Fe, S and O. Trace concentrations of Ca, Mg, Al, Si and K are possible.
Ti-oxide	Ti-oxide. Final transformation product of Ti-oxide
Other	Uncombusted remains of "coal". Predominantly C and O.
Unmatched	Describes unclassified fly ash particles, which cannot be allocated into a specific class. Varying proportions of Al, Si, Ca, Mg, K, Fe, Ti, O, C and S.

In general, six common groups have been identified in South African fly ashes (van Alphen, 2007). These include aluminosilicate, Ca-Fe-bearing aluminosilicate glass, K bearing aluminosilicate glass, quartz and Si rich glasses, Ca(Mg) rich oxides and Fe-rich oxides. Kaolinite (aluminosilicate), which is Al-Si-O phase, was the predominant fly ash phase for all three fly ash samples. It includes metakaolinite, silicon spinel and mullite (Table 4.8). The second most abundant phase kaolinite (carbonate) represents the interaction of kaolinite and calcite. Kaolinite(pyrite/carbonate), quartz, kaolinite(CaMg), Quartz60Kaol40, Quartz80Kaol20 and Iron-oxide/pyrite, were present in minor to trace proportions. All remaining phases are described in table 4.8. The Ca from Ca-oxide and CaMg-oxide fly ash phases should be readily available to

neutralise acidic water (Reactive CaO). Technically, the Ca in kaolinite (pyrite, carbonate), kaolinite (carbonate) and kaolinite (CaMg) is probably not immediately available to neutralise, but with time should become available (slow release CaO).

Algorithms were developed to predict the element proportions based on raw counts. Using the predicted CaO content and the volume-percent phase proportions (Table 4.7) the proportion of “reactive CaO” and “slow release CaO” was calculated (Table 4.9).

Table 4.9: Calculated CaO

	Arnot, %	Kriel, %	Hendrina, %
“Reactive CaO”	2.67	4.26	2.39
“Slow release CaO”	2.93	3.94	1.82
Total	5.61	8.20	4.21

In theory, neutralisation hierarchy from good to poor, with respect to CaO neutralisation of AMD, in this sequence was Kriel, Arnot and Hendrina.

4.4 PARTICLE SIZE ANALYSIS

The particle size distribution (PSD) of the fly ash samples was determined to predict the reactivity of the fly ash in neutralising AMD according to the technique described in section 3.3. As mentioned earlier, the surface CaO effects neutralisation and surface area is directly related to the particle size of the material. The PSD of fly ash could vary depending on combustion conditions of power plant boilers. Vadapalli *et al.* (2007) investigated the influence of fly ash particle size on its capacity to neutralise AMD. It was clearly demonstrated that quicker neutralisation reaction times and higher alkaline pH was achieved with fly ash enriched with finer ash particles compared to those enriched with coarse ash particles. Further, that study indicated that the removal of toxic elements and sulphate was enhanced with the finer fly ash fraction as compared to the coarser fly ash fraction due to the greater reactive

surface area. The PSD of these fly ash samples was determined by a Malvern Masterizer particle size analyser with a 300 mm lens.

Table 4.10 lists the percentage of fine and coarse fractions of the fly ash samples used in this study in terms of volume percentage.

Table 4.10: Particle size distribution of Arnot, Kriel and Hendrina fly ash

	10 %	50 %	90 %
Arnot fly ash	6.00 μm	26.00 μm	81.82 μm
Kriel fly ash	9.89 μm	47.25 μm	172.01 μm
Hendrina fly ash	3.84 μm	16.31 μm	48.16 μm

The particle size distribution in Table 4.10 is interpreted as “10, 50 or 90 % less than a particle size (μm) e.g. Arnot fly ash has 10 % of its particles $<6.00 \mu\text{m}$. Hendrina fly ash constitutes finer particles with 50 % of its particles being $<16.31 \mu\text{m}$ and 90 % $<48.16 \mu\text{m}$. Arnot fly ash has slightly larger particles with 90 % of its particles being $<81.82 \mu\text{m}$ whilst Kriel is significantly larger than the other fly ash samples with 90 % of its particles being $<172 \mu\text{m}$. The expected reactivity hierarchy based on particle size distribution was Hendrina fly ash, Arnot fly ash followed by Kriel fly ash.

4.5 SUMMARY OF FLY ASH CHARACTERISATION

Titrimetric and XRF analyses confirmed the concentration of CaO present in Arnot, Kriel and Hendrina fly ash, with Kriel fly ash containing the largest concentration of 9.1 % CaO followed by Arnot with 6.1 % CaO and then Hendrina with 5.7 %. SEM analysis was employed to predict the neutralisation potential hierarchy based on CaO content. The neutralisation hierarchy for the three fly ash samples as determined by titrimetric, XRF and SEM methods, from good to poor, was predicted as Kriel > Arnot > Hendrina. The titrimetric methods gave results of 9.1 %, 6.1 % and 5.7 % CaO for Kriel, Arnot and Hendrina fly ash respectively. XRF analysis followed a similar trend to that obtained from titrimetric analysis producing 10.4 %, 5.3 % and 4.6 % for Kriel, Arnot and Hendrina fly ash respectively. The CaO content of limestone was 93 % and 72 % for lime. What this implies is that lesser volumes of

limestone and /or lime would be required to neutralise acidic waters. However, the literature review (**Chapter 2**) revealed that limestone is only capable of increasing the pH of AMD to neutral levels and sulphate attenuation is limited. The CaO content determined by SEM is less than that determined by titrimetric and XRF methods. Accurately characterising elemental distributions, element proportions and mineralogical characteristics is difficult due to the high proportion of amorphous phases in the ash, irrespective of the techniques applied (van Alphen, 2007).

In view of the fact that particle size distribution of the fly ash particles would influence the effectiveness and rate of neutralisation, the particle size distribution was determined (section 4.4). Hendrina fly ash contained finer ash in size compared to Hendrina whilst Kriel fly ash contained significantly larger particle size fractions as shown in Table 4.10, section 4.4. An additional factor taken into consideration was fly ash transportation costs to the mine for AMD treatment. Kriel fly ash would have to be purchased due to contractor agreements at site whilst Arnot and Hendrina were freely available. The major cost associated here was transportation costs. Although Arnot and Hendrina demonstrated similar CaO concentrations and Hendrina had finer ash particles, the distance between Arnot power plant and the source of AMD to be treated was less than Hendrina power plant and would result in reduced costs for treatment (Table 4.11). Thus, for this treatment to be economically feasible, Arnot power plant fly ash was selected for the study.

Table 4.11: Estimated distance between power plants and AMD sites

Power plant	Landau Colliery
Arnot	50 km
Hendrina	80 km
Kriel	60 km

4.6 CHEMICAL COMPOSITION OF AMD

Two different qualities of AMD emanating from Landau colliery namely Skoongesig and Toeseep AMD were selected for this study due to the volumes available, quality and their detrimental environmental impacts. Both AMD samples were analysed by Inductively Coupled Plasma spectroscopy (ICP) and Ion Chromatography (IC) to determine the elemental concentration. Table 4.12 gives the chemical composition of the Skoongesig AMD and Table 4.13 provides the chemical composition of Toeseep AMD.

Table 4.12: Chemical Composition of Skoongesig AMD

COMPONENT	SKOONGESIG AMD
pH	2.79
Conductivity (mS/cm)	7.52
Aluminium (mg/l) Al	200
Barium (mg/l) Ba	0.10
Boron (mg/l) B	27
Beryllium (mg/l) Be	<0.01
Cadmium (mg/l) Cd	0.51
Cobalt (mg/l) Co	7.1
Chromium (mg/l) Cr	0.13
Copper (mg/l) Cu	<0.01
Iron (mg/l) Fe	5000
Manganese (mg/l) Mn	38
Nickel (mg/l) Ni	3.8
Lead (mg/l) Pb	<0.02
Strontium (mg/l) Sr	0.8
Zinc (mg/l) Zn	16
Sulphate (mg/l) SO ₄	5700

The Skoongesig AMD was found to be of very low pH and contained high concentrations of aluminium (200 mg/l), iron (5000 mg/l) and sulphate (5700 mg/l)

(Table 4.12). This source of AMD contained much higher sulphate concentrations of 5700 mg/l than those reported in the literature review except for the GYP-CIX treatment process (Table 2.9). The high concentrations of sulphate would provide a good comparison study of fly ash versus alternate treatment processes. The solution had a reddish brown colour due to the high iron content. Laboratory and large scale neutralisation experiments were conducted aimed at neutralising the AMD and reducing the concentrations of those critical elements namely iron, sulphate and aluminium.

Table 4.13: Chemical Composition of Toeseep AMD

COMPONENT	TOESEEP AMD
pH	2.58
Conductivity (mS/cm)	11.33
Aluminium (mg/l) Al	401
Barium (mg/l) Ba	0.13
Boron (mg/l) B	2.12
Beryllium (mg/l) Be	<0.005
Cadmium (mg/l) Cd	1.18
Cobalt (mg/l) Co	1.55
Chromium (mg/l) Cr	<0.005
Copper (mg/l) Cu	<0.005
Iron (mg/l) Fe	5186
Manganese (mg/l) Mn	54.7
Nickel (mg/l) Ni	2.10
Lead (mg/l) Pb	0.94
Strontium (mg/l) Sr	3.43
Zinc (mg/l) Zn	9.82
Sulphate (mg/l) SO ₄	24400

The chemical composition of Toeseep AMD (Table 4.13) was similar to the Skoongesig AMD (Table 4.12) except that sulphate concentration in the Toeseep AMD was excessively high at 24400 mg/l. Aluminium in the Toeseep AMD (Table

4.13) was almost double that found in Skoongesig AMD (Table 4.12) at 401 mg/l. Iron concentrations for both AMD samples were similar (Tables 4.12 and 4.13).



CHAPTER 5

BEAKER AND LARGE SCALE NEUTRALISATION EXPERIMENTS

Chapter 5 presents the results of the investigation of the active neutralisation of AMD with fly ash utilising fresh Arnot fly ash and Skoongesig and Toeseep AMD from Landau colliery. The critical difference between these two types of AMD is that Toeseep contains significantly higher concentrations (>18000 mg/l) sulphate than Skoongesig AMD. The raw material selected for use in this chapter were characterised and the rationale for their selection was detailed in **Chapter 4**. These experiments are conducted firstly at beaker scale (500 ml AMD) and thereafter large scale experiments (250 l AMD). At each stage of the neutralisation experiments the following conditions were investigated:

- pH and EC,
- Iron, aluminium and sulphate concentrations.

The sulphate results of these experiments were compared to those achieved by alternate treatment technologies as described in **Chapter 3**.

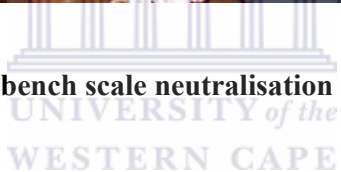
5.1 BEAKER SCALE NEUTRALISATION EXPERIMENTS WITH SKOONGESIG AMD

Beaker scale neutralisation experiments were conducted to demonstrate the neutralisation potential of Arnot fly ash. Various quantities of fly ash were added to 500 ml of AMD at pre-determined fly ash:AMD ratios. The following fly ash:AMD ratios were studied: 1:1, 1:2, 1:3, 1:5 and 1:10. Fresh AMD samples were firstly added to the beakers and stirred by overhead stirrers at 250 rpm/min for approximately 30 min to allow the AMD to reach room temperature. The reason for the use of overhead stirrers was that with magnetic stirrers the iron in the fly ash tended to become attached to the magnet whilst reciprocating shakers did not suspend all the ash (Klink, 2006). The stirring rate of 250 rpm/min provided adequate

agitation without sample spillage. The fly ash was then weighed in beakers and slowly added to AMD with continuous stirring (Figure 5.1).



Figure 5.1: Stirrer unit for bench scale neutralisation experiments



5.1.1 Results of beaker scale experiments with Skoongesig AMD

The experimental results of beaker scale neutralisation experiments are presented and discussed in this section. Beaker scale experiments were performed with automatic overhead stirrers as described in section 5.1 and illustrated in Figure 5.1. The pH and conductivity (EC) of each mixture was monitored at regular time intervals to establish the neutralisation potential and maximum pH attainable at the various ratios listed in section 5.1. The 1:1 ratio applied 500 g Arnot fly ash to 500 ml Skoongesig AMD and the 1:10 ratio utilised 50 g Arnot fly ash to neutralise 500 ml Skoongesig AMD. The graph in Figure 5.2 illustrates the pH and EC trends with time for the beaker scale neutralisation experiments.

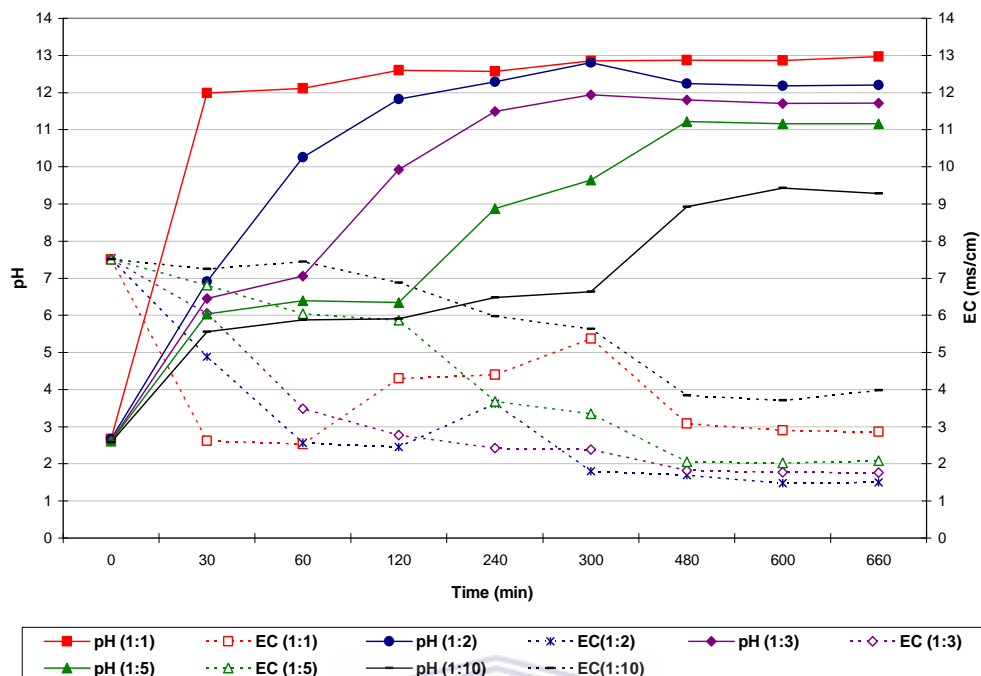
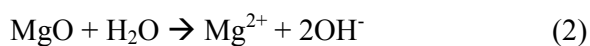


Figure 5.2: Variation in pH and EC for different ratios of fly ash:AMD in beaker scale neutralisations experiments with Skoongesig AMD and Arnot fly ash

A rapid increase in pH from 2.67 to 12.97 was noted within the first 30 minutes of the reaction for the 1:1 fly ash:AMD ratio (Figure 5.2). The pH of all other ratios increased at slower rates, depending on the ratios, with a corresponding decrease in conductivity in each case. The dissolution and hydrolysis of oxide components such as CaO and MgO (equations 1 and 2) from fly ash contributes to an increase in solution pH (Petrik *et al.*, 2006).



An increase in conductivity was noted for the 1:1 and 1:2 ratios within 120 and 240 minutes respectively, in conjunction with a decline in the pH slope. This was possibly due to the release of certain metals species from the fly ash at the corresponding pH. Buffering zones were detected for the 1:10 and 1:5 ratios at pH (5.5-6.0) and pH (6.3-6.5) respectively. These buffering zones are associated with the oxidation and

hydrolysis of Fe^{2+} (Stumm and Lee, 1961). The associated release of H^+ ions slows down the neutralisation process due to increased acidity. The absence of buffering zones with the lower ratio experiments indicates the ability, probably due to the excess fly ash present, to overcome the buffering capacity of the AMD. The pH equilibrated at $\text{pH} > 11$ for all ratios except the 1:10 ratio at various times depending on the fly ash:AMD ratio. The final pH values showed decreasing trends with larger ratios and the conductivity results were vice versa. The two factors that dictated the final solution pH and rate of reaction in the neutralisation reactions are the ratio of fly ash:AMD and the contact time. Owing to the large mass of fly ash applied, the 1:1 ratio resulted in a thick slurry, which altered the efficiency of agitation and made separation of the final liquid from solids via filtration methods difficult. Further, the extremely rapid rise in pH proved this ratio to be less viable for practical purposes since control of the endpoint may be difficult. Alternately, in comparison to all ratios tested, the pH of the 1:3 ratio steadily increased to neutrality within an hour and eventually stabilised at a pH of 11.67 after 240 minutes. All reactions were terminated when the pH stabilised at 660 minutes. The solids (fly ash fraction) settled efficiently and separation of the two phases was accomplished without any difficulties.



The liquid portions were separated via filtration through a $0.2 \mu\text{m}$ Millipore filter for aluminium and total iron analysis by ICP and sulphate analysis by IC. The iron, aluminium and sulphate trends for the various ratios are graphically depicted in Figures 5.3-5.5. The concentrations of all elements are presented on a logarithmic scale. Original AMD refers to the bulk solution prior to neutralisation with fly ash.

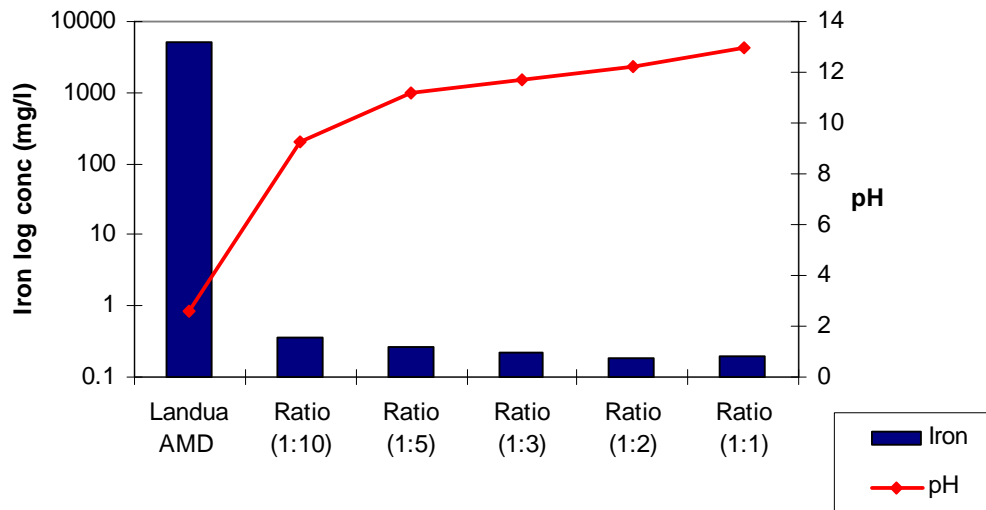


Figure 5.3: Effect of fly ash neutralisation on iron attenuation at varying pH endpoints and fly ash:AMD ratios.

There was a decreasing trend in iron concentration as the fly ash:AMD ratios decreased (1:10 → 1:1) and a corresponding increase in pH at 660 minutes. In comparison to the original concentration of 5000 mg/l, all ratios achieved a > 99% reduction in iron concentration at pH values >7. Ratios 1:2 and 1:1 achieved almost total iron removal at pH values >12 and EC values <2 mS/cm. This is comparable to the high cost membrane and ion exchange technologies discussed in **Chapter 2**. The metal precipitation and ion exchange technology applied by Feng *et al* (2000) produced > 99 % iron reduction but with an initial concentration of only 942 mg/l iron. Feng *et al.* (2000) also suggested that the iron precipitates out as hydroxides and oxyhydroxides. Gitari *et al.* (2008) conducted research into the factors that control the solubility of major inorganic contaminants in coal mine wastewater. AMD was neutralised with fly ash at 1:3 and 1:15 ratios. The solid residues underwent mineralogical analysis whilst thermodynamic modelling with PHREEQC was applied to calculate the saturation indices of selected mineral phases. Gitari's investigation indicates that an initial decrease of Fe^{3+} occurs at pH 4-4.5 possibly as $Fe(OH)_3$ and schwertmannite, $(Fe_8O_8(OH)_{12}(H_2O)_{26})$ in the presence of high sulphate concentrations at both ratios. At pH values >5.5, a significant decrease in total iron concentration was observed and attributed to the precipitation of $Fe(OH)_3$ when Fe^{2+} is oxidised followed by hydrolysis. Further to his investigations, PHREEQC

simulation indicated that the solution was over-saturated with $\text{Fe}(\text{OH})_3$ and goethite (FeOOH) throughout the neutralisation reaction for both ratios.

