WATER TREATMENT TECHNOLOGIES FOR REMOVAL OF ACID, SULPHATE AND METALS

A.J. GELDENHUYS M.Ing

Thesis submitted for the degree Philosophiae Doctor in Chemical Engineering at the North-West University (Potchefstroom Campus)

Promoter:	**Prof. F.B. Waanders**
Co-Promoter:	**Dr. J.P. Maree**

2004
Potchefstroom

DECLARATION

I, Andries Johannes Geldenhuys, hereby declares before a Commissioner of Oaths:

1. That, all the material submitted for the degree PhD in Chemical Engineering at the North-west University (Potchefstroom Campus) has not previously been submitted for a degree at any other university
2. That, this submission takes place with due recognition given to my copyright where applicable

Signed at PRETORIA on this 13th day of APRIL 2005

A J Geldenhuys

[illegible]

[illegible] by me and that the deponent has acknowledged that he/she knows and understands the contents of this statement. This statement was sworn to/affirmed before me and deponent's signature/mark/thumbprint was placed thereon in my presence –

PRETORIA op/on 2005/04/13 om/at 18 35

3446591-7
InSP

(HANDTEKENING) KOMMISSARIS VAN EDE
(SIGNATURE) COMMISSIONER OF OATHS

FRANCOIS KOEN

VOLLE VOORNAME EN VAN IN DRUKSKRIF
FULL FIRST NAMES AND SURNAME IN BLOCK LETTERS

GARSFONTEIN SAPD

BESIGHEIDSADRES (STRAATADRES)
BUSINESS ADDRESS (STREET ADDRESS)

InSP

RANG/RANK

SA POLISIE
SA POLICE

SUID-AFRIKAANSE POLISIEDIENS
DIE TAKBEVELVOERDER
THE BRANCH COMMANDER
2005 -04- 13

ABSTRACT

A great deal of research effort has been undertaken to find an effective solution to the problem of acid mine drainage. Indeed, South African legislation requires mining companies to respect environmental regulations by minimising water intake from local municipalities and providing a rehabilitation plan. In order for the South African mining industry to remain competitive, the proposed solutions have to be not only efficient but also economic. This is the reason for the use of a waste material being attractive for water treatment and an integrated treatment technology being developed to treat water to different quality levels. The main objectives of this study were to develop more cost-effective treatment processes specific to the needs of the mining industry in southern Africa and to investigate the technical and environmental feasibility of utilising an alkaline waste product from the local paper industry as stabilising agent for acid mine residues.

All the research and development work was carried out on laboratory and pilot scale plants. Five papers, with the present author as principal contributor, will form the basis of this thesis, of which one has been published and four are being peer-reviewed, presented at international conferences (locally and overseas) and published in the proceedings of the various conferences. Another five papers, with the author as co-author, have also been presented at international conferences and are being published in the proceedings of these conferences, and are included in this thesis.

The results of the laboratory and pilot scale studies have been incorporated into the design and implementation of the following full-scale plants:

- A limestone handling and dosing system to supply slurried limestone of constant density to the neutralisation plant was constructed and commissioned during 2001 at Navigation Section of Landau Colliery, Witbank
- A limestone handling and dosing system, including a fluidised-bed limestone neutralisation plant, was constructed and commissioned during 2001, at Ticor, Empangeni
- An iron(II)-oxidation and fluidised-bed limestone neutralisation plant was constructed and commissioned during 2002 at BCL, Selebi-Phikwe, Botswana

- A limestone handling and dosing system, to supply slurried limestone of constant density to the neutralisation plant, was constructed and commissioned during 2003, at Kromdraai Colliery, Witbank
- An iron(II)-oxidation and fluidised-bed limestone neutralisation plant was constructed and commissioned during 2004, at the Navigation Section of Landau Colliery, Witbank

These plants consist of specific units (stages) of the completely integrated process, developed by the CSIR:Environmentek over the past four years. These stages are:

- Heating unit: Production of CaO (quick lime) and CO_2-gas from burned coal and precipitated $CaCO_3$ (limestone)
- Limestone neutralisation and partial sulphate removal to a level of 1 900 mg/ℓ
- $Ca(OH)_2$ (hydrated lime) stage: CaO contacted with the acid water to produce $Ca(OH)_2$
- Lime treatment stage: Partial sulphate removal as $CaSO_4$ (gypsum) to below 1 200 mg/ℓ, and full removal of magnesium and other metals
- pH adjustment stage: CO_2 from the heating unit applied to reduce the pH to 8.6 while $CaCO_3$ precipitates
- Barium sulphide treatment or biological sulphate removal treatment: Removal of sulphate to below 200 mg/ℓ
- Production (regeneration) of barium sulphide: Heating barium sulphate from the above stage
- Stripping of H_2S either from the barium sulphide or the biological sulphate removal processes. H_2S is contacted with Fe(III)-rich water for elemental sulphur production.

UITTREKSEL

'n Uitgebreide navorsingsondersoek is geloods om 'n effektiewe manier van waterbehandeling te vind vir suur mynwater en probleme wat daarmee gepaardgaan. Suid-Afrikaanse wetgewing vereis dat myne die omgewing met versigting hanteer deurdat die aankoop van water vanaf die munisipaliteit beperk word tot 'n minimum en 'n rehabilitasieprogram in plek moet wees. Vir die Suid-Afrikaanse mynbou-industrie, om koste-effektief en kompeterend te wees, moet die behandelingsprosesse effektief en ekonomies wees. Daarom is die gebruik van 'n afvalproduk as alternatief tot alkaliese medium, so 'n aantreklike opsie en het gelei tot die ontwikkeling van 'n geintegreerde behandelingstegnologie. Hierdie tegnologie behels die behandeling van swak kwaliteit water, afkomstig vanaf myne, tot spesifieke vlakke, afhangend van wat die eindbestemming van hierdie water is. Die hoofdoel van hierdie proefskrif was om 'n meer koste-effektiewe manier van waterbehandeling te ontwikkel wat voldoen aan die behoeftes van die mynbou-industrie in Suid-Afrika. Ook is daar intensief gekyk na die tegniese en omgewingsvatbaarheid van die gebruik van kalksteen, 'n afval produk vanaf die plaaslike papierindustrie, as alkaliese medium tot neutralisering van suur mynuitvloeisels.

Alle navorsingswerk en ontwikkeling is gedoen in 'n laboratorium en loodskaalaanleg. In die hoedanigheid as hoofouteur, is vyf artikels gelewer, waarvan een gepubliseer is. Die ander vier artikels is geproeflees en aangebied op internasionale konferensies, plaaslik sowel as oorsee, asook gepubliseer in die verrigtinge van die onderskeie konferensies. Hierdie vyf artikels vorm die basis van die proefskrif terwyl 'n verdere vyf ander artikels, waarby die skrywer as mede-outeur opgetree het, as aanvullende materiaal aangebied word.

Die resultate van die laboratorium- en loodskaalaanleg studies het gelei tot die ontwerp, oprigting en inwerkstelling van die volgende volskaal aanlegte:

- Kalksteen behandelings- en doseringsisteem om vloeibare kalksteen met konstante digtheid te lewer aan neutraliseringsaanleg – opgerig en inwerking gestel gedurende 2001 te Navigation seksie van Landau Colliery, Witbank
- Kalksteen behandelings- en doseringsisteem en gefluidiseerde bed kalksteen neutraliseringsaanleg – opgerig en inwerking gestel gedurende 2001 te Ticor, Empangeni

- Yster(II)-oksidasie and gefluidiseerde bed kalksteen neutraliserings aanleg – opgerig en inwerking gestel gedurende 2002 te BCL, Selebi-Phikwe, Botswana
- Kalksteen behandelings- en doseringsisteem om vloeibare kalksteen met konstante digtheid te lewer aan neutraliseringsaanleg – opgerig en inwerking gestel gedurende 2003 te Kromdraai Colliery, Witbank
- Yster(II)-oksidasie and gefluidiseerde bed kalksteen neutraliserings aanleg – opgerig en inwerking gestel gedurende 2004 te Navigation seksie van Landau Colliery, Witbank

Bogenoemde aanlegte bestaan uit een of meer van die volgende stadiums van die geintegreerde proses soos ontwikkel oor die afgelope vier jaar deur die WNNR:

- Verhittingseenheid – produksie van CaO en CO_2-gas deur steenkool verbranding, $CaCO_3$ presipitasie
- Kalksteen neutralisasie en gedeeltelike sulfaatverwydering (tot 1 900 mg/ℓ)
- $Ca(OH)_2$ stadium – CaO word gekontak met suur water om $Ca(OH)_2$ te produseer
- Kalkbehandelingstadium – gedeeltelike sulfaatverwydering as $CaSO_4$ (gips) tot 1 200 mg/ℓ, volledige verwydering van magnesium en ander metale
- pH verstelling na neutraal - CO_2 afkomstig vanaf verhittingseenheid verlaag die pH tot 8.6 terwyl $CaCO_3$ presipiteer
- Barium sulfied behandelingstadium of Biologiese sulfaatverwydering – sulfaat word verwyder tot 200 mg/ℓ en laer
- Produksie van barium sulfied - verhit barium sulfaat vanuit bogenoemde stadium
- Stroping van H_2S vanaf die barium sulfied proses of die biologiese sulfaat verwyderingsproses. H_2S word dan in kontak met Fe(III) ryke water vir swawel produksie gebring

PREFACE

Increasing exploitation of the natural water resources in southern Africa will necessitate widespread exploitation of non-conventional sources, such as municipal and industrial wastewater. The direct use of wastewater, as well as being an economically attractive option of utilising supplies, represents prevention of pollution and eutrophication and exploits a guaranteed source of supply which can be tailored to meet specific requirements. The advanced treatment options described in this thesis may be utilised to further these objectives.

This thesis reports the results of research conducted at the Council for Scientific and Industrial Research, in the Division for Water, Environment and Forestry Technology (CSIR: Environmentek), situated in Pretoria, on newly developed water treatment technologies during the past four years. The author was personally involved in the research and development of these technologies and processes as well as in the construction and running of laboratory and pilot scale units and the commissioning of full scale plants. The purpose of this thesis is to present basic principles and general process guidelines based on operational experience with the various processes employed for the production of re-usable water from mining effluents, resulting from coal mines and the mining of heavy minerals.

Numerous full scale plants, based on specific stages of the developed technology, have been designed by Wates, Meiring & Barnard and constructed by Thuthuka Project Management, both of which are industrial partners of the CSIR. These plants were operated by the CSIR under the supervision of the author as process engineer for a period of 12 – 24 months in order to optimise the processes. He also provided on-site training to mine operators in order to ensure efficient running and understanding of the technology. These full scale, operational plants are listed in the *Abstract* of this thesis.

GLOSSARY

Acid mine drainage:	Acid water that is rich in iron and is produced when pyrites (Fe_2S) is oxidised in water due to the presence of air and iron oxidising bacteria
Fluidised-bed reactor:	A column type reactor packed with solid material (e.g. limestone). A gas is moved through the reactor at a high enough rate to expand the volume inside the reactor
Limestone:	Ore containing primarily $CaCO_3$
Slaked lime:	$Ca(OH)_2$
SRB	Sulphate Reducing Bacteria
Unslaked lime:	CaO

CONTENTS

Abstract 3

Uittreksel 5

Preface 7

Glossary 8

Chapter 1: Literature Overview 12

- **1.1 Mining of Heavy Minerals** 13
- **1.2 Nickel-Copper-Cobalt Mining** 14
- **1.3 Coal Mining** 16
  - **1.3.1 Introduction to Coal** 16
  - **1.3.2 Coal Formation and Composition of Coal Macerals** 17
  - **1.3.3 Mineral Matter** 17
  - **1.3.4 Coal Mining and the Environment** 19
  - **1.3.5 Origin of Acid Mine Drainage** 19
  - **1.3.6 Geochemistry of Acid Mine Drainage** 21
- **1.4 Conventional Treatment Options for Acid Mine Drainage and Acidic Solutions** 24
- **1.5 Alternative Neutralisers** 25
- **1.6 Further Treatment** 27
- **1.7 Novel Integrated Technology for Treatment of Acid Mine Drainage and Effluents** 30
- **1.8 Legal requirements** 34

Chapter 2: Papers 1 to 8 35

- **2.1 Introduction to Papers** 35
- **Paper 1:** Geldenhuys,A.J., Maree, J.P., de Beer, M. and Hlabela, P. 2003. An integrated limestone/lime process for partial sulphate removal, The *J. South African Institute of Mining and Metallurgy*, **103**(6), 345 – 353. 37

- **Paper 2:** Geldenhuys, A.J. & Maree, J.P. Synthetic organic polymers (PAC6 and 3095) as coagulants/flocculants for optimisation of an integrated limestone/lime neutralisation process for partial sulphate removal, *Proceedings 5th Annual Industrial Water Management* 47 *and Treatment Symposium*, 15 – 16 May 2002, Johannesburg, South Africa.

Paper 3: Geldenhuys, A.J., Maree, J.P., Strobos, G., Smit, N. and Buthelezi, B. Neutralisation and partial sulphate removal of acid leachate in a heavy minerals plant with limestone and lime, *Proceedings 6th International Conference on Acid Rock Drainage*, 12 – 18 July 2003, Cairns, Australia. 71

Paper 4: Geldenhuys, A.J., Maree, J.P., Fourie, W.J., Bladergroen, B.J. and Tjati, M. Acid mine drainage treated electrolytically for recovery of hydrogen, iron(II) oxidation and sulphur production, *Proceedings 8th International Congress on Mine Water and the Environment*, 19 – 22 October 2003, Johannesburg, South Africa. 75

Paper 5: Maree, J.P., de Beer, M., Geldenhuys, A.J., Strobos, G, Greben, H., Judels, C. and Dreyer. Comparison of the combined limestone/lime and combined limestone/biological sulphate removal process for treatment of acid mine water, *Proceedings 8th Hard Rock Mining Conference: Issues Shaping the Industry*, 7 – 9 May 2002, City Colorado, USA. 92

Paper 6: Adlem, C.J.L., Geldenhuys, A.J., Maree, J.P. and Strobos, G.J. Examining the implementation of limestone neutralisation technology in the mining and industrial sector to neutralise acid and reduce sulphate pollution, *Proceedings 5th Annual Industrial Water Management and Treatment Symposium*, 15 – 16 May 2002, Johannesburg, South Africa. 95

Paper 7: Maree, J.P., Hlabela, P., Geldenhuys, A.J., Nengovhela, R., Mbhele, N. and Nevhulaudzi, T. Treatment of mine water for sulphate and metal removal using barium sulphide, *Proceedings Waste Management, Emissions & Recycling in the Metallurgical & Chemical Process Industries*, 18 – 19 March 2004, Johannesburg, South Africa. 111

Paper 8: Maree, J.P., Netshidaulu, I., Strobos, G., Nengovhela, R. and Geldenhuys, A.J. Integrated process for biological sulphate removal and sulphur recovery, *Proceedings Water Institute of Southern Africa (WISA) Biennial Conference & Exhibition*, 2 – 6 May 2004, Cape town, South Africa. 127

Concluding Discussion 140
Acknowledgements 149
Bibliography 150
Appendix A List of Additional Papers and Posters 153
Appendix B List of Confirmations 163

CHAPTER 1: LITERATURE OVERVIEW

The generation of acid mine drainage (AMD), from working or abandoned mines, and its discharge into the surrounding environment is a cause of serious environmental pollution. At present, AMD is becoming a problem as increasing numbers of mines are facing closure, which will finally lead to the shutting down of whole coalfields. Pumps, which currently keep these mines dry, are removed and consequently the groundwater returns to its pre-mining levels leading to AMD. The treatment, or the prevention, of such pollution by current means is costly and the legal requirement to treat it is also likely to become a more pressing requirement.

The problem with treatment is that the available technologies for dealing in an environmentally friendly way with AMD. Until recently, the standard practice was to treat AMD with lime. This produces a ferruginous (iron bearing) waste material which is often too variable in quality to represent a useful source of ochre. Such waste has to be disposed of in a tailings dam if possible or to landfill. The many technologies proposed for treatment of mine drainage are usually expensive and complex. Liming is also not sustainable because of the requirement for lime and the need for disposal space. This research looked into the feasibility of replacing lime treatment of AMD with other technologies which, not only offer a more sustainable solution, but also cost effective answers to water issues that may become major problems. Without this industry accepting responsibility and realising the extent of the pollution by mine water, detrimental effects on the environment and its water resources will result, especially in a semi-arid country like South Africa.

In this section, an in-depth overview is given of the available literature on specifically coal mining. The history of coal and the geochemistry of coal mine drainage in Southern Africa will be discssed. The mining of heavy minerals in South Africa also adds to the list of many polluters of ground water resources on which one paper will focus. A neighbouring country of South Africa, Botswana, also very arid in climate, produces acid water, resulting from a nickel-copper-cobalt mine, operating as BCL Limited at Selebi-Phikwe. In general, focus will be on coal mining, which is one of South Africa's biggest role players in the mining industry. Overall, the focus will be on the origin and background of these different mining operations: how they contribute to water pollution and how their adverse impact on the environment can be mitigated, assisted and guided from a legislation point of view. The responsibility for treating AMD is a crucial issue. As it was not foreseen, when the pumping of water in mines began, that there would be a problem of AMD, there were no funds set aside to meet the considerable financial implications. When mining started, there was also little or no concern about potential environmental problems that might result from such industrial activity.

AMD events are more pernicious than, for example incidents involving nitrate or oil, because the pollutant is not broken down in the environment. Whilst nitrates may be utilised by aquatic organisms and oil may eventually be broken down to carbon dioxide and water, metal pollutants will remain in the environment in one form or another. Metals may be concentrated or dispersed in the environment and without treatment, there will be no control over where these concentrated or dispersed metals will deposit. In the meantime there will be an extended period in which the local environment will suffer the effects of the pollution.

However, AMD is not a new problem. The mining industry in South Africa is therefore under pressure to find solutions for the seriously degradation of the aquatic habitat and quality of water supplies for which they are responsible. Academic and industrial partnerships have investigated a range of mine water treatment technologies to assist in water treatment and remediation. There is currently no consensus on what is the ideal solution, and it may be that each AMD case will require its own treatment solution.

1.1 MINING OF HEAVY MINERALS

Although not as prominent and well-known as the mining of coal, gold and diamonds in South Africa, Ticor Limited (TOR) is involved in the mining, processing and smelting of mineral sands. TOR in South Africa is a heavy minerals sand mining and processing operation, near Richards Bay (http://au.biz.yahoo.com/p/t/tor.ax.html). The operation is based on three alluvial, high grade, placer, mineral sand deposits, namely Hillendale, Fairbreeze and Gravelotte, with reserves of 16 million tonnes of valuable heavy minerals. These deposits yield ilmenite, zircon, rutile and leucoxene which are primarily sources of titanium dioxide feedstock for the paint, paper and plastic's industries. The company produces about 200 000 tonnes of chloride grade and about 50 000 tonnes of sulphateable feedstock per year and will manage about 11% of the world's titanium feedstock supply. Approximately 250 000 tonnes of titania slag and 140 000 tonnes of pig iron are also produced (http://au.biz.yahoo.com/p/t/tor.ax.html).

In the mining and processing operations where these minerals, high in pyrites and low in calcite/dolomite are processed, acid is generated which requires neutralisation in the processing plant where acid is leached into the wash water. This water needs to be treated to a quality suitable for re-use in the metallurgical process, or to a higher quality rendering it suitable for discharge into the Empangeni sewage system, 200 km north of Durban, Kwazulu-Natal. For re-use the water should be neutral and under-saturated with respect to gypsum. For discharge into the sewage system the sulphate concentration should be less than 500 mg/ℓ (as SO_4). Acid mine water is generally neutralised with lime. Disadvantages associated with lime are the costs and maintenance of the slaking equipment as well as hazards, associated with handling. The cost of powdered limestone ($CaCO_3$) in South Africa, a by-product from the paper industry, is 60% lower than conventional lime. Lime has been successfully replaced by limestone as neutralising agent while no compromises have been made on the quality of the discharge water or that of the final products.

The legislative requirements governing effluents resulting from industries are set out in the Water Act (Act 36 of 1998) which is discussed later in this introductory review.

1.2 NICKEL-COPPER-COBALT MINING

Botswana's rapid economic growth, which began in the 1970's, continued into 1997. Much of the growth is attributed to the country's successful program of mineral exploration and development. The mining sector, mostly on the strength of diamonds, accounted for about 33% of the gross domestic product. Nickel and copper also played significant roles in the national economy. BCL Limited is operating nickel-copper-cobalt mines and a smelter at Selebi-Phikwe, about 350km northeast of the capital, Gabarone, and processes 450t/day of ore (Van Tonder *et al.*, 2000)

At BCL, Mine waste discard, that contains pyrites, is produced during mining operations and poses problems of acid leachate. This leachate contains high concentrations of acid, sulphate and metals. The operations consist of underground mining, concentration of the copper and nickel components of the ore by means of flotation, and smelting of the concentrate to produce copper and nickel. The main flows of water into the underground workings include cooling water (with high NaCl content from the ice plant), groundwater (fissure water) and water recycled with the coarse waste backfill. These streams are currently mixed and returned to surface where the combined stream of 350 m^3/h water is neutralised (Van Tonder *et al.*, 2000).