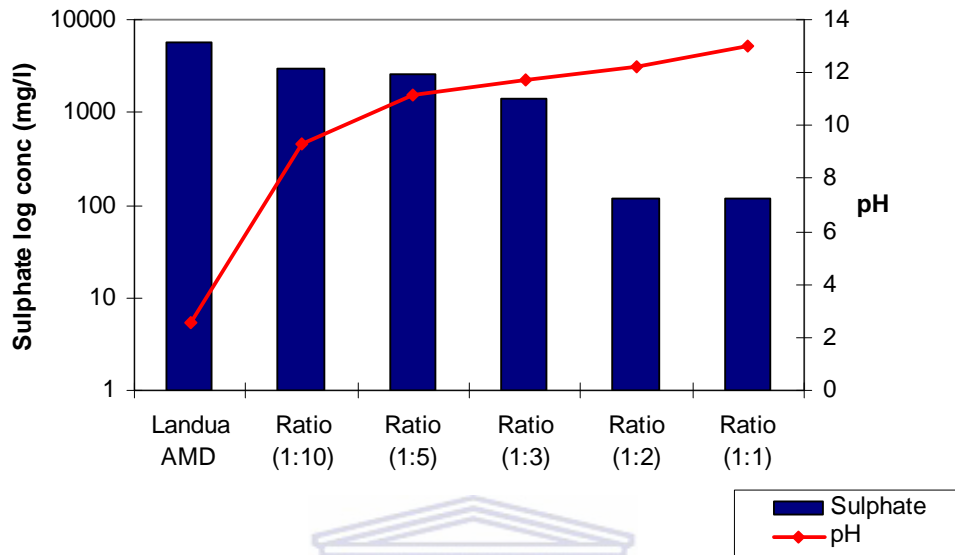


Figure 5.4: Effect of fly ash neutralisation on sulphate attenuation at varying pH endpoints and fly ash:AMD ratios

Approximately 50% and 98% reduction in sulphate concentration was achieved with the 1:10 and 1:1 ratios respectively. As was seen with iron, the decreasing trend followed the increase in pH values for the different ratios. Almost total reduction in sulphate was achievable at pH values >12 . Below this pH value, only partial sulphate reduction was achieved. These include ratios 1:3, 1:5 and 1:10 with final pH values <12 .

Research conducted by O'Brien, 2000 suggested that sulphate concentrations are probably controlled by the precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) at low pH and ettringite ($\text{Ca}_6\text{Al}_2\text{O}_6(\text{SO}_4)_3 \cdot 32\text{H}_2\text{O}$) at high pH with other metal species. The investigations conducted by Gitari *et al.* (2008) revealed that at pH values >5.5 , gypsum precipitates out of solution and the calculated saturation indices also indicated that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), barite (BaSO_4) and celestite (SrSO_4) was at saturation or near saturation throughout the neutralisation reaction. Sulphate concentrations are further reduced at pH >6.0 , where high concentrations of sulphate are adsorbed during $\text{Fe}(\text{OH})_3$ precipitation. At pH >8.0 , the formation of Al-Si-Ca-

SO₄ rich mineral phases were identified and attributed to a further decrease in concentration (Gitari, 2008).

In comparison to the various alternate technologies discussed in Chapter 2, the capacity to reduce the sulphate concentrations in the AMD source with fly ash was excellent.

Table 5.1: Comparison of treatment technologies for sulphate attenuation

Technology	Sulphate Reduction (%)
Chemical Treatment	
Lime/Limestone	59
Savmin	89
Fly ash	98
Membrane Systems	
Reverse Osmosis	99
Electro-dialysis reversal	93
Ion exchange	
GYP-CIX	99
Biological Sulphate Removal	
Bioreactors	90

Fly ash treatment of AMD, in particular sulphate attenuation, was comparable to membrane and ion exchange technologies and even better than other chemical treatment regimes utilising lime/limestone (Table 5.1). The simplicity and lower financial implications renders the fly ash treatment of AMD a superior alternative.

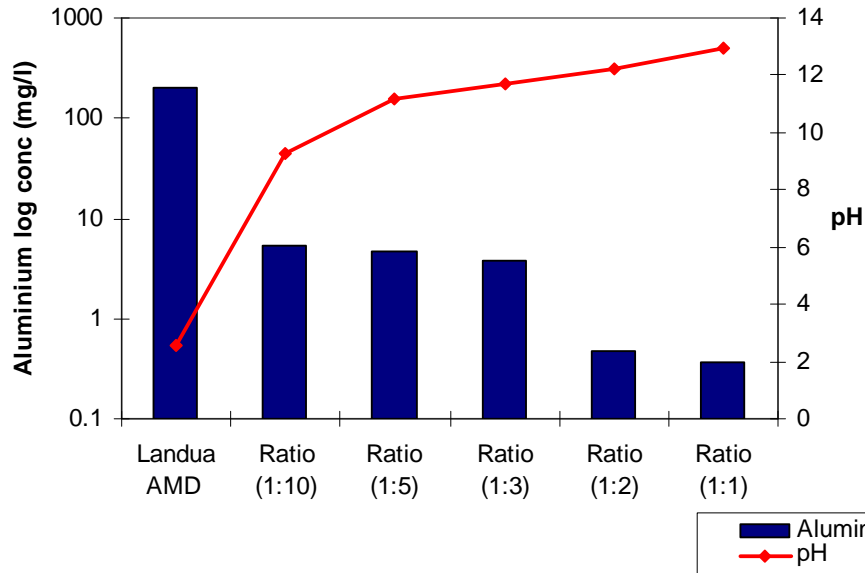


Figure 5.5: Effect of fly ash neutralisation on aluminium attenuation at varying pH endpoints and fly ash:AMD ratios

Aluminium concentrations decreased with an increase in pH (Figure 5.5) within 660 minutes. The initial aluminium concentration was reduced from 200 mg/l to 0.37 mg/l for ratio 1:1, resulting in a 99 % decrease at pH values >12. The variation in aluminium concentration is attributable to the formation of a variety of mineral phases at various pH values. These mineral phases include jurbanite, basaluminite, boehmite, gibbsite and diaspore at various pH levels (Gitari *et al.*, 2008). Gitari *et al.* (2008) also highlighted the fact that sulphate further influences the presence of these mineral phases e.g. gibbsite is not stable in acid sulphate waters and precipitated only as the sulphate concentration reduced. Gibbsite's presence was observed in the pH range 5.53 and 9.12. The calculated saturation indices indicated that both gibbsite and boehmite were over-saturated in the pH range 5.49-9.88.

The initial neutralisation experiments were monitored for 660 minutes. The AMD and fly ash contact times were increased in further experiments to determine the stability of the neutralisation reaction i.e. if the pH or EC changes. An additional ratio 1:20 was added to this batch of experiments in an attempt to reduce the final sludge volumes. The 1:1 to 1:3 neutralisation reactions are depicted in Figure 5.6 and the 1:5 to 1:20 neutralisation reactions are depicted in Figure 5.7.

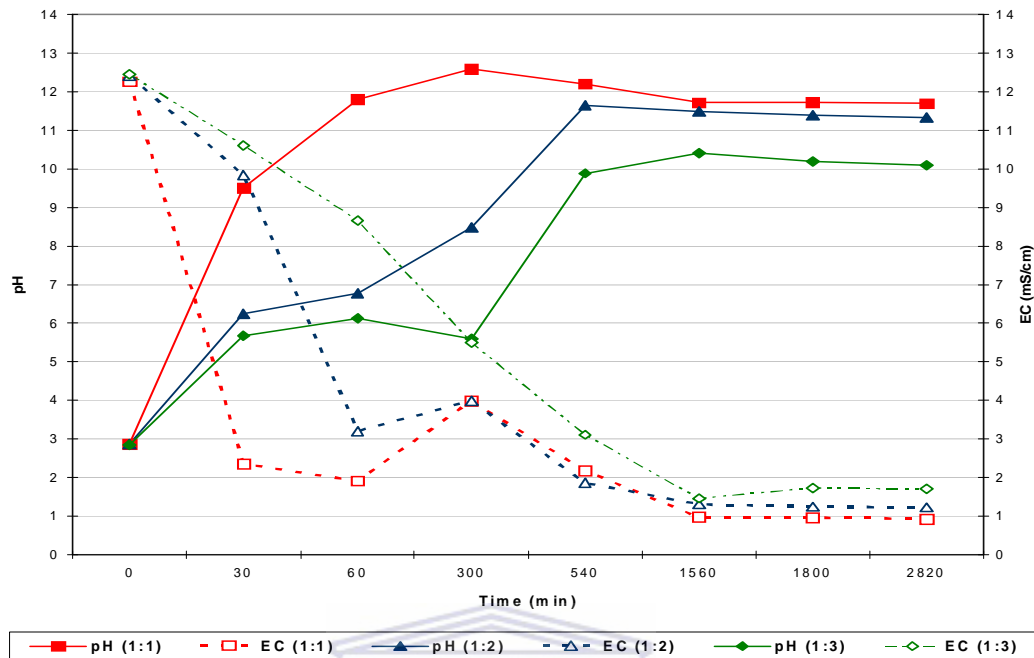


Figure 5.6: Variation in pH and EC with extended contact time for the 1:1 to 1:3 ratios with Skoongesig AMD and Arnot fly ash

A similar rapid initial increase in pH was noted for the 1:1 ratio (Figure 5.6). Of particular importance, was the rise in conductivity observed between 1 and 5 h for both the 1:1 and 1:2 ratios. This was also evident in the first experiments (Figure 5.2). This could be attributed to the release of calcium and silica from the fly ash. The Ca^{2+} release could have initiated gypsum precipitation and triggered the increase in pH at that point in the reaction (300 minutes and $\text{pH} > 5$) for the 1:2 and 1:3 ratios. Buffering zones were detectable at similar pH values identified in the initial experiment. The pH stabilised after approximately 47 h at pH values > 10 . The AMD and fly ash contact was maintained for an additional 20 h after which time the experiment was terminated. During this period the pH changed only slightly from 10.4 to 10.2 for the 1:3 ratio. The results for the larger ratios i.e. 1:5, 1:10 and 1:20 are depicted in a separate graph due to the difference in time scales. The pH for these ratios stabilised faster than the lower ratios.

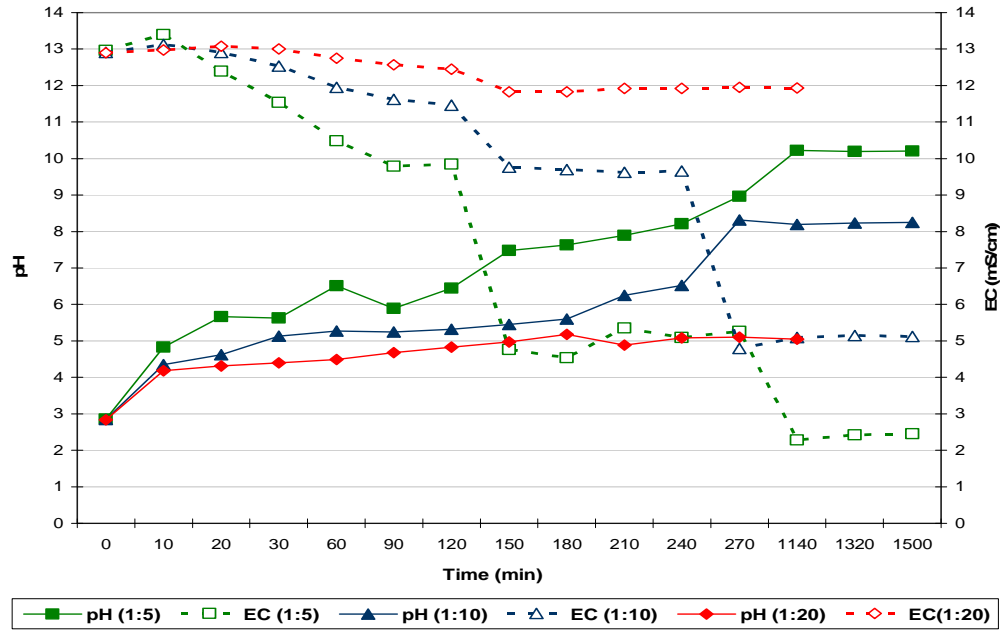


Figure 5.7: Variation in pH and EC with extended contact time for the 1:5 to 1:20 ratios with Skoongesig AMD and Arnot fly ash

The above neutralisation experiments were terminated once stable values for pH and EC were obtained. The 1:20 ratio was ineffective in obtaining neutrality (pH ~5.1) and reaction equilibrium was reached within 4.25 h. The pH and EC stabilised at 5.05 and 11.93 mS/cm respectively. The 1:5 and 1:10 ratios displayed buffering zones between pH 5 and 6 for extended periods. The buffering was overcome after approximately 2.5 hrs after which the pH steadily increased. The 1:5 ratio achieved a final pH of 10.2 and 1:10 a final pH of 8.25. These ratios took much longer to achieve neutral pH values in comparison to the lower ratios i.e. 1:1, 1:2 and 1:3. The lower ratios could be either advantageous whereby the faster reactions could result in more AMD being treated in a shorter time period or disadvantageous whereby larger volumes of fly ash are utilised resulting in the handling of greater sludge volumes and control of the neutralisation reactions could prove difficult. Further, more efficient mixers are available to be utilised at large scale which could result in faster neutralisation times for the higher ratios which would then reduce the volumes of sludge generated by the neutralisation process. These factors are to be considered when applying the technology at large scale.

5.1.2 Summary of beaker scale neutralisation experiments

Neutralisation experiments conducted at beaker scale, treating 500 ml of AMD with fly ash have proven that fly ash can effectively neutralise AMD whilst efficiently reducing the concentration of sulphate, iron and aluminium. At ratios of 1:1, 1:2, 1:3, 1:5 and 1:10, Arnot fly ash neutralised Landau AMD within different time periods and the final pH values, which were mostly >10 was maintained for extended periods. The significant decrease in sulphate concentration at the various ratios was notable. Greater than 90 % sulphate removal was observed. Fly ash treatment of AMD, in particular sulphate attenuation, was comparable to membrane and ion exchange technologies and even better than other chemical treatment regimes utilising lime/limestone. Iron was almost entirely removed from solution for all ratios and pH values >7. Aluminium concentrations decreased consistently with decreasing ratios. Overall >95 % aluminium reduction was achieved.

Whilst the 1:1, 1:2 and 1:3 fly ash:AMD ratios were most efficient in neutralising the AMD and achieved optimum reduction in iron, sulphate and aluminium concentrations, the volume of fly ash utilised and resulting sludge was far in excess of the other ratios. Practically, this could lead to difficulties with regards to handling and disposal of such large volumes of sludge and increased costs for the transportation of fly ash. Further, the reaction rate was rapid based on the time taken to reach neutral pH values. The 1:5 or 1:10 ratios on the other hand, achieved neutral pH values within a less rapid time period and acceptable reduction in iron, sulphate and aluminium. Based on these factors, a ratio between 1:3 and 1:10 was tested in large scale experiments. This study has showed that it is possible to control the rate of neutralisation and the pH endpoint by adjusting the ratio of fly ash:AMD.

5.2 LARGE SCALE NEUTRALISATION EXPERIMENTS

Having observed the potential of fly ash to neutralise and ameliorate AMD at beaker scale, it was prudent to test the technology at large scale. These experiments were expected to provide further information with regards to the process conditions for full scale implementation of the technology. The same source of fly ash and AMD material utilised in the beaker experiments were initially applied in the large scale

experiments. Following the results of the initial tests, AMD from another source, with significantly higher sulphate concentrations, were also applied in large scale experiments. The rationale behind this was again to determine the effectiveness of sulphate reduction whilst neutralising AMD with fly ash.

5.2.1 Large scale mixer design

The following variables were considered when identifying a suitably designed large scale mixer:

- Efficient agitation
- Slurry density and flocculation
- Bulk solids separation and handling
- Water recovery

The mixing tank was a 250 l stainless steel tank, fitted with a turbulator aerator. The turbulator design was such that air intake was made possible to achieve optimum iron oxidation with efficient agitation of the fly ash/AMD mixture (Figure 5.8). The slight conical base of the tank allowed for quick and simple separation of the sludge from the liquid after settling of the solids. The top view in Figure 5.9 shows the extra baffle plates that were added to enhance mixing. The stirrer was set at a rate of 1000 rpm.



Figure 5.8: Large scale mixer with 250 l tank capacity and turbulator/aeration unit.



Figure 5.9: Agitation and aeration achieved with large scale mixer

5.2.2 Large scale neutralisation experiments of 1:3 to 1:10 Arnot fly ash:Skoongesig AMD ratios

Beaker scale experiments indicated that ratios ranging from 1:1 to 1:10 were suitable to neutralise the AMD efficiently and achieved good reduction in the concentrations of iron, sulphate and aluminium. However, the 1:1 to 1:2 ratios produced excessive sludge and the increase in pH was extremely rapid whilst the 1:3 and 1:10 ratios produced lesser sludge and the pH increased at a slower, more controllable rate. Hence, it was decided to test different ratios, but greater than the 1:2 ratio. The following ratios were tested at large scale:

- FA:AMD (1:3)
- FA:AMD (1:4)
- FA:AMD (1:5)
- FA:AMD (1:10)

Figure 5.10 illustrates the pH and EC trends with time for the large scale neutralisation experiments.

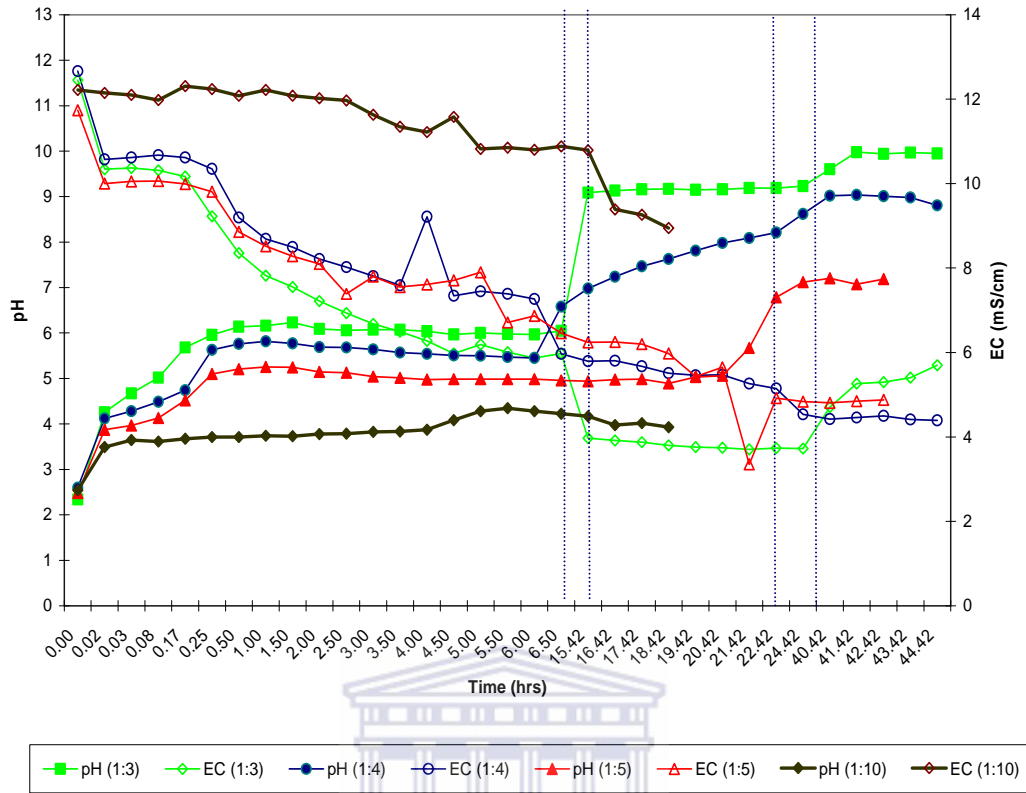


Figure 5.10: Variation in pH and EC for different ratios of fly ash:AMD (in large scale neutralisations experiments with Skoongesig AMD and Arnot fly ash)

The 1:10 ratio was terminated within 20 h since the pH did not increase to neutral levels and stabilised at a pH of ~4.2. The 1:3 ratio increased steadily and achieved a stable pH >9. Due to the long reaction time of ~44 h and since manual data logging was conducted, some data were not recorded for both pH and EC for a period of 9 h. The time lag is indicated by the vertical lines in Figure 5.10 and was evident for the 1:3 ratio which increased in pH from 6.05 to 9.09 within the 9 hour period where no pH and EC results were recorded. Automatic data loggers are recommended for continuous monitoring. In comparison to the beaker experiments, break through the buffer zone seemed to have taken much longer at all ratios. Further, the 1:10 performed better with regards to neutralising the AMD at beaker scale than large scale experiments. Beaker scale experiments achieved pH values >7, however the large scale experiments did not. This could be attributed to various factors. Firstly, a change in fly ash composition and/or mineralogy of the fly ash, due to re-sampling,

could significantly alter the potential and rate of neutralisation. The ash that was re-sampled was not confirmed by additional characterisation. As mentioned in **Chapter 1**, the coal source and boiler conditions influence the chemical composition or mineralogy of fly ash as well as mixing conditions. The variability in fly ash composition implies that a set formula or standard procedure may not always be suitable when neutralising AMD with different qualities of fly ash. Alternately, the agitation rate and other design parameters could further influence the rate at which neutralisation is achieved. The 1:4 ratio followed a similar trend to the 1:3 ratio and reached neutral pH levels after ~15.4 h. The EC displayed a gradual and continuous decreasing trend except for one data point at 60 hrs which spiked. There was no corresponding trend in pH when the spike occurred and this was attributed to analytical error. Also by means of extrapolation, it was determined that the 1:5 ratio achieved a pH of 7 after ~22 h with a consistent decreasing trend in EC. A buffering region was observed similar to that observed with the beaker experiments which continued over an extended period between pH 5.6 and 6.0. The buffering zone persisted for 12 h for the 1:5 ratio, 5 h for the 1:4 ratio and 2 h for the 1:3 ratio. As was noted with the beaker scale experiments, the buffering in this range is attributed to the oxidation and hydrolysis of Fe^{2+} (Stumm and Lee, 1961). Increased ratios, utilising more fly ash could overcome this buffering zone.