Central to the water network is the Mill Return Water Sump (MRWS). The used-water streams are recycled to the MRWS, from where the concentrator circuit is supplied with water. Lime is used to adjust the pH of the return water to 8.5 in the MRWS. This water is used in the concentrator circuit as transport medium and to facilitate separation. The pH of the water is the main quality consideration for the concentrator as high salinity levels do not pose a problem. In the copper-nickel concentration processing plant, solid waste material containing 5% pyrite is produced. The coarse fraction of the solid waste material is discarded underground as backfill, while the fine waste is discharged onto a tailings waste dump. These wastes give rise to acidic leachate due to pyrite oxidation. Lime is used to neutralise 350 m^3/h of underground mine water (with an acidity of 235 mg/ℓ as $CaCO_3$) and 60 m^3/h of tailings dump seepage (with an acidity of 5000 mg/ℓ as $CaCO_3$). Excess water is used for the cooling and granulation circuit in the smelter. The smelter intake water chloride concentration should be limited to 5 mg/ℓ to prevent pitting corrosion in the smelter cooling jackets. For this purpose surface water is piped from a local dam (Van Tonder *et al.*, 2000).

BCL currently experiences the following water-related problems:

- Neutralised water is discharged into a public stream at a rate of 300 m^3/h. The effluent quality does not meet the permitted level of 500 mg/ℓ sulphate.
- The neutralisation cost is high due to the use of imported lime.
- Excessive acid seepage has resulted in deterioration of the land area adjacent to the tailings dump.
- The water intake of 300 - 400 m^3/h is expensive.

A modelling exercise was carried out during 1999 to audit and simulate the water network of BCL with the aim to identify the optimum water management strategy (Van Tonder, *et al*, 2000). It was found that discard leachate could be neutralised with limestone to minimise chemical cost. It should be treated, before being mixed with less polluted streams, to achieve maximum sulphate removal through gypsum crystallisation and precipitation. The latter will result in reduced gypsum scaling in the metallurgical plant.

1.3 COAL MINING

1.3.1 Introduction to coal

Coal has been described and classified by many scientists. Grainger *et al.* (1981) delineated coal as an organic sedimentary rock, formed by the action of temperature and pressure on plant debris. Coal is a complex mixture of organic matter consisting of mainly carbon, hydrogen and oxygen, together with some small amounts of nitrogen, sulphur and trace elements.

Sanders (1996) referred to coal as a generic term which belongs to a family of solid fossil fuels with a wide range of physical and chemical compositions. Coal is actually a heterogeneous rock composed of different kinds of organic matter which vary in their proportions in different coals. He also noted that no two coals are absolutely identical in nature, composition or origin and proposed that "coal is a compact stratified mass of metamorphosed plants which have, in part, suffered arrested decay to varying degrees of completeness".

According to Grainger *et al.* (1981), the rank of coal can be described as the degree of metamorphism to which coal has been subjected after burial. It then results in the transformation of the original peat swamp through the progressive stages of brown coal (lignite), sub-bituminous, and bituminous coals to anthracite and the meta-anthracites. The rank is then defined as the level to which coal has reached in this coalification series (Falcon *et. al.*, 1981). Rank also refers to the degree of maturity or metamorphism or coalification achieved by a coal through the process of time, temperature, and pressure as a result of depth of burial or proximity to heat following peat accumulation. The progressive change from peat into coal passes through a number of stages, namely:

Peat → Lignite → Bituminous → Semi-anthracite → Anthracite → Graphite (Falcon, 1988).

1.3.2 Coal formation and composition of coal macerals

Neavel (1981) stated that "Macerals" are organic substances derived from plant tissues and cell contents that were variably subjected to decay, incorporated into sedimentary strata, and then altered physically and chemically by natural processes. Each of the materials recognised as belonging to a specific maceral class has physical and chemical properties that depend upon its composition in the peat swamp and the effects of subsequent metamorphic alteration. For applications in coal utilisation it is often sufficient to group the macerals together as vitrinite, exinite (or liptinite) and inertinite (Grainger *et al.*, 1981). In South African coals, a fourth maceral group has been identified, i.e. semi-fusinite. By means of optical examination, the different macerals in coal can be distinguished. Macerals may be differentiated from one another on the basis of morphology, relief, size, shape, colour, reflectance and, origin in some cases (Falcon *et al.*, 1986).

1.3.3 Mineral matter

Table 2 lists the most abundant and common mineral groups found in South African coals, namely: clays, carbonates, sulphides, quartz and glauconite (Falcon & Snyman, 1986).

Table 2 Distribution of the common minerals in South African coals (Falcon & Snyman, 1986)

Group of minerals	**Minerals**	**Chemical Formula**
Clay minerals	Kaolinite	$Al_2Si_2O_5(OH)_4$
	Illite	$(K,H)Al_2(Si,Al)_4O_{10}(OH)_2$
	Montmorillonite	$(\frac{1}{2}Ca,Na)_{0\text{-}7}(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4.nH_2O$
Carbonates	Calcite	$CaCO_3$
	Dolomite	$(Ca,Mg)(CO_3)_2$
	Aragonite	CaCO3 (orthorhombic)
	Siderite	$FeCO_3$
Sulphides	Pyrite	FeS_2
	Marcasite	FeS_2
Oxides	Haematite	Fe_2O_3
Silicates	Quartz	SiO_2

Mineral particles are evident in coal sections and form a major portion of the ash (Grainger *et al.*, 1981). Falcon *et al.* (1986) stated that the forms in which minerals occur in coal fall into two major categories: one of which includes the intrinsic inorganic matter which was present in the original living plant tissue; a second, which includes the extrinsic or induced forms of mineral matter. Intrinsic inorganic matter is trapped in coal in the form of sub-microscopic mineral grains and as organo-metallic complexes. The extrinsic mineral may be primary or syngenetic, and arises from the accumulation by means of wind and water or precipitation in situ (Falcon *et al.*, 1986).

According to Stach *et al.* (1982), the inorganic matter in coal can be classified into three groups:

- Inorganic matter from the original plants;
- Inorganic – organic complexes and minerals which formed during the first stage of the coalification process; or which were introduced by water or wind into the coal deposits as they were forming;
- Minerals deposited during the second phase of the coalification of the coal, by ascending or descending solutions in cracks.

Coal has a significant inorganic material content, varying from less than 3-4%(m/m) to more than 40%(m/m). There is general agreement in the literature that clays, sulphides, carbonates and quartz are the most common minerals in coals (Alpern *et al.*, 1984).

1.3.4 Coal mining and the environment

By its very nature and scale, mining makes a marked and visual impact on the environment. Mining is, moreover, implicated as a significant contributor to water pollution, the prime reason being that most of South Africa's geological formations, which are mined, contain pyrites which oxidise to form sulphuric acid when exposed to air and water. The scarcity of water in South Africa is exacerbated by pollution of the surface- and ground- water resources. Typical pollutants of the aquatic environment include industrial effluents and acid mine drainage.

Mine water in the Upper Olifants River Catchment in Mpumalanga (upstream of Loskop Dam) is at times discharged into local streams, resulting in local acidification and regional salination of surface water resources. Pollution of surface water can be prevented by collecting and treating mine water to a quality where it can be re-used without restriction (Cleanwater 2020 Initiative). Although mine water in the Olifants River Catchment currently amounts to only 4,6% of the total water usage, it contributes 78,4% of the sulphate load.

Mine water in the catchments of the Witbank Dam and Middelburg Dam is rich in calcium, magnesium, sulphate and acid pH. This is due to oxidation of pyrites to sulphuric acid in the mined coal and coal waste, followed by neutralisation with dolomite that is also present in the mined coal.

1.3.5 Origin of acid mine drainage

Coal mine drainage, also known as acid mine drainage (AMD) or acid rock drainage (ARD), is a natural consequence of mining activity where the excavation of mineral deposits (metal bearing or coal), below the natural ground level, exposes sulphur containing compounds to oxygen and water. Recently, it has become possible to mine ores substantially below the groundwater level which can cause surface waters to run over exposed ore seams and elicit similar chemical mechanisms and acid formation (Maree *et al.* (1997)).

Many have given definitions of what they understand under the term "AMD". AMD can be described as drainage resulting from, or caused by, surface mining, deep mining or coal refuse piles that are typically highly acidic with elevated levels of dissolved metals. The formation of AMD is primarily a function of the geology, hydrology and mining technology employed for a specific mine site. AMD is formed by a series of complex geochemical and microbial reactions that occur when water comes into contact with pyrite, amongst other iron disulphide minerals, in coals, refuse or the overburden of a mining operation. The resulting water is usually high in acidity and dissolved metals. The metals remain in solution until the pH rises to a level where precipitation occurs.

When mining began, it was only possible to mine those ores that were at or above ground level. As technology and mining engineering improved, it became possible to excavate horizontal shafts, adits, leading away from the mine to drain groundwater into local low lying river valleys and provide access to lower levels. It later became possible to pump water from deep mines, artificially lowering the groundwater level in the vicinity. When pumping ceases, groundwater floods the mine and will eventually approach the original groundwater level and may cause environmental problems. As the water rises it will eventually reach the levels where adits were built to drain the mine water into river valleys (Kuyucak, 1998).

Oxidation reactions, often biologically mediated, take place which affect the sulphur compounds that often occur in coal seams. Whilst a mine remains dry these sulphur compounds normally generate sulphates in solid form. The metals occurring in these minerals are often incorporated into these salts. When water flows through the mine, they dissolve and this acidic, metal-containing mixture comprises the initial AMD discharge. AMD is a problem because the vast majority of natural life only viable at a neutral or near neutral pH, i.e. 7. The drainage acidifies local watercourses and either kills or stunts the growth of river biota. Effects are even more pronounced on vertebrate life such as fish than on the plant and unicellular life (Maree *et al.*, 1997).

Metals contained in drainage are also of concern, particularly iron. Its presence in the water is a problem, due more to its physical properties than its toxic effects. Iron may be found in two forms, ferrous and ferric. When AMD is generated it will generally be in the ferrous form, but is changed in the presence of oxygen to ferric iron (Fe^{3+}) when it forms semi-solid particles, which are bright orange. Very small concentrations in water are capable of generating large volumes of ferric precipitates which cover the surfaces of land and streams close to the point of discharge. This effectively smothers the environment, prevents life from flourishing, and coats the gills of vertebrate lifeforms such as fish and causes fatalities. The metal is, however, not inherently toxic. Not all mine drainage is acidic. Some are close to neutral but the presence of ferric iron leads to the possibility of precipitation and causes environmental problems as outlined earlier.

1.3.6 Geochemistry of acid mine drainage

The geochemistry of AMD has been the subject of numerous investigations with Rose & Cravotta (1998) being a general reference on the subject. The composition of coal mine drainage ranges widely, from acidic to alkaline and with typical elevated concentrations of sulphate (SO_4), iron (Fe), manganese (Mn) and aluminium (Al) as well as common elements such as calcium, sodium, potassium and magnesium. With fewer intermediate or extreme values, the pH most commonly ranges either between 3-4.5 or 6-7. A key parameter is the acidity, which can be commonly described as the amount of base required to neutralise the solution. In coal mine drainage, major contributors to acidity are ferrous and ferric Fe, Al and Mn as well as free hydrogen ions.

When pyrite is oxidised, it releases dissolved Fe^{2+}, SO_4^{2-} and H^+ and is known as AMD. This process is followed by the further oxidation of Fe^{2+} to Fe^{3+} and the precipitation of the iron as a hydroxide ("yellow boy") or similar substances, producing more H^+. Neutral mine drainage with high SO_4^{2-}, and possibly elevated Fe and Mn, forms with the neutralisation of acidic solutions by limestone or similar materials. If appreciable Fe or Mn is present, these neutral solutions can become acid on oxidation and result in the precipitation of the Fe and Mn.

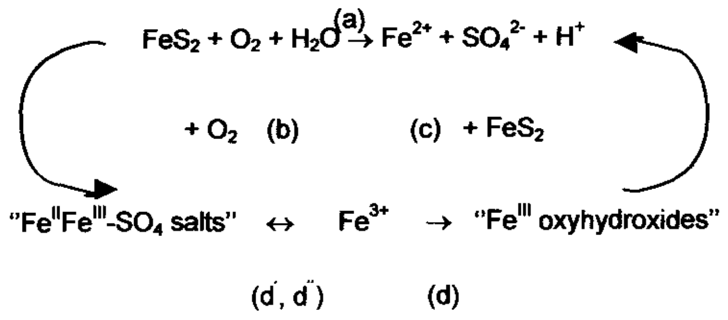
The rate and extent of AMD formation in surface coal mines are controlled by a number of factors. An increase in acidity of the drainage tends to be the result of more abundant pyrite in the overburden as well as decreasing particle size of the pyrite. Furthermore, acid formation is accelerated by iron-oxidising bacteria and low pH values. The presence of limestone or another neutraliser has an adverse effect on the rate of acid formation. The limiting factor in acid formation is the access to air which contains the oxygen needed for pyrite oxidation. Both access to air and pyrite surface exposure are promoted by crushing of the pyrite-bearing rock. The oxygen can gain access either by molecular diffusion through the air-filled pore space in the spoil, or by air flow which is driven through the pore space by temperature or pressure gradients. The complexity of these interactions and other factors results in the forecast and remediation of AMD to be site specific.

Serious degradation of the aquatic habitat and the quality of water supplies, owing to the toxicity, corrosion, incrustation and other effects from dissolved constituents, can be ascribed to coal mine drainage, which can be either acidic or alkaline. AMD is a result of interactions of certain sulfide minerals with oxygen, water and bacteria, as illustrated in Figure 3. Steps (a) to (d) correspond with reactions 2-5, respectively. Steps (d') and (d") represent the formation of iron-sulphate minerals (sources of acidity, ferric ions and sulphate).

According to Davis (1981) and Hawkins (1984), the iron disulphide minerals pyrite (FeS_2) and, less commonly, marcasite (FeS_2), are the principle sulphide bearing minerals in bituminous coal. Upon oxidation, acidic solutions can also be generated from pyrrhotite (FeS), arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$) and other sulphide minerals containing Fe, Cu, As, Sb, Bi, Se and Mo. These minerals are, however, uncommon in coal beds.

The stoichiometric reaction that best describes the oxidation of pyrite is commonly given as:

$$FeS_2 + 3.75\ O_2 + 3.5\ H_2O = Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H^+ + \text{heat} \qquad [1]$$



Overall reaction: $FeS_2 + 3.75\ O_2 + 3.5\ H_2O \rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H^+ + \text{heat}$ [1]

Steps:

(a) $FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$

(b) $Fe^{2+} + 0.25\ O_2 + H^+ \rightarrow Fe^{3+} + 0.5\ H_2O$

(c) $FeS_2\ 14\ Fe^{3+}\ 8\ H_2O \rightarrow 15\ Fe^{2+}\ 2\ SO_4^{2-} + 16\ H^+$

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

(d') $2\ Fe^{3+} + Fe^{2+} + 4\ SO_4^{2-} + 14\ H_2O \rightarrow Fe^{II}Fe^{III}(SO_4)_4{\bullet}14H_2O$

(d″) $3\ Fe^{3+} + K^+ + 2\ SO_4^{2-} + 6\ H_2O \rightarrow KFe_3^{III}(SO_4)_2(OH)_6 + 6\ H^+$

Figure 3 A model for the oxidation of pyrite. (Modified from Stumm & Morgan, 1981 by Rose & Cravotta, 1998)

The oxidation of sulphur and iron (Figure 3, reactions a and b respectively) by gaseous or dissolved O_2, can be mediated by various species of sulphur- and iron-oxidising bacteria (Thiobacillus spp.). According to others (Temple & Delchamps, 1953; Kleinman *et al.* 1981; Ehrlich, 1990), these bacteria produce enzymes which catalyse the oxidation reactions and use the energy released to transform inorganic carbon into cellular matter.

In reaction (c), (Figure 3) dissolved ferric iron (Fe^{3+}) from reaction (b) is the oxidising agent for pyrite and finally, part of the Fe precipitates as $Fe(OH)_3$ (Figure 3, reaction d).

Intuitively, pH best indicates the severity of AMD. However, acidity or total alkalinity of a solution probably outcompete this inclination. Acidity is the basic requirement of a solution in order to be neutralised and includes the requirement to neutralise acid generated by Fe-, Al- and Mn-hydrolysis. This is illustrated by reactions (b) and (d) in Figure 3 and the following two reactions:

$$Al^{3+} + 3\ H_2O \rightarrow Al(OH)_3 + 3\ H^+ \qquad [2]$$

$$Mn^{2+} + 0.5\ O_2 + H_2O \rightarrow MnO_2 + 2\ H^+ \qquad [3]$$

According to work done by Ott (1986), Fe^{3+}, Fe^{2+}, Mn^{2+}, Al^{3+} and H^+ are the main components of acidity in mine drainage from coal mines. Payne & Yates (1970) found that other species that precipitate as hydroxides or oxides, including Mg^{2+}, H_2CO_3 and H_2S, can also contribute to acidity. Many methods express acidity as milligrams of $CaCO_3$ per litre of solution, based on the following relationship:

$$2\ H^+ + CaCO_3 \rightarrow Ca^{2+} + CO_2 + H_2O \qquad [4]$$

From reaction [4], 2 moles (2.0g) of H^+ are neutralised by 1 mole (100.1g) of $CaCO_3$.

1.4 CONVENTIONAL TREATMENT OPTIONS FOR ACID MINE DRAINAGE AND ACIDIC SOLUTIONS

The use of lime to neutralise AMD and precipitate metals (active treatment system) is considered, in the context of this thesis, as the standard against which other methods are compared as it has been the conventional treatment choice for many years. Lime treatment is simple and robust, and the benefits and drawbacks are well known owing to long established usage. It does, however, present several environmental problems. The material produced after treatment with the lime is metal rich and usually contains a significant amount of water. The presence of metals means that it will often require special waste disposal facilities that add to the costs of disposal. The water content increases the volume and mass of the waste which means that money is wastefully being spent to dispose of water, both in transport and landfill fees. The general methods to reduce the water content are often labour or energy intensive that also increases costs and, moreover, are often unable to keep pace with the flow of material from the treatment system. Alternatives must provide some advantage over the lime treatment either in the use of materials, the disposal of waste, or the production of usable materials. These questions are addressed in the research described in this thesis.

In conventional lime neutralisation processes, acid is neutralised and metals and sulphate are precipitated in the form of metal hydroxides and gypsum ($CaSO_4$), respectively, as shown in Equation [5]. The mixture of precipitates is referred to as "sludge".

$$Ca(OH)_2 + Me^{2+}/Me^{3+} + H_2SO_4 \leftrightarrow Me(OH)_2/Me(OH)_3 + CaSO_4 + H_2O \qquad [5]$$

Air is frequently used to oxidise the ferrous to ferric iron during precipitation to obtain sludges that are more chemically stable (MEND Report, 1994, Kuyucak, 1998). The sludge produced, is allowed to settle in ponds or clarifiers/thickeners. The settled sludge is disposed of in specifically designed ponds for storage in perpetuity.

Depending on site factors, lime neutralisation facilities range from the simple addition of lime to the tailings pipelines to facilities, and sludge dewatering equipment. The water strength (solid concentration) and the sophistication of the treatment process have been found by many to affect the sludge solids content. As a result, sludge densities may vary from 1 to 30% solids. The process parameters are set to obtain denser, less voluminous sludge. Major process parameters affecting sludge characteristics include: the rate of neutralisation; rate of oxidation; Fe^{2+} to Fe^{3+} ratio; concentration of ions; ageing; recycle of settled sludge; temperature; and crystal formation (Kuyucak & Sheremata, 1995, Zinck & Griffith, 2000, Kuyucak *et al.,* 1999).

1.5 ALTERNATIVE NEUTRALISERS

Under controlled conditions, limestone, in contrast to lime, can remove acidity and precipitate metals (e.g. Al, Cu and Fe^{3+}) producing higher density sludges. CO_2 gas is released as $CaCO_3$ (s) dissociates in AMD as illustrated in equations 6 and 7.

$$CaCO_3 + H_2SO_4 \leftrightarrow CaSO_4 + H_2O + CO_2 \qquad [6]$$

$$CaCO_3 + Fe_2(SO_4)_3 + 3H_2O \leftrightarrow 3CaSO_4 + 2Fe(OH)_3 + 3CO_2 \qquad [7]$$

CO_2 forms carbonate ions which act as a buffer system and sets an upper limit on the pH (maximum pH 6.5) and also affects the rate and amount of lime consumption. The precipitates may settle very slowly because of their small particle size. Removal of a broad range of metals and ferrous iron cannot be achieved since they require higher pH levels than 6.5. A combined-limestone/lime process is suggested for removal of a wide range of metal ions.

Magnesium hydroxide ($Mg(OH)_2$) usage can result in a lower volume of metal hydroxide sludge when it is properly applied due to the higher solubility of $MgSO_4$ than $CaSO_4$. $Mg(OH)_2$ can also remove metals through surface adsorption. However, $Mg(OH)_2$ prevents the pH from exceeding 9. Depending on the pH requirements, it can be used in conjunction with lime.