5.2.3 Large scale neutralisation experiments at 1:6 fly ash:AMD ratio with varying agitation rates

Based on the results of the preliminary large scale experiments, which indicated positive trends towards neutralisation, a 1:6 ratio of Arnot fly and Skoongesig AMD was tested at two different agitation rates. Increased agitation rates may possibly increase the rate of reaction and allow the use of lower ratios and ultimately smaller ash volumes. The experiments were conducted individually at rates of 1000 and 1500 rpm. The reaction was terminated within a shorter time period in comparison to the experiments conducted in section 5.2.3 since the primary objective was to determine the effectiveness of varying agitation rates. 5200 l Skoongesig AMD was added to the tank and stirred to equilibrate. 33 kg of Arnot fly ash was added to the AMD with continuous stirring. The pH was monitored at regular time intervals with a

portable Hanna pH/EC meter. Figure 5.11 illustrates the variation in pH with time between the two rates of agitation at a 1:6 Arnot fly ash:Skoongesig AMD ratio.

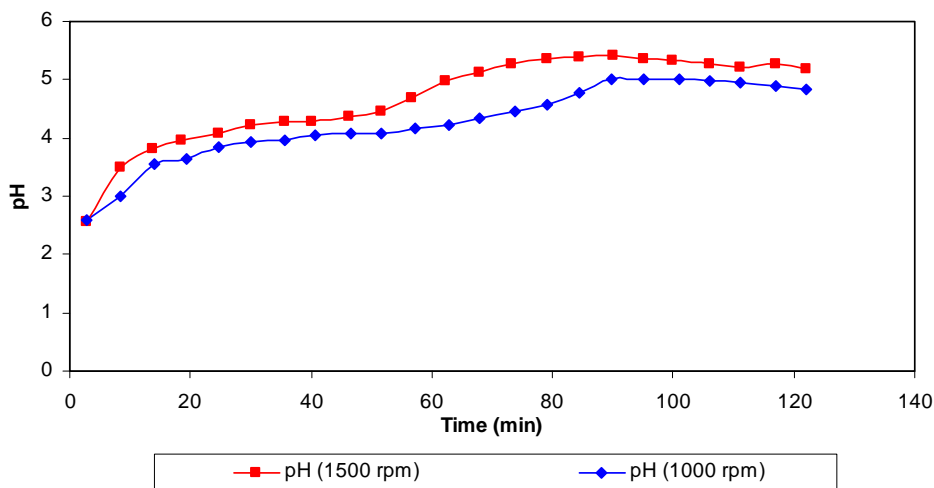


Figure 5.11: Effect of varying agitation rates on the pH of the 1:6 Arnot fly ash:Skoongesig AMD neutralisation ratio

The increase in pH, as shown in Figure 5.11, increased slightly faster at the higher agitation rate of 1500 rpm in comparison to 1000 rpm. The pH stabilised at approximately pH 5 for both the 1000 and 1500 rpm experiments. The buffering zone which was observed in Figure 5.10 cannot be detected in this study due to the shortened reaction time. Samples were extracted at the various time intervals and analysed by Inductively Coupled Plasma Spectroscopy (ICP). Elemental concentrations of iron, sulphate and aluminium, for the 1500 rpm experiment are depicted in Figures 5.12-5.14 respectively.

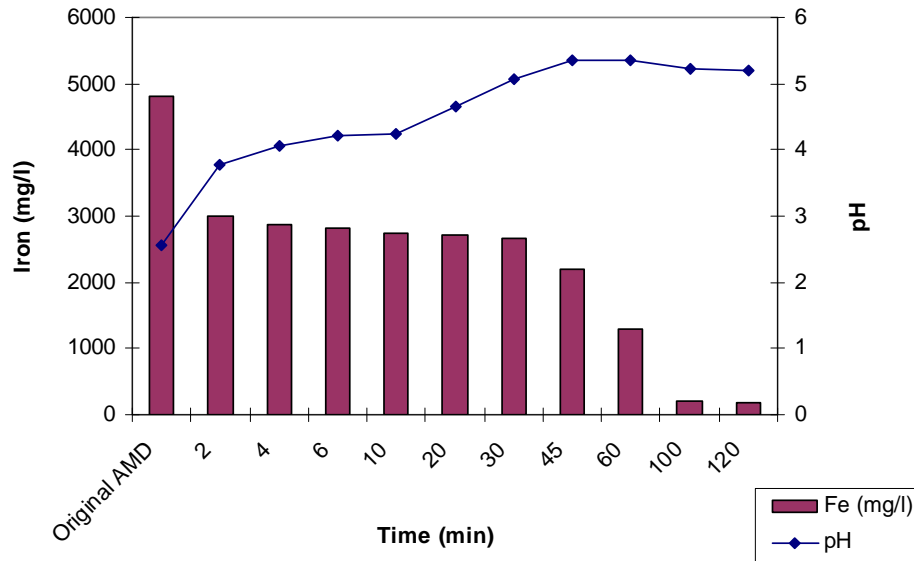


Figure 5.12: Iron reduction with pH variation: neutralisation of 1:6 fly ash:AMD

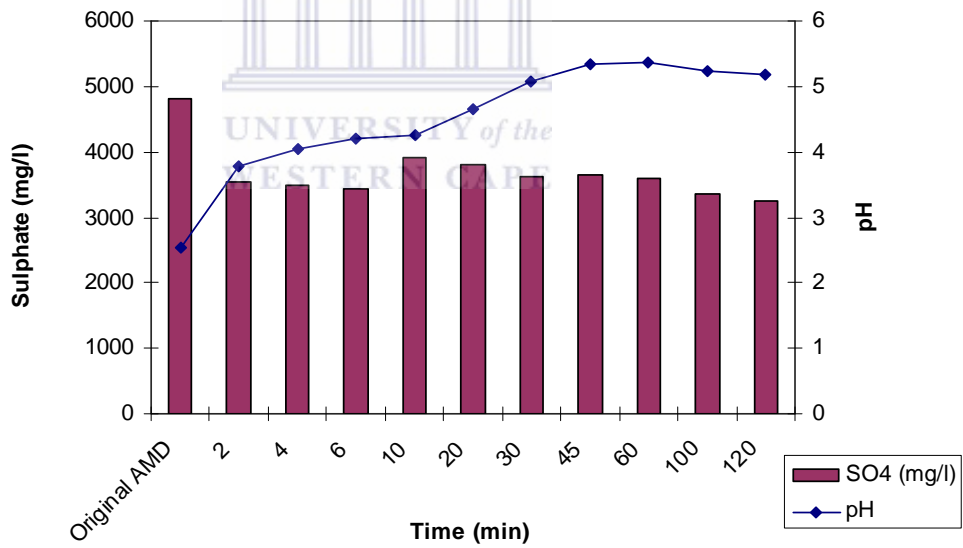


Figure 5.13: Sulphate reduction with pH variation: neutralisation of 1:6 fly ash:AMD

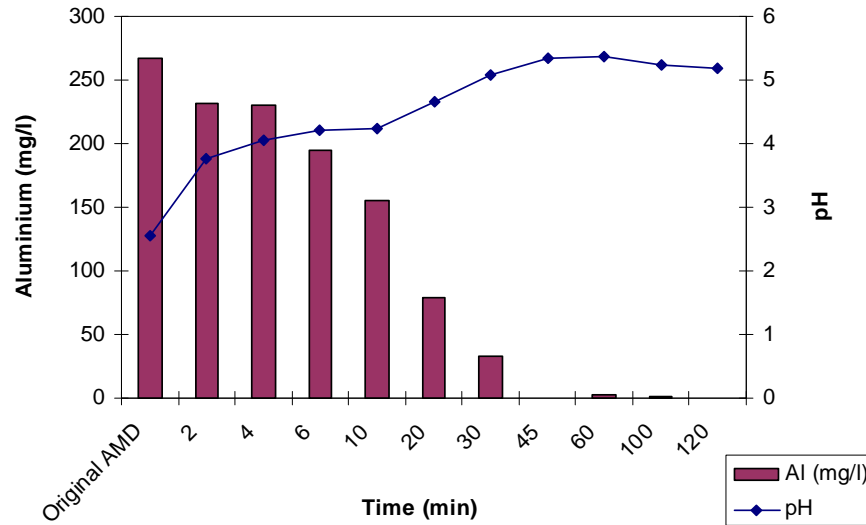


Figure 5.14: Aluminium reduction with pH variation: neutralisation of 1:6 fly ash:AMD

The decreasing iron concentration corresponded with the increasing pH trend (Figure 5.12). A significant decrease was noted as the pH rose above pH 5, attributed to the precipitation of $\text{Fe}(\text{OH})_3$ when Fe^{2+} is oxidised followed by hydrolysis. A 96 % total reduction in iron concentration was achieved at the end of the reaction. Sulphate concentrations (Figure 5.13) varied depending on the pH level over the 2 hour contact time but the results showed only a 32 % reduction being achieved. Greater sulphate reduction is expected at the higher pH values that can be attained by extending the contact time. Another contributing factor is that the volume of fly ash applied was perhaps insufficient, resulting in lesser Ca^{2+} being released and thereby minimizing gypsum precipitation. With larger quantities of fly ash applied to the neutralization process, greater concentrations of Ca^{2+} would be available to combine with SO_4^{2-} enhancing gypsum precipitation. The integrated limestone/lime process only achieved a 59 % reduction in sulphate concentration at pH values >12 (see Table 2.2). Aluminium reduction was in excess of 99 % at a final pH of 5.17 (Figure 5.14). The aluminium concentration was observed to decrease significantly as the pH increased beyond 5 as the various mineral phases, in particular gibbsite are formed (Gitari, 2008).

5.2.4 Large scale neutralisation experiments at 1:6 fly ash:AMD ratio

Since the 1:6 ratio of fly ash:AMD did not reach neutral pH values within the 6 hour contact time in the previous experiments, the experiment was repeated with an extended contact time of 225 min to determine if the buffer zone could be overcome and the pH increased further with a corresponding decrease in elemental concentrations. The experiment was conducted under similar conditions with a 1:6 ratio of Arnot fly ash and Skoongesig AMD and a 1500 rpm stirring rate. The trends during the 225 minute contact time revealed very interesting results. Figure 5.15 illustrates the pH trend with time for the 1:6 Arnot fly ash Skoongesig ratio.

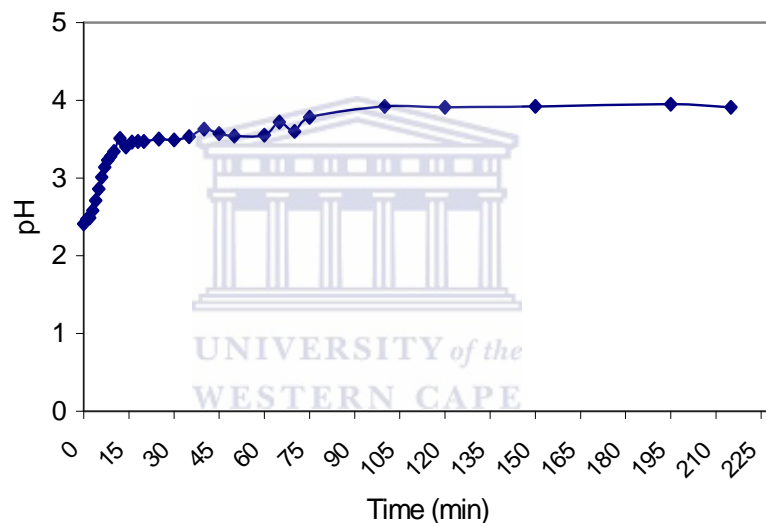


Figure 5.15: pH development at 1:6 fly ash:AMD ratio with extended reaction time

The pH rose at an extremely slow rate and reached a maximum pH of only 4.0 after 105 min (Figure 5.15). This was vastly different to the previous 1:6 experiment which reached a pH of >5 in <30 min in section 5.2.3 (Figure 5.11). Since a new batch of fly ash from Arnot power plant was sampled for these experiments, it was probable that the chemical properties of the fly ash may have altered which could influence its neutralisation capabilities.

The fresh fly ash sample was re-analysed and a notable difference in Loss-on-ignition (LOI) was identified between the fly ash utilised in previous experiments and this

experiment. The LOI, which measures the amount of unburned carbon remaining in the fly ash, is considered to be a significant chemical property for further ash utilisation, in particular in the cement industry where air entraining agents, which impart freeze-thaw resistance to concrete, are adsorbed by the unburned carbon in fly ash thereby destroying the freeze-thaw resistance (Osvalda, 2007; Külaots, 2003). This property was determined by the method described in section 3.3. Table 5.2 tabulates the variability in LOI observed with the original Arnot fly ash and the re-sampled Arnot fly ash.

Table 5.2: Loss on ignition (LOI) of Arnot fly ash

	LOI
Original Arnot fly ash	3.2
Re-sampled Arnot fly ash	6.6

The unburned carbon in the fresh ash was determined to be 6.6 %, which was more than double the carbon content of the original ash of 3.2 % (Table 5.2). Factors resulting in high unburned carbon content in fly ash are ambiguous. Various authors (French *et al.*, 2007) dispute the possibility of the unburned carbon being due to the coal quality, boiler conditions or both. Changes in boiler conditions that affect combustion efficiency could impact on calcite transformation, thereby resulting in increased unburned carbon and reduced free lime content in the fly ash. Such variability's in the fly ash used for neutralisation purposes impacts on the neutralisation reaction as was seen in Figure 5.16. The fly ash neutralisation process would have to be a flexible process and allow for adjustments to cater for changes in the neutralisation process. Since the fly ash with high unburned carbon content was ineffective for neutralisation, a new batch was obtained from Arnot fly ash. The LOI of the new batch of fly ash was determined to 2.5 % and utilised in subsequent experimentation.

5.2.5 Large scale neutralisation experiments at 1:6 ratio with Arnot fly ash and Toeseep AMD

The large scale 1:6 ratio experiment was repeated over a longer contact time with freshly sampled fly ash from Arnot power plant. Toeseep AMD, which had significantly higher sulphate concentrations (>20 000 mg/l) was utilised for the experiment. The presence of excessive sulphate concentration would aid in ascertaining the effectiveness of sulphate attenuation. Fresh Arnot fly ash was sampled and analysed. The unburned carbon content was confirmed to be 2.5 % prior to conducting neutralising experiments (Table 5.2). The 1:6 ratio neutralisation reaction was repeated and the contact time was extended to 100 hours at an agitation speed of 1500 rpm.

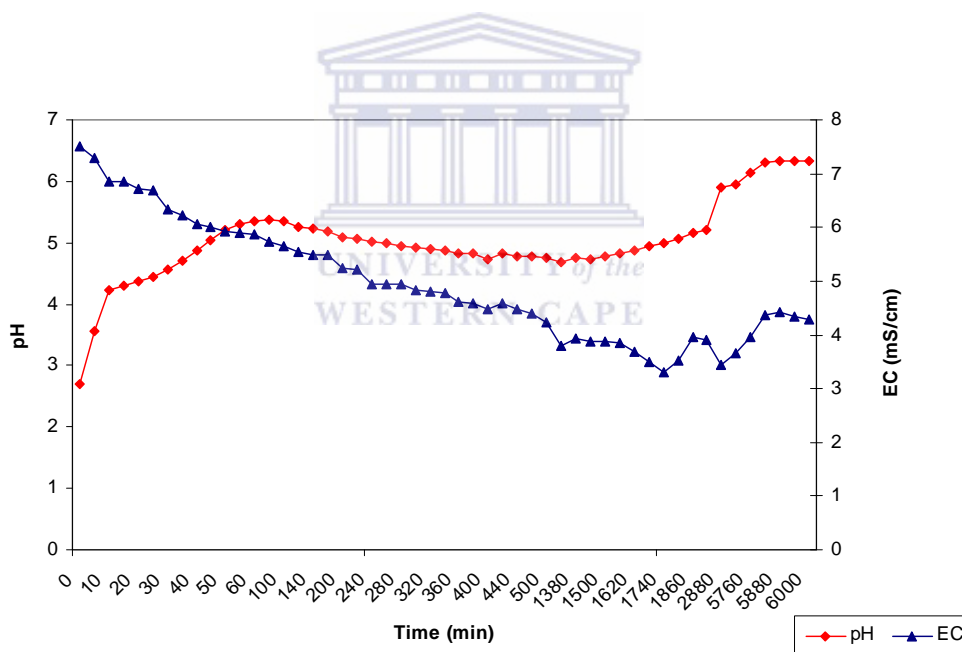


Figure 5.16: Variation in pH and EC for fly ash:AMD at 1:6 ratio with extended reaction time

The pH trends (Figure 5.16) were similar to those obtained in the initial experiment (Figure 5.11). The pH rose steadily and reached pH 5 within the first hour (Figure 5.16). Thereafter, a buffer zone was detected between pH 5 and 6. The buffer zone persisted over a very long time period (~ 45 h). The buffering of the reaction was

eventually overcome and the pH stabilised again at 6.33 at which point the reaction was terminated. The EC decreased continuously, even during the pH buffer zone and the final EC value of 4.3 was obtained. Liquid and solid samples were extracted at various time intervals and elemental iron, sulphate and aluminium analysis was performed.

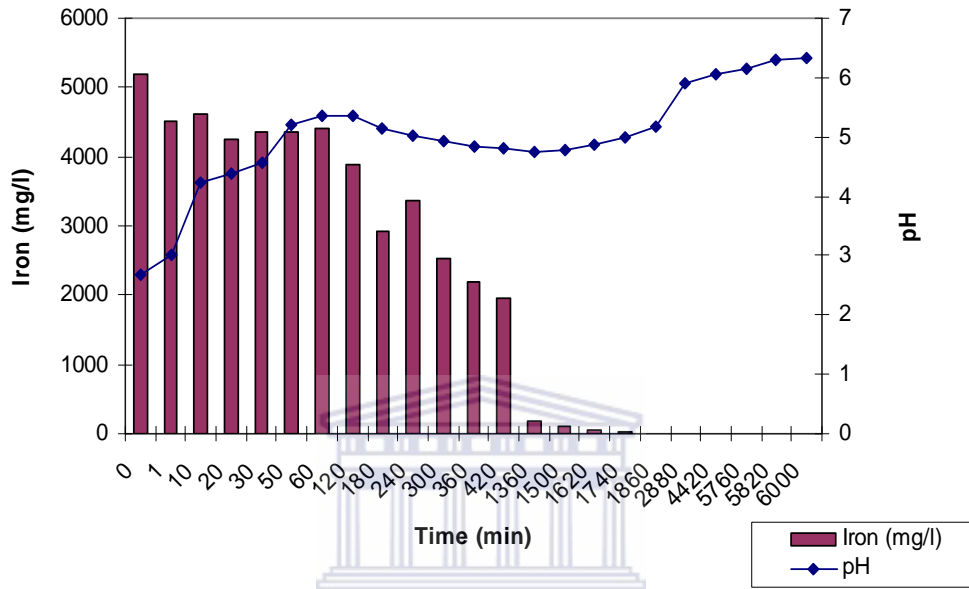


Figure 5.17: Iron attenuation with pH variation: neutralisation of Toeseep AMD with Arnot fly ash at 1:6 ratio

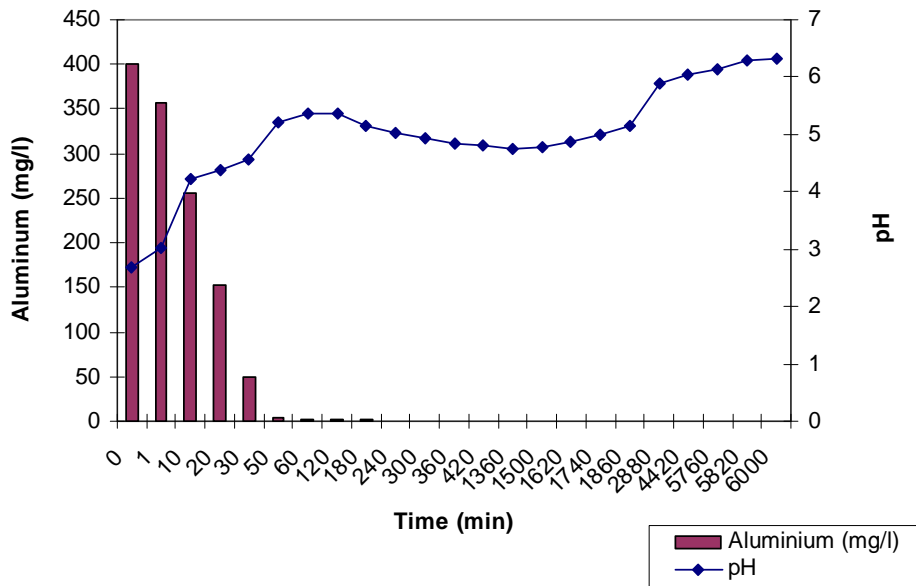


Figure 5.18: Aluminium attenuation with pH variation: neutralisation of Toeseep AMD with Arnot fly ash at 1:6 ratio

Reduction in iron (Figure 5.17) and aluminium (Figure 5.18) concentrations was most effective, achieving 99.99 % reduction, primarily since the pH exceeded the pH levels at which optimum removal of iron and aluminium occurs. This corresponds to a pH of > 5 where optimum iron oxidation and precipitation of various mineral species of aluminium occurred.