Limestone and other materials that produce alkalinity can affect the generation of AMD in two ways. If water contacting pyritic materials is alkaline, or if alkaline conditions can be maintained in the pyritic material, the acid-generating reactions may be inhibited so that little or no AMD forms. Alternatively, once AMD has formed, its interaction with alkaline materials may neutralise the acidity and promote the removal of Fe, Al and other metals. Hence, water with high SO_4^{2-} and low Fe may be indicative of earlier AMD generation.

The carbonate mineral, limestone ($CaCO_3$), is the main mineral providing alkalinity for the process to be described. Carbonate minerals may occur as layers of limestone in the overburden above coal, as cement in sandstone or shale, or as small veins cutting the rock. The initial reaction with an acid solution is:

$$CaCO_3 + 2\ H^+ \rightarrow Ca^{2+} + H_2CO_3 \qquad [8]$$

If a gas phase is present, the H_2CO_3 may partly decompose and exsolve into the gas phase, i.e.:

$$H_2CO_3 \rightarrow CO_2 + H_2O \qquad [9]$$

Upon further neutralisation of AMD with carbonate to pH values of greater than 6.3, the product is bicarbonate (HCO^{3-}):

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad [10]$$

When it is necessary to lower the pH to between 6.5 - 8.5 in the final effluent, following treatment to a much higher pH, the pH is adjusted to the desired level with CO_2.

1.6 FURTHER TREATMENT

Treatment technologies are commonly categorised as either passive or active. The main purpose of both types is to lower total acidity, raise pH and lower toxic metal and sulphate concentrations. Passive treatment approaches are economically attractive, but have some significant limitations. They are best suited to waters with low acidity (<800 mg/ℓ), low flow rates (<50 ℓ/sec) and, therefore, low acid loads, where the key outcome is near neutral pH. Passive systems cannot handle acid loads in excess of 100-150 kg of $CaCO_3$ per day. When specific metal removal targets need to be achieved, as opposed to simple neutralisation, most passive treatment technologies are unsuitable.

Although not limited by tight operational parameters, as in the case of passive systems, the unlimited chemical flexibility of active systems comes at a price, which proves to be one of the biggest challenges in the field of water treatment. Active treatment systems can be engineered to accommodate essentially any pH, flow rate and daily acid load. Economic considerations (i.e. capital and ongoing operational cost) play a big role in determining the viability of active treatment systems.

A broad range of active treatment approaches is available for dealing with AMD. Physical, chemical and biological approaches include one or more of the following:

- pH control or precipitation
- Electrochemical oxidation
- Biological mediation/redox (sulphate reduction)
- Coagulation/Flocculation
- Crystallisation

pH control/precipitation with inorganic alkaline amendments is the most common and cost effective form of general purpose AMD treatment. A large variety of natural, manufactured or by-product alkaline reagents, are available, with their use generally dictated by availability and cost. Alkaline reagents treat AMD by increasing the pH and promoting the precipitation of heavy metals, generally as hydroxide complexes. The successful implementation and sustainability of 'pH control' active treatment systems requires the selection of a reagent appropriate for the treatment task and an efficient mixing and dispensing mechanism. Conventional alkaline reagents that are readily available in South Africa to treat AMD include hydrated lime and the carbonate mineral, limestone out of a list of reagents. Although the capital and operating costs of such systems are relatively high, they employ well established technology and are highly reliable. A key limitation of fixed plant systems is the need to deliver affected water, regardless of the number of discrete AMD sources. Mixing and dosing systems employing the CSIR's technology (*Limestone Handling and Dosing System*) provides the reagent dispensing capacity of a large fixed plant system. The *Integrated Limestone/Lime Treatment Technology* was developed in response to the problems that passive treatment systems face in using limestone efficiently. Together with this treatment technology, the *Limestone Handling and Dosing System* has been developed to replace the conventional storage of the alkali in a hopper and automatic feeding with a screw-feeder.

The Limestone Handling and Dosing System, which is the first technology of its kind to be built on full scale, can be designed to accommodate any load capacity. It consists of the following items:

- A concrete slab with a slope of 7° onto which the $CaCO_3$ powder is dumped and stored. The $CaCO_3$ powder is slurried with a water jet and collected in a slurry tank through gravity flow
- A slurry tank with stirrer which acts as a mixing chamber for the acid water and $CaCO_3$
- A ball valve in the slurry tank to maintain the water at a specific level in the tank by dosing tap or clarified water.
- A $CaCO_3$- recycle slurry pump that withdraws some of the slurried $CaCO_3$ of higher density from the slurry tank or clear water through a water jet, passing through a density meter onto the $CaCO_3$ dump to keep slurried the $CaCO_3$ concentration constant. The slurried $CaCO_3$ is returned by gravity via the sloped concrete slab back to the slurry tank. The slurried $CaCO_3$ concentration is controlled by the density meter which activates/stops the recycle pump at pre-set low/high values, respectively.
- A transfer pump to feed slurried $CaCO_3$ from the limestone make-up tank.

The system provides the benefit of using environmentally benign, very low cost limestone aggregate that is locally available as a waste product from the paper industry. As the carbonate dissolves and neutralises the AMD, CO_2 builds up in the reactor and can be recirculated. Key benefits of systems in which lime is partially replaced by limestone, include the generation of high levels of alkalinity, partial sulphate removal and efficient use of low cost limestone.

Electrochemical oxidation uses electrical techniques to oxidise Fe^{2+} to Fe^{3+} in AMD while generating hydrogen (H_2) electrolytically to be utilised as energy later on in the treatment of AMD by means of the Biological Sulphate Removal Process.

Biological mediation/redox (sulphate reduction) – Microbial Reactor Systems (MRS) are fully engineered and process controlled systems for harnessing chemical and biological processes to further remove sulphates in AMD to below 200 mg/ℓ. This process follows directly after the AMD has been fully neutralised and sulphates removed to below the saturation level of gypsum, i.e. 1 200 mg/ℓ, by means of the Integrated Limestone/Lime Treatment Technology. These systems consist of a sulphate reducing bioreactor and H_2S scrubbing process for sulphur recovery. The successful performance of MRS is reliant on the continued growth of sulphate reducing bacteria (SRB), which require temperatures between 25 - 35°C.

Coagulation/Flocculation - Following neutralisation and partial sulphate removal with limestone and lime, fine particles (precipitates) in suspension need to be aggregated to improve solid/liquid separation or sedimentation in clarifiers. Coagulation is a specific type of aggregation, which leads to the formation of compact aggregates, called flocs. The addition of coagulants, such as inorganic Al^{3+} or Fe^{3+} salts or organic 'polymers', help to electrically neutralise or destabilise electronegative colloids and bridge the neutral particles. Important parameters are the type of polymer and external stirring.

Crystallisation – the Integrated Limestone/Lime Treatment Technology and BaS Treatment Technology offer new methods for lowering soluble sulphate concentrations in water that has already been subjected to lime treatment. It is possible to lower sulphate concentrations to below 200 mg/ℓ using these approaches.

1.7 NOVEL INTEGRATED TECHNOLOGY FOR TREATMENT OF ACID MINE DRAINAGE AND EFFLUENTS

Both the environmental aspects and the economics of metal and coal mining operations worldwide are being affected by AMD. The latter can have significant impacts on the economics of a mining operation. This is due to the corrosive effects of acid water on the mine infrastructure, the limitations it places on water reuse and discharge and the expense incurred implementing effective closure options. While AMD minimisation and control must remain the focus of mine-site water management strategies, when acid generation is unavoidable, appropriate passive or active treatment technologies need to be implemented. As mentioned earlier, passive treatment systems are economically attractive but have some significant limitations. They are best suited to treating low flow rates and therefore low acidity.

Newly developed technology resulted in active treatment systems that can accommodate any flow rate, pH and acid load and are not limited by operational parameters. Because every mine site is unique as are its water issues, these newly developed systems can be designed and engineered to cost effectively deliver the required water quality of such a site. The cost effectiveness is achieved by designing the system in such a way that the treated water can either be reused in the plant, thus decreasing the amount of water purchased, or the water can be utilised for irrigation purposes or even discharged into a water course.

An integrated process (active treatment system), consisting of various treatment stages has been developed by CSIR: Environmentek in an effort to solve the current AMD situation and other acid water related issues, especially in the mining industry. Depending on the specific requirements, i.e. to what level of quality the mine needs to treat its water and the water quality and flow-rate that require treatment, this process can be adapted by omitting some of the stages. It offers huge cost benefits compared with existing processes, for example, over the conventional way of neutralising acid water with lime, sodium hydroxide or sodium carbonate. These chemicals have the disadvantage that they require accurate dosing to prevent under- or over-dosage, which result in pH fluctuations. When pumped through pipelines of a mine water system, corrosion (low pH) or scale formation (high pH) will result which can adversely affect the whole system, necessitating shut-down for maintenance repair.

The use of limestone as neutralising agent has the following benefits:

- Direct chemical cost savings, utilising limestone, a waste product from local paper industry
- No pH-control required, as limestone dissolution occurs mainly at below pH 7
- Limestone is easy to handle and store as it contains 15% moisture which eliminates dust problems
- Limestone is non-hazardous and environmentally friendly

The completely integrated process has been recently developed and consists of the following stages, illustrated in Figure 4:

- Heating unit for the production of CaO (quicklime) and CO_2 from burned coal and $CaCO_3$ (limestone) precipitation.
- Limestone neutralisation and partial sulphate removal to 1 900 mg/ℓ
- $Ca(OH)_2$ (hydrated lime) stage, where CaO is contacted with acid water to produce $Ca(OH)_2$.
- Lime treatment, to partially remove the sulphates as $CaSO_4$ (gypsum) to below 1 200 mg/ℓ and full removal of magnesium and other metals.
- pH adjustment stage where the CO_2 from the heating unit is applied to reduce the pH to 8.6 while $CaCO_3$ precipitates.
- Two options: Removal of sulphate to below 200 mg/ℓ as barium sulphate by means of barium sulphide treatment, or biological sulphate removal.
- Regeneration of barium sulphide for reuse by heating the barium sulphate produced from the preceding stage.
- Stripping of H_2S, either from the barium sulphide process or the biological sulphate removal process, to be contacted with Fe(III) rich water for elemental sulphur production.

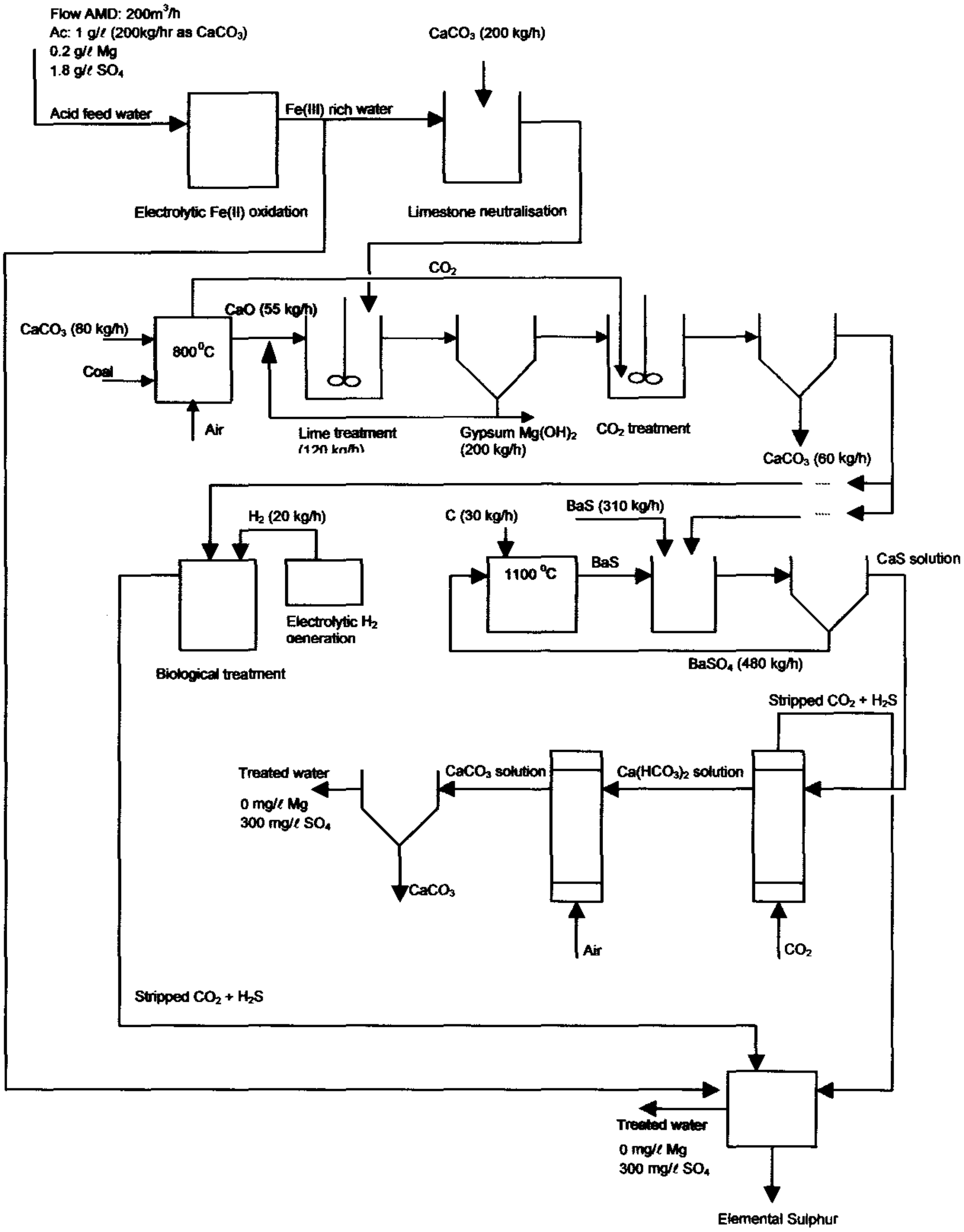


Figure 4 Process flow diagram of the completely integrated process for neutralisation and removal of acidity, sulphate and metals from AMD

In the completely integrated process, limestone is economically utilised to completely neutralise AMD and acid process water. The sulphate concentrations in these waters are lowered to 1 900 mg/ℓ. With the addition of lime at this stage, the sulphate concentration is further reduced to below the saturation level of gypsum, i.e. 1 200 mg/ℓ. Metals are now also being fully removed from the water. CO_2, generated during the limestone roasting stage, is then used to adjust the pH to 8.5 and to achieve $CaCO_3$ crystallisation, which can be recycled to the limestone roasting stage.

Either the biological sulphate removal stage or the BaS treatment stage can now be applied to achieve removal of sulphates to below 200 mg/ℓ, i.e. the recommended sulphate level for discharge water. H_2S gas, generated during both of these stages as a by-product, is stripped and contacted with Fe(III) rich water to produce elemental sulphur which is a valuable product. The Fe(III) rich water results from the Fe(II) oxidation stage prior to limestone neutralisation which is inevitable as acid will start forming without oxidation of Fe(II).

The Biological Sulphate Removal Process is an anaerobic treatment in which a reducing environment is produced and the proliferation of sulphate reducing bacteria (SRB) is encouraged. ***(Although this thesis contains a paper on biological treatment, it only focuses on chemical treatment technologies. See Appendix A for Paper 9 on, "The Sustainability of Biologically Treated Nickel/Copper Mine Effluent Suitable for Irrigation")*** These bacteria use sulphate in their metabolism, producing hydrogen sulphide which combines with metals such as copper, cadmium and zinc to form insoluble sulphides. Another product of SRB metabolism is the production of alkalinity, thereby raising the pH of the mine water. Naturally, these bacteria utilise sugar and ethanol as carbon source which is economically unfeasible. Electrolytically generated hydrogen has been successfully implemented as substitute for sugar and ethanol as energy source. Hydrogen is electrolytically generated on-site by means of stainless steel (type 316) electrodes in KOH (3%) as the electrolyte. An asbestos sheet of 3mm thickness serves as diaphragm between anodes and cathodes in the electrolytic cell as both hydrogen and oxygen are generated.

In the BaS treatment stage, sulphates are removed from the water as $BaSO_4$ which is converted back to BaS for re-use. This conversion is achieved by heating the $BaSO_4$ to a specific temperature.

The final, unsolicited waste product after either of these two stages is hydrogen sulphide gas (H_2S), which is stripped and contacted with a small part of the Fe(III) rich water, resulting from the Fe(II) oxidation stage, that yields pure, elemental sulphur.

1.8 LEAGAL REQUIREMENTS

The treatment processes that are widely applied mainly to acid water, have one goal in mind: to comply with legislative requirements before discharge to the receiving water body. The legislative requirements imposed on industrial effluent derive primarily from the National Water Act (Act 36 of 1998), as laid down by the Department of Water Affairs & Forestry in consultation with the SABS and as published in the Government Gazette. The Act states that the ultimate aims of water resource management are to achieve the sustainable use of water for the benefit of all users and to recognise that the protection of the quality of water is necessary to ensure sustainability of the nation's water resources in the interests of all water users. In this Act it is required that any person who uses water for industrial purposes shall purify or otherwise treat such water in accordance with requirements prescribed in the Government Gazette. Before a permit for discharge of water is granted, all efforts should be made to ensure effective utilisation of the water through recycling or alternative applications. One specific alternative would be to pass the water on to a responsible local authority who then can treat it for use. Certain criteria are prescribed to be met before discharge water is accepted by such an authority.

In Chapter 4 of the National Water Act (Government Gazette (Parliament of the republic of South Africa), 1998), the use and discharge of water are dealt with in detail in order to down the basis for regulation. Water use is defined broadly, and includes pumping and storing water, activities which reduce stream flow, waste discharges and disposals, controlled activities which impact detrimentally on a water resource, removing underground water for certain purposes, and recreational use of water. In general, a water use must be licensed under a general authorisation and before any permit for discharge is granted, all efforts should be made to ensure optimum use of water through recycling or alternative processes. The Department of Water Affairs & Forestry uses a so-called Waste Load Allocation to lay down allowable discharge parameters from some major industries. In theory, a Waste Load Allocation is the amount of tolerable discharge to a water body whilst monitoring the water quality at a usable level for the designated users.

CHAPTER 2: PAPERS 1 - 8

2.1 INTRODUCTION TO PAPERS

This thesis describes research and development work conducted on laboratory and pilot scale plants, situated at numerous mines across South Africa and one in Botswana. The results have been utilised in the design of full scale plants at some of these sites of which a few have already been constructed and commissioned. Others are in the design process and being finalised.

Eight of the nine papers, which comprise this thesis, were arranged in chronological order to conform to the requirements of the University of the North-West (Potchefstroom Campus) for the degree of Philosophiae Doctor. It is required that "the work should clearly demonstrate advanced original research and/or creative work which must also constitute a real and major advance to the technology of engineering science or practice". All of the papers have been presented at local or international scientific conferences are fully referenced in this chapter.

Papers 1 to 3 describe the development of the fluidised-bed limestone neutralisation process during laboratory and pilot scale studies. It was also demonstrated that iron(II) needs to be oxidised to iron(III) upstream of the limestone neutralisation stage as direct treatment of iron(II)-rich water results in scaling of the limestone particles with gypsum and ferric hydroxide.

Paper 4 describes an innovative and cost-effective way of generating hydrogen to be utilised as an energy source for SRB in an anaerobic biological treatment process. Hydrogen was generated on-site which eliminates the need for purchasing it from a local supplier and resulting in the process not being cost-effective. To date, sugar and ethanol were utilised as energy source for these bacteria. **Paper 9**, which describes the biological process, has been placed under Appendix A, as the other eight papers describe research that is chemically based.

Paper 5 compares the chemical neutralisation and partial sulphate removal from AMD, to the biological process that has the same aim.

Paper 6 presents practical information on the implementation of a full scale limestone neutralisation process which replaces the existing method of neutralising AMD with lime. The process has been successfully implemented at a mine site in South Africa and has been in continuous operation for almost two years to date.

Paper 7 describes an alternative process for removing sulphates from AMD to below 200 mg/ℓ by means of chemical treatment, i.e. initially the AMD is neutralised with lime resulting in the removal of sulphates to below 1 200 mg/ℓ. The sulphates are then further removed to a lower level of < 200 mg/ℓ.

Paper 8 proves that hydrogen, generated electrolytically (Paper 4), is the most cost-effective energy source for SRB. It also addresses other issues like energy utilisation efficiency of feed water with hot gas, rate of sulphate removal by SRB and the effect of biologically related issues.

Paper 9 was included in this thesis for completeness. The paper addresses the treatment of effluent from a copper mine and is included in Appendix A. Papers 1 - 8 involve the chemical treatment of mine effluent and the utilisation of AMD as a medium for generating hydrogen as a useful by-product and energy source for SRB, while Paper 9 concentrates on the biological treatment of mine effluent.

PAPER 1: Geldenhuys,A.J., Maree, J.P., De Beer, M. and Hlabela, P. 2003. An integrated limestone/lime process for partial sulphate removal, *J.S.A. Inst.Mining Metallurg.*, **103**(6), 345 – 353.

In the investigation of lime being largely replaced with limestone in order to achieve neutralisation and partial removal of sulphates from acid mine water, discharged by a coal mine near Witbank in Mpumalanga, the main objectives were:

- ✓ To determine the effect of limestone on the chemical composition of the coal processing water before and after treatment
- ✓ To determine the effect of various parameters on the rate of gypsum and $CaCO_3$ precipitation
- ✓ To determine the characteristics of the gypsum and $CaCO_3$ sludge produced

The following findings resulted from the investigation:

- ✓ Acid mine water can be neutralised effectively from a pH of 2.1 to 7.7 and the sulphate concentration being lowered from 3 000 mg/ℓ to 1 900 mg/ℓ
- ✓ With lime treatment, as a follow-up stage to limestone neutralisation, the sulphate concentration was further reduced by means of gypsum crystallisation to below the original target of 1 200 mg/ℓ, i.e. 1 100 mg/ℓ
- ✓ With lime treatment, pH values of 12 and higher were reached and magnesium was fully removed by gypsum crystallisation.
- ✓ To lower the high pH, CO_2 sparging resulted in $CaCO_3$ precipitation was recycled to the limestone neutralisation stage and utilised as additional alkali
- ✓ For design purposes, a contact time of 1 hour was needed for the neutralisation stage with limestone and 2 hours for the gypsum crystallisation stage. The surface areas of the limestone and lime played a major role in the rate of neutralisation and crystallisation
- ✓ When replacing lime with limestone for neutralisation purposes and partial sulphate removal, an alkali cost saving of up to 62% could be achieved. Lime was only added to lower the sulphate concentration to below the saturation level of gypsum, i.e. 1 500 mg/ℓ, to ensure complete removal of sodium and magnesium thereby preventing scaling of pipelines

Paper 1 was peer-reviewed and published in The Journal of the South African Institute of Mining and Metallurgy

Paper 1 was also presented as a poster by J P Maree at the Hard Rock Mining 2002 Conference, Westminister, Colorado, USA (See Poster 1, Appendix A).

An integrated limestone/lime process for partial sulphate removal

by A.J. Geldenhuys, J.P. Maree, M. de Beer, and P. Hlabela*

Synopsis

This paper will focus on two topics, namely (1) an innovative process for the neutralization and partial sulphate removal of acid streams produced during coal mining and processing and (2) optimization of this integrated neutralization process by adding small amounts of synthetic organic polymers.

The integrated lime and limestone process has been developed to neutralize acid mine water and to remove sulphate (to less than 1 200 mg/*l*), magnesium and metals. Limestone and lime treatment is the most cost-effective technology for neutralization and partial sulphate removal of acidic/sulphate-rich water to sulphate levels of less than 1 500 mg/*l* due to precipitation of magnesium and removal of the associated sulphate fraction (through gypsum crystallization). Neutralized mine water of this quality may be suitable for irrigation.

The process consists of the following stages:

1. Limestone ($CaCO_3$) neutralization to raise the pH to 7 and CO_2-production.
2. Lime ($Ca(OH)_2$) treatment to pH 12 for $Mg(OH)_2$ precipitation and gypsum ($CaSO_4.2H_2O$) crystallization.
3. pH adjustment with CO_2 recovered from stage 1 and $CaCO_3$ precipitation.

Retention times of 1 hour, 4 hours and $^1/_2$ an hour were required by stages 1, 2, and 3 respectively. The sulphate level was reduced to 1 094 mg/*l*, which is less than the original aim of 1 200 mg/*l*. Chemical costs associated with neutralization, using limestone instead of lime, are reduced by 69% in the integrated limestone/lime process.

The overflow water from the clarifier of each of the above stages generally contains a wide variety of colloidal impurities that may cause the water to appear turbid or may impart colour. This results in very slow sludge settling rates that cause overflow water with a high degree of turbidity and colour. There are a number of successive or simultaneous stages involved in the agglomeration of particles.

To get optimum neutralisation of the acid water and partial sulphate removal to below the saturation level of gypsum (i.e. 1 500 mg/*l*), maximum sludge recovery is needed. The higher the concentration of seed crystals, the larger the surface area. Therefore, effective removal of suspended and colloidal matter from the overflow of each stage is required and can be achieved by coagulation and flocculation. The polymers PAC6 and 3095 were effectively used as coagulant and flocculant respectively. The addition of these polymers resulted in a clear overflow in each of the above stages with a very low turbidity.

Introduction

By its very nature and scale, mining makes a marked and visual impact on the environment. Mining is, however, implicated as a significant contributor to water pollution, the prime reason being that most of our geological formations that are mined contain pyrites, which oxidize to form sulphuric acid when exposed to air and water. The scarcity of water in South Africa is exacerbated by pollution of the surface and groundwater resources. Typical pollutants of the aquatic environment include industrial effluents and acid mine drainage.

Mine water in the Upper Olifants River Catchment in Mpumalanga (upstream of Loskop Dam) is at times discharged into local streams, resulting in local acidification and regional salination of surface water resources. Pollution of surface water can be prevented by collecting and treating mine water to a quality where it could be re-used without restriction (Cleanwater 2020 Initiative). Although mine water in the Olifants River Catchment currently amounts to only 4.6% of the total water usage, it contributes 78.4% of the sulphate load.

Mine water in the catchment of the Witbank Dam and Middelburg Dam are rich in calcium, magnesium, sulphate and acid pH. This is due to oxidation of pyrites in the coal ore and coal waste to sulphuric acid Equation [1], followed by neutralization with dolomite. which is also present in the coal ore. When the pH is below 5.5, water can be toxic to plant and fish life and corrosive to pipelines and equipment.

$$2FeS_2 + 7^1/_2O_2 + 7H_2O \rightarrow 2Fe(OH)_3 + 4H_2SO_4 \quad [1]$$

Sulphate needs to be removed from effluents for the following reasons:

---

* *CSIR, Division of Water, Environment and Forestry Technology, Pretoria.*

© *The South African Institute of Mining and Metallurgy, 2003. SA ISSN 0038-223X/3.00 + 0.00. Paper received May 2002; revised paper received Mar. 2003.*

- Prevention of salination of surface water—discharge recommended concentration <500 mg/*l*.
- Prevention of scaling—when no Na or Mg is present, the saturation level = 1 500 mg/*l* SO_4
- Biocorrosion
- Acid corrosion—when acid water is neutralized with lime, scaling of the equipment by the unstable water is produced, and malfunctioning of dosing equipment and settling of particles in pipelines and valves occur. The latter often causes blockages, which may result in under-dosage, which in turn may lead to acid corrosion.

Typical sulphate removal processes are the biological sulphate removal process, RO and EDR. The integrated limestone/lime treatment process can be used for neutralization of acid water and partial sulphate removal to below the saturation level of gypsum, i.e. 1 200 mg/*l*. The benefits of this process are:

- Limestone treatment is the most cost-effective treatment for neutralization of acid water, and partial sulphate removal to levels of 2 000 mg/*l* can be achieved
- With high lime treatment (pH >11), sulphate can be reduced further to 1 200 mg/*l* through gypsum crystallization and magnesium precipitation
- Scaling and corrosion problems are reduced during re-use of the water in the mines
- Discharge water needs to meet certain quality requirements in accordance with environmental legislation.

Earlier investigations[1–3] showed that acid mine water can be neutralized effectively by limestone. Maree *et al.*[4] also found that the sulphate concentration in acid mine water can be reduced from 15 000 to 2 000 mg/*l* through limestone neutralization.

Limestone and lime treatment of acid water were effectively introduced to the water reclamation field at the Navigation Colliery near Witbank. Considerable attention has been paid to the clarification of the treated water in order to remove small particles by combining them into larger aggregates by coagulation and flocculation. These particles are mainly of chemical origin as limestone and lime are added to the system, which results in the production of $Mg(OH)_2$, $CaSO_4.2H_2O$ and $CaCO_3$.

The process of destroying the stabilizing forces and causing aggregation of clay colloids is referred to as *chemical coagulation* (Benefield *et al.*[5]). It can also be referred to as the addition of a chemical to water or sewage so as to precipitate, usually, a metal hydroxide that catches and so removes from the water most of the tiny suspended particles. The chemical lessens the surface charge of the suspended matter, unlike flocculation. Flocculation can be considered the agglomeration of destabilized particles into microfloc, and later into bulky floccules which when settled can be called floc. Flocculation can be promoted by gentle stirring (mechanical flocculation) or by adding chemicals (flocculants).

Synthetic organic polymers such as PAC6 and Type 3095 can be used effectively as coagulants and flocculants. These polymers are long-chain molecules comprised of many monomers. Polymers typically have a helical molecular structure comprised of carbon chains with ionizing groups attached. When the groups are ionized in solution, an electrical repulsion is created, which causes the polymer to assume the shape of an extended rod. As the ionized groups become attached to colloidal particles the charges are neutralized and the polymer starts to coil and form a dense floc with favorable settling properties.

The associated environmental impact is a growing concern related to water and effluent treatment. The sludges,which result from the process and which are not recycled back to the respective stages of treatment, are inert and do not contain any toxic metals. These sludges are therefore sent through a filter press to produce a 'cake' that can be discharged. Waste sludge withdrawn from the bottom of the reactor can contain between 0 and 30% $CaCO_3$ (m/m dry basis), depending on the limestone excess that is applied. If the sludge contains a significant amount of $CaCO_3$, it might be cost effective to combine the waste sludge with acid feed water prior to discharge in order to achieve maximum utilization of the $CaCO_3$.

The main objectives of this investigation, where limestone instead of only lime is used to neutralize and remove sulphates partially from acid mine water, were:

- To determine the chemical composition of the coal-processing water before and after treatment
- To determine the effect of various parameters on the rate of gypsum and $CaCO_3$ crystallization
- To determine the sludge characteristics of the gypsum and $CaCO_3$ produced
- To determine the effect of the polymers (as coagulant/flocculant) on the chemical composition of the coal-processing water before and after treatment in all stages of the treatment process (settling rate of sludge and clarity of overflow water)
- To determine the optimum dosage of coagulant/flocculant for each stage of the treatment process (concentration).

Materials and methods

Feed Water

A synthetic solution (diluted sulphuric acid), similar to leachate from a waste coal dump, was used as feed water for batch studies in beakers. The solution contained 3 g/*l* acidity (as H_2SO_4) and 160 mg/*l* Mg. For batch or continuous studies on a pilot scale, acid mine water was used for treatment in all stages (limestone, lime and CO_2 treatment) of the process (see Table I for chemical composition of the feed water).

Table I

Chemical composition of acid mine water fed to the limestone/lime treatment process

Parameter	pH mg/l	SO_4^{2-} mg/l	Ca mg/l	Mg mg/l	Na mg/l	Mn mg/l	Cl⁻ mg/l	Alkalinity mg/l
Acid feed water	2.10	3 000	420	160	41	17	16	-3 000

Feedstock

Waste powder limestone ($CaCO_3$) from paper industries was used in the limestone neutralization stage of the process. For the gypsum crystallization stage, unslaked lime ($Ca(OH)_2$) was used. The limestone was analysed for its calcium, magnesium and alkalinity content. Calcium and magnesium were determined with EDTA, while the alkalinity content was determined by dissolving it in a stoichiometrically excessive amount of hydrochloric acid. This excess amount of hydrochloric acid was titrated with sodium hydroxide (see Tables II and III for chemical composition of powder lime and limestone respectively).

The polymers that were used as coagulant and flocculant respectively are PAC6, which is poly-aluminium-hydroxy chloride with a specific gravity of 1.3 (only available as solution) and Type 3095 (granules), poly-acrylamide which is a co-polymer of acrylamide and acylic acid with a molecular weight of about 15 000 000 g/mole. These chemicals were supplied by Montan Chemicals, Germiston. The coagulant was used as received, while a stock solution of 2.5 g of Type 3095 flocculant per litre distilled water was made up on a weekly basis. For dissolving the flocculant in distilled water, a small amount of methanol was first added to the granules to assure effective granular dissolution.

Batch studies in beakers and batch and continuous studies on pilot scale

Neutralization studies

Batch studies (no feed water) were conducted in 1 *l* beakers at atmospheric pressure to study the kinetics of acid water neutralization with limestone and lime. Samples were taken regularly and analysed for pH, calcium, magnesium, sulphate, alkalinity and MLSS (mixed liquid suspended solids). The same variables as for batch studies were measured during continuous studies (constant feed water) for different hydraulic retention times.

Table II

Chemical composition of powder lime ($Ca(OH)_2$)

Bulk density (kg/m³)	Available $Ca(OH)_2$ (min%)	Available CaO (min%)	Total CaO (min%)	MgO (max%)	Al_2O_3 + Fe_2O_3 (max%)	SiO_2 (max%)	Acid insolubles (max%)
560	94	71	72	1	0.3	0.5	1

Particle size: fine powder, 100% passing 90 micron

Table III

Chemical composition of powder limestone ($CaCO_3$)

$CaCO_3$ (%)	$Ca(OH)_2$ (%)	Ca (mg/g)	Mg (mg/g)	Na (mg/g)	K (mg/g)	Moisture (%)
97.02	3.87	354.08	5.66	11.17	0.43	24

Percentages based on dried basis

Sludge settling studies

Batch studies were conducted in the laboratory in 1 *l volumetric cylinders* at atmospheric pressure and ambient temperature to study the efficiency of the two polymers, PAC6 and 3095 as coagulant and flocculant respectively. The polymers were added separately to the effluents of these three stages as follows:

Primary effluent
(limestone neutralization): 3095 → flocculant
Secondary effluent (lime treatment for gypsum crystallization): 3095 → flocculant
Tertiary effluent
(CO_2 treatment for $CaCO_3$ precipitation): PAC6 → coagulant
3095 → flocculant

Each effluent was stirred at a medium stirring rate for 1 minute, whereafter increasing amounts of polymer were injected into the solution (effluent). For the tertiary effluent, an additional stirring of 1 minute between the coagulant and flocculant addition was allowed. These tests enable quantification of the influence of the mentioned polymers as effective coagulants/flocculants by means of polymer concentration, settling rate and clarity. Based on the studies conducted in the laboratory, the optimum amount of polymer was used in each consecutive step of the process at pilot plant scale to demonstrate the effective settling of the various sludges and clear overflow water on a larger scale. These cylindrical tests should be used only for the evaluation of the operation, chemical dosage and removal of contaminants. They are not valid for evaluating the size of the clarifier or to simulate a reactor-clarifier, but serve merely as guidelines.

Equipment and procedure

A mobile pilot plant at Navigation Coal Mine near Witbank, with a capacity of $10 m^3$/day was used for on-site treatment of the mine water. A $CaCO_3$-handling and dosing system (see Figure 1) was designed and implemented for treating the acid mine water in the first stage of the process at the pilot plant (see Figure 2).

Limestone neutralization using a $CaCO_3$-handling and dosing system (Figure 1)

The $CaCO_3$-handling and dosing system, which is the first technology of its kind to be built on full scale, has a capacity of 10 *Ml*/day and consists of the following items:

- A concrete slab with a slope of 7° onto which the $CaCO_3$ powder is dumped and stored. The $CaCO_3$ powder is slurried with a water jet and collected in a slurry tank through gravity flow.
- A slurry tank with stirrer, which acts as a mixing chamber for the acid water and $CaCO_3$ as well as recovery of CO_2 gas.
- A ball valve in the slurry tank to maintain the water level at a specific height by dosing tap or clarified water.
- $CaCO_3$ recycle slurry pump, which withdraws some of the slurried $CaCO_3$ of higher density from the slurry tank or clear water through a water jet onto the $CaCO_3$ dump to keep the $CaCO_3$ concentration at a constant level. The slurried $CaCO_3$ is returned by gravity via the sloped concrete slab back to the slurry tank. The $CaCO_3$ concentration is controlled by the load cells underneath the slurry tank, which activate/stop the recycle pump at preset low/high values.

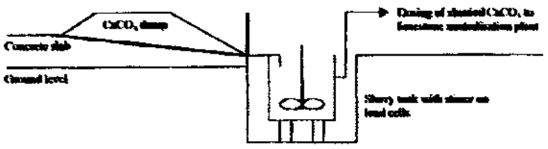


Figure 1—Schematic illustration of $CaCO_3$-handling and dosing system

- A transfer pump, feeding slurried $CaCO_3$ into the limestone make-up tank.

Stage 1: Limestone neutralization

Acid feed water from the plant and slurried limestone from the $CaCO_3$-handling and dosing system were pumped into a reactor onto which a stirrer was fixed. The overflow from the reactor went into a clarifier from where sludge was recycled back to the reactor.

Stage 2: Gypsum crystallization

Lime ($Ca(OH)_2$) was fed to a second reactor, containing the neutralized water of the neutralization stage from the first reactor. Fine particles that washed out from the reactor, were allow to settle in a clarifier and were returned to the reactor via a recycle pump.

Stage 3: CO_2-dosing system

During this stage, CO_2 recovered from the limestone neutralisation stage was bubbled through the treated water of the gypsum crystallization stage. The $CaCO_3$ that precipitated during this stage was recycled to the first stage where limestone was used for neutralization of the acid water.

In all three stages, the polymer(s) was added to the effluent in the overflow between the reactor and clarifier for rapid mixing to disperse the polymer(s) homogeneously and to enabe good contact between the effluent and polymer(s). In each clarifier, slow speed agitation was provided by recycling a part of the sludge back to its reactor by means of a variable speed pump to enable the growth of the aggregates into voluminous flocs by collision and entrapment of the suspended matter.

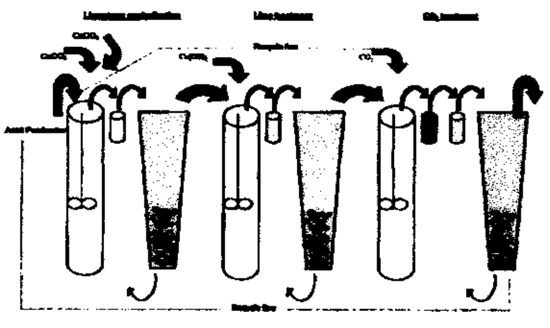


Figure 2—Schematic illustration of the limestone neutralization-, gypsum crystallization- and CO_3-precipitation system on pilot plant scale

Programme

Neutralization studies

Batch studies on gypsum crystallization and $CaCO_3$ crystallization

The following parameters were varied to evaluate and optimize the rate of gypsum crystallization:

- Settling rate of sludge (200, 100, 75, 50, 30, 20 and 10%)
- Over-saturation concentration

Continuous studies on gypsum crystallization and $CaCO_3$ crystallization

The quality of the water from the gypsum crystallization stage was studied on a continuous basis at various hydraulic retention times (HRT), varying between 0.2 and 3.5 hours.

Sludge settling studies

Batch studies on coagulation/flocculation

The concentration of polymer added was varied to evaluate and optimize the efficiency of the polymers as coagulant/flocculant by measuring the clarity and settling rate of each trial.

Continuous studies on coagulation/flocculation

The quality of the water before and after treatment for the various stages of the process was studied at the pilot plant on a continuous basis at different hydraulic retention times.

Analysis

Samples were collected regularly and filtered through Whatman No. 1 filter paper. Determinations of pH and sulphate were carried out manually according to procedures described in Standard Methods[6]. Calcium and magnesium were recorded with the ICP method for metals. Alkalinity was determined by titrating with sodium hydroxide to pH 7.0. Clarity was determined with a spectrophotometer, measured in NTU (Nephelometric Turbidity Unit).

Results and discussion

Water quality

The chemical composition of the acid mine feed water and the water qualities after each of the three stages of treatment are listed in Table IV.

From Table IV, it can be noted that limestone ($CaCO_3$) can be used effectively in the integrated process for neutralization of acid water (HRT = 1 hour). When discard leachate was treated with limestone, the pH of the water was raised from 2.10 to 7.68 in the neutralization reactor. A decrease of 96.6% in the acidity of the water after limestone neutralization is a result of the following reaction:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4.2H_2O.2H_2O + CO_2 + H_2O \qquad [2]$$

When the water is under-saturated to gypsum ($CaSO_4.2H_2O$), acidity removal is achieved at a high rate. Once the water is saturated to gypsum, further dissolution of $CaCO_3$ is limited by the rate at which gypsum crystallizes out of solution.