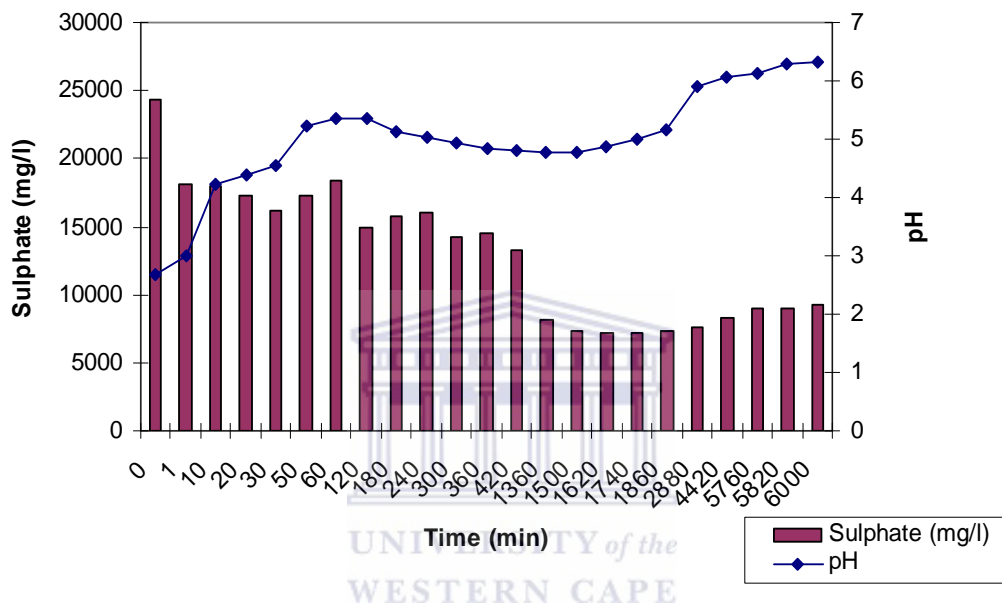


Figure 5.19: Sulphate attenuation with pH variation: neutralisation of Toeseep AMD with Arnot fly ash at 1:6 ratio

Sulphate was only reduced by 68 % (Figure 5.19). The largest reduction in sulphate concentration was probably achieved via gypsum precipitation at pH >5.5 and possibly to a smaller extent via adsorption during $\text{Fe}(\text{OH})_3$ precipitation (Gitari, 2008). However, the pH did not rise much higher than 6, whereby precipitation of various mineral phases did not occur, resulting in less sulphate being extracted from the waters. In comparison to alternate treatment technologies discussed in **Chapter 2**, the 1:6 ratio at large scale, performed better than the lime/limestone treatment but poorly with respect to other treatment processes such as the membrane system and ion exchange which achieved >90 % reduction in sulphate. Based on the beaker studies, lower ratios, with more fly ash, are expected to further increase the pH, thereby resulting in further sulphate reduction.

5.2.6 Morphology of solids by scanning electron microscopy

The 96 hour solid residue sample from the 1:6 Arnot fly ash:Toeseep AMD experiment was subjected to Computer Controlled Scanning Electron Microscopy (CCSEM), as detailed in section 3.3, to determine the mineralogy and elemental partitioning of the solids recovered after neutralisation of AMD with fly ash. Table 5.3 tabulates the phase distribution between the original fly ash and the solid residue recovered from the 1:6 Arnot fly ash:Toeseep AMD neutralisation reaction at 96 hours.

Table 5.3: Volume-% fly ash phase distribution of fly ash and 96 hour solid residue sample from 1:6 Arnot fly ash:Toeseep AMD neutralisation reaction

	Fly ash	96 hour solid residue
Ca-sulphate	<0.1	<0.1
Ca-Oxide/CaMg-Oxide	2.7	0.6
Iron oxide/Fe-S-Oxide	1.0	3.1
Kaolinite/mullite	70.0	55.6
Kaolinite(pyrite,carbonate)	0.4	0.4
Kaolinite(carbonate)	7.4	11.1
Kaolinite(pyrite)	0.8	6.2
Orthoclase	1.4	1.9
Quartz60Kaol40	3.9	5.0
Quartz80Kaol20	4.4	5.4
Quartz	7.6	10.3
TiOxide	0.1	0.1
Other	0.0	0.3
Total	99.7	100.0

There were notable differences in the phase proportions between the original fly ash and the solid residue covered from the neutralisation reaction as determined by CCSEM (Table 5.3). A notable variation in the proportion of Ca-oxide/CaMg oxide was observed between the original fly ash and the 96 hour solid residue sample. The original fly ash contained a 2.7 % Ca-oxide/CaMg oxide which reduced to 0.6 % in

the 96 hour solid residue sample (Table 5.3). This was due to the release of Ca^{2+} which is released from the fly ash and neutralises the AMD. The Ca^{2+} combines with SO_4^{2-} ions in the AMD and precipitates out as gypsum. The increase in the % iron oxide from the Arnot fly ash to the 96 hour solid residue sample was attributed to the precipitation of iron from the AMD during neutralisation. Figure 5.20 illustrates the presence of iron oxide on the surface of the 96 hour solid residue sample. Marker A points to the presence of iron oxide rimming the aluminosilicate particle. Marker B points to an aggregated quartz particle entrained with iron oxide.

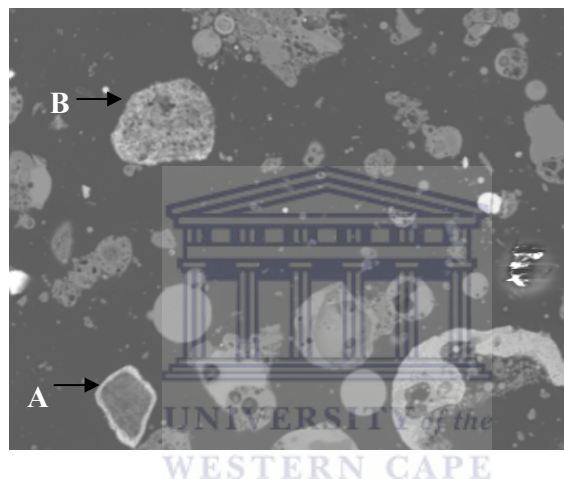


Figure 5.20: Iron-oxide rimming aluminosilicate particle as observed by CCSEM analysis

It can be deduced from SEM-EDS analysis (Table 5.3) that the mechanism of the reaction is the dissolution of the soluble surface salts upon fly ash particles. The dissolved salts react with the acidic metals and ions in the AMD and the minerals either precipitate on the surface of the large spheres or fill in gaps between the small spheres leading to aggregation.

5.2.7 Summary of large scale neutralisation experiments

Large scale neutralisation experiments showed potential for Arnot fly ash to neutralise AMD at specific fly ash:AMD ratios. The lower ratios ranging from 1:3 to 1:5 were most effective in neutralising the AMD whilst those greater than 1:5 were less efficient unless the contact time was extended. Iron and aluminium reduction was effective, with >99 % reduction achieved, at all ratios achieving near neutral or neutral pH's. Sulphate concentrations were reduced by 68 %, however the data indicated that pH values >7 are necessary for optimum sulphate reduction. In comparison to alternate treatment technologies discussed in Chapter 2, the 1:6 ratio at large scale, performed better than the lime/limestone treatment but was less efficient than embrane systems and ion exchange which achieved >90 % reduction in sulphate. Based on beaker scale experiments, lower ratios, with more fly ash, are expected to further increase the pH, thereby achieving better sulphate attenuation. The change in rate of neutralisation from the beaker to large scale experiments and unsuccessful attempt at neutralisation with the 1:6 ratio due to high unburned carbon content in the fly ash, highlighted two important factors in the neutralisation of AMD with fly ash. The first being that process conditions e.g. stirring rates could alter the rate of the neutralisation reaction and the second was that variability in fly ash composition and AMD composition could alter the efficiency of neutralisation and thus impact on elemental reduction. Thus, a standard procedure would not always be applicable for different qualities of fly ash applied for AMD neutralisation and amelioration. The process should be monitored and either the contact time increased or more fly ash added to adjust to the correct pH endpoint to achieve maximum sulphate attenuation. Fly ash could offer a significantly less expensive and less complex alternate to technologies e.g. RO, EDR and ion exchange with similar, if not better results. In comparison to the commonly used limestone process, fly ash was capable of raising the pH of the AMD to higher levels thereby reducing sulphate more efficiently. Ultimately, the results clearly indicated that fly ash could be effectively applied to neutralise AMD and achieve optimum reduction of iron, aluminium and sulphate at the required pH.

CHAPTER 6

FEASIBILITY STUDY OF FLY ASH VERSUS LIMESTONE TREATMENT OF AMD

6.1 INTRODUCTION

Based on the results obtained in **Chapter 5**, this chapter demonstrates the feasibility of implementing the active neutralisation process at pilot scale in comparison to the conventionally used limestone treatment process. The potential to employ an integrated waste management scheme, based upon the use of fly ash for AMD treatment is presented.

6.2 BACKGROUND

6.2.1 Limestone Neutralisation

Traditionally, limestone is used for the neutralisation and partial sulphate removal of acidic mine waters through gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) precipitation prior to discharge. Sulphate removal is limited by the solubility of gypsum and is thus not effective in reducing sulphate concentrations. Anglo Coal in South Africa has implemented the use of limestone in the High Density Sludge (HDS) plant (Maree *et al.*, 2004). To date, two full-scale limestone make-up and dosing plants have been installed at Landau Colliery. The first was installed at the Navigation Plant and the second at Kromdraai opencast mine. The Navigation plant limestone system consists of the following (Maree *et al.*, 2004) (Figure 5.1):

- Limestone slab
- Density meter
- Recycle pump
- Mixing Tank
- Dosing Tank
- Transfer pumps

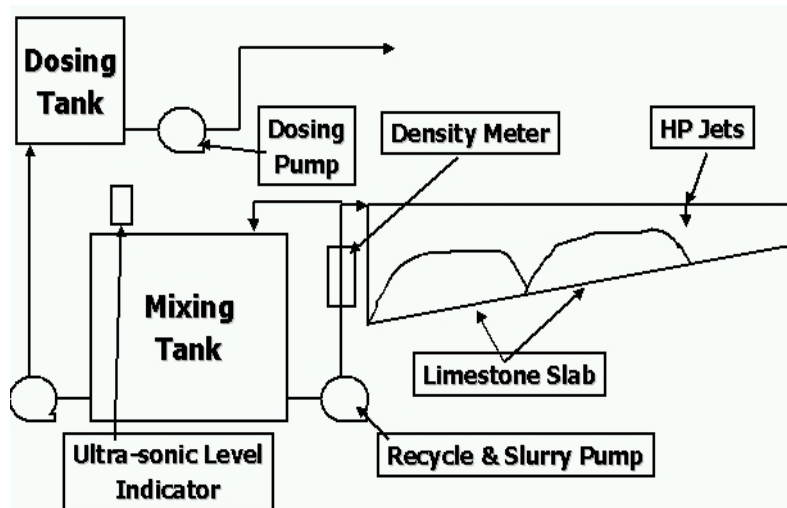


Figure 6.1: Limestone mixing and dosing plant (Greiben *et al.*, 2004)

Limestone is dumped onto the inclined concrete limestone slab and slurried (5-15%) with a water jet (Figure 6.1). The density of the slurry, which is monitored continuously with an on-line density meter, controls the direction of the water. When the slurry density reaches the set value, the water jet sprays on the lower end of the slab where the slurry gravitates into the CaCO_3 -slurry make-up tank. Transfer pumps transfer the limestone slurry from the mixing tank to the dosing tank (Figure 6.1) where it is dosed to the conditioning tank containing the AMD. Electrical conductivity, pH, and sulphate measurements are made at this stage. After mixing, the slurry is transferred to the aeration tank to oxidise the iron and strip CO_2 . Flocculant is added to the turbo-circulator for enhanced settling. The settled sludge or underflow is recycled while the liquid portion or overflow is transferred to the raw water dam for use as make-up for the coal processing plant.

The feed water, conditioning tank, aeration tank and turbo-circulator are sampled every eight hours to ensure that optimum iron oxidation and neutralisation is occurring. The samples are monitored for pH, EC, acidity as mg/l CaCO_3 , ferrous iron as mg/l Fe (II) and alkalinity as mg/l CaCO_3 .

6.2.2 Fly ash as an alternative to limestone neutralisation

The free alkalinity imparted by CaO and other ash components and the fact that fly ash has a very high surface area and small particle size make South African fly ash a good neutralisation agent and AMD ameliorant.

The potential of using South African fly ash as a liming substitute was investigated, at both bench and large scale, in active acid mine drainage treatment systems in **Chapter 5**. Two waste products (i.e. AMD and fly ash), were reacted together in an active treatment system and produced much cleaner effluent waters. Sulphate removal was excellent depending on the final pH and the EC decreased significantly.

Long term performance and stability criteria were assessed for application of fly ash as well as the insoluble, pH neutral, bulk solid residues derived from the neutralisation process as an in-situ barrier suitable for ash walling in the passive treatment of AMD or as backfill material in mines (Reynolds, 2004; 2006). The stability, leaching characteristics and performance of fly ash residues or ash with various additives as backfill materials useful for underground placement has been determined (Petrik *et al.*, 2006, Gitari *et al.*, 2008). The physical and chemical properties that were ascertained included characteristics such as hardness, strength as well as the chemistry and long term phase transition kinetics of solid fill material that may in future be in contact with acid mine drainage or seepage waters.

In order to determine the feasibility of using fly ash as passive AMD treatment system over a long term period it was necessary to monitor the quality of water. Passive column studies were assessed with different combinations of various South African fly ash and AMD sources (Reynolds, 2004: 2006). The permeate water (also termed leachate) recovered after passive percolation of AMD through columns of fly ash of various lengths was analysed for chemical composition to understand the changes to water quality over time and to model systems in which long term contact between ash and raw AMD may occur.

It was found that fly ash as well as the solid residues recovered after active neutralisation are suited to be utilised to treat AMD in-situ in passive systems as reactive barriers or underground as backfill in mined out areas to control AMD generation (Petrik *et al.*, 2006, Gitari *et al.*, 2008). AMD water quality significantly improved during permeation through fly ash and the mineralogy of the fly ash changed due to contact with the AMD (Reynolds, 2004; 2006). Column leaching showed excellent improvement in terms of toxic element removal within the first few days and over the longer term.

Although clear mineralogical changes were not discernable by XRD, the fact that the columns blocked over time indicated agglomeration or coalescence of ash particle by insoluble precipitates that formed upon contact of AMD with fly ash (Reynolds, 2004; 2006). This showed the potential of ash walling as a reactive barrier to direct AMD flows. Iron precipitated as minerals such as oxyhydroxides with low crystallinity. Sulphate precipitated in the form of gypsum or ettringite.

The long term chemical changes within backfill and the influence of acid waters on the chemical stability of backfill (e.g. influence of AMD entering from another section of the mine) were investigated (Petrik *et al.*, 2006). Simulated AMD was percolated through fly ash and solid residues recovered from the neutralisation step, in column leaching studies in order to model the chemical and mineralogical changes that could be expected over time when solid residues are placed underground as fill or backfill material in possible contact with AMD flows. The solid residues from the neutralisation reaction were compared to blends with unreacted fly ash to give mixtures of varying ratio (5, 25 and 40% unreacted fly ash) or with solid residues blended with 6% cement on a dry weight basis or with fly ash only (Petrik *et al.* 2006). The solid residues by themselves performed somewhat similarly to the solid residue/fly ash combinations and considerably better than the Portland cement amended blend, once again highlighting their suitability as backfill material, than standard ash/cement binder combinations. It was noteworthy that ash as binder replaces cement successfully (Petrik *et al.*, 2006).

Finally, it was demonstrated that ash and solid residues recovered after contact with AMD to be suitable as feedstock materials for the preparation of high capacity zeolite

adsorbents (Hendricks, 2005 & Somerset, 2005 & 2008). The ash and solid residues recovered from the reaction of two wastes, AMD and fly ash, were successfully converted to zeolite Y (Hendricks, 2005), faujasite, sodalite and zeolite A (Somerset, 2005; 2008) via alkaline hydrothermal synthesis at 600°C. The synthesis method at 100°C, which is less energy consuming, also successfully produced a zeolite adsorbent, zeolite P with a high ion exchange capacity from the solid waste residues (Hendricks, 2005). Despite its low surface area zeolite P prepared at the lower temperature had a high adsorption capacity and its removal efficiency for toxic elements was good and generally higher than the removal efficiency of a commercial zeolite and resins for the treatment of post –neutralisation effluent. Leaching tests showed that the zeolites prepared from solid waste residues were safe for landfill disposal.

Applications of fly ash and derivatives for water treatment, mine backfilling, lining and walling were thus shown to be feasible. An active system using fly ash as the alkaline material for AMD remediation provides a realistic low cost alternative to existing processes and passive systems employing fly ash. Its derivative presents an environmentally benign alternative ameliorant for AMD.

6.3 COMPARISON OF LIMESTONE AND FLY ASH FOR NEUTRALISATION OF AMD WITH HIGH SULPHATE CONCENTRATION

6.3.1 Experimental Results of Chemical Characteristics of Neutralising Material, Neutralisation Reaction and Treated AMD

Table 6.1 tabulates the data and results for the acidity and sulphate analysis of Toeseep AMD. The acidity, as detailed in **Chapter 3, Section 3.3**, was determined by titration with NaOH to pH 8.3. Demineralised water was added to 25 ml of AMD sample to allow adequate coverage of the pH electrode used for the titration. The initial pH of the AMD was 3.48, which was gradually increased by the addition of 0.1 N NaOH in small increments to a pH of 8.30. The acidity was then calculated as per the formula in **Chapter 3, Section 3.3**. The sulphate was analysed by ion chromatography.

Table 6.1: Determination of acidity and sulphate concentration of Toeseep AMD

Replicate 1	
AMD, ml (V)	12.5
0.1 N NaOH , normality (N)	0.1
Titration of AMD with NaOH solution (ml)	pH
0 (initial)	3.48
30.5	8.30
Replicate 2	
AMD, volume (ml)	12.5
0.1 N NaOH , normality (N)	0.1
Titration of AMD with NaOH solution (ml)	pH
0 (initial)	3.44
30.9	8.30
acidity (meq/l)	245.6
molar mass of CaCO ₃ (g/mol)	100.09
acidity (mg/l CaCO₃)	12291
Analysis of AMD	
SO₄²⁻ (mg/l)	17100

The Toeseep acidity was calculated as an average of two replicate analyses and determined to be 12291 mg/l as CaCO₃. The sulphate concentration of the Toeseep AMD was 17100 mg/l.

The data and results for the determination of the CaCO₃ content of the neutralising material are tabulated in Table 6.2. Table 6.2 tabulates the titration of the filtrate collected after addition of HCl to limestone and fly ash and subsequent calculation of the CaCO₃ concentration as detailed in **Chapter 3, section 3.3**.



Table 6.2: Determination of CaCO₃ content of limestone used at Navigation Plant

	Limestone		Arnot fly ash		Hendrina fly ash		Kriel fly ash	
Mass of sample (g)	2.5		25		25		25	
Volume of 1N HCl (ml)	100		100		100		100	
Volume of filtrate (ml)	95		72.9		76		66	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Titration volume of NaOH (ml)	0	48.3	0	31.5	0	34.9	0	11.6
pH of titration mixture	2.04	7.04	0.70	7.05	0.70	7.03	1.92	7.06
Alkalinity titrated (eq)	0.049		0.067		0.063		0.088	
Mass of CaCO₃ titrated (g)	2.456		1.874		1.773		2.461	
Amount of CaO (%)			7.49		7.09		9.85	
Amount of CaCO₃ (%)	98		13		13		18	

The amount of CaCO_3 in limestone is about 80 % higher than in fly ashes. As such, larger volumes of fly ash, than limestone, were added in the neutralisation experiments that follow. Kriel fly ash showed the highest amount of CaCO_3 (18 %) in comparison to Arnot and Hendrina which both resulted in 13 % CaCO_3 . The limestone neutralisation ratio was 1:40 limestone:AMD whilst the fly ashes were experimented at two ratios of 1:4 and 1:7.

The data and results of the limestone neutralisation reactions at 1:40 ratio, as well as the % solids and % water content are presented in Table 6.3. In Table 6.3, the time and pH of the neutralisation reaction is presented firstly. This is followed by the determination of the % solids and water content. The acidity and sulphate concentration of the treated AMD, termed process water, from the limestone neutralisation reaction is listed in Table 6.4. The acidity was determined by standard methods and sulphate analysed by ion chromatography as described in **Chapter 3, section 3.3**. An average of duplicate acidity analyses is reported.