Table IV

Water qualities of feed water and treated water of each of the three stages of treatment

Parameter	Acid feed water	Limestone neutralization	Flocculation	Gypsum crystallization through lime treatment	Flocculation	$CaCO_3$ precipitation through CO_2 treatment	Coagulation + Flocculation
pH	2.10	7.20	7.68	11.71	12.26	9.46	8.50
SO_4^{2-} (mg/*l*)	3 000	1 890	1 900	1 100	1 094	1 199	1 219
Alkalinity (mg/*l*)	-3 000	108	100	960	940	71	50
Ca (mg/*l*)	420	638	636	994	829	530	542
Mg (mg/*l*)	160.00	147.00	147.00	0.22	0.00	2.88	3.03
Al (mg/*l*)	556.00	0.30	0.39	0.00	0.00	0.74	1.11
Na (mg/*l*)	41.00	46.40	40.00	45.60	47.00	45.30	46.80
Mn (mg/*l*)	17.00	13.02	13.00	0.00	0.00	0.00	0.01

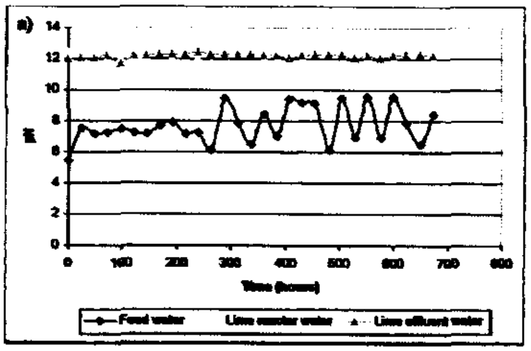
The stability of the treated water with respect to calcium carbonate is determined by the pH, calcium and alkalinity values of the treated water. The alkalinity of the treated water was 100 mg/*l* (as $CaCO_3$) owing to the escape of CO_2 from the solution and can be ascribed to the following reaction:

$$H_2CO_3 \rightarrow H_2O + CO_2 \quad [3]$$

This is a benefit as the increased buffer capacity contributes to stabilizing the pH of the water (Table IV). Sulphate was reduced from 3 000 to 1 900 mg/*l* after neutralization with limestone. The calcium concentration increased during treatment from 420 to 636 mg/*l*. Only partial manganese removal (17 to 13 mg/*l*) was achieved, which can be expected if the pH is not raised to values higher than 7.8. Manganese removal is only achieved at pH 9.5.

The relationship between pH in the gypsum crystallization reactor and the sulphate in solution is evident from Table IV and Figures 3a and b in which the temporal behaviour of pH and SO_4^{2-} are illustrated over a period of 28 days. It can be further concluded that sulphates in the neutral water can be reduced effectively with lime treatment during gypsum crystallization to levels below the original aim of 1 200 mg/*l* SO_4^{2-}, i.e. 300 mg/*l* below the saturation level of gypsum (1 500 mg/*l*), by raising the pH to 12.26 (HRT = 2.72 hours). Because of the removal of sulphates to this low level, no scaling of pipelines in the plant where the treated water is re-used, will occur as the treated water is well below the saturation level of gypsum. The water is also suitable for irrigation as 1 200 mg/*l* is a typical limit for such practice. Improved sulphate removal is achieved when magnesium is removed at the high pH level of 12.26 after lime treatment. The magnesium concentration at pH 7.68 was 140 mg/*l* while at pH 12.26, the magnesium content dropped to zero, due to magnesium hydroxide precipitation. The calcium concentration increased from 636 to 829 mg/*l* due to the dissolution of lime ($Ca(OH)_2$). This phenomenon can be explained by the following reaction:

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4.2H_2O \quad [4]$$



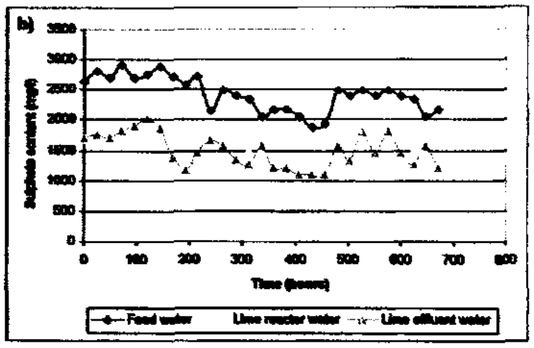


Figure 3—Levels of pH and SO_4^{2-} of the neutralized water during gypsum crystallization with lime over a period of 28 days at HRT of 2.72 hours

Rate of gypsum crystallization and $CaCO_3$ precipitation

During limestone treatment, neutralization occurs with the soluble $Ca(OH)_2$ resulting in a 96.6% decrease in acidity and an increase in pH and Ca concentration in the bulk water.

It has been shown by Maree *et al.*[4] that the above-mentioned increase in dissolved Ca concentration can result in super-saturation with respect to gypsum and concomitant precipitation with sufficient reaction time. The level to which SO_4^{2-} was removed was determined by the solubility product of gypsum, which is a function of the Ca and SO_4^{2-} concentrations as well as the ionic strength of the solution.

Maximum sulphate removal can be achieved during alkali treatment by raising the pH to 12 and higher for magnesium precipitation and removal of sulphate associated with magnesium by means of gypsum crystallization. During gypsum crystallization, the gypsum concentration was found to have a major influence on the rate of sulphate removal.

This phenomenon, which is illustrated in Table V and Figure 4, concurs with the findings of Maree *et al.*[4], who stated that the rate of crystallization is influenced by the concentration of gypsum seed crystals.

The rate of neutralization takes place in two stages, a fast first phase and a slow second phase. The first phase is associated with the neutralization of pure H_2SO_4 solutions. Clayton *et al.*[7] proposed the following equation:

$$-dc/dt = K.S.C_{ab} \qquad [5]$$

where $-dc/dt$ is the reaction rate, K the rate constant per unit surface area, S the total available surface area of $CaCO_3$ and C_{ab} the concentration of H_2SO_4.

It can therefore be concluded that the rate of gypsum crystallization is directly proportional to the surface area of the gypsum, which is illustrated in the following equation:

$$d[CaSO_4.2H_2O]/dt = k[CaSO_4.2H_2O](S)[C-C_0]^2 \qquad [6]$$

where $d[CaSO_4.2H_2O]/dt$ represents the rate of crystallisation, k the reaction rate constant, $[CaSO_4.2H_2O](S)$ the surface area of the seed crystals, C the initial concentration of calcium sulphate in solution and C_0 the saturated concentration of calcium sulphate in solution.

Figure 5 is an illustration of the removal of sulphates through gypsum crystallization from the neutralized water, if sufficient time is provided, compared to that of the limestone neutralization process. It is evident from the decrease of the sulphate content of the water that about 2 hours are required to reduce the sulphates in the water to 1 100 mg/*l* during the gypsum crystallization stage with lime treatment.

Water, which is under-saturated with respect to gypsum, can be produced by adjusting the pH with CO_2 from the high levels of 12 and higher to a level where $CaCO_3$ has a low solubility. Figure 6 shows the relationship between pH and Ca concentrations in solution. It can be seen that calcium was reduced from 1 100 mg/*l* at pH 13.30 to 487 mg/*l* at pH 8.80 due to $CaCO_3$ crystallization.

Table V

Water qualities of feed water and treated water of each of the three stages of treatment

Sludge concentration (g/*l*)	1	10	50	200
Reaction rate (g/*l*. day)	38.02	52.70	102.53	125.76

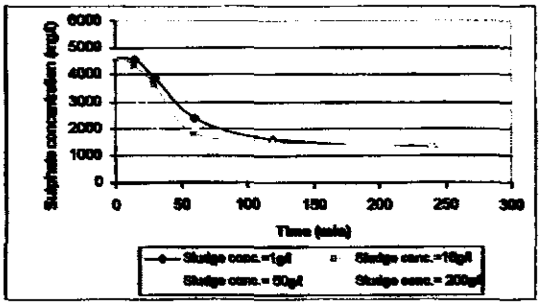


Figure 4—Effect of sludge concentration on rate of gypsum crystallization at pH 12

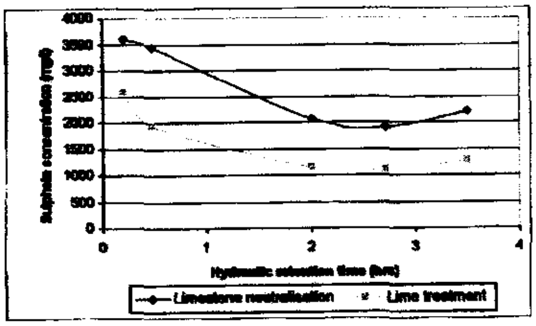


Figure 5—Effect of different retention times on rate of limestone neutralization and gypsum crystallization

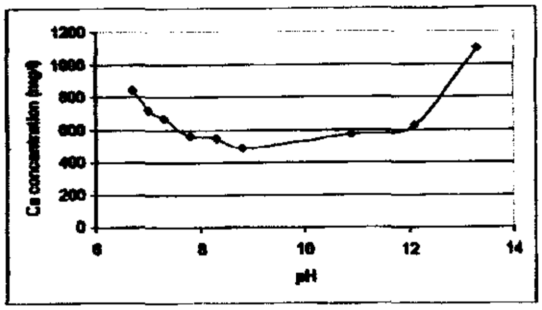


Figure 6—Relationship between pH and Ca concentration

The fact that CO_2 bubbling into the treated water of the gypsum crystallization stage resulted in an immediate decrease in pH and that it needed a very short retention time, makes it almost impossible to determine the effect of various parameters on the rate of $CaCO_3$ precipitation. The pH of the water was adjusted to 8.50 after CO_2-bubbling and the calcium concentration decreased from 829 to 487 mg/*l* as $CaCO_3$ crystallized out.

According to Loewenthal and Marais[8], the saturation, under-saturation and super-saturation states of $CaCO_3$ are theoretically identified by the activity product of Ca^{2+} and CO_3^{2-} species that is compared with the solubility product constant k_{sp} for $CaCO_3$. Above the solubility product, $CaCO_3$ will precipitate out of the water and if below the solubility product, $CaCO_3$ will dissolve. The rate of precipitation or dissolution is described by the following equation:

$$-d\left[Ca^{2+}\right]/dt = kS\left\{\left(Ca^{2+}\right)^{1/2}\left(CO_3^{2-}\right)^{1/2} - k_{sp}^{\ 1/2}\right\}^2 \qquad [7]$$

where k is the precipitation rate constant, S the surface area of $CaCO_3$ growth/dissolution sites and () the activity in moles/*l*. Adlem[9] further stated that this equation can be described as practical for the design of softening plants. The rate of precipitation depends on k, S and the term in brackets. Although k is affected to an unknown extent by crystal structure, S depends on size, mass and structure of the crystals. By controlling S and the degree of super-saturation (term in brackets), the rate of precipitation or dissolution of $CaCO_3$ can be determined.

Table VI

Suspended solids content of the gypsum sludge at different dilutions before settling and settling rate after 24 hours

Reactor	**Dilution (%)**						
	200	**100**	**75**	**50**	**30**	**20**	**10**
Gypsum crystallization							
Suspended solids before settling (mg/*l*)	26 500	11 135	10 015	5 630	2 825	1 985	1 110
Settling rate of gypsum sludge (m/h)	0.101	0.293	0.428	0.633	0.904	1.171	2.483

Conditions: HRT in crystallization reactor: 2.72 hours

Sludge characteristics

The suspended solids content and settling rate of the gypsum sludge after 24 hours settling time are shown in Table VI at different dilutions.

For the gypsum sludge, the settling rate increased from 0.101 to 2.483 m/h as the dilution decreased from 200 to 10%. A low sludge settling rate (0.101 m/h) would therefore be expected in the gypsum crystallization reactor where the sludge solids content is high (26 500 mg/*l*), while a high sludge settling rate (2.483 m/h) can be expected in the sludge separation stage where the solids content is low (1 110 mg/*l*). The sludge concentration can be controlled by withdrawing sludge from the bottom of the reactor in which the solids content would be at a maximum.

As mentioned earlier, the $CaCO_3$ sludge, produced through CO_2 bubbling of the treated water of the gypsum crystallization stage, had a wide variety of particle sizes which made it almost impossible to determine settling rates. These results are supported by the conclusions made by Pontius[6] in which he stated that individual particle behaviour is influenced or hindered by the presence of other particles and that the flow characteristics of the bulk suspension can be affected. With increased particle concentration, the free area between particles is reduced, causing greater interparticle fluid velocities and alteration of flow patterns around particles. Consequently, the settling velocity of a suspension is generally less than that of a discrete particle. When the size, shape or density of particles in a suspension is not uniform, individual particles will have different settling velocities and smaller particles tend to be dragged down by the motion of larger particles.

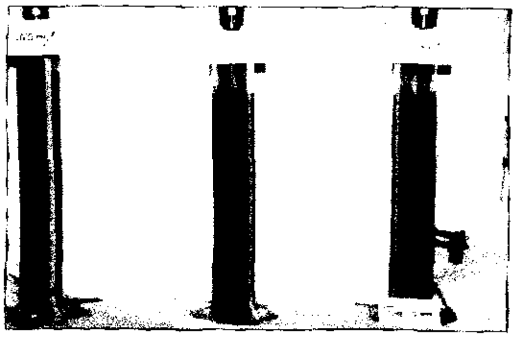
Effect of polymers for settling reasons on chemical composition of treated water

To optimize the process, settling of the various sludges in the three stages was improved by the addition of the polymers PAC6 and 3095 as coagulant and flocculant respectively to the effluents. The addition of limestone, lime, CO_2 and polymeric substances to the secondary effluents in the various pH ranges had the following effects on its inorganic composition, as illustrated in Table VI.

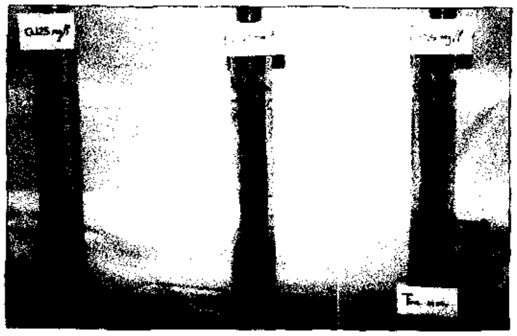
The presence of Al ions in the various secondary effluents played an important role in the achievement of optimum clarification during limestone, lime and CO_2 treatment. This is due to the formation of gelatinous Al-precipitated compounds that is illustrated in the decrease of Al concentration, from 556 mg/*l* to zero, in each of the three stages of the process. It can therefore be concluded that the Al content in the polymers used as coagulant or flocculant did not affect the final quality of the treated water. Al precipitated in the same way as Fe and Mn and can be treated as for inert sludge. Metal hydroxides are inert and therefore do not oxidize like metal sulphides under standard conditions to form H_2SO_4 and metals in solution.

Optimum dosage of polymeric additions for improved settling of sludges

It is known that particles in the relatively dilute solutions did not act as discrete particles but coalesced during sedimentation (Metcalf and Eddy[10]). As coalescence or flocculation occurs, the mass of the particle increases and it settles faster. The extent to which flocculation occurs depends on the opportunity for contact, which varies with a number of variables. One of these variables is the concentration of the particles.



Photograph 1—Effect of various concentrations of flocculant 3095 on settling rate of sludge from stage 1—time 0 min



Photograph 2—Effect of various concentrations of flocculant 3095 on settling rate of sludge from stage 1—time 10 min

Table VII

Effect of polymer concentration on the settling rate of the sludges produced in the three consecutive stages of the treatment process (including polymer cost)

Stage 1: Limestone neutralization

Polymer concentration (mg/*l* treated water)	0.000	0.125	0.250	0.500	1.000	1.250	1.500
Sludge settling rate (m/h)	1.30	4.62	5.10	5.04	5.37	5.79	5.91
Cost to treat 1m³ water (cents)	0.00	0.28	0.55	1.10	2.20	2.75	3.30

Stage 2: Gypsum crystallization with high lime treatment

Polymer concentration (mg/*l* treated water)	0.000	0.250	0.500	0.750	1.250	1.750	2.000
Settling rate (m/h)	0.21	0.67	0.84	1.64	2.58	3.44	5.81
Cost to treat 1m³ water (cents)	0.00	0.55	1.10	1.65	2.75	3.85	4.40

Stage 3: $CaCO_3$ precipitation with CO_2 treatment

Polymer concentration (mg/*l* treated water)	0.000	0.400	0.500	0.625	1.000	1.250	1.500
Settling rate (m/h)	0.00	19.98	20.04	20.10	22.08	20.34	20.16
Cost to treat 1m³ water (cents)	0.00	4.13	4.35	4.63	5.45	6.00	6.55

A number of experiments was conducted at various polymer concentrations and the rate of settling of the sludges as well as clarity of the treated water were studied. Photographs 1 and 2 illustrate these actions. These results (including cost estimates) are also listed in Table VII.

The contacting particles tended to settle as a zone, maintaining the same relative position with respect to each other. As the particles in this region settled, a relatively clear layer of water was produced above the particles in the settling region. In the case of stages 1 and 2, an identifiable interface developed between the more or less clear upper region and the hindered settling region. The rate of settling in the hindered settling region is a function of the concentration of solids and their characteristics. As settling continued, a compressed layer of particles began to form on the bottom of each cylinder in the compression settling region. The particles in this region apparently formed a structure in which there is close physical contact between the particles. As the compression layer formed, regions containing successively lower concentrations of solids than those in the compression region extend upward in the cylinder. In the case of stage 3, such a small concentration of sludge was formed and settling of the sludge with an addition of a coagulant and flocculant was obtained within a few seconds.

Inefficient coagulation/flocculation resulted from an overdose of polymer to the system or from intense or prolonged agitation. If excessive polymer is added, the segments may saturate the surfaces of colloidal particles so that no sites are available for the formation of polymer bridges. This can restabilize the particles and may or may not be accompanied by charge reversal. A very narrow optimum exists for the polymer and overdosing or underdosing will result in restabilization of the colloids. Intense or prolonged mixing may destroy previously formed bridges and lead to restabilization.

An inverse relationship exists between the optimum polymer dosage and the concentration of colloids to be removed. This can be explained as follows: at low colloid concentrations a large excess of polymer is required to produce a large amount of precipitate that will enmesh the relatively few colloidal particles as it settles. At high colloid concentrations, coagulation/flocculation will occur at a lower chemical dosage because the colloids serve as nuclei to enhance precipitate formation.

Depending on the settling rate of the sludge, the clarity of the overflow water and the cost of polymer added for sufficient sludge settling, the optimum concentration of polymer can be determined. Dosages of only 0.50 to 1.0 mg/*l* are needed for effective settling of the sludge in the first stage of the process with a settling rate of 5.04 to 5.37 m/h. In the second stage of the process only 0.75 to 1.25 mg/*l* of the polymer is needed to achieve a settling rate of 1.635 to 2.58 m/h. For the third stage, the addition of a coagulant first, followed by a flocculant, necessary to achieve good settling of the very fine $CaCO_3$ sludge. Only 0.005 ml/*l* of the coagulant PAC6 and 0.4 mg/*l* of flocculant 3095 were needed for effective sludge settling. A specific combination of coagulant:flocculant exists and from there the above optimum amount of this specific combination had been experimentally determined.

Economic feasibility

Neutralization and sulphate removal from water to a level where the water quality is suitable for re-use in the process, for irrigation purposes or for discharge into the sewerage network, can be achieved with limestone ($CaCO_3$) and slaked lime ($Ca(OH)_2$). For re-use in some areas of the plant, treated water may need to be under-saturated with respect to gypsum to prevent gypsum scaling of equipment. Due to the removal of magnesium, sulphate associated with magnesium and the solubility product of gypsum, which allows lower sulphate concentrations at higher calcium concentrations in solution, sulphate can be removed to lower levels with lime (pH is raised to 12.26) than with limestone (pH is raised to 7.68). Therefore, maximum benefits can be achieved by combining limestone neutralization with lime treatment for neutralizing the water, for complete magnesium removal and for sulphate removal to less than 1 200 mg/*l*.

The bulk of the solution can be neutralized with limestone (which is much cheaper than lime), followed by lime treatment for metal removal as well as partial sulphate removal. Further treatment of the high pH water with CO_2 (which is generated during limestone neutralization and gypsum crystallization) will not only adjust the pH of the water to neutral levels but $CaCO_3$ of high quality can also be produced and then recycled to the limestone neutralization stage.

A comparison between the cost associated with neutralizing 1 g/*l* acidity by using limestone and lime, is illustrated in Table VIII. It can be noted that acid water can be neutralized 69% more cheaply, using limestone instead of lime.

Table VIII

Comparison between chemical costs for neutralizing 1g acid with limestone and lime

Chemical	Molecular mass (g/l)	Purity (%)	Chemical cost (R/t)	Cost of removal of 1g acid (R/Ml acid)
Limestone	100	80	150	190
Slaked lime	74	85	700	610

Table IX

Chemical cost of sulphate removal by means of limestone neutralization and gypsum crystallization

Chemical	Minimum sulphate level (mg/l)	Chemical cost (R/t)	Chemical usage(t/t sulphate)	Cost of sulphate removal (R/t sulphate)
Limestone	1 900	150	1.04	156
Slaked lime	1 200	700	0.77	539

The cost for removing of sulphate to a certain level by means of limestone and lime is listed in Table IX.

It can be noted from Table VIII that the addition of polymers to the effluents of the various stages of the process, to ensure fast enough settling of the sludges, is inevitable. Because of the higher settling rates through the usage of coagulants/flocculants, big savings will be made on capital cost, as much smaller clarifiers are needed. The quality of the treated water was also greatly improved in terms of clarity. Clarity improvement of 63, 92 and 99% can be achieved for the overflow water of the secondary settling sludges in the process by the addition of very small quantities of polymeric substances to the sludges. Settling of these sludges was improved by 74, 90 and 100% in the three consecutive stages of the process.