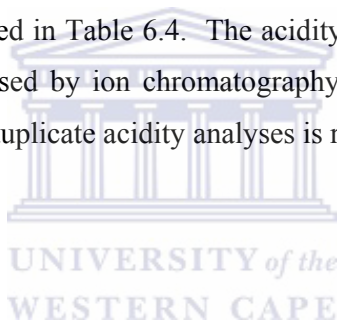


Table 6.3: Limestone neutralisation reaction data and % solid and water content results

Limestone, mass (g)		12.50
AMD, volume (ml)		500
Neutralisation Reaction , speed (rpm)		250
	time (min)	pH
	0	2.81
	60	5.79
	121	5.92
	180	6.07
	240	6.06
	300	6.08
	360	6.07
	360	settling
	470	separation of liquid and solids
Process water, volume (ml)		380
Residual solids, wet mass (g)		124.67
Dried at 105 °C for over 12 hr		
Dry mass (g)		15.23
Water content (%)		87.8
Solid content (%)		12.2

Table 6.4: Acidity and sulphate concentration of treated AMD from the limestone neutralisation reaction

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
	0		0
	4.90		5.06
	10.1		8.30
	8.30		10.05
Acidity (meq/l)	102.3		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO₃)	5118		
Sulphate, SO₄²⁻ (mg/l)	9680		

The data and results of the Arnot fly ash neutralisation reactions at 1:7 ratio, as well as the % solids and % water content are presented in Table 6.5. The results are presented as detailed above for the limestone neutralisation reaction. The acidity and sulphate concentration of the treated AMD, termed process water, from the Arnot fly ash neutralisation reaction is listed in Table 6.6. The results are presented as detailed for the limestone neutralisation reaction.

Table 6.5: Arnot fly ash neutralisation reaction data and % solid and water content results (1:7 ratio)

Fly ash, mass (g)		71.43
AMD, volume (ml)		500
Neutralisation Reaction , speed (rpm)		250
	time (min)	pH
	0	2.74
	80	5.33
	120	5.30
	182	5.51
	300	5.36
	300	settling
	358	separation of liquid and solids
Process water, volume (ml)		380
Residual solids, wet mass (g)		179.22
Dried at 105 °C for over 12 hr		
Dry mass (g)		77.77
Water content (%)		56.6
Solid content (%)		43.4

Table 6.6: Acidity and sulphate concentration of treated AMD from the Arnot fly ash neutralisation reaction (1:7 ratio)

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
0	5.15	0	4.97
13.95	8.30	14.0	8.30
Acidity (meq/l)	141.8		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO₃)	7099		
Sulphate, SO₄²⁻ (mg/l)	W12720		

The data and results of the Arnot fly ash neutralisation reactions at 1:4 ratio, as well as the % solids and % water content are presented in Table 6.7. The acidity and sulphate concentration of the treated AMD, termed process water, is listed in Table 6.8. The data and results are presented as detailed for the Arnot fly 1:4 ratio neutralisation reaction.

Table 6.7: Arnot fly ash neutralisation reaction data and % solid and water content results (1:4 ratio)

Fly ash, mass (g)		125.00
AMD, volume (ml)		500
Neutralisation Reaction , speed (rpm)		250
	time (min)	pH
	0	2.74
	80	5.78
	120	5.87
	180	5.94
	300	5.93
	300	settling
	363	separation of liquid and solids
Process water, volume (ml)		320
Residual solids, wet mass (g)		299.23
Dried at 105 °C for over 12 hr		
Dry mass (g)		134.45
Water content (%)		55.1
Solid content (%)		44.9

Table 6.8: Acidity and sulphate concentration of treated AMD from the Arnot fly ash neutralisation reaction (1:4 ratio)

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
	0	0	5.38
	17.0	8.55	8.30
Acidity (meq/l)	86.5		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO ₃)	4330		
Sulphate, SO ₄ ²⁻ (mg/l)	9530		

The data and results of the Hendrina fly ash neutralisation reactions at 1:7 ratio, as well as the % solids and % water content are presented in Table 6.9. The acidity and sulphate concentration of the treated AMD, termed process water, is listed in Table 6.10. The data and results are presented as detailed for the Arnot fly neutralisation reaction.

Table 6.9: Hendrina fly ash neutralisation reaction data and % solid and water content results (1:7 ratio)

Fly ash, mass (g)		71.43	
AMD, volume (ml)		500	
Neutralisation Reaction , speed (rpm)		250	
	time (min)	pH	EC (mS/cm)
	0	2.83	9.77
	60	5.93	7.34
	120	5.78	6.92
	180	5.53	6.75
	240	5.43	6.55
	300	5.35	6.39
	362	5.26	6.28
	362		settling
	425		separation of liquid and solids
Process water, volume (ml)		390	
Residual solids, wet mass (g)		173.00	
Dried at 105 °C for over 12 hr			
Dry mass (g)		72.66	
Water content (%)		58.0	
Solid content (%)		42.0	

Table 6.10: Acidity and sulphate concentration of treated AMD from the Hendrina fly ash neutralisation reaction (1:7 ratio)

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
0	4.86	0	5.08
13.50	8.30	13.60	8.30
Acidity (meq/l)	137.5		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO₃)	6883		
Sulphate, SO₄²⁻ (mg/l)	11560		

Hendrina fly ash neutralisation reaction data and results at 1:4 ratio are presented in Table 6.11 and 6.12. The data and results are presented as for the previous experiments. Table 6.11 tabulates the neutralisation reaction data and % solid and water content. Table 6.12 tabulates the acidity determination data and results and sulphate content of the process water.

Table 6.11: Hendrina fly ash neutralisation reaction data and % solid and water content results (1:4 ratio)

Fly ash, mass (g)		125.00
AMD, volume (ml)		500
Neutralisation Reaction , speed (rpm)		250
	time (min)	pH
	0	2.80
	60	6.03
	120	5.94
	182	5.84
	240	5.76
	300	5.66
	360	5.51
	360	settling
	415	separation of liquid and solids
Process water, volume (ml)		325
Residual solids, wet mass (g)		287.09
Dried at 105 °C for over 12 hr		
Dry mass (g)		125.50
Water content (%)		56.3
Solid content (%)		43.7

Table 6.12: Acidity and sulphate concentration of treated AMD from the Hendrina fly ash neutralisation reaction (1:4 ratio)

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
0	5.25	0	5.08
6.1	8.30	Sample split and discarded	
Acidity (meq/l)	61.4		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO₃)	3073		
Sulphate, SO₄²⁻ (mg/l)	7910		

Kriel fly ash neutralisation reaction data and results at 1:7 ratio are presented in Table 6.13 and 6.14. The data and results are presented as for the previous experiments. Table 6.13 tabulates the neutralisation reaction data and % solid and water content. Table 6.14 tabulates the acidity determination data and results and sulphate content of the process water.

Table 6.13: Kriel fly ash neutralisation reaction data and % solid and water content results (1:7 ratio)

Fly ash, mass (g)	71.43
AMD, volume (ml)	500
Neutralisation Reaction , speed (rpm)	250
time (min)	pH
0	2.70
67	5.73
160	5.49
210	5.74
280	5.42
280	settling
330	separation of liquid and solids
Process water, volume (ml)	385
Residual solids, wet mass (g)	176.89
Dried at 105 °C for over 12 hr	
Dry mass (g)	79.29
Water content (%)	55.2
Solid content (%)	44.8

Table 6.14: Acidity and sulphate concentration of treated AMD from the Kriel fly ash neutralisation reaction (1:7 ratio)

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
	0	0	5.01
	11.7	21.5	8.30
Acidity (meq/l)	113.9		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO₃)	5702		
Sulphate, SO₄²⁻ (mg/l)	9850		

Kriel fly ash neutralisation reaction data and results at 1:4 ratio are presented in Table 6.15 and 6.16. The data and results are presented as for the previous experiments. Table 6.15 tabulates the neutralisation reaction data and % solid and water content. Table 6.16 tabulates the acidity determination data and results and sulphate content of the process water.

Table 6.15: Kriel fly ash neutralisation reaction data and % solid and water content results (1:4 ratio)

Fly ash, mass (g)	125.00
AMD, volume (ml)	500
Neutralisation Reaction , speed (rpm)	250
time (min)	pH
0	2.67
67	6.31
160	6.19
210	6.35
280	6.45
280	settling
340	separation of liquid and solids
Process water, volume (ml)	315
Residual solids, wet mass (g)	308.18
Dried at 105 °C for over 12 hr	
Dry mass (g)	139.64
Water content (%)	54.7
Solid content (%)	45.3

Table 6.16: Acidity and sulphate concentration of treated AMD from the Kriel fly ash neutralisation reaction (1:4 ratio)

Acidity of process water			
Process water, volume (ml)	10	Process water, volume (ml)	10
Process water diluted, volume (ml)	100	Process water diluted, volume (ml)	100
0.1 N NaOH, normality (N)	0.1015	0.1 N NaOH, normality (N)	0.1015
Titration volume of NaOH solution (ml)	pH	Titration volume of NaOH solution (ml)	pH
	0		0
	4.0		3.65
Acidity (meq/l)	37.0		
Molar mass of CaCO ₃ (g/mol)	100.09		
Acidity (mg/l CaCO ₃)	1854		
Sulphate, SO ₄ ²⁻ (mg/l)	5820		

6.3.2 Discussion of results obtained for the comparison of limestone versus fly ash neutralisation of Toeseep AMD

All the data and results obtained from the neutralisations experiments in **Section 6.5.2** are tabulated in Table 6.17. This allowed a detailed comparison of process conditions and results from the neutralisation of AMD with limestone and various fly ashes. The individual experiments are allocated test numbers in Table 6.17

Table 6.17: Comparison of result for limestone and fly ash treatments of high sulphate Toeseep AMD

NOTE: This cost comparison does not consider the additional costs of the biological process needed after limestone treatment

	Test number	1	2	3	4	5	6	7
AMD	pH	2.81	2.74	2.74	2.83	2.80	2.70	2.67
water quality	Acidity (mg/l as CaCO ₃)	12 291	12 291	12 291	12 291	12 291	12 291	12 291
	Sulphate concentration (mg/l)	17 100	17 100	17 100	17 100	17 100	17 100	17 100
Neutralisation	Neutralising material	Limestone	Arnot FA	Arnot FA	Hendrina FA	Hendrina FA	Kriel FA	Kriel FA
	Alkalinity (% as CaCO ₃)	98	13	13	13	13	18	18
	Reaction time (hours)	6.0	5.0	5.0	6.0	6.0	4.7	4.7
Material usage	(kg/m ³ of AMD)	25	143	250	143	250	143	250
Recovered water	pH	6.1	5.4	5.9	5.3	5.5	5.4	6.4
	Acidity (mg/l as CaCO ₃)	5 118	7 099	4 330	6 883	3 073	5 702	1 854
	Sulphate concentration (mg/l)	9 680	12 720	9 530	11 560	7910	9 850	5 820
Residual sludge	Settling time (hours)	1.8	1.0	1.1	1.1	0.9	0.8	1.0
	Mass recovered (kg/kg material used)	10	2.5	2.4	2.4	2.3	2.5	2.5
	Solid content (%)	12	43	45	42	44	45	45

	Test number	1	2	3	4	5	6	7
Costs	Neutralising material price (R/t)	97.60	0	0	0	0	0	0
	Flocculant cost (R/kg sludge)	0.0007	0	0	0	0	0	0
	Neutralisation cost (R/m ³ of AMD) excluding transport	2.62	0	0	0	0	0	0
	Transport cost (R/t)	72.40	55	55	55	55	55	55
	Neutralisation cost (R/m ³ of AMD) including transport	4.28	7.86	13.75	7.86	13.75	7.86	13.75
	Acidity removal cost (R/kg as CaCO ₃) including transport	0.62	1.51	1.73	1.45	1.49	1.19	1.32
	Sulphate removal cost (R/kg) including transport	0.60	1.79	1.82	1.42	1.50	1.08	1.22



In the case of fly ash (Table 6.17), a larger mass was used because of the lower CaCO_3 content (13-18 % CaCO_3 for fly ash versus 98 % for limestone) (Table 6.17) of fly ash for treatment of the contaminated AMD tested (Table 6.17). Less fly ash was needed for treatment of the Skoongesig AMD, which contained lesser sulphate concentrations, than the Toeseep AMD (**Chapter 5**). This simulation used only enough fly ash to bring water to a comparable pH as could be achieved with limestone. A pH of about 7.5 is the maximum that can be attained using limestone, whereas fly ash can increase the pH to higher levels as required, depending on the quantity used and the contact time. The AMD was neutralised in 6 hours with limestone whilst the fly achieved neutralisation in 5 hours. The residual acidity and sulphate loads are still high in all cases at the pH attained for both limestone and fly ash. The sulphate, TDS and toxic element content could be further reduced by achieving a higher pH with fly ash either using a longer contact time or more ash.

A limestone dosage of 25 kg/m^3 (Table 6.17: test 1) led to a similar decrease in acidity and sulphate load compared to fly ash at higher dosages of 143 kg/m^3 for Kriel fly ash (Table 6.17: test 6), 250 kg/m^3 for Hendrina and Arnot fly ash (Table 6.17: tests 3, 5). Kriel fly ash at 250 kg/m^3 (Table 6.17: test 7) allowed for a more significant decrease in acidity and sulphate load, because of its higher alkalinity. Higher fly ash dosages would achieve complete neutralisation of AMD, but may not be applicable in the current primary liming plant as the limits of pump ability of the sludge may be reached, due to high solid contents.

Acidity expressed as mg/l as CaCO_3 , was reduced from 12291 mg/l to 1850 mg/l when using Kriel fly ash over 4.7 hours (Table 6.1: test 7) at a dosage of 250 kg/m^3 of AMD compared to limestone, in which case the acidity was only reduced to 5120 mg/l as CaCO_3 over 6 hours. The kg/m^3 of AMD dosage used for limestone was however lower. The simulation shows that limestone is somewhat efficient as neutralising agent but does not achieve high sulphate removal from AMD.

In the simulated study a reduction of about 40 % of the usual efficiency of neutralisation was observed in the case of limestone, compared to that currently achieved on a full scale plant (Maree *et al.* 2004). This loss of efficiency was likely

caused by the conditions applied in the simulated study. It is expected that the results of the simulation given here using fly ash show a similar reduction in efficiency. Thus the fly ash neutralisation capacity can be expected to increase proportionately, and the corresponding cost reduced, when comparison is made to a full scale system.

The sludge obtained after limestone treatment had to settle for 2 hours before the overflow could be extracted, while 1 hour was sufficient in the case of fly ash, indicating a quicker processing time. Since the fly ash sludge settled fairly rapidly, it was predicted that flocculants will not be necessary, whereas in the case of limestone these are routinely used. Limestone utilisation produced 10 kg of sludge per kg of material used, while with fly ash, the sludge produced amounted to only 2.3 - 2.5 kg per kg of material used. Dewatering of the fly ash sludge was thus more effective. The sludge obtained after limestone treatment only contained ~12 % solids, while the fly ash sludge contained 42 – 45 % solids. Due to improved separation of phases after treatment with fly ash a higher proportion of treated water could be recovered.

Limestone needs to be mined, crushed and purchased at R 97.6 per ton at the time of the investigation (2007). Fly ash alternatively is freely available from the power plants in the vicinity. Limestone needs to be transported for long distances at R 72.4 per ton at the time of the investigation. The transport cost for fly ash was quoted at R 55 per ton by truck at the time (2007) of the investigation. Alternative means of transport, such as by train or by trucks returning after coal delivery, should be considered to reduce costs.

The utilisation of fly ash for AMD treatment will reduce the costs associated with long term storage of fly ash (storage in large dumps, remediation of storage leachate). Fly ash, specifically Kriel fly ash, was most cost effective with regards to neutralisation and sulphate reduction. This cost comparison did not consider the additional costs of the biological process needed after limestone treatment. The costs associated with purchase of material and transport make limestone treatment less cost effective than fly ash, whilst costs using Kriel fly ash were comparative to that of limestone at the various treatment stages. However, the costs for biological sulphate removal are not included and this will raise the costs for limestone treatment.

Potgieter-Vermaak (2006) conducted a comparison of limestone, dolomite and fly ash for the treatment of AMD. The results were similar with regards to the pH achieved in this study and highlighted the fact the fly ash was far more efficient with regards to sulphate removal. The cost comparison conducted, based on only chemical treatment, showed that the running costs for fly ash was almost half that of limestone and dolomite. Cost savings of 48 % could be achieved when fly ash is applied instead of limestone. Akcil and Koldas, (2006) also commented on the inefficiency and complexity of limestone treatment when treating high ferrous iron water.

The results of the comparative study has highlighted the many advantages of utilising fly ash instead of limestone for AMD treatment even though larger volumes of fly ash are required.

6.4 CURRENT LIMESTONE PRACTICE

The treatment of AMD with sulphate concentration of 17 100 mg/l using limestone and fly ash was compared in a simulated study to obtain a circum neutral pH, according to current operational capacity of the liming process at Navigation plant in which AMD with a high sulphate content is treated. The AMD treated is made up of discard dump seepage and rain water stored in the toe dam and referred to as Toeseep water. This water is the same as that experimented with in the large scale experiments

in **Chapter 5**. The integrated treatment plant used at Navigation section of Landau colliery consists of the following treatment stages (Maree *et al.*, 2004):

- CaCO_3 handling and dosing system where CaCO_3 is introduced in the form of slurry.
- CaCO_3 neutralisation (Primary Liming Plant (PLP)), consisting of a fluidised bed reactor and sludge separator. Compressed air is used at this stage for iron oxidation and subsequent precipitation.
- Heating unit where feed water is sprayed through spiral jet nozzles while hot air is flowing upwards.
- Biological sulphate removal using ethanol as the carbon and energy source, H_2S stripping using CO_2 produced during calcium carbonate treatment, aerobic treatment for removal of residual organic material and CaCO_3 precipitation.

The current AMD treatment, typically using limestone as a neutralising agent, has several drawbacks.

- In the primary liming plant (PLP), only neutralisation of AMD takes place. Moderate sulphate removal is achieved, without reduction of toxic elements content. After treatment with limestone, the water generally has a sulphate concentration >3000 mg/l and is not suitable for industrial activities unless it is further treated with the biological process, introducing additional costs. Only after the treatment by the biological plant, which further reduces the saturation index of gypsum, is the quality of water suitable for industrial applications.
- Limestone cannot be stored in a silo due to its high moisture content. It needs to be dosed in slurry form. It is abrasive and contains stones which cause blockages in pipes.
- The recovered water is separated from solids using flocculants, with considerable cost implications.
- The sludge that settles down after treatment is pumped to a lined hazardous waste storage area. Storage costs per annum are estimated to be high. The sludge has a very high water content reducing water recovery.

- The neutralised water needs to be further treated for instance by use of biological systems, where sulphate concentration may be reduced to 250 mg/l. A pre-treatment is required, using a costly agent: lime. The biological process is energy and carbon feed (ethanol) consuming (Greben *et al.*, 2004). It is very sensitive to temperature and pH fluctuations and may take several months to equilibrate after start-up. As the process may result in toxic H₂S release, the redox reactions must be carefully controlled. Moreover, the bacteria used in the process may be pathogenic.

6.5 ADVANTAGES OF SUBSTITUTING LIMESTONE WITH FLY ASH FOR AMD NEUTRALISATION

The advantages of using fly ash instead of limestone for the treatment of AMD would include its lower cost, and the fact that it is readily available in large quantities in close proximity to the coal mine where the acidic waters are found.

In general, the limestone utilised in the neutralisation of AMD needs to be mined and crushed as well as transported for long distances, resulting in wear on infrastructure such as roads, as well as pollution and environmental degradation of mined out source areas, whereas the ash does not require further mining or crushing and is available in close proximity. The utilisation of fly ash for AMD treatment will reduce the cost of environmental rehabilitation associated with the storage of fly ash. The cost of long term ash storage will be reduced or avoided and environmental remediation costs resulting from fly ash leaching while in lagoon storage will also be minimised.

The quality of the recovered water after neutralisation with fly ash was significantly improved, as shown in **Chapter 5**, and thus there may be significant processing advantage in replacement of limestone with fly ash. The percentage sulphate reduction achieved was excellent at bench scale and comparable to membrane systems and ion exchange and better than other chemical treatment regimes discussed in **Chapter 5**. Further stages in the limestone treatment process e.g. flocculation could be eliminated and their cost reduced since the burden of pollutants in the recovered water would be lower. Since the solid residues settle out of suspension very readily, the flocculation stage could be eliminated with potential cost savings.

Depending on the process conditions chosen in the neutralisation process, different qualities of water may be recovered after treatment with fly ash. Should the pH of AMD be brought to approximately pH 6 with fly ash, further treatment of water may be necessary in the sulphate removal process (SRP) to remove the remaining sulphate. It would be more appropriate to raise the pH to between 9 and 10 to remove the major, minor and trace elements to the maximum and thereafter adjust the pH to more circum neutral values for reuse or discharge. Decreasing the pH of the water to required levels will be easily accomplished since the buffering capacity of elements such as iron, aluminium and other toxic metals is reduced as a result of their precipitation as metal hydroxides and subsequent removal in the solid fraction. The quality of the remediated water should make it suitable for reuse and possible release and would minimise its impact on RO and EDR water treatment systems.

The possible reuse, of solid residues resulting from the neutralisation process, as backfill material could provide an answer to the problem of AMD generation. The possibility exists for the production of a durable, stable and environmentally benign fill material in backfilling of mines, by use of the residues already available in bulk on site after the neutralisation process requiring no further purchasing and importation of other suitable material. Long term costly and hazardous waste storage of AMD sludge remaining after limestone treatment would also be avoided. In the long term, it can be expected that the amount of AMD to be treated at the mine will be significantly minimised by preventing air ingress by backfilling the voids left underground after coal extraction. Backfilling will also add to the economic lifetime of mines and allow a greater degree of extraction of coal.