Conclusions

- Acid water can be neutralized effectively with limestone instead of lime. In addition, sulphate is removed to 1 900 mg/*l* (as SO_4)
- After limestone neutralization, the sulphate content of the treated water can be further reduced to less than the original aim of 1 200 mg/*l* by means of lime treatment to a pH level of 12 and higher. When pH values of 12 and higher are reached, gypsum crystallization will take place and magnesium will be fully removed from the water
- The CO_2 produced during the limestone neutralization stage can be used to reduce the high pH of the treated water after gypsum crystallization. The $CaCO_3$ formed during this stage is recycled to the limestone neutralization stage for re-us
- The contact time required between limestone and lime and the water depends on the surface area of the limestone and the lime. For design purposes, a contact time of 1 hour is needed for neutralization of acid water with limestone and 2 hours for maximum sulphate removal with lime treatment
- Depending on the required level of sulphate removal, cost savings of up to 61.5% can be achieved by the integrated limestone/lime process, compared to the well-known lime neutralization process that is commonly used by acid water treatment plants
- Due to the very low concentration of Al in the treated water of the process after each stage of treatment, it can be concluded that the polymers used for coagulation/flocculation had no effect on the chemical composition of the treated water after limestone and lime treatment for neutralization and partial sulphate removal
- A contact time of 1 minute between polymer addition for coagulation/flocculation reasons was found to be sufficient for effective settling of the secondary effluents of the three consecutive stages in the process.
- The settling rates of the secondary sludges in the process were increased by 74.2, 91.9 and 100% respectively for the three stages by the addition of PAC6 as coagulant to the third stage and 3095 as flocculant to all three stages of the process. Because of higher settling rates, the clarity of the effluents was also improved greatly.
- Depending on the required level of sludge settling and effluent clarity of the treated water after each stage in the process, large cost savings can be achieved by the addition of a specific amount of polymer to each of the stages.

References

1. Maree, J.P. and du Plessis, P. Neutralisation of acid mine water with calcium carbonate. *Wat. Sci. Tech.*, 26(9), 1994. pp. 285–196.
2. Maree, J.P., du Plessis, P. and van der Walt, C.J. Treatment of acidic effluents with limestone instead of lime. *Wat. Sci. Tech.*, 26(1-2), 1992. pp. 345–355.
3. Maree, J.P., van Tonder, G.J., Millard, P. and Erasmus, T.C. Pilot-scale neutralisation of underground mine water, *Wat. Sci. Tech.*, 34(10), 1996. pp. 141–149.
4. Maree, J.P., de Beer, M., Strydom, W.F. and Christie, A.D.M. Limestone neutralisation of acidic effluent, including metal and partial sulphate removal, *IMWA. Proceedings of the 1998 Symposium of IMWA*, 1998. Johannesburg, South Africa.
5. Benefield, L.D., Judkins, J.F. and Weand, B.L. *Process Chemistry for water and wastewater treatment*. United States. Prentice-Hall, Engelwood Cliffs. N.J. 1982. p. 510.
6. APHA. *Standard methods for the examination of water and wastewater treatment. 12th ed.* American Public Health Association. New York, McGraw-Hill. 1985.
7. Clayton, J.A., de Villiers, M.G., Maree, J.P. and Pienaar, G. Calcium carbonate neutralization of acidic effluents in a fluidised bed, *Proceedings of The 1998 Southern Africa Industrial Water Symposium*, 1990. Johannesburg, South Africa.
8. Loewenthal, R.E. and Marais, G.v.R. *Carbonate chemistry of aquatic systems: theory and application*. United States. Ann Arbor Science Publishers, 1976. p. 433.
9. Adlem, C.J.L. *Treatment of sulphate-rich effluents with the barium sulphide process*, M-Dissertation, 1997. p. 107.
10. Pontius, F.W. *Water quality and treatment*. United States. McGraw-Hill, 4th ed. 1990. p. 1195.
11. Metcalf and Eddy. *Wastewater Engineering: Treatment, disposal and re-use.* United States. McGraw-Hill, 3rd edition. 1991. p. 1334. ●

PAPER 2: Geldenhuys, A.J. & Maree, J.P. Synthetic organic polymers (PAC6 and 3095) as coagulants/flocculants for optimisation of an integrated limestone/lime neutralisation process for partial sulphate removal, *Proceedings 5th Annual Industrial Water Management and Treatment Symposium*, 15–16 May 2002, Johannesburg, South Africa.

This investigation arose from a need to improve the poor settling rates of gypsum- and $CaCO_3$-sludge in the combined limestone/lime process. These settling rates were very slow and caused the overflow water from each stage to have a high degree of turbidity and colour. The effectiveness in terms of cost and water overflow quality, using two polymeric substances to improve settling of the sludges, was extensively investigated in order to formulate design criteria for settling tanks (clarifiers) in full scale neutralisation and sulphate removal plants.

The main objectives were:

- ✓ To determine the effect the polymers had on the chemical composition of the water, before and after treatment
- ✓ To determine the optimum dosage of polymer and contact time between polymer and sludge for each stage in the combined limestone/lime process
- ✓ To evaluate the economic efficiency of the polymeric substances
- ✓ To produce design criteria for settling tanks in each of the three stages of the combined limestone/lime process

Type 3095 flocculant, which is poly-acrylamide in granule form, was effectively utilised to serve as flocculant after both the lime treatment stage (gypsum crystallisation) and the CO_2 treatment stage ($CaCO_3$ precipitation). The $CaCO_3$ sludge, resulting after CO_2 treatment in the third stage of the process, requires the use of a coagulant prior to the flocculant to enable the growth of aggregates into sizeable flocs. PAC6, which is a poly-(aluminium-hydroxy) chloride and only available in solution, was successfully introduced to the process as coagulant. The gypsum sludge, resulting from the first stage of the process (limestone neutralisation), did not need any polymeric addition for improvement of sludge settling, although the suitability of PAC6 as flocculant was evaluated at this stage and presented in this paper.

For design purposes, the results are such that the required settling rates of the various sludges, the essential clarity of the overflow water, and the cost of the amount of additive are listed. From these results, a full scale limestone neutralisation and iron(II)-oxidation plant has been designed, constructed and commissioned in January 2004 to treat toe-seep from a coal discard dump near Witbank.

Paper 2 was presented orally by A J Geldenhuys at the 5th Annual Industrial Water Management and Treatment Symposium

SYNTHETIC ORGANIC POLYMERS (PAC6 AND 3095) AS COAGULANTS/FLOCCULANTS FOR OPTIMISATION OF AN INTEGRATED LIMESTONE/LIME NEUTRALISATION PROCESS FOR PARTIAL SULPHATE REMOVAL

Institute for International Research

A J GELDENHUYS and J P MAREE

CSIR, Division of Water, Environment and Forestry Technology, P O Box 395,

Pretoria, 0001, South Africa

(Tel no: +27 12 841 4178, Fax no: +27 12 841 2506, Email: ajgeldenhuys@csir.co.za)

KEYWORDS: Limestone neutralisation, gypsum crystallisation, $CaCO_3$ precipitation, acidic effluents, partial sulphate removal

ABSTRACT

Limestone and lime treatment is the most cost-effective technology for neutralisation and partial sulphate removal of acidic/sulphate-rich water to sulphate levels of less than 1 200 mg/ℓ due to precipitation of magnesium and removal of the associated sulphate fraction (through gypsum crystallisation). Neutralised mine water of this quality may be suitable for irrigation or re-use in mine applications. The overflow water from the clarifier of each of the above stages generally contains a wide variety of colloidal impurities that may cause the water to appear turbid or may impart colour. This results in very slow sludge settling rates that causes overflow water with a high degree of turbidity and colour.

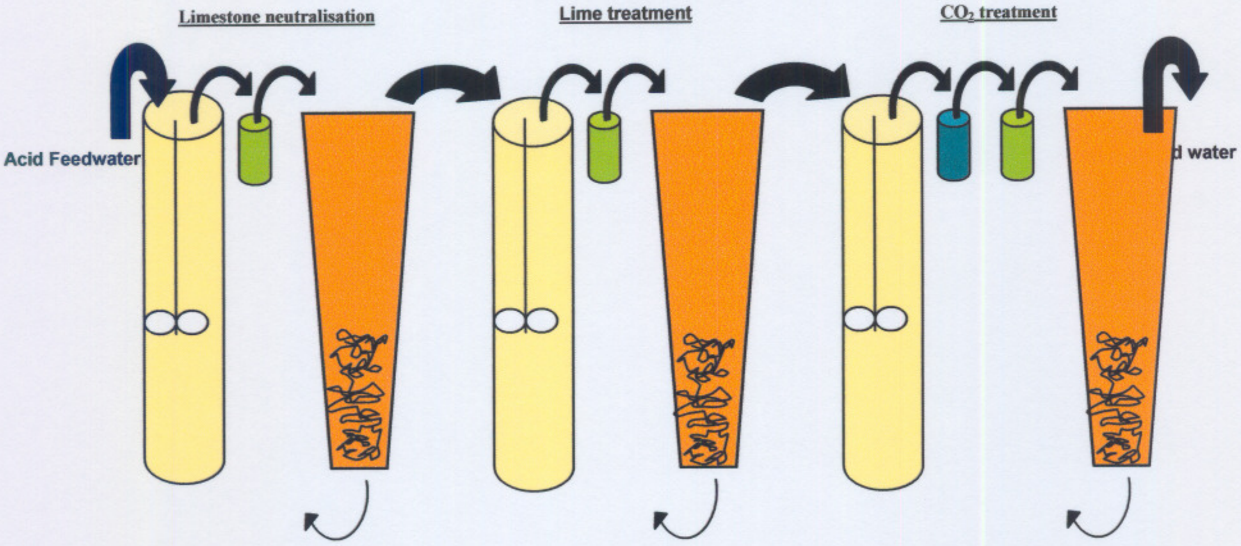
There are a number of successive or simultaneous stages involved in the agglomoration of particles. This paper describes the use of two of these stages in an innovative process for the neutralisation and partial sulphate removal of acid streams produced during coal mining and processing. In this process, the integrated lime and limestone has been developed to treat water for removal of magnesium, metals and sulphate (to less than 1 200 mg/ℓ). The process consists of the following stages:

1. Limestone ($CaCO_3$) neutralisation to raise the pH to 7 and CO_2-production.
2. Lime ($Ca(OH)_2$) treatment to pH 12 for $Mg(OH)_2$ precipitation and gypsum ($CaSO_4$) crystallisation.
3. pH adjustment with CO_2 recovered from Stage 1 to enable $CaCO_3$ precipitation for re-use in Stage 1.

In an earlier study it was found that the rate of gypsum crystallisation is directly proportional to the surface area of the gypsum. To get optimum neutralisation of the acid water and partial sulpate removal to below the saturation level of gypsum (i.e. 1 200mg/ℓ), maximum sludge recovery is needed. The higher the concentration of seed crystals the larger the surface area. Therefore, effective removal of suspended and colloidal matter from the overflow of each stage are required and can be achieved by coagulation and flocculation. The polymers, PAC6 and 3095 were effectively used as coagulant and flocculant respectively. The addition of these polymers resulted in a clear overeflow in each of the above stages with a very low turbidity.

1 INTRODUCTION

Lime clarification is applied throughout the world in water treatment. Its most extensive use is in the purification of surface waters for domestic and industrial use. Limestone and lime clarification were effectively introduced to the water reclamation field at the Navigation Colliery near Witbank. The integrated limestone/lime treatment process (Figure 1) comprises three consecutive stages which may be carried out seperately in different pieces of equipment (reactors, clarifiers, and coagulant/flocculant mixing tanks).



Reactor	Clarifier	Coagulation: PAC6	Flocculation: 3095	Overflow	Sludge recycling

Figure 1: Block diagram of integrated limestone/lime treatment process

The clarification system at the Navigation treatment plant consists of the following items:

1. A limestone reactor for mixing the limestone and acid feedwater thoroughly during limestone neutralisation, and has a retention time of 1 hour. A flocculant storage- and feed tank for dosing flocculant: 3095 into the overflow from the reactor to a clarifier. In the clarifier, the clarified effluent is seperated from the sludge. The sludge produced in the clarifier is recirculated to the reactor by means of a variable speed peristaltic pump. The sludge density is controlled by the recirculation and draw-off rates.
2. A lime reactor, in which the neutralised water from Stage 1 (limestone neutralisation) is thoroughly mixed with lime (retention time: 2.72 hours) to achieve $Mg(OH)_2$ precipitation and gypsum ($CaSO_4$) crystallisation. A flocculant storage- and feed tank for dosing flocculant: 3095 into the overflow from the reactor to a second clarifier. For handling the sludge and clarified effluent of

the lime treatment stage as well as the next stage (CO_2 treatment), the same applies as for limestone neutralisation.

3. A mixed reactor for pH adjustment by decrease the pH of the treated water resulting from Stage 2 to enable $CaCO_3$ precipitation for re-use in Stage 1. A retention time of 30 minutes was used. A coagulant and flocculant storage- and feed tank for dosing coagulant: PAC6 and flocculant: 3095 in serie into the overflow from the reactor to a third clarifier.

Considerable attention has come to be directed at the removal of small particles by combining them into larger aggregates by coagulation and flocculation. These particles are mainly of chemical origin as limestone and lime are added to the system which result in the production of $Mg(OH)_2$, $CaSO_4$ and $CaCO_3$.

Water contains many compounds, which can be classified into three categories:

- Suspended solids – These products may be mineral in origin (sand, silt, clays, etc.) or organic (products resulting from the decomposition of plant or animal matter, humic or fulvic acids, for example). Added to these compounds are microorganisms such as bacteria, plankton, algae and viruses. These substances, in particular, are responsible for turbidity and colour.
- Colloidal particles (less than 1 micron) – These are suspended solids of the same origin as the above but of smaller size and with a settling rate that is extremely slow. They are also responsible for turbidity and colour.
- Dissolved substances (less than several nanometres) – These are usually cations or anions. Part of the organic matter is also dissolved. Gases are also present (O_2, CO_2, H_2S, etc.).

Colloidal particles that cause colour and turbidity are difficult to separate from water because the particles will not settle by gravity and are so small that they pass through the pores of most common filtration media. To be removed, the individual colloids must aggregate and grow in size. Aggregation is not only by the small size of the particles but more importantly by the fact that physical and electrical forces keep the particles separated from each other and prevent the collisions that would be necessary for aggregation to occur. Thus colloids are particles that cannot settle naturally and for which surface area factors are most important. These factors determine the stability of colloidal suspensions. In fact, colloids are subject to two major forces:

✓ Van der Waals attraction, which relates to the structure and form of colloids as well as to the type of medium,

✓ The electrostatic repulsive force, which relates to the surface charges of the colloids.

In order to destabilise the suspension, it is necessary to overcome the energy barrier. To accomplish this and, thereby, promote the agglomoration of colloids, it is neceassary to reduce the electrostatic forces. This destabilisation is brought about by coagulation (Benefield *et al.*[1]).

Chemical agents can be used to promote colloid aggregation by destroying the forces that stabilise colloidal particles. Mechanisms responsible for destabilisation of inorganic clay colloids have been identified through extensive research studies and are well understood. The process of destroying the stabilising forces and causing aggregation of clay colloids is referred to as *chemical coagulation* (Benefield *et al.*[1]). It can also be referred to as the destabilization of colloidal particles brought about by the addition of a chemical reagent known as a flocculant. *Flocculation* can be adressed as the agglomeration of destabilized particles into microfloc, and later into bulky floccules which can be settled called floc. The introduction of another reagent, called a flocculant may promote the formation of the floc.

According to Pontius[2], the process of coaggulation as practised in water treatment can be considered as three separate and sequential stages: coagulant formation, particle destabilisation, and interparticle collisions. Coagulant formation and particle destabilization occur in rapid-mixing tanks; interparticle collisions occur predominantly in flocculation tanks. The major factors affecting the coagulation/flocculation processes in diverse ways are: (1) coagulant/flocculant dosage; (2) pH; (3) colloid concentration, often measured by turbidity; (4) anions or cations in solution; and (5) mixing effects.

Synthetic organic polymers can be effective as coagulants. These polymers are long-chain molecules comprised of many monomers. Polymers typically have a helical molecular structure comprised of carbon chains with ionising groups attached. When the groups are ionised in solution, an electrical repulsion is created which causes the polymer to assume the shape of an extended rod. As the ionised groups become attached to colloidal particles the charges are neutralized and the polymer starts to coil and form a dense floc with favourable settling properties.

The main objectives of this investigation were:

- To determine the effect of the polymers on the chemical composition of the water before and after treatment
- To determine the optimum dosage of coagulant/flocculant for each stage of the treatment process (concentration)
- To determine the efficiency of the polymers (as coagulant/flocculant) on the chemical composition of the coal processing water before and after treatment in all stages of the treatment process (settling rate of sludge and clarity of overflow water)
- To determine the economic feasibility of the polymers used as coagulant/flocculant

2 MATERIALS AND METHODS

2.1 Feed Water

Acidic leachate from a waste coal dump, was used as feed water for *batch studies* on laboratory scale in beakers and *continuous studies* on pilot plant scale. The relevant chemical composition of this leachate is listed in Table I.

Table I. Chemical composition of acidic mine leachate as feedwater

Parameter	Acid feed water
pH	2.10
SO_4^{2-} (mg/ℓ)	3 000
Ca (mg/ℓ)	420
Mg (mg/ℓ)	160
Na (mg/ℓ)	41
Mn (mg/ℓ)	17
Cl^- (mg/ℓ)	16
Acidity (mg/ℓ)	3 000

2.2 Feedstock

Waste powder limestone ($CaCO_3$) from paper industries was used in the limestone neutralisation stage of the process. For the gypsum crystallisation stage, unslaked lime ($Ca(OH)_2$) was used. The limestone was analysed for its calcium, magnesium and alkalinity content. Calcium and magnesium were determined with EDTA, while the alkalinity content was determined by dissolving it in a stoichiometrically excessive amount of hydrochloric acid. This excess amount of hydrochloric acid was titrated with sodium hydroxide (see Tables II & III for chemical composition of powder lime and limestone respectively).

Table II. Chemical composition of powder lime ($Ca(OH)_2$)

Bulk density (kg/m^3)	Available $Ca(OH)_2$ (min %)	Available CaO (min %)	Total CaO (min%)	MgO (max%)	Al_2O_3 + Fe_2O_3 (max%)	SiO_2 (max%)	Acid insolubles (max%)
560	94	71	72	1	0.3	0.5	1

Particle size: Fine powder, 100% passing 90 micron

Table III. Chemical composition of powder limestone ($CaCO_3$)

$CaCO_3$ (%)	$Ca(OH)_2$ (%)	Ca (mg/ℓ)	Mg (mg/ℓ)	Na (mg/ℓ)	K (mg/ℓ)	Moisture (%)
97.02	3.87	354.08	5.66	11.17	0.43	24

Percentages based on dried basis

The polymers that were used as coagulant and flocculant respectively are PAC6, which is Poly-aluminium-hydroxy chloride with a specific gravity of 1.3 (only available as solution) and 3095 (granules), Poly-acrylamide which is a co-polymer of acrylamide and acylic acid with a molecular weight of about 15 000 000 g/mole. These chemicals were supplied by Montan Chemicals, Germiston. The coagulant was used as received while a stock solution of 2.5g of 3095 flocculant per litre distilled water was made up on a weekly basis. For dissolving the flocculant in distilled water, a small amount of methanol was first added to the granules to assure effective granular dissolution.

2.3 *Batch studies and continuous studies*

Batch studies were conducted in the laboratory in 1ℓ volumetric cylinders at atmospheric pressure and ambient temperature to study the efficiency of the two polymers, PAC6 and 3095 as coagulant and flocculant respectively. These polymers were used to enhance settling of the various sludges produced in the three consecutive stages of the limestone/lime treatment process (Figure 1). The polymers were added separately to the effluents of these three stages as follows:

Primary effluent (limestone neutralisation):	3095	→	flocculant
Secondary effluent (lime treatment for gypsum crystallisation):	3095	→	flocculant
Tertiary effluent (CO_2 treatment for $CaCO_3$ precipitation):	PAC6	→	coagulant
	3095	→	flocculant

Each effluent was stirred at a medium stirring rate for 1minute whereafter increasing amounts of polymer were injected into the solution (effluent). To assure thorough mixing of the polymer and solution, it was further stirred for 1 minute at the same rate. For the tertiary effluent, an additional stirring of 1 minute between the coagulant and flocculant addition was allowed. At various time intervals, the interface of the settling region was marked and 30mℓ samples were withdrawn from the the top part of each cylinder (representing overflow) and analysed for turbidity until a settling time of 30 minutes have been reached. These measurements enable quantification of the influence of the mentioned polymers as effective coagulants/flocculants by means of polymer concentration, settling rate and clarity. Cylindrical tests should be used only for the evaluation of the operation, chemical dosage and removal of contaminants. It is not valid for evaluating the size of the clarifier or to simulate a reactor-clarifier but serves merely as guidelines.

Based on the studies conducted in the laboratory, the optimum amount of polymer was used in each consecutive step of the process at pilot plant scale to demonstrate the effective settling of the various sludges and clear overflow water on larger scale.