The waste solid residues can furthermore be transformed into zeolite adsorbent. By selling such value added zeolite materials manufactured from the solid residues would represent a source of income. These adsorbents are also excellent at removing toxic elements from water representing another cost saving opportunity by reducing the cost of maintenance and replacement of RO or RO-EDR systems, by reducing the load of dissolved species in waters currently submitted to these systems for polishing.

CHAPTER 7

TREATMENT OF CIRCUM-NEUTRAL MINE WATER

7.1 INTRODUCTION

Circum-neutral mine waters, often referred to as Ca-Mg waters, are produced when acidic mine water undergoes partial neutralisation due to the surrounding geology. If the acidic mine water flows past dolomite rock, it is partially neutralised and in the process some metal contaminants are precipitated while sulphates may precipitate as gypsum or be adsorbed on metal hydroxides. As a result, circum-neutral mine waters contain lower sulphate concentrations than acid mine water and at pH 6.5, the concentration of toxic metals are near or below the acceptable effluent limits. The water does however; contain considerable concentrations of sulphate, calcium, magnesium and manganese (Banks *et al.*, 1997). Coal mining operations in South Africa are known to produce large quantities of circum-neutral water contaminated with a considerable amount of sulphate. As such, in addition to treating acidic mine water, this section describes the treatment of circum-neutral water emanating from the Middleburg mine with fly ash, to ascertain its capacity for sulphate attenuation in Ca-Mg sulphate waters that are naturally low in iron and aluminium..

Circum-neutral mine water from Middleburg mine was collected in 10 l containers and stored under refrigeration to preserve the sample. The mine water was initially analysed to determine its chemical composition (Table 7.1).

Table 7.1: Chemical composition of circum-neutral mine water from Middleburg mine

COMPONENT	CIRCUM-NEUTRAL MINE WATER
pH	7.16
Conductivity (mS/cm)	5.3
Aluminium (mg/l) Al	0.01
Barium (mg/l) Ba	<0.005
Boron (mg/l) B	0.09
Beryllium (mg/l) Be	<0.005
Cadmium (mg/l) Cd	<0.005
Cobalt (mg/l) Co	0.31
Chromium (mg/l) Cr	0.01
Copper (mg/l) Cu	0.02
Iron (mg/l) Fe	0.17
Lead (mg/l) Pb	0.04
Manganese (mg/l) Mn	28
Nickel (mg/l) Ni	0.20
Zinc (mg/l) Zn	0.11
Calcium (mg/l) Ca	480
Magnesium (mg/l) Mg	820
Sodium (mg/l) Na	25
Potassium (mg/l) K	32
Chloride(mg/l) Cl	<0.1
Nitrate (mg/l) NO ₃	<0.1
Sulphate (mg/l) SO ₄	4560

The contamination level of the circum-neutral mine water was not as high as the Toeseep AMD utilised in this study (**Chapter 4**). The pH of the circum-neutral mine was already neutral at 7.16 and the toxic element concentrations were lower than the AMD utilised in this study. The iron and aluminium concentrations of 0.17 and 0.01 mg/l respectively were far lower than the 5000 mg/l and 200 mg/l aluminium

contained in Landau AMD. The anions, calcium, magnesium and in particular sulphate concentrations were elevated.

Experiments were conducted with fly ash from Arnot, Duvha and Hendrina power plants. The experiments were conducted at beaker scale with 500 ml AMD. Fly ash was added to the circum-neutral water with constant stirring. The pH was monitored and the reaction terminated when the pH of the solution reached a pH 9. This was based on findings in **Chapter 5**, where sulphate was reduced significantly at pH >6.0 via adsorption and reduced even further at pH >8.0 due to the formation of Al-Si-Ca-SO₄ rich mineral phases. A further consideration for maintaining a maximum pH of 9 was that for discharge purposes, the pH would again have to be adjusted to neutrality resulting in further costs. As such, the quantity of fly ash applied in the treatment process was based on increasing the pH only slightly to achieve sulphate removal. The ratios applied are tabulated in Table 7.2.

Table 7.2: Selected ratios for treatment of circum-neutral mine water with Arnot and Duvha and Hendrina fly ash

	Ratios of fly ash to mine water		
Arnot fly ash	1:250	1:500	1:1000
Duvha FA	1:250	1:500	1:1000
Hendrina	1:50	1:100	1:250

Much less fly ash was added since the pH of the mine water was neutral. The ratios for Hendrina fly ash were lower than that utilised for Arnot and Duvha fly ash. Lower ratios were applied for the Hendrina fly ash due to its lower CaO content as determined in Chapter 4.

7.2 RESULTS OF FLY ASH TREATMENT OF CIRCUM-NEUTRAL WATER

Figures 7.1-7.4 illustrates the effect of fly ash on the attenuation of sulphate and iron concentration in circum-neutral mine water. The circum-neutral mine waters' initial pH of 7.1 was raised to pH 9.0 within 1 hour at all ratios.

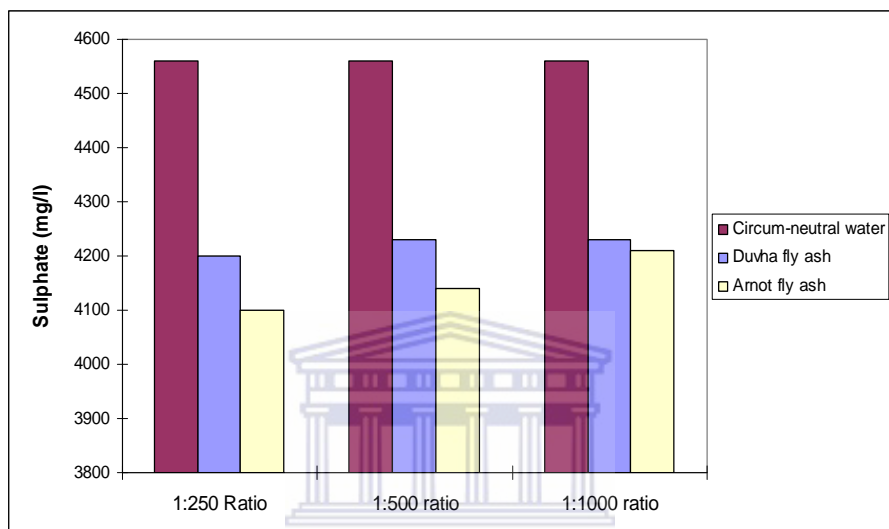


Figure 7.1: Effect of Arnot and Duvha fly ash treatment on sulphate concentration in circum-neutral mine water

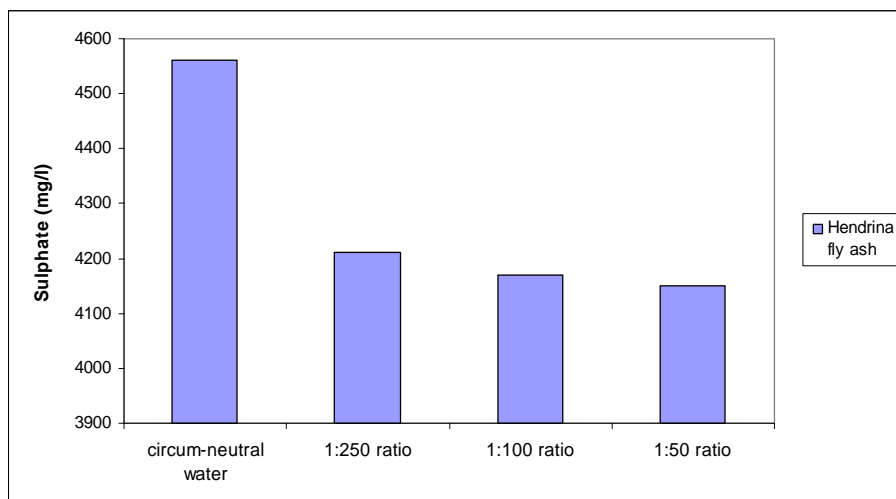


Figure 7.2: Effect of Hendrina fly ash treatment on sulphate concentration in circum-neutral mine water

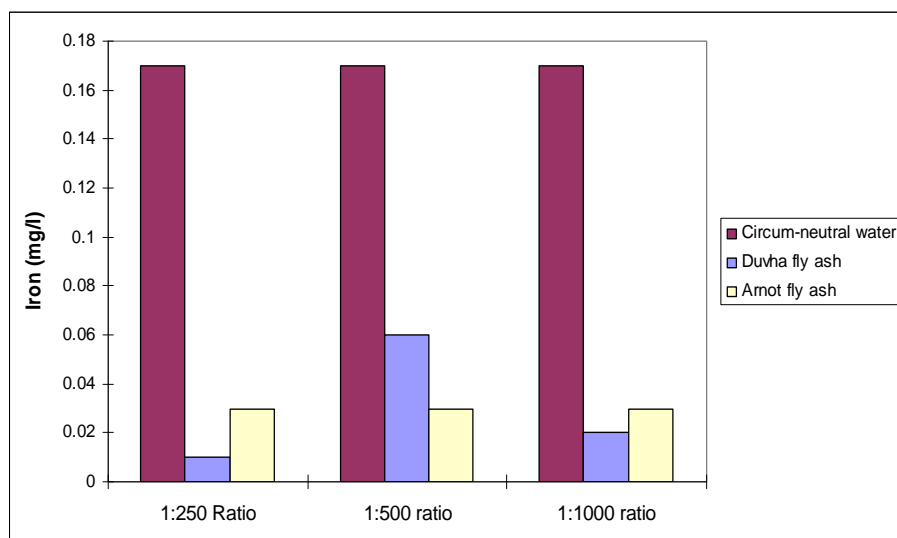


Figure 7.3: Effect of fly ash treatment on iron concentration in circum-neutral mine water at pH 9

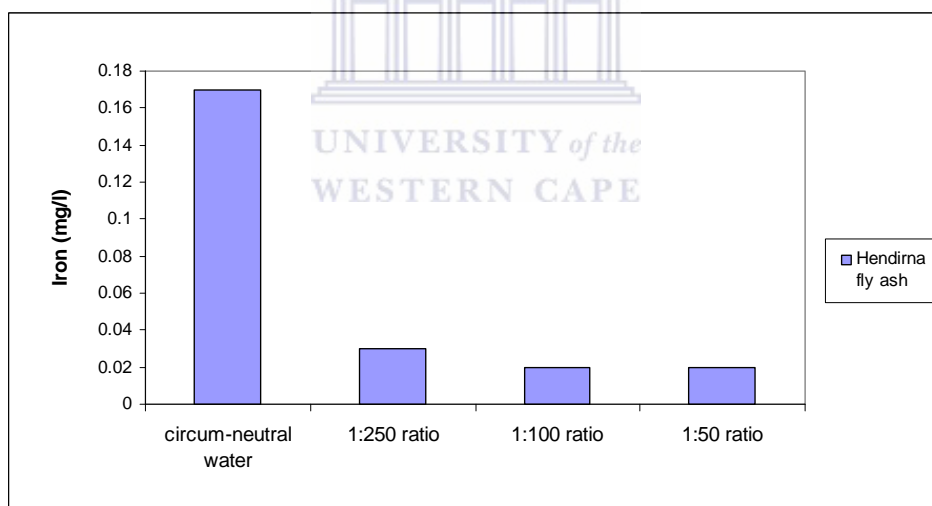


Figure 7.4: Effect of Hendrina fly ash treatment on iron concentration in circum-neutral mine water at pH 9

In previous beaker scale experiments (Chapter 5), a pH > 8.0 resulted in >90 % sulphate reduction, at specific fly ash:AMD ratios. Treatment of circum-neutral mine waters with fly ash did not achieve significant sulphate reductions. Greater quantities of fly ash (lower fly ash:AMD ratios) resulted in more sulphate reduction, but again this was not significant. Duvha and Arnot fly ash achieved a maximum sulphate

reduction of 7.8 % and 10 % respectively at the 1:250 ratio (Figure 7.1). Hendrina fly ash achieved a similar reduction in sulphate of 9 %, but with the smaller ratio of 1:50 (Figure 7.2). This proved that the lower CaO content of Hendrina fly ash renders it less effective, since more fly ash is required than Arnot and Duvha to achieve similar results with regards to sulphate attenuation. The initial iron concentration of 0.17 mg/l in the mine water was almost totally removed by all fly ashes (Figure 7.3, 7.4). Hendrina fly ash was as efficient as Arnot and Duvha fly ash in reducing the iron concentration at the smaller ratios. This low initial iron concentration in the circum-neutral mine water could be an important contributor to the low percentage of sulphate reduction, since at pH values >6.0, high concentrations of sulphate are adsorbed during Fe(OH)₃ precipitation (Gitari *et al.*, 2008). Further, the low amount of fly ash used in the experiments and a pH of 9 could be insufficient to allow sufficient attenuation of sulphate. This phenomenon is explained further by Madzivire *et al.*, (2009) during treatment of circum-neutral mine water. The acidity generated by the formation of aluminium and iron (oxy) hydroxides and oxyhydroxysulphate complexes facilitates lime dissolution and subsequent Ca²⁺ and OH⁻ release. Sulphate attenuation is enhanced via the formation of gypsum when the Ca²⁺ combines with SO₄²⁻ (Madzivire *et al.*, 2009). Further, Madzivire *et al.*, (2009) reported that at pH values >12, sulphate attenuation was enhanced. With larger quantities of fly ash applied, greater concentrations of Ca²⁺ would be available for gypsum precipitation.

7.3 SUMMARY FLY ASH TREATMENT OF CIRCUM-NEUTRAL WATER

Results from the treatment of circum-neutral mine water have shown that, the quality of this type of mine water could also be improved with fly ash. However, sulphate attenuation was not significant in comparison to AMD waters due to two primary factors. The first being the influence of iron and aluminium concentrations, which tend to aid sulphate attenuation via adsorption during precipitation of the (oxy) hydroxides and oxyhydroxysulphate complexes. Secondly, addition of larger quantities of fly ash as were applied in AMD treatment would render more Ca²⁺ available for gypsum precipitation and subsequent sulphate attenuation. The experiments conducted in this study utilised minimum quantities of fly ash, aimed only at increasing the pH to 9.0. As was reported in circum-neutral water treatment

conducted by Madzivire *et al.*, (2009), at pH values >12 , sulphate attenuation was enhanced. Additional experimentation with large quantities of fly ash and higher pH values is recommended as it is expected that more fly ash would increase the pH further and subsequently aid in further sulphate attenuation.



CHAPTER 8

DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

8.1 INTRODUCTION

This chapter provides a summary of the discussion of results and conclusions drawn. Recommendations and areas for further and future research are made based on the results of this study. The investigations undertaken in this study were initiated due to concerns with regards to the environmental impact of fly ash and the detrimental nature of AMD generated at mines, in particular coal mines. Two major concerns were the highly acidic nature and significant sulphate concentrations of AMD.

The literature study revealed that existing treatment technologies have limited capabilities with respect to sulphate reduction and those that have enhanced capability are associated with exorbitant treatment costs. Mutual beneficiation associated with the application of fly ash for AMD treatment and prevention has demonstrated potential for large scale active neutralisation of AMD. The objectives of this thesis were to determine the effectiveness of utilising fly ash for active AMD neutralisation, sulphate attenuation and the feasibility thereof in comparison to alternate treatment technologies. A further objective was to determine the effect of fly ash treatment on sulphate in circum-neutral waters.

The Mpumalanga coal mining region was selected as the study area due to the abundance of mining that occurs in the region and the localised power plants. The sample streams were selected based on the results of the characterisation study conducted. Beaker scale neutralisation experiments were conducted as a baseline prior to large scale neutralisation experiments. The results at each stage were compared to data obtained from literature. Following the neutralisation experiments, a feasibility study was conducted, comparing fly ash with limestone for AMD neutralisation and treatment. Standard laboratory procedures were applied for the analysis of liquid and solids samples.

8.2 BEAKER AND LARGE SCALE NEUTRALISATION EXPERIMENTS

Beaker scale neutralisation experiments confirmed that fly ash could successfully be applied for the removal of iron and aluminium rich sulphate containing AMD. The relative quantities of soluble bases (oxides) in fly ash and hydrolysable constituents in AMD dictate whether the final solution at a given contact time will have a dominant acid or basic character. The trend that was observed was that the higher volume of fly ash added to AMD, the quicker was the reaction time and the greater the attenuation of sulphate, iron and aluminium. The pH increased with a corresponding decrease in the electrical conductivity, and varied depending on the ratio of fly ash:AMD selected or volume of ash applied: 1:1 (pH 12.9), 1:2 (pH 12.2), 1:3 (pH 11.7), 1:5 (pH 11.1) and 1:10 (pH 9.3). Sulphate was attenuated in excess of 90%, from 5700 mg/l to 120 mg/l, via adsorption during $\text{Fe}(\text{OH})_3$ precipitation and the gypsum formation. Fly ash performance with regards to sulphate attenuation was better than limestone and comparable to membrane and ion exchange treatment technologies. Iron was almost completely removed (>99 %) at pH values >7 via $\text{Fe}(\text{OH})_3$ precipitation. Aluminium also achieved a 99% reduction via the formation of various minerals, primarily gibbsite. Optimum ratios of fly ash:AMD ranged between 1:3 and 1:10.

Large scale neutralisation experiments demonstrated the possibility of applying the fly ash technology at full scale AMD treatment plants. Experimental ratios ranged from 1:3 to 1:10 fly ash:AMD. Comparative experiments showed that the rate of agitation influenced the rate of reaction. With most ratios applied, the final pH was less than that achieved with beaker experiments resulting in lesser sulphate attenuation. The pH ranged from pH 9.9 (1:3 ratio) and pH 7.7 (1:5 ratio). The maximum pH obtained at large scale with the 1:10 ratio was 4.2. It was postulated that changes in fly ash composition and/or mineralogy as well as process conditions, could have influenced the pH values and ultimately the neutralisation process and elemental attenuation. Therefore fly ash treatment process should be adapted for the different qualities of fly ash applied for AMD neutralisation and amelioration. Based on the results of the initial large scale experiments, a 1:6 ratio was selected for further large scale experiments. At this ratio, elemental attenuation trends, similar to those observed in the beaker experiments, were also seen. However, the lower pH values resulted in a

lesser sulphate reduction of only 68 %, even after the long contact time, with a 1:6 ratio and final pH of 6.33. In comparison, the integrated limestone/lime process only achieved a 59 % reduction in sulphate concentration at pH values >12. Greater sulphate reduction is expected with fly ash at the higher pH values as was seen with beaker studies. Reduction of iron and aluminium at this ratio was excellent (>99 %). The LOI, which measures the amount of unburned carbon remaining in the fly ash, was found to influence the neutralisation. Fly ash with high unburned carbon of 6.6 % hindered an increase in pH possible due to reduced free lime content in the fly ash. The presence of high percentages of unburned carbon could be attributable to variations in coal quality, boiler conditions or both. In comparison to the commonly used limestone process, fly ash was capable of raising the pH of the AMD to higher levels thereby reducing sulphate more efficiently.

8.3 FEASIBILITY STUDY OF FLY ASH VERSUS LIMESTONE TREATMENT OF AMD

A comparative study of fly ash versus limestone treatment of AMD was conducted based on the neutralisation potential, sulphate removal and to a smaller degree, costs. Three different fly ash samples namely, Arnot, Hendrina and Kriel fly ash was compared to limestone. In the case of fly ash, a larger mass was used because of the lower CaCO_3 content (13-18 % CaCO_3 for fly ash versus 98 % for limestone) of fly ash for treatment of the very contaminated AMD tested (>17000 mg/l sulphate). Reaction times were comparable for all neutralising material and Kriel fly ash achieved the lowest reaction time. Kriel fly ash achieved 66 % attenuation in sulphate whilst limestone only achieved 43 % at similar pH levels. The reduction in acidity was most pronounced with Kriel fly ash reducing the acidity from 12300 mg/l as CaCO_3 to 1850 mg/l as CaCO_3 . When using limestone, the acidity was only reduced to 5120 mg/l as CaCO_3 . When the reaction time for the Kriel fly ash was extended, the acidity was almost completely reduced. Settling rates were better with the fly ash which would eliminate the use of flocculants as is currently done with limestone treatment. A higher percentage of water recovery was also achieved with fly ash. Fly ash, more specifically Kriel fly ash, was most cost effective with regards to neutralisation and sulphate. This cost comparison did not consider the additional costs of the biological process that is needed after limestone treatment. The

comparison highlighted the advantages of utilising fly ash in comparison to limestone and demonstrated its cost effectiveness.

8.4 TREATMENT OF CIRCUM-NEUTRAL MINE WATER WITH FLY ASH

In addition to AMD, an abundance of Ca-Mg sulphate rich circum-neutral mine water is also generated during mining operations. Fly ash treatment, aimed at sulphate attenuation was investigated at beaker scale at pre-determined fly ash:AMD ratios. These ratios were much larger using much less fly ash than initial experiments conducted with AMD since the mine water was already neutral and only a slight increase to pH 9 was required. Iron and aluminium were detected in only very low concentrations in the circum-neutral mine water and were almost completely removed after the addition of fly ash. Sulphate attenuation was minimal, decreasing from 4560 mg/l to 4100 mg/l at a 1:250 ratio and a maximum 10 % in attenuation was achieved. The explanation behind this was 1) the restricted amount of fly ash added and low pH did not allow sufficient gypsum precipitation and 2) the low iron concentration inhibited sulphate adsorption which occurs during $\text{Fe}(\text{OH})_3$ precipitation. With larger volumes of fly ash applied, greater concentrations of Ca^{2+} would be available for gypsum precipitation.