2.4 *Equipment and procedure*

A mobile pilot plant at Navigation Coal Mine near Witbank, with a capacity of 10m^3/day was used for on-site treatment of the acid mine water. The design and operational parameters for the mobile plant are summarised in Figure 1 and Table IV.

Table IV. Design parameters for the three consecutive stages of the treatment process as illustrated in Figure 1

Parameter	Limestone reactor	Limestone clarifier	Lime reactor	Lime clarifier	CO_2 reactor	CO_2 clarifier
Diameter (m)	*	*	1.220	1.220	0.600	1.220
Base area (m^2)	*	*	1.169	1.169	0.283	1.169
Height (m)	*	*	0.850	2.100	0.800	2.100
Volume (m^3)	*	*	0.994	2.821	0.226	2.821
Hydraulic retention time (HRT, hours)	1	-	2.72	-	0.5	-

* *Full scale plant in operation*

In all three stages, the polymer(s) was added to the effluent in the overflow between the reactor and clarifier for rapid mixing to disperse the polymer(s) homogeneously for enabling good contact between the effluent and polymer(s). In each clarifier, slow speed agitation was provided by recycling a part of the sludge back to its reactor by means of a variable speed pump to enable the growth of the aggregates into voluminous flocs by collision and entrapment of the suspended matter. Another reason for recycling a partial of separated solids (the sludge) is to provide nuclei for better coagulation and flocculation. The rest of the sludge is disposed of.

2.5 *Programme*

2.5.1 *Batch studies on coagulation/flocculation*

The concentration of polymer added was varied to evaluate and optimise the efficiency of the polymers as coagulant/flocculant by measuring the clarity and settling rate of each trial.

2.5.2 Continuous studies on cogulation/flocculation

The quality of the water before and after treatment for the various stages of the process were studied at the pilot plant on a continuous basis at the hydraulic retention times listed in Table 4.

2.6 Analytical

The samples were collected regularly and filtered through Whatman No 1 filter paper. Determinations of pH and sulphate were carried out manually according to procedures described in Standard Methods (APHA[3]). Calcium and magnesium were recorded with the ICP Method for metals. Alkalinity was determined by titrating with sodium hydroxide to pH 7.0. Clarity was determined with a spectrophotometer, measured in NTU (Nephelometric Turbidity Unit). The measurement of turbidity is based on comparison of the intensity of light scattered by a sample as compared to the light scattered by a reference suspension under the same conditions.

3 RESULTS AND DISCUSSION

3.1 Water quality

The chemical composition of the acid mine feed water and the water qualities after each of the three stages of treatment are listed in Table V (samples were taken in each reactor and after each polymer addition)

Table V. Water qualities of feed water and treated water of each of the three consecutive stages of the limestone/lime treatment process (see key notes in Figure 1)

Parameter	Acid feed water	Limestone neutralisation	Flocculation	Gypsum crystallisation through lime treatment	Flocculation	$CaCO_3$ precipitation through CO_2 treatment	Coagulation + Flocculation
pH	2.71	6.2	6.47	11.71	11.72	9.46	8.5
SO_4^{2-} (mg/ℓ)	14 200	8 800	6 200	2 200	2 600	2 800	2 400
Alkalinity (mg/ℓ)	-12 000	-3 200	-7.6	1 460	1 840	120	100
Ca (mg/ℓ)	434	538	537	994	1 330	630	626
Mg (mg/ℓ)	301	317	316	0.224	0.229	4.78	5.57
Al (mg/ℓ)	556	10.1	0.385	0	0	0.074	1.11
Na (mg/ℓ)	22.8	86.4	91.9	85.6	91.4	85.3	113
Fe(II) (mg/ℓ)	4 356	4 356	4 356	58	58	58	58
Fe_{Total} (mg/ℓ)	3 060	3 280	2 630	0.394	0.036	0.276	0.989

To optimise the process, settling of the various sludges in the three stages were improved by the addition of the polymers PAC6 and 3095 as coagulant and flocculant respectively to the effluents. The addition of limestone, lime, CO_2 and polymeric substances to the secondary effluents in the various pH ranges had the following effects on its inorganic composition, as illustrated in Table V:

a) Limestone ($CaCO_3$) can be used effectively in the integrated process for neutralisation of acid water. When discard leachate was treated with limestone, the *pH* of the water was raised from 2.71 to 6.20 in the neutralisation reactor. To achieve further reduction of sulphate to the level of 2 200mg/ℓ, lime was added to the neutralised effluent. The pH and Ca content increased to 11.71 and 994 mg/ℓ respectively, due to gypsum crystallisation in the second stage of the process. The high pH of 11.71 after lime addition to the water was corrected by bubbling CO_2 through the treated water until a pH of 8.50 had been reached.

b) The acidity of the water after limestone neutralisation was initially increased owing to the addition of hydroxide ions, but was subsequently reduced by the precipitation of carbonate as $CaCO_3$ and hydroxide as $Mg(OH)_2$. The Mg concentration was not affected by the addition of lime *per se*, but was reduced as a result of the precipitation of $Mg(OH)_2$ at pH levels of >10.8.

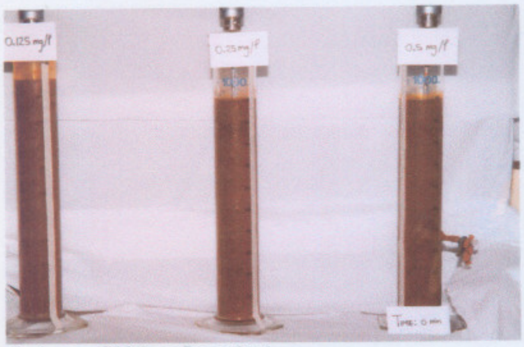
c) The presence of Al ions in the various secondary effluents played an important role in the achievement of optimum clarification during limestone-, lime- and CO_2-treatment. This is due to the formation of gelatinous Al-precipitated compounds that is illustrated in the decrease of Al concentration, from 556 mg/ℓ to zero, in each of the three stages of the process. It can therefore be concluded that the Al content in the polymers used as coagulant or flocculant did not affect the final quality of the treated water.

3.2 Optimum polymer dosage

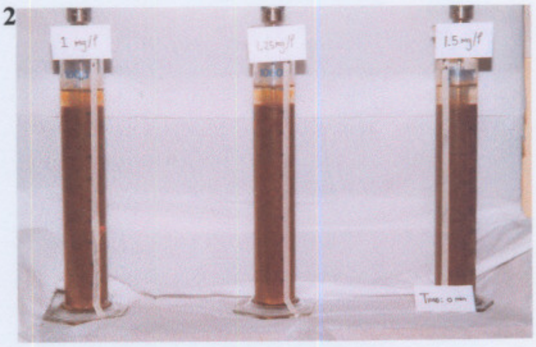
It is known that particles in the relatively dilute solutions did not act as discrete particles but coalesced during sedimentation (Metcalf & Eddy[4]) . As coalescence or flocculation occurs, the mass of the particle increases and it settles faster. The extent to which flocculation occurs is dependent on the opportunity for contact, which varies with a number of variables. One of these variables are the concentration of the particles. The settling rates for various concentrations of particles (polymer) which were added to the three consecutive stages of the process individually, are photographic illustrated in Tables VI, VII and VIII.

Table VI. Photographic illustration of the settling of the sludge in the limestone neutralisation stage (stage 1) of the limestone/lime treatment process with increasing concentration of polymer 3095 as flocculant (including values for clarity and cost)

1



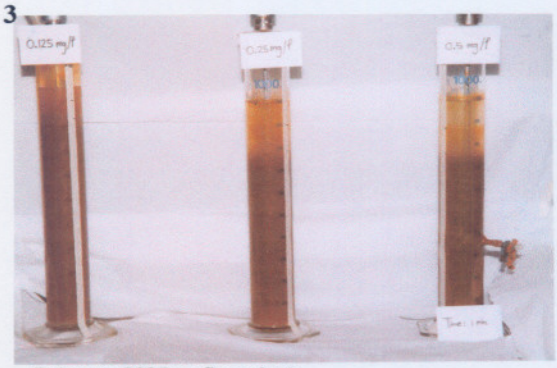
2



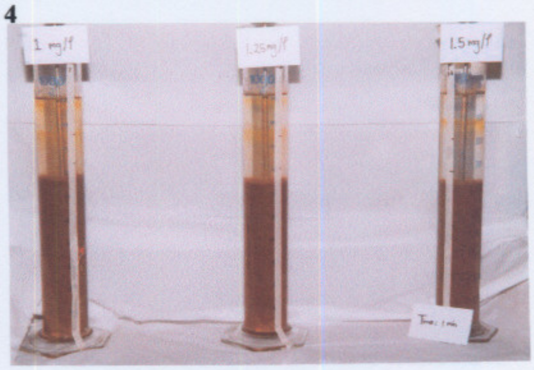
Polymer: 3095 as flocculant
Settling time: 0 minutes – directly after flocculant dosage

C: 0.125 T: out of spec. SR: 4.620 R: 0.275	C: 0.250 T: out of spec. SR: 5.100 R: 0.550	C: 0.500 T: out of spec. SR: 5.040 R: 1.100	C: 1.000 T: out of spec. SR: 5.370 R: 2.200	C: 1.250 T: out of spec. SR: 5.790 R: 2.750	C: 1.500 T: out of spec. SR: 5.910 R: 3.300

3



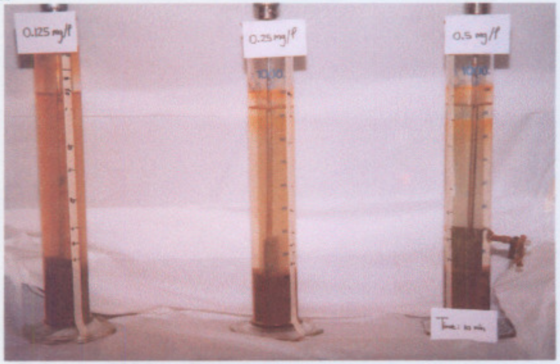
4

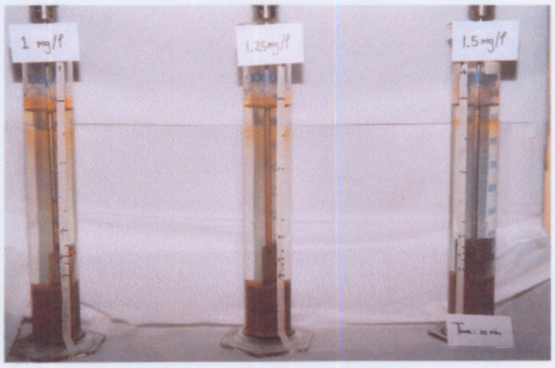


Polymer: 3095 as flocculant
Settling time: 1 minute after flocculant dosage

T: 862	T: 357	T: 319	T: 264	T: 247	T: 283

56





Polymer: 3095 as flocculant
Settling time: 10 minutes after flocculant dosage

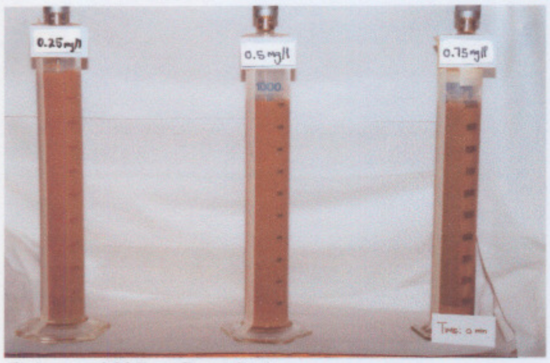
T: 163	T: 110	T: 154	T: 111	T: 173	T: 237

C – Polymer (3095) concentration (mg/ℓ)
T - Turbidity (NTU)

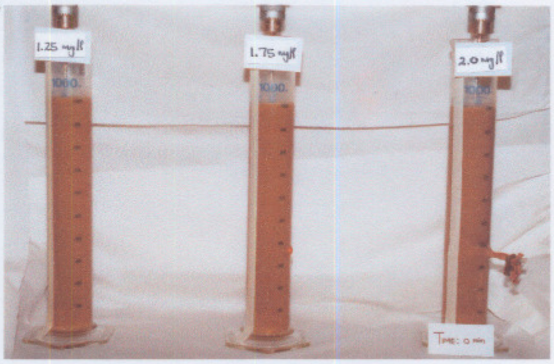
R - Cost (c/m^3)
SR - Settling rate (m/h)

Table VII. Photographic illustration of the settling of the sludge in the lime treatment stage (stage 2) of the limestone/lime treatment process with increasing concentration of polymer 3095 as flocculant (including values for clarity and cost)

1



2

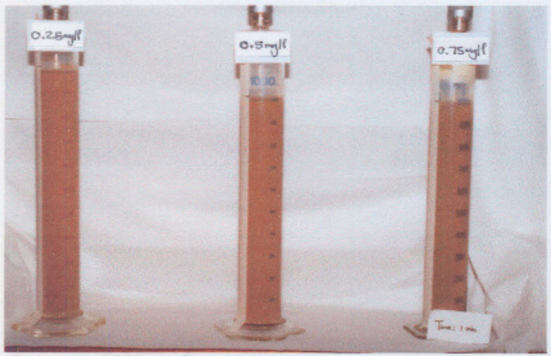


Polymer: 3095 as flocculant

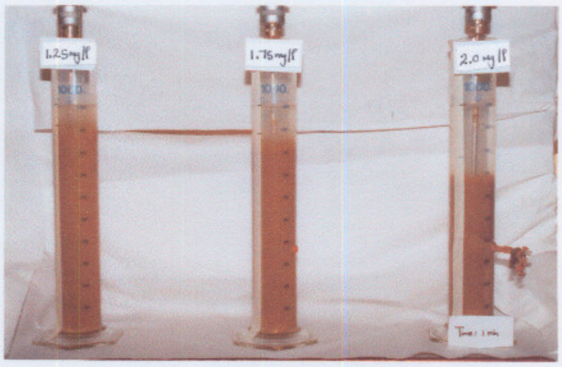
Settling time: 0 minutes – directly after flocculant dosage

C: 0.250 T: out of spec. SR: 0.672 R: 0.550	C: 0.500 T: out of spec. SR: 0.840 R: 1.100	C: 0.750 T: out of spec. SR: 1.635 R: 1.650	C: 1.250 T: out of spec. SR: 2.580 R: 2.750	C: 1.750 T: out of spec. SR: 3.440 R: 3.850	C: 2.000 T: out of spec. SR: 5.610 R: 4.400

3



4

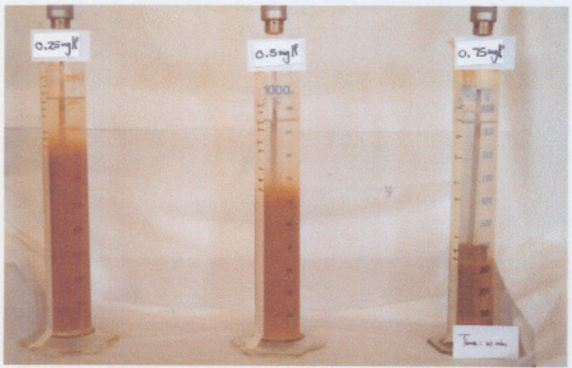


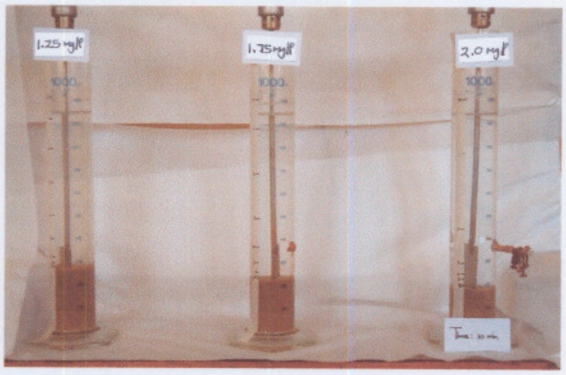
Polymer: 3095 as flocculant

Settling time: 1 minute after flocculant dosage

T: out of spec.	T: 3308	T: 276	T: 72.7	T: 22.6	T: 11.5

5 6





Polymer: 3095 as flocculant

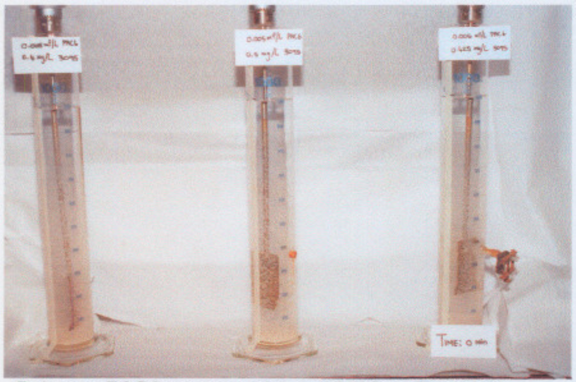
Settling time: 10 minutes after flocculant dosage

T: 10.6	T: 37.8	T: 18.5	T: 10.7	T: 10.5	T: 7.86

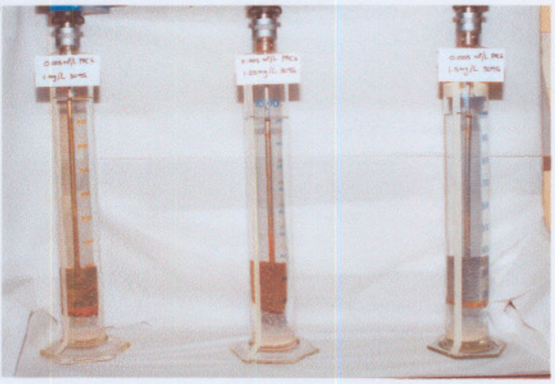
C – Polymer (3095) concentration (mg/ℓ)
T - Turbidity (NTU)
R - Cost (c/m^3)
SR - Settling rate (m/h)

Table VIII. Photographic illustration of the settling of the sludge in the CO_2 treatment stage (stage 3) of the limestone/lime treatment process with increasing concentration of polymers PAC6 and 3095 as coagulant/flocculant respectively (including values for clarity and cost)

1



2

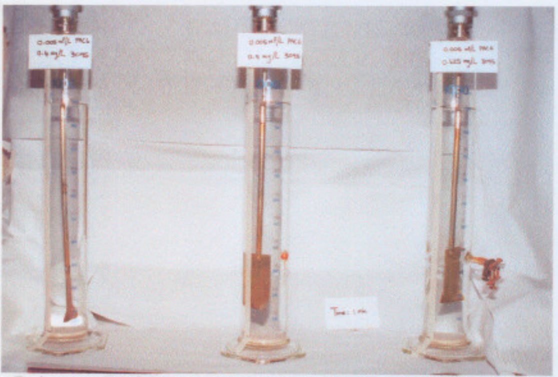


Polymer: PAC6 as coagualnt and 3095 as flocculant

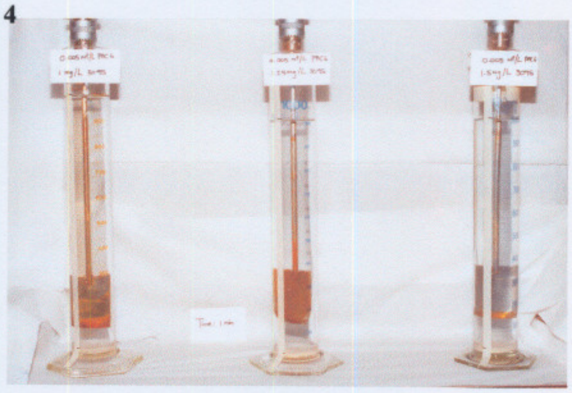
Settling time: 0 minutes – directly after coagulant/flocculant dosage

C: 0.400	C: 0.500	C: 0.625	C: 1.000	C: 1.250	C: 1.500
T: 1891	T: 1891	T: 1891	T: 1891	T: 1891	T: 1891
SR: 19.980	SR: 20.040	SR: 20.100	SR: 22.080	SR: 20.340	SR: 20.160
R: 4.130	R: 4.350	R: 4.625	R: 5.450	R: 6.000	R: 6.550

3



4



Polymer: PAC6 as coagulant and 3095 as flocculant

Settling time: 1 minute after coagulant/flocculant dosage

T: 3.83	T: 1.16	T: 0.122	T: 0.105	T: 0.099	T: 0.115

0.005 mℓ/ℓ PAC6 as coagulant was added and stirred for 1 minute before 3095 was added

C – Polymer (3095) concentration (mg/ℓ)

T - Turbidity (NTU)

SR - Settling rate (m/h)

R - Cost (c/m³)

The photo's listed in Tables VI, VII and VIII, are an illustration of the liquid's tendency to move up through the interstices of the contacting particles. As a result, the contacting particles tended to settle as a zone (or 'blanket'), maintaining the same relative position with respect to each other. As the particles in this region settled, a relatively clear layer of water was produced above the particles in the settling region. In the case of stages 1 and 2, an identifiable interface developed between the more or less clear upper region and the hindered settling region, as illustrated in Tables VI and VII. The rate of settling in the hindered-settling region is a function of the concentration of solids and their characteristics. As settling continued, a compressed layer of particles began to form on the bottom of each cylinder in the compression-settling region. The particles in this region apparently formed a structure in which there is close physical contact between the particles. As the compression layer formed, regions containing successively lower concentrations of solids than those in the compression region extend upward in the cylinder. In the case of stage 3, such a small concentration of sludge was formed and settling of the sludge with an addition of a coagulant and flocculant was obtained within a few seconds.