8.5 RECOMMENDATIONS

In order to further elucidate aspects of the fly ash treatment technology, the following recommendations are put forward:

- More experimental work needs to be conducted at large scale, with larger fly ash volumes to attain higher pH values to ascertain optimum sulphate attenuation capabilities. Automatic data logging is recommended to identify optimum contact times and associated changes in pH.
- Further neutralisation experiments need to be conducted to determine the maximum percentage unburned carbon in fly ash that will be tolerable for neutralisation.

- Additional neutralisation experiments, using a wider range of fly ash from various sources would aid in delimiting the optimum conditions necessary for neutralisation.
- Additional neutralisation experiments with Ca-Mg sulphate rich circum-neutral mine water, with the addition of larger volumes of fly ash to achieve pH values >9.0. This will elucidate the sulphate attenuation capabilities of fly ash in circum-neutral mine waters.
- Test the fly ash treatment technology at pilot scale.

8.6 SIGNIFICANCE OF THE STUDY

The results of this study have shown that fly ash could be successfully applied for the neutralisation of acid mine drainage (AMD) and effectively reduce the sulphate load in the treated water. Iron and aluminium which was also present in significant concentrations was almost completely removed. In comparison to alternate treatment technologies, fly ash performance with respect to sulphate attenuation, was more effective than the conventionally applied limestone treatment and was comparable to technologies like membrane system and ion exchange. Fly ash thus provides for a cost efficient, alternate technology for AMD neutralisation and amelioration. Treatment of fly ash with AMD has the simultaneous advantage of neutralising two sources of waste streams.

The large scale experiments have shown the potential to apply this technology at pilot and full scale plants. Further, this technology has shown the potential to treat circum-neutral mine waters.

The limitation of the technology lies with the quality of fly ash and AMD. Variations in the chemical composition and mineralogy of fly ash could influence the neutralisation reaction and the same is true if the AMD quality varies. Thus,

operating conditions may have to be adapted and process controls at full scale treatments are necessary



CHAPTER 9

REFERENCES

Adriano D.C., Page, A.L., Elseewi, A.A., Chang, A.C. and Straughan, A. (1980). Utilisation and disposal of fly ash and other coal residues in terrestrial ecosystems: A review. *Journal of Environmental Quality* 9: 333-334.

Akcil, A and Koldas, S. (2006). Acid mine drainage: causes, treatment and case studies. *Journal of Cleaner Production* 14: 1139-1145.

APHA. (1985). Standard Methods for the Examination of Water and Wastewater. 12th Edition, American Public Health Assoc, New York, USA.

Aptel, P. and Buckley, C.A. (1996). Categories of Membrane Operations. In: *Water Treatment Membrane Processes*. Mallevalle, J., Odendaal, P.E. and Wiesner, M.R., (eds), McGraw-Hill. 2.1-2.24.

American Society for Testing and Materials. 2003. Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete. Designation ASTM C618.

Banks, D., Younger, P.L., Arnesen, R.L., Egil, R., Iversen, E.R. and Banks, S.B. (1997) Mine-water chemistry: the good, the bad and the ugly. *Environmental Geology* 32(3): 157-174.

Buckley, C.A. and Hurt, Q.E. (1996). Membrane Applications: A Contaminant-Based Perspective. In: *Water Treatment Membrane Processes*. Mallevalle, J., Odendaal, P.E. and Wiesner, M.R., (eds), McGraw-Hill. 3.1-3.24.

Camacho, L.M. and Munson-McGee, S.H. (2006). Anomalous transient leaching behaviour of metals solidified/stabilised by pozzolanic fly ash. *Journal of Hazardous Materials* 137:144-151.

Carlson, C.L. and Adriano, D.C. (1993). Environmental impacts of coal combustion residues. *Journal of Environmental Quality* 22: 227-247.

du Plessis, G.H. and Swartz, J.A. (1992). Tubular reverse osmosis treatment of Secunda mine water: a pilot plant investigation. *Water Science and Technology* 25: 193-201.

Edwards, K.J., Bond, P.L., Gihring, T.M. and Banfield, J.F. (2000) An archaeal iron-oxidising extreme acidophile important in acid mine drainage. *Science* 287: 1796-1799.

Eskom. (2008). Annual Report, *Business and sustainability performance review*. Eskom, South Africa.

Eskom Method 304. (2006). *Determination of alkalinity of water: Electrometric titration*.

Eskom Method 412. (2006). *Metal analysis of raw, potable and waste water by inductively coupled plasma atomic emission spectrometry (ICP)*.

Eskom Method 307. (2006). *Determination of anions in water by ion chromatography with conductivity measurements: chromatographic method*.

Feng, D., Aldrich, C. and Tan, H. (2000). Treatment of acid mine water by use for heavy metal precipitation and ion exchange. *Mineral engineering* Vol. 13, No. 6, pp 623-642.

Fisher, G.L. and Natusch, F.S. (1979). Size dependence of the physical and chemical properties of coal fly ash. In: Karr c Jnr. (ed) *Analytical methods for coal and coal products* 1979, Vol III Academic Press, New York. 489-541.

French, D. and Smitham, J. (2007). Fly ash characteristics and feed coal properties. CSIRO Energy Technology, *Research Report 73*, May 2007.

Geldenhuys, A.J., Maree, J.P., de Beer, M. and Hlabela, P. (2001). An integrated limestone/lime process for partial sulphate removal. *Conference on Environmentally Responsible Mining in South Africa*, CSIR, Pretoria, South Africa.

Gitari, W.M., Petrik, L.F., Etchebers, O., Key D.L. and Okujeni, C. (2008). Utilisation of fly ash for treatment of coal mines wastewater: Solubility controls on major inorganic contaminants. *Fuel* 87: 2450-2462.

Gitari, W.M., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E. and Okujeni, C. (2008). Passive neutralisation of acid mine drainage by fly ash and its derivatives: A column leaching study. *Fuel*; 87:1637-1650.

Greben, H.A., Maree, J.P., Singmin, Y. and Mnqanqeni, S. (2004). Biological sulphate removal from acid mine effluent using ethanol as carbon and energy source. *Water Science and Technology* 42: 339-344.

Günther, P., Mey, W. and van Niekerk, A. (2006). A sustainable mine water treatment initiative to provide potable water for a South African city – A public-private partnership. *Water in Mining Conference*. Brisbane. Australia.

Hendricks, N.R. (2005). *The application of high capacity ion exchange adsorbent material synthesized from fly ash and acid mine drainage, for the removal of heavy and trace metals from secondary co-disposed process waters*. MSc Thesis, University of Cape Town, South Africa.

Ilgner, H.J. (2000). The benefits of ashfilling in South African coal mines. *12th International Conference on Coal Research (ICCR)*, Sandton, South Africa.

International Network for Acid Prevention (INAP) (2003), Treatment of sulphate in mine effluents. Lorax Environmental. Available at www.inap.com.

Juby, G.J.G. (1992). Membrane desalination of service water from gold mines. *Journal of the South African Institute of Mining and Metallurgy* 92: 65-70.

Klink, M.J. (2006). *The potential use of South African coal fly ash as a neutralisation treatment option for acid mine drainage*. MSc thesis, University of Western Cape, South Africa, 2006.

Külaots, I., Hurt, R.H. and Suuberg, E.M. (2004). Size distribution of unburned carbon in coal fly ash and its implications. *Fuel* 83: 223-230.

Kippax P. Measuring particle size using modern laser diffraction techniques. Available at www.analytica-world.com/articles/e/61205/.

Madzivire, G., Petrik, L.F., Gitari, W.M., Balfour, G., Vadapalli, V.R.K. and Ojumu, T.V. (2009). Role of pH on sulphate removal from circumneutral mine water using coal fly ash. *International Mine Water Conference*, South Africa.

Maree, J.P.. (2006). *Personal communication*.

Maree, J.P., Van Tonder, G.J., & Millard, P. (1996). Underground neutralisation of mine water with limestone. *Water Research Commission Report No. 609/1/96*, Pretoria, South Africa.

Maree, J.P., Stobos, G., Greben, H., Netshidaulu, E., Steyn, E.; Christie, A. and Günther, P. (2001). Biological treatment of mine water using ethanol as energy source. *Conference on Environmentally Responsible Mining in South Africa*. Pretoria. South Africa.

Maree, J.P. and du Plessis, P. (1994). Neutralisation of acid mine water with calcium carbonate. *Water Science and Technology* 29(9):285-296.

Maree, J.P., Stobos, G., Greben, H., Netshidaulu, E., Steyn, E., Christie, A. and Günther, P. (2004). Treatment of acid leachate from coal discard using calcium

carbonate and biological sulphate removal. *Mine Water and the Environment* 23:144-151.

Malleville, J., Odendal, P.E. and Wiesner, M.R. (1996). Water treatment membrane process. AWWA, Lyonnaise des Eaux, WRC of SA, McGraw-Hill: New York, (Eds).

Mattigod, S.V., Rai, D., Eary, L.E. and Ainsworth, C.C. (1990). Geochemical factors controlling the mobilisation of inorganic constituents from fossil fuel combustion residues: I. Review of the major elements. *Journal of Environmental Quality* 19: 188-201.

O'Brien, R.D. (2000). *The Neutralisation of Acid Mine Drainage by Fly Ash*. MSc Thesis, University of Cape Town, South Africa.

Osvolda, S. (2008). Burning and physico-chemical characteristics of carbon in ash from a coal fired power plant. *Fuel* 87:1207-1216.

Petrik, L.F., White, R.A., Klink, M.J., Somerset, V.S., Burgers, C.L. and Fey, M.V. (2003). Utilisation of South African fly ash to treat acid coal mine drainage, and production of high quality zeolites from the residual solids. *International Ash Utilisation Symposium*, Kentucky, USA.

Petrik, L.F., Burgers, C., Gitari, W., Surender, D., Reynolds, K., Ellendt, A., Etchebers, O., Vadapalli, V.R., Key, D. and Iwuoha, E. (2006). Stability and neutralisation capacity of potential mine backfill material formed by neutralisation of fly ash and acid mine drainage. *Water Research Commission Report 1458/1/06*.

Pilat, B.V. (2003). Industrial application of electrodialysis reversal systems. *Desalination* 158: 87-89.

Potgieter-Vermaak, S.S., Potgieter, J.H., Monama, P. and Van Grieken, R. (2006). Comparison of limestone, dolomite and fly ash as pre-treatment agents for acid mine drainage. *Minerals Engineering* 19: 454-462.

Reynolds, K. (2004). The use of fly ash for ash walling of acid mine drainage. *Eskom Research Report, RES/RR/02/19247*.

Reynolds, K. (2004). Utilisation of fly ash for AMD treatment. *Eskom Research Report, RES/RR/03/20887*.

Reynolds, K. (2006). The use of ash walling for the treatment and control of AMD. *Eskom Research Report, RES/RR/04/23405*, July 2006.

Ridgway, H.F. and Flemming, H.C. (1996). Membrane Biofouling. In: *Water Treatment Membrane Processes*. Mallevialle, J., Odendaal, P.E. and Wiesner, M.R., (eds), McGraw-Hill. 6.1-6.62.

South African National Standard for Drinking Water, SANS 241:2006, ISBN-0626-18876-8.

Skoog, D.A., Holler, F.J. and Nieman, T.A. (1998). Principles of instrumental analysis. 5th Edition: Saunders College Publishing.

Schoeman, J.J. and Steyn, A. (2001). Investigation into alternative water treatment technologies for the treatment of underground mine water discharged by Grootvlei Proprietary Mines Ltd into the Blesbokspruit in South Africa. *Desalination* 133: 13-30.

Sibilski, U. (2001). Anglogold desalination pilot plant project. *Conference on Environmentally Responsible Mining in South Africa*.

Skousen, J.G., Sexstone, A. and Ziemkiewicz P.F. (2000) Acid mine drainage control and treatment. Reclamation of Drastically Disturbed Lands. American Society of Agronomy. Agronomy 41.

Somerset, V.S., Petrik, L.F. and White, R.A., Klink, M.J., Key, D. and Iwuoha, E.I. (2005) Alkaline hydrothermal zeolites synthesised from high SiO₂ and Al₂O₃ co-disposal fly ash filtrates. *Fuel* 84: 2324-2329.

Somerset, V., Petrik, L. and Iwuoha, E. (2008) Alkaline hydrothermal conversion of fly ash precipitates into zeolites 3: The removal of mercury and lead ions from wastewater. *Journal of Environmental Management* 87:125-131.

Steward, B.R., Daniels, W.L. and Jackson, M.L. (1997). Evaluation of leachate quality from co-disposed coal fly ash and coal refuse. *Journal of Environmental Quality* 26: 1417-1424.

Stumm, W. and Lee, G.F. (1961). Oxygenation of ferrous iron. *Industrial and Engineering Chemistry*, 53: 143.

Summers, K.C., Rupp, G.L. and Gherini, S.A. (1983). Physical-chemical characteristics of utility solid wastes. *Research report EPRI EA-3236*, Electrical Power Research Institute, Palo Alto, CA, USA.

Taylor, J.S. and Jacobs, E.D. (1996). Reverse Osmosis and Nanofiltration. In: *Water Treatment Membrane Processes*. Mallevalle, J., Odendaal, P.E. and Wiesner, M.R., (eds), McGraw-Hill. 9.1-9.70.

The Water Wheel. (2005). World first: Full-scale BioSURE Plant Commissioned. pg 19-21, May/June 2005

Twardowska, I. (1990). Buffering capacity of coal mine spoils and fly ash as a factor in the protection of the aquatic environment. *The Science of the Total Environment* 91: 177-189.

Vadapalli, V.R.K., Petrik, L., Fester, V., Slatter, P. and Sery, G. (2007). Effect of fly ash particle size on its capacity to neutralise acid mine drainage and influence on the rheological behaviour of residual solids. *Proceedings of the World of Coal Ash Conference*, Covington, Kentucky, USA.

Van Alphen C. (2007). Automated mineralogical analysis of coal and ash products – Challenges and requirements. *Minerals Engineering* 20: 496-505.

Van Den Berg, J.J., Cruywagen, L., De Necker, E. and Hodgson, F.D.I. (2001). The suitability and impact of power station fly ash for water quality control in coal opencast mine rehabilitation. *Water Research Commission Report No. 745/1/01*.

Warren, C.J. and Dudas, M.J. (1984). Weathering processes in relation to leachate properties of alkaline fly ash. *Journal of Environmental Quality* 13(4): 530-538.

Water Sewage & Effluent (2006). Acid Mine Drainage – the BioSURE solution”, 26(3): 39-41.



**APPENDIX A: DETERMINATION OF ALKALINITY OF WATER
ELECTROMETRIC TITRATION**

METHOD NUMBER 304	PAGE 1 OF 3
REV 6	

**DETERMINATION OF ALKALINITY OF WATER
ELECTROMETRIC TITRATION**

BASIS OF METHOD

This method covers the rapid, routine control measurement of alkalinity to predesignated end points of waters that contain no materials that buffer at the end point or other materials that interfere with titration by reason of colour, precipitation, etc.

The sample is titrated with standard acid to a designated pH, the end point being determined electrometrically.

INTERFERENCES

1. Suspended solids may interfere in electrometric titrations by making the glass electrode sluggish.
2. Similarly, the development of a precipitate during titration may make the glass electrode sluggish and cause high results.
3. Variable results may be experienced with waters containing oxidising or reducing substances, depending on the equilibrium conditions and the manner in which the sample is handled.
4. Although oily matter, soaps, suspended solids and other waste materials may interfere with the pH measurement, these materials may not be removed to increase precision, because some are an important component of the acid- or alkali-consuming property of the sample.

SAMPLE PREPARATION

The analysis should be carried out as soon as possible after sampling: No sample preparation is required.

TIME REQUIRED FOR ANALYSIS

Approximately 6 minutes per sample, although this may vary considerably from sample to sample.

METHOD NUMBER 304	PAGE 2 OF 3
REV 6	

REAGENTS

1. 0.02 N HNO₃: Measure 1.4 ml of 65 % HNO₃ into a 50 ml of milli-q water. Precautionary measures must be taken handling acid. Cool, and make up to the mark in a 1000 ml volumetric flask.
2. Standardise the 0.02 N HNO₃ against 0.02 N sodium carbonate.
3. 0.002 N sodium carbonate for standardisation: Weigh 1.06 g of sodium carbonate and dissolve in UHP water and make up to the mark in a 1000 ml volumetric flask.
4. 0.002 N QC Standard: Weigh 1.06 g of sodium carbonate and dissolve in UHP water and make up to the mark in a 1000 ml volumetric flask.

ANALYTICAL PROCEDURE

1. Calibrate the instrument as instructed in method 300.
2. Pipette 25 ml of sample into a beaker and adjust the temperature to 25°C ± 2°C as per method 300.
3. Analyse the QC standard before analysing the samples and check that the results are within the limits of the control chart.
4. If required, flush the assembly until no more bubbles appear in the titration tube.
5. Press <user method> on keyboard and recall method will appear on the screen. Press 11 and <enter>.
6. On the screen "set pH" will appear on the screen and then press <start>.
7. The instrument will start the titration with 0.02 N HNO₃ automatically, until the end points are reached.
8. Alkalinity results displayed as follows:
RS1 = "P Alkalinity"
RS2 = "M Alkalinity"
RS3 = "Total Alkalinity"
9. All samples are analysed in duplicate.
10. If alkalinity is very high, pipette 5 ml of the sample and continue as per step 5. The supervisor must be notified prior to analysis to change instrument settings. The final results are calculated automatically by the instrument.
11. If alkalinity is still too high titrate 5 ml of sample with standardised 0.2 N HNO₃. The supervisor must be notified prior to analysis to change instrument settings. The final results are calculated automatically by the instrument.

METHOD NUMBER 304	PAGE 3 OF 3
REV 6	

VALIDATION OF ANALYTICAL DATA

Analytical data is validated according to procedure P529.

REFERENCES

Standard Methods for the Examination of water and Wastewater 20th edition 1998, pp 2-26.
Instruction Manual for Metrohm 702 SM Titrino

COMPILED BY: _____ DATE: _____
D Surender (QC Co-ordinator)

AUTHORISED BY: _____ DATE: _____
J Reeves (QA Manager)



APPENDIX B: DETERMINATION OF ANIONS IN WATER BY ION CHROMATOGRAPHY WITH CONDUCTIVITY MEASUREMENTS: CHROMATOGRAPHIC METHOD

METHOD NUMBER 307	PAGE 1 OF 6
REV 6	

DETERMINATION OF ANIONS IN WATER BY ION CHROMATOGRAPHY WITH CONDUCTIVITY MEASUREMENTS CHROMATOGRAPHIC METHOD

BASIS OF METHOD

A water sample is injected into a stream of carbonate-bicarbonate eluant and passed through a series of ion exchangers. The anions of interest are separated on the basis of their relative affinities for a low capacity, strongly basic anion exchanger (guard and separator column). The separated anions are directed onto a strongly acidic cation exchanger (suppressor column) where they are converted to their highly conductive acid form and the carbonate-bicarbonate eluant is converted to weakly conductive carbonic acid. The separated anions in their acid form are measured by conductivity. They are identified on the basis of retention time as compared to standards. Quantity is preformed by measurement of peak area or peak height.

This gives the parameters for the use of a Dionex type AS14 anion separator and AG14 anion guard column set using a microbore (2mm ID) system. This column set offers improved separation of all analytes but with a similar analysis time to the AS4A type column set, and shorter analysis time than the AS12A type column set.

INTERFERENCES

1. Any substance that has a retention time coinciding with that of any anion to be determined will interfere.
2. A high concentration on any one ion interferes with the resolution and retention characteristics of other anions.
3. Spurious peaks may result from contaminants in reagent water, glassware, or sample processing apparatus.
4. Organic species, if present, will interfere with the fluoride ion.

SAMPLE PREPARATION

1. Remove sample particulates by filtering through a pre-washed 0.2 μm pore diameter membrane filter.
2. The sample may require dilution in order for the anion values to be as close as possible to the standard values.

METHOD NUMBER 307	PAGE 2 OF 6
REV 6	

TIME REQUIRED FOR ANALYSIS

- ± 20 minutes for instrument stabilisation
- ± 15 minutes per calibration run
- ± 15 minutes per sample run

SPECIAL APPARATUS

1. ICS-1500 Ion chromatograph Unit operating on Chromeleon Software, comprises of an injection valve, a sample concentration column, a temperature-compensated small-volume conductivity cell, and a personal computer. The ion chromatograph shall be capable of 0.05 to 2.50 ml.min⁻¹ eluent at a pressure of 1 400 to 6.900 kPa.
2. An inject valve with sample loop (2µl) and a temperature-compensated small-volume conductivity cell.
3. Anion separator column (Dionex type AS14 column is suitable) with styrene divinylbenzene-based low-capacity pellicular anion-exchange resin capable of resolving Cl⁻, F⁻, NO₃⁻, NO₂⁻, Br⁻, and SO₄²⁻, with column length of 2 x 250 mm.
4. Guard column (Dionex type AG14 column is suitable), identical to separator column except 2 x 50 mm, to protect separator column from fouling by particulates or organics.
5. Anion micromembrane suppressor or anion self-regenerating suppressor for removal of cations from the eluent stream.
6. An electronic integrator or computer-based integration station.

REAGENTS

1. Deionised water with a conductivity of less than 0.5 µScm⁻¹ and filtered through a 0.22 µm membrane filter to remove particulates.
2. Eluent solution: (See manufacturers recommendations for the particular column set used.) For the Dionex type AS14 and AG14 set use 1.0 mM sodium bicarbonate and 3.5 mM sodium carbonate. Weigh 8.4 g sodium bicarbonate and 37.1 g sodium carbonate into a beaker and dissolve in deionised water. Dilute the solution to 500 ml with deionised water. This stock may be kept for 1 year in a polypropylene bottle. Pipette 20 ml of this stock into a 2 litre volumetric flask, dilute to volume with deionised water, mix well and transfer to the eluent reservoir.

METHOD NUMBER 307	PAGE 3 OF 6
REV 6	

- Reagent solution 0.025 N, H₂SO₄. Measure 27 ml of concentrated H₂SO₄ (measuring cylinder) and slowly (observing safety requirements for acids) add to a beaker containing approximately 300 ml deionised water. Dilute to 1 l (this is approximately 1 N). dilute 100 ml of this solution to 4 l with deionised water (NB this reagent is not required if electronic suppression is available).
- Standard anion solutions, 1 000 mg l⁻¹. Prepare a series of standard anion solutions by weighing the indicated amount of salt, dried to a constant weight at 105 °C and dissolved in 1 000 ml of demineralised water. The salts used for the preparation of the standards must be of the best quality ie GUARANTEED REAGENT (GR Grade) from Merck, ANALYTICAL REAGENT (AR Grade) from Riedel-de Haen or a suitable supplier. Store in plastic bottles in a refrigerator, these solutions are stable for at least 1 year.

Anion	Salt	Amount (g.l ⁻¹)
Cl ⁻	NaCl	1.6485
NO ₃ ⁻	NaNO ₃	1.3707
NO ₂ ⁻	NaNO ₂	1.4998
SO ₄ ²⁻	Na ₂ SO ₄	1.4785

- Combined working standard solution 1: Pipette the following volumes of the standard solutions (prepared in 4) into a 1 l volumetric flask.

Cl ⁻	50.0 ml	(50.0 mg l ⁻¹)
NO ₂ ⁻	10.0 ml	(10.0 mg l ⁻¹)
NO ₃ ⁻	25.0 ml	(25.0 mg l ⁻¹)
SO ₄ ²⁻	100.0 ml	(100 mg l ⁻¹)

- Remaining work standards. Pipette 50.0 ml aliquots of Standard Solution 1 into each of the volumetric flasks given below, and dilute to volume the concentrations of the solutions are in brackets.

Standard Volumetric Flask	2 100.0 ml	3 250 ml	4 500 ml	5 1 000 ml
Cl ⁻	25.0	10.0	5.0	2.5
NO ₂ ⁻	5.0	2.0	1.0	0.5
NO ₃ ⁻	12.5	5.0	2.5	1.25
SO ₄ ²⁻	50.0	20.0	10.0	5.0

The working standards must be prepared weekly.

METHOD NUMBER 307	PAGE 4 OF 6
REV 6	

ANALYTICAL PROCEDURE

1. Prepare System

Set up the ion chromatograph according to the operation manual, using the following conditions:

Flow rate : 1.20 ml.min⁻¹
 Suppressor : 31mA
 Cell Heater : 35°C

Set up the integrator or data station according to the appropriate operation manual. (For integrators, a chart speed of 0.5 cm.min⁻¹ and attenuation of 256, 512, or 1024 mV is usually suitable.) Adjust other parameters after the first injection, using the procedure recommended in the operation manual. Allow to equilibrate to a stable pressure and conductivity reading. With the conditions given the pressure should be between 200-3000 psi and conductivity 17-20 µS.cm⁻¹. Offset the conductivity to zero.

2. Calibrate System

Using a disposable syringe, or by autosampler if available, inject a portion of standard 3 into the ion chromatograph. When the chromatogram is complete, use the peak retention data to set up the calibration parameters in the integrator or data station (refer to the operation manual). The calibration is stable for one week.

For the Dionex AS14 column type, the approximate retention times are:

Cl ⁻	4.55 minutes
NO ₂ ⁻	5.61 minutes
NO ₃ ⁻	8.99 minutes
SO ₄ ²⁻	12.60 minutes

Perform a 5-point calibration by injecting each of the standards in turn as required by the calibration programme.

METHOD NUMBER 307	PAGE 5 OF 6
REV 6	

3. Analysing of Samples

Steps to be followed:

- 3.1 Sort samples according to logging-in sequence and pour into the sample vials in the sample tray.
- 3.2 Switch on the computer, printer, autosampler and the ion chromatography system.
- 3.3 Check the chromeleon server on the right side of the computer, it will take about 1 minute to start.
- 3.4 When the chromeleon server is running idle, double click on the chromeleon icon. NB. A problem may arise with starting of the server but that may be rectified by putting the Dongel (green piece of metal) in and out at the back of the CPU.
- 3.5 Click on panels
- 3.6 Click on ICS-1500 system AS40 panel.
- 3.7 Click on start up, the message (Pump ECD Devise is not remote) will appear, and then press OK.
- 3.8 Click on connected, then start up again.
- 3.9 The pump will switch on and the system will take about 20 minutes to stabilize.
- 3.10 Simultaneously press CONTROL and TAB buttons.
- 3.11 Click on sequence, then select the month of the sequence on which samples should be run. Once the sequence has been sorted out, the analysis can be started by clicking on BATCH START and then START THE SAMPLE BATCH.
- 3.12 After the run has been completed, check if any of the analysed peaks exceed the highest calibration concentration for that then make appropriate dilutions and then analyze again.

4. Reporting of Results

Value obtained	Report to
Below LOD	If result is less than the LOD report as less than the LOD of this method
Between LOD and < 100 mg/l	1 decimal places
Between 100 mg/l and < 1000 mg/l	To the nearest ten
Above 1000 mg/l	To the nearest hundred

METHOD NUMBER 307	PAGE 6 OF 6
REV 6	

CALCULATIONS

No calculations are required, as the concentrations are calculated directly by the personal computer. However, remember to account for any dilutions that may have been made.

SAMPLE STORAGE AND PRESERVATION

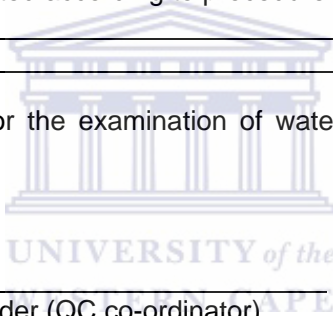
On-line analysis should be performed as close to the sample point as possible keeping the sample line as short as possible. See Procedure P511.

VALIDATION OF ANALYTICAL DATA

Analytical data validated according to procedure P529.

REFERENCES

Standard Methods for the examination of water and wastewater 20th Edition, page 4-6



COMPILED BY: _____ DATE: _____
D Surender (QC co-ordinator)

AUTHORISED BY: _____ DATE: _____
J Reeves (QA Manager)

APPENDIX C: METAL ANALYSIS OF RAW, POTABLE AND WASTE WATER BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP)

METHOD NUMBER 412	PAGE 1 OF 10
REV 1	

METAL ANALYSIS OF RAW, POTABLE AND WASTE WATER BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP)

BASIS OF METHOD

Measurement of atomic emission by optical spectroscopy. Nebulization of samples and transportation of the aerosol produced to the plasma torch, where excitation occurs. Production of characteristic atomic-line emission spectra by a radio frequency inductively coupled plasma (ICP) and monitoring of the intensity of the lines by means of a charge injection device. Processing and controlling of the photon current from the charge injection device by the computer system. Use of the background correction technique to compensate for variable background contribution to the determination of the elements. This method is for the determination metal elements in raw, potable and wastewater using OPTIMA 5300DV instrument.

SAFETY PRECAUTIONS

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound needs to be treated as a potential health hazard. From this viewpoint, reduce exposure to these chemicals to the lowest possible level by whatever means available.

Wear gloves and safety spectacles when handling concentrated acids.

METHOD NUMBER 412	PAGE 2 OF 10
REV 1	

RANGE OF APPLICATION

Table 1: List elements, for which this method applies, along with the wavelength, range and detection limit.

Element	λ (nm)	Range (mg/l)	LOD (ppm)
Al	396.1	0-1	0.005
B	208.8	0-10	0.004
Ba	233.5	0-10	0.005
Be	234.8	0-1	0.005
Cd	226.5	0-10	0.005
Co	228.6	0-10	0.005
Cr	267.7	0-10	0.005
Cu	324.7	0-10	0.005
Fe	259.9	0-10	0.005
Mn	260.5	0-10	0.005
Ni	231.6	0-10	0.005
Pb	220.3	0-10	0.007
Sr	407.7	0-0.5	0.005
Zn	213.8	0-10	0.005

For the purpose of this method, total metals are defined as soluble metals at pH<2.

The analytical range of this manual has been restricted to improve performance. Samples that do not fall within the ranges as specified in Table 1, will be diluted with deionized water, until they do.

METHOD NUMBER 412	PAGE 3 OF 10
REV 1	

INTERFERENCES

The method is free from inter-elemental interferences, as the spectral lines chosen are free from interference.

SAMPLE PREPARATION

1. Glassware, sample vessels, reagents, standards and blank solution

All volumetric glassware (pipettes and volumetric flasks only), should be of grade A quality. Glassware should be cleaned by rinsing with 1:9 (v/v) nitric acid, followed by deionized water before use. All storage containers for standard solutions should be soaked in 1:9 (v/v) nitric acid overnight and rinsed with deionized water before use. All sample vessels to be rinsed with demineralised water. Before use, each sample vessel should be rinsed at least once with at least 5 ml of the solution to be analysed.

Water used for dilutions, should have an element content that is negligible, compared to the smallest concentrations to be determined in the samples. Deionized water is suitable for this purpose.

2. Nitric acid

To prevent the possible introduction of foreign mineral contaminants, acid of at least analytical reagent grade is required.

REAGENTS

1. Metal stock solution

Ampoules /ready-made standard solutions containing the different elements are commercially available and are made up according to the recommendations of the manufacturer. All materials bought are, where possible, traceable to reference materials. Shelf life is two years, if stored in high quality polyethylene containers.

METHOD NUMBER 412	PAGE 4 OF 10
REV 1	

2. Multi-element standard solution (prepared by analyst)

HIGH STD: Prepared by pipetting 10ml of 1000mg/L stock of each element into a 1000ml volumetric flask. For Al and Be a 100ml of a 10mg/L prepared standard is pipetted. For Sr a 50ml of a prepared 10mg/L standard is pipetted. 4ml HNO₃ is added to the 1000ml volumetric flask and made up in deionized water. Store in DURAN PYREX glass bottles. Shelf life is 12 months.

NEW STD: Prepared by pipetting 200ml of the HIGH STD into a 1000ml volumetric flask, 4ml HNO₃ is added and made up in deionized water. Store in DURAN PYREX glass bottles. Shelf life is 12 months.

<i>Element</i>	HIGH STD(mg/l)	NEW STD(mg/l)
Al	1.0	0.2
B	10.0	2.0
Ba	10.0	2.0
Be	1.0	0.2
Cd	10.0	2.0
Co	10.0	2.0
Cr	10.0	2.0
Cu	10.0	2.0
Fe	10.0	2.0
Mn	10.0	2.0
Ni	10.0	2.0
Pb	10.0	2.0
Sr	0.5	0.1
Zn	10.0	2.0

METHOD NUMBER 412	PAGE 5 OF 10
REV 1	

3. Multi-element quality check standard solution (prepared by analyst)

HIGH STD (FOR THE QC): Prepared by pipetting 10ml of a 1000mg/l of each element into a 1000ml volumetric flask, except Al and Be of which 1ml of each is pipetted, 4ml HNO₃ is added and made up in deionized water. Store in DURAN PYREX glass bottles. Shelf life is 12 months.

QC: Prepared by pipetting 100ml of the HIGH QC STD into a 1000ml volumetric flask, 4ml HNO₃ is added and made up in deionized water. Store in DURAN PYREX glass bottles. Shelf life is 12 months.

<i>Element</i>	(QC) mg/l
Al	0.1
B	1.0
Ba	1.0
Be	0.1
Cd	1.0
Co	1.0
Cr	1.0
Cu	1.0
Fe	1.0
Mn	1.0
Ni	1.0
Pb	1.0
Sr	0.2
Zn	1.0

4. Blank solution (4 ml HNO₃/l prepared by Analyst)

2 ml of nitric acid made up to 500 ml. Store in a DURAN PYREX glass bottle.

5. Argon gas

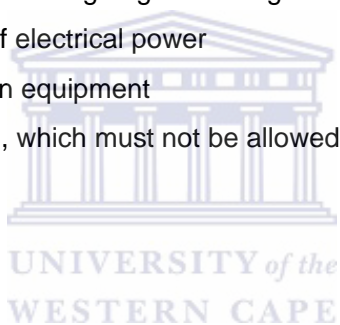
Spectrographic grade argon gas at a regulated pressure of above 700 kPa (Minitank)

METHOD NUMBER 412	PAGE 6 OF 10
REV 1	

ANALYTICAL PROCEDURE

1. Equipment

- The OPTIMA 5300DV SPECTROPHOTOMETER, which includes the ICP Emission Source and the Optical system
- The host computer and printer
- AS 93PLUS Autosampler
- The recirculator and refrigeration unit(chiller) for the SCD Detector
- Atlas Copco Compressor
- Spectrographic grade argon gas at a regulated pressure of 700 kPa.
- Suitable source of electrical power
- Suitable extraction equipment
- Suitable drainage, which must not be allowed to overflow



METHOD NUMBER 412	PAGE 7 OF 10
REV 1	

2. Procedure

- 2.1 The steps described in 2.3 should, if followed in sequence, generally lead to satisfactory accomplishment of the task, but may not always be the most efficient approach. Analysts should take note that certain parts of the sequence should normally be carried out in the specified order. Groups can usually be swapped around to obtain better efficiency. The torch compartment will purge with argon for about 45 seconds, before attempting to ignite the plasma (this time delay is computer controlled).
- 2.2 Experience has demonstrated that failure of this method to perform satisfactorily can rarely be ascribed to human error. It is usually caused by instrumental malfunction. The nature of such malfunctioning is often unique, and beyond the scope of this method, or even that of the THERMO JARRELL ASH User's Guide. When problems are encountered, they should be discussed with other authorised users, or the service engineer, as indicated in the Instrument Logbook. An entry to this effect should also be made in the instrument Logbook.

3. Steps

1. Sort samples according to registration sequence.
2. Confirm that there is power to the refrigeration unit.
3. Confirm that there is sufficient Argon gas pressure in the lines by noting the reading on the pressure gauge. It must be 550 kPa or more
4. If it is not, then the Argon mini tanks must be checked.
5. Confirm that there is extraction by observing the draught meter above the spectrometer in the clean lab. It must read around 300 Pascals.
6. Should there have been a general power failure, note that the switch on sequence is as follows:
 - GAS
 - CHILLER
 - COMPRESSOR
 - INSTRUMENT
 - COMPUTER
7. Switch on the computer.
8. On the desktop, double click on **WINLAN 32** to load the software.
9. A **DIGNOSTICS** window will confirm the communication between the **AUTOSAMPLER, RF GENERATOR** and **COMPUTER**. Then it will disappear, if not then an error message will appear, attend to the problem on the error message and the wait for the communication to be established, if this is not successful then proceed to step 54.
10. Using the mouse, click on the **PLASMA CONTROL PANEL** icon.
11. This will bring up an information window confirming the status of the controller and the plasma discharge.

METHOD NUMBER 412	PAGE 8 OF 10
REV 1	

12. Check that the settings are: **RF POWER** – 1300 Watts, **AUXILIARY FLOW** – 0.2 L/min, **NEBULIZER FLOW** – 0.75 L/min, **PUMP RATE** – 2.5 ml/min.
13. Click **ON**, to ignite plasma.
14. If this is not successful then an error message will appear, click on **OK** and the **PLASMA CONTROL PANEL** will reappear. Then try igniting again, if this is not successful then proceeds to step 54.
15. Autosampler table must be loaded to the **OPTIMA 5300DV** computer
16. To do this, click on the **SAMPLE INFO** icon. This will bring up a sample information editor window.
17. Click on **SAMPLE ID** column, start typing the sample information, i.e. **Submission Id, Sample Id** and **User Id**
18. Continue typing according to the LIMS sequence until all the samples have been entered
19. Now right click on the **AUTOSAMPLER LOCATION** column, select **COLUMN FILL** from the drop down menu window will open where a starting location and the sample number range has to be entered. Click **OK** and the location of the sample will be calculated automatically.
20. From the menu select **FILE SAVE AS**, select **SAMPLE INFO FILE** and name the file **SET1B** and then print the sample list and use the list to pour out samples.
21. From the menu click **FILE** then **OPEN- METHOD**, then a method window will pop up, then select **SET1B** then **OK**.
22. Click on **METHOD EDITOR** icon then a window will open.
23. Confirm that **WASH** is set on **BETWEEN SAMPLES** and that the rinse time is at least 30seconds by clicking on sampler then autosampler. Then close the method editor window.
24. Click on **AUTO** icon and select **SET UP**, confirm that the method name is **SET1B** and the sample info is **SET1B**.
25. Confirm that the data is being saved by checking the **SAVE DATA**, double click on open and name the table as would like data to be saved.
26. If it is an unattended run, double click on **SET** under **AUTOSHUTDOWN**, a window will appear then check the **SHUTDOWN** box and select the option required after an automated analysis.
27. Confirm that the **wash before shutdown** and **turn off plasma and pump** boxes have been checked if it is an overnight run.
28. Now select **ANALYZE** from the **AUTO** window, click on **REBUILD LIST** to load the new sample info table.
29. Confirm the sample and standard / QC positions on the autosampler racks.
30. Place the samples, standards and QC's in the relevant positions on the autosampler racks. Ensure that there is sufficient solution in each vial and that the vials are correctly placed in their positions to avoid unnecessary repeats.
31. Confirm that there is sufficient water in the rinse station reservoir.

METHOD NUMBER 412	PAGE 9 OF 10
REV 1	

32. Remember that each sample vessel should be rinsed at least once with at least 5 ml of the solution to be analysed
33. Check sample transport system for air bubbles, leaks and smoothness of transport. Rectify any problems before continuing.
34. Then click on **ANALYSE ALL** to start running the samples.
35. If this is to be an unattended overnight run then ensure that the terminating action selected is **SHUTDOWN**.
36. As the run begins, check that all the components are functioning properly.
37. When the run has been completed click on **OK**. For an overnight run the instrument will shut down automatically.
38. Ensure that the plasma has been rinsed with UHP water for at least 2-3 minutes.
39. Switch the plasma power supply (RF power) off, using the **PLASMA CONTROL** icon and clicking on **OFF**. An audible click will be heard, do not worry, this is normal.
40. Unclamp the feeder tubes.
41. Unclamp and turn off the rinse station pump.
42. Sign and update printout results.
43. Take the samples found to be out of range and dilute as required.
44. Re-run these dilutions and do not forget to add the dilution factor in the sample table.
45. **File the raw data and send the report.**
46. The OPTIM 5300DV follows the following autosampler protocol.
47. The first step is to standardise all elements in the method.
48. The next step is to analyse a quality control sample.
49. Should the QC fail then it will re-analyse the quality control, should the QC fail again then it will re-standardise all the elements. It will then analyse the QC again. Should it fail a third time, it will re-analyse for the fourth time, if it fails then it will stop. At this stage try solving the problem and restart the run and should it fail again repeat it once more using a different set of standards. Should this prove unsuccessful proceed to step 54.
50. Should it have passed the QC at any stage, the programme will proceed with analysing the first 20 samples.
51. After which it will then analyse another QC. If this QC passes it will analyse the next 20 samples and continue in this manner until the run is completed. At the completion of the run a QC will be analysed.
52. If at any time a QC should fail, the instrument will re-standardise all the elements and analyse the QC again. If the QC passes it will RE ANALYSE the previous 20 samples. Should the QC still fail, it will read the QC once more. Should the QC now pass it will RE-ANALYSE the previous 20 samples, but should it have failed it will stop the autosampler run.
53. Any failures linked to gross errors such as plasma shutoff, empty QC vials; etc must not be entered into the spreadsheet, as they will cause artificial widening of the limits.
54. Contact the local service engineers at PERKIN ELMER at the telephone number stated in the logbook.

METHOD NUMBER 412	PAGE 10 OF 10
REV 1	

In order to ease the above procedure (not replace it) a checklist (WAC FORM NO.6, REV.2) has been devised and must be utilised before every calibration. These checklists must be filed.

Final reporting policy

Value obtained	Report to
Below LOD	If result is less than the LOD report as less than the LOD of this method
Between LOD and < 1 mg/l	2 decimal places
Between 1 mg/l and < 10 mg/l	1 decimal place
Between 10 mg/l and < 100 mg/l	To the nearest unit
Between 100 mg/l and < 1000 mg/l	To the nearest ten
Above 1000 mg/l	To the nearest hundred

REFERENCE

- 1.0 OPTIMA 5000 SERIES Hardware Guide.
Preliminary Part Number: 0993-7625
Publication Date: April 2004
- 2.0 Concepts, Instrumentation and Techniques in ICP-OES
By Charles B. Boss and Kenneth J. Fredeen.

VALIDATION OF ANALYTICAL DATA

Refer to procedure P506.

COMPILED BY: _____ DATE: _____

AUTHORISED BY: _____ DATE: _____