Inefficient coagulation/floccualtion resulted from an overdose of polymer to the system or from intense or prolonged agitation. If excessive polymer is added, the segments may saturate the surfaces of colloidal parfticles so that no sites are available for the formation of polymer bridges. This can restabilise the particles and may or may not be accompanied by charge reversal. A very narrow optimum exists for the polymer and overdosing or underdosing will result in restabilisation of the colloids. Intense or prolonged mixing may destroy previously formed bridges and lead to restabilisation.

An inverse relationship exists between the optimum polymer dosage and the concentration of colloids to be removed. This can be explained as follows: at low colloid concentrations a large excess of polymer is required to produce a large amount of precipitate that will enmesh the relatively few colloidal particles as it settles. At high colloid concentrations, coagulation/flocculation will occur at a lower chemical dosage because the colloids serve as nuclei to enhance precipitate formation.

Depending on the settling rate of the sludge, the clarity of the overflow water and the cost of polymer added for sufficient sludge settling, the optimum concentration of polymer can be determined. Dosages of only 0.50 to 1.0 mg/ℓ are needed for effective settling of the sludge in the first stage of the process with a settling rate of 5.04 to 5.37 m/h. Nearly 33% of the sludge had already been settled after 1 minute of polymer dosage. In the second stage of the process only 0.75 to 1.25 mg/ℓ of the polymer are needed to achieve a settling rate of 1.635 to 2.58 m/h. For the third stage, the addition of a coagulant first, followed by a flocculant are necessary to achieve good settling of the very fine $CaCO_3$ sludge. Only 0.005 mℓ/ℓ of the coagulant PAC6 and 0.4

mg/ℓ of flocculant 3095 were needed for effective sludge settling. A specific combination of coagulant:flocculant exists and from there the above optimum amount of this specific combination had been experimentally determined. For design purposes, the photographic illustrations and values for the above variables are listed in Tables VI, VII and VIII for the three consecutive stages of the process.

3.3 Polymer efficiency

The efficiency of the polymers used in each of the three consecutive stages is directly related to the settling rate of the sludge and the clarity of the overflow water. The effect of polymer concentration on sludge settling rate and clarity of the overflow water of the three stages are illustrated in Figures 2, 3 and 4.

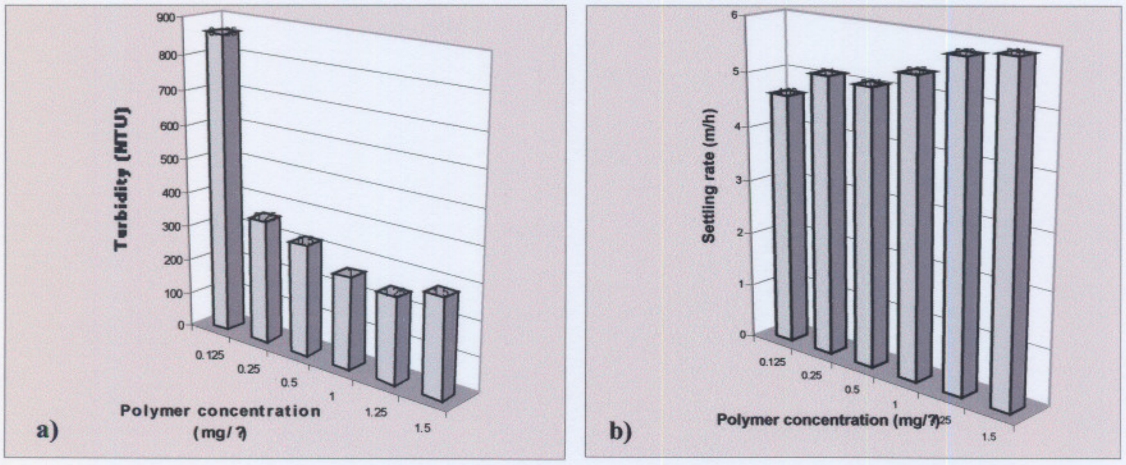


Figure 2: Illustration of the effect of polymer concentration on clarity of the overflow water (a) and sludge settling rate (b) for stage 1

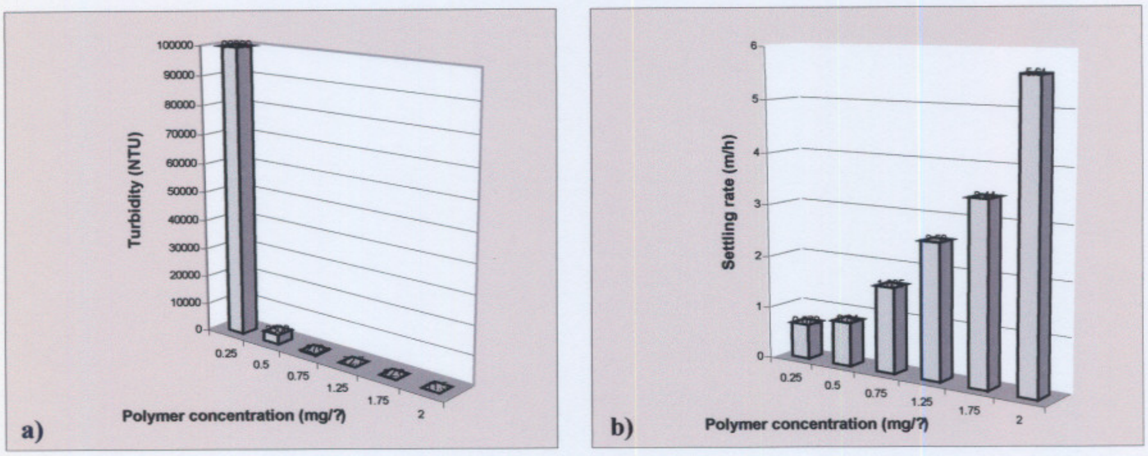


Figure 3: Illustration of the effect of polymer concentration on clarity of the overflow water (a) and sludge settling rate (b) for stage 2

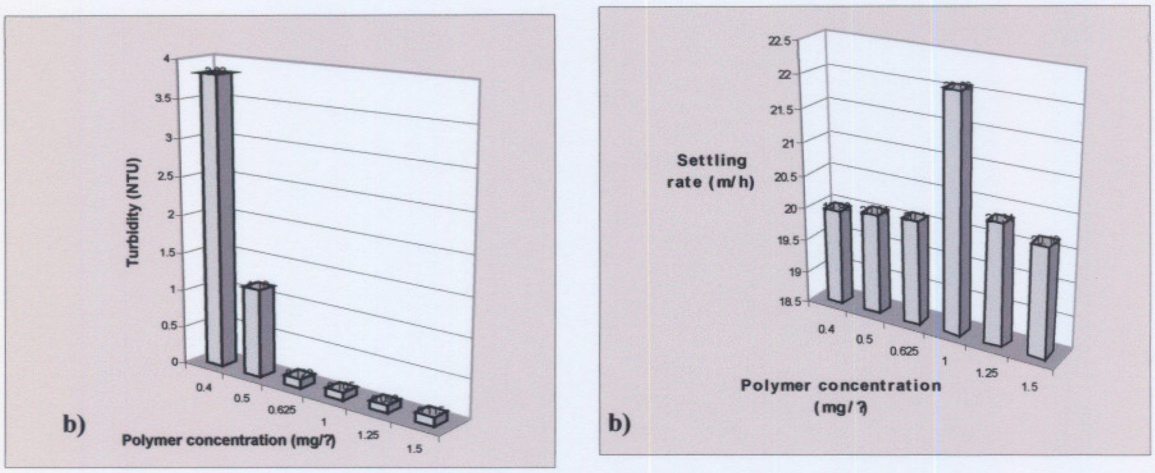


Figure 4: Illustration of the effect of polymer concentration on clarity of the overflow water (a) and sludge settling rate (b) for stage 3

The turbidity of the clarified effluents are a parameter that are very sensitive to the mode of operation of the limestone-, lime- and CO_2-treatment units (i.e. chemicals used, overflow rate and retention time and sludge recirculation rate) and can be manipulated by the use of suitable coagulant or flocculant aids.

A reasonable relationship exists between turbidity and suspended solids for the settled secondary effluents from this process. From Figures 2, 3 and 4, it can be noted that:

- With increasing polymer concentration, the color of the overflow water from the settled secondary effluent in the first and second stage of the process, changed sequentially from dark brown to transparent. For the third stage of the process, the very fine $CaCO_3$ particles settled immediately after polymer addition and the overflow water had an almost perfect clarity of 3.83 NTU (turbidity) within 1 minute's time.
- For stages 1 and 3, the settling rate of the sludges remained fairly constant with increasing polymer concentration. For stage 3, a linear increase in settling rate resulted from increasing polymer concentration.

3.4 Economic feasibility

Neutralisation and sulphate removal from water to a level where the water quality is suitable for re-use in the process or discharge into the sewerage network, can be achieved with limestone ($CaCO_3$) and slaked lime ($Ca(OH)_2$). It can be noted from Table IX that the addition of polymers to the effluents of the various stages of the process, to ensure fast enough settling of the sludges, are inevitable.

Table IX. **Effect of polymer concentration on the settling rate of the sludges produced in the three consecutive stages of the treatment process**

Stage 1: Limestone neutralisation							
Polymer concentration (mg/ℓ)	0.000	0.125	0.250	0.500	1.000	1.250	1.500
Settling rate (m/h)	1.30	4.62	5.10	5.04	5.37	5.79	5.91
Cost (c/m^3)	0.00	0.28	0.55	1.10	2.20	2.75	3.30
Stage 2: Gypsum crystallisation with high lime treatment							
Polymer concentration (mg/ℓ)	0.000	0.250	0.500	0.750	1.250	1.750	2.000
Settling rate (m/h)	0.21	0.67	0.84	1.64	2.58	3.44	5.61
Cost (c/m^3)	0.00	0.55	1.10	1.65	2.75	3.85	4.40
Stage 3: $CaCO_3$ precipitation with CO_2 treatment							
Polymer concentration (mg/ℓ)	0.000	0.400	0.500	0.625	1.000	1.250	1.500
Settling rate (m/h)	0.00	19.98	20.04	20.10	22.08	20.34	20.16
Cost (c/m^3)	0.00	4.13	4.35	4.63	5.45	6.00	6.55

The limestone/lime neutralisation process will be overall more cost effective, because of the higher settling rates that will not only save on capital cost, as much smaller clarifiers are needed for sludge settling, but will also produce overflow waters from secondary effluents of a much higher quality in terms of clarity. Clarity improvement of 63, 92 and 99% can be achieved respectively for the overflow water of the secondary settling sludges in the process by the addition of very small quantities of polymeric substances to the sludges (see Tables VI, VII and VIII). Settling of these sludges were improved by 74, 90 and 100% in the three consecutive stages of the process (see Table IX).

4 CONCLUSIONS

- Due to the very low concentration of Al in the treated water of the process after each stage of treatment, it can be concluded that the polymers used for coagulation/flocculation had no effect on the chemical composition of the treated water after limestone and lime treatment for neutralisation and partial sulphate removal.
- A contact time of 1 minute between polymer addition for coagulation/flocculation reasons was found to be sufficient for effective settling of the secondary effluents of the three consecutive stages in the process.
- The settling rates of the secondary sludges in the process were increased by 74.2, 91.9 and 100% respectively for the three stages by the addition of PAC6 as coagulant to the third stage and 3095 as flocculant to all three stages of the process.
- Clarity of the secondary effluents were improved by almost 100% for all three stages of the process, as the water clarity before polymer addition for the various stages were >99 999.
- Depending on the required level of sludge settling and effluent clarity of the treated water after each stage in the process, large capital cost savings can be achieved by the addition of a specific amount of flocculant to the first two stages and a coagulant and flocculant to the third stage of the process.

5 REFERENCES

1. Benefield, L.D., Judkins, J.F. and Weand, B.L. *Process Chemistry for water and wastewater treatment.* United States. Prentice-Hall, Inc., Engelwood Cliffs, N.J. 1982. Pp. 510.
2. Pontius, F.W. *Water quality and treatment.* United States. McGraw-Hill, Inc. 4th ed. 1990. Pp. 1 195.
3. APHA, *Standard methods for the examination of water and wastewater treatment.* 12th ed. American Public Health Association. New York, McGraw-Hill, 1985.

4. Metcalf & Eddy. *Wastewater Engineering: Treatment, disposal and re-use.* United States. McGraw-Hill, Inc. 3rd ed. 1991. Pp.1 334.

PAPER 3: Geldenhuys, A.J., Maree, J.P., Strobos, G., Smit, N. and Buthelezi, B. Neutralisation and partial sulphate removal of acid leachate in a heavy minerals plant with limestone and lime, *Proceedings 6th International Conference on Acid Rock Drainage*, 12–18 July 2003, Cairns, Australia.

Ticor SA produces zircon, rutile and ilmenite from mining sand dunes on the Natal coast. The plant produces 85 m^3/h of acid water that needs to be treated for re-use in the metallurgical process leaching circuits. A portion of the process water has to be blended with the Empangeni sewage system (discharge water) to prevent build-up of soluble ions. The stream is required to have a sulphate content of less than 2 200 mg/ℓ.

Initially, during 2001, a combined limestone/lime treatment plant was designed, constructed and commissioned to treat acid water, resulting from the process. It comprised a primary neutralisation stage utilising limestone and a secondary neutralisation stage employing lime. With this combined process, the sulphate concentration in the water was lowered to 1 150 mg/ℓ. During an attempt to optimise the process and further save on alkali cost, the lime treatment stage was abandoned and only limestone utilised to neutralise the acid water (pH 6.5) and lower the sulphate concentration from 5 100 mg/ℓ to 2 200 mg/ℓ to comply with the above mentioned minimum requirements from the local municipality.

During this investigation, the following findings were made:

- ✓ Aeration of the acid water after the primary neutralisation stage resulted in CO_2 removal. Consequently lime was completely replaced by limestone for neutralisation of the acid water resulting from the process
- ✓ Sulphate concentration in the acid water was lowered from 5 100 mg/ℓ to 2 200 mg/ℓ to render the water acceptable for re-use in the plant or for discharge into the local sewerage system
- ✓ The quality of the treated water could be controlled and any build-up of ions in the water avoided
- ✓ Savings of R1M per annum were achieved by replacing lime with limestone
- ✓ *Paper has been presented as a poster by A J Geldenhuys at the 6th International Conference on Acid Rock Drainage. (See Poster 2 in Appendix A).*

Neutralisation and Partial Sulfate Removal of Acid Leachate in a Heavy Minerals Processing Plant With Limestone and Lime

A J Geldenhuys[1], J P Maree[1], G Strobos[1], N Smit[2] and B Buthelezi[2]

ABSTRACT

In mining and processing operations where minerals, high in pyrite and low in calcite/dolomite are processed, acid is generated, which needs to be neutralised. Ticor at Empangeni in South Africa (SA) produces rutile (TiO_2), leucoxene (TiO_2 plus iron compounds), titanium (Ti), zircon (Zi) and ilmenite (TiO_2 plus iron compounds). Neutralisation is required in the processing plant where acid is leached into the wash water. This water needs to be treated to a quality suitable for re-use in the metallurgical process or to a higher quality to make it suitable for discharge into the Empangeni sewage system (SA). For re-use the water needs to be neutral and under-saturated with respect to gypsum while for discharge into the sewage system the sulfate concentration needs to be reduced to less than 500 mg/L (as SO_4). Acid mine water is generally neutralised with lime. Disadvantages associated with lime are the costs and maintenance of the slaking equipment as well as hazards, associated with handling of the alkali. The cost of powdered limestone ($CaCO_3$) in South Africa, a by-product, is 50 - 60 per cent cheaper than lime.

A technology has been developed where limestone is used for neutralisation of acid mine water instead of lime. This development includes:

- **Limestone handling and dosing system**. A novel, robust system has been developed where waste $CaCO_3$ from the paper industry is slurried to a constant density. A full-scale plant was constructed to evaluate its performance (Figure 4). The dosing system consists of an inclined slab onto which the limestone is stored and from where it is slurried into a make-up tank. The density of the slurry in the make-up tank is controlled via a loadcell that measures the weight of the tank (operated at constant volume) and activates/deactivates the spray of the recycle slurry onto the slab.
- **Integrated limestone neutralisation/lime treatment process**. In this process powdered $CaCO_3$ is used for neutralisation and partial sulfate removal of acid leached from the coal washing plant. The sulfate concentration can be further reduced to below the saturation level of gypsum (ie 1200 mg/L) through gypsum crystallisation by means of lime treatment, resulting in metal precipitation (eg Fe^{3+} and Al^{3+}).
- **CO_2-treatment for $CaCO_3$ precipitation**. The pH of the lime treated water can be adjusted to pH levels of 8.5 and lower using CO_2. The CO_2, generated during limestone neutralisation (Equation 2), can be captured and used in this stage of the process.

The first two stages (limestone- and lime neutralisation) of this technology have been implemented on full-scale at Ticor to treat the effluent of the process. The constructed plant is 80 m^3/hr and differs from coal processing plants by way of not containing Fe(II) and Fe(III) in the water. The CO_2-treatment stage (Stage 3) will soon be implemented at IHM as part of a program to optimise the technology for maximum benefits.

PAPER SUMMARY

The limestone handling and dosing system (see Figure 1), which is the first technology of its kind, was built on full-scale and has a capacity of 10 Mℓ/day. It consists of the following units:

- Concrete slab with a slope of seven degrees onto which the $CaCO_3$ powder is dumped and stored. The $CaCO_3$ powder is slurried with a water jet and collected in a slurry tank through gravity flow.
- Slurry tank with stirrer which acts as a mixing chamber for the acid water and $CaCO_3$ as well as recovery of CO_2- gas.
- Ball valve in the slurry tank to maintain the water level at a specific height in the tank by dosing tap or clarified water.
- $CaCO_3$-recycle slurry pump which withdraws some of the slurried $CaCO_3$ of higher density from the slurry tank or clear water through a water jet onto the $CaCO_3$ dump to keep the $CaCO_3$ concentration at a constant level. The slurried $CaCO_3$ is returned by gravity via the sloped concrete slab back to the slurry tank. The $CaCO_3$ concentration is controlled by a density meter, developed by Environmentek, CSIR (SA). The density meter measures the mass of a fixed slurry volume on a continuous basis by means of a loadcell.
- Transfer pump, feeding slurried $CaCO_3$ into the limestone make-up tank.

FIG 1 - Limestone handling and dosing system.

The neutralisation plant consists of the following stages (Figures 1 and 2):

- limestone neutralisation;
- lime treatment and gypsum crystallisation;
- filter press; and
- CO_2-treatment for $CaCO_3$-precipitation.

In the neutralisation process (Figure 4), effluent from the Hot Acid Leach Plant (HAL) is fed to the $CaCO_3$-neutralisation stage (C1) from where the water flow by gravity to the lime treatment/gypsum crystallisation stage (C2). The overflow of C2 is running via a surge tank to the filter press, which is fed on a batch basis. The effluent of the filter press is discharged into a second surge tank from where water is pumped to the CO_2-treatment stage (C3). Powdered $CaCO_3$ and slaked lime are fed via ring-lines to C1 and C2 respectively to control the pH at five in C1 and between nine and 12 in C2. The $CaCO_3$ concentration in the ring-line is kept at 10 g $CaCO_3$/100 ml slurry by controlling its density. The relationship between $CaCO_3$-concentration and density is given by Equation 1. The plant has been designed for the CO_2, produced in C1, to be

---

1. CSIR, Water, Environment and Forestry Technology, PO Box 395, Pretoria 0001, South Africa.
2. Ticor, PO Box 20010, Empangeni 3880, South Africa.

FIG 2 - Photo of $CaCO_3$ -neutralisation (right column, C1) and lime treatment/gypsum crystallisation (left column, C2) stages.

FIG 3 - Photo of CO_2 -treatment stage (C3).

transported with a compressor to C3 for adjusting the pH to 8.5 or lower. $CaCO_3$ that is produced during this stage can then be recycled back to the neutralisation stage (C1) in the process.

$$CaCO_3 \text{ - concentration (kg/L)} = -10.34X^2 + 99.30X - 88.88 \quad (1)$$

where:

X = density in kg/L.

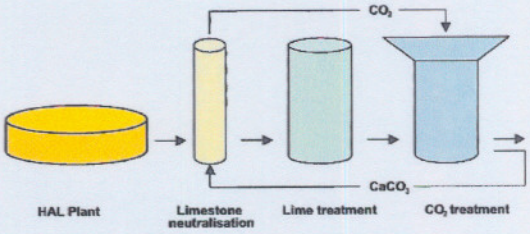


FIG 4 - Process flow diagram of combined limestone/lime neutralisation process.

DISCUSSION OF RESULTS ON FULL-SCALE PLANT

The quality of the acid feed water and after each stage of treatment is listed in Table 1.

TABLE 1

Water qualities of the acid feed water and treated water after each treatment stage.

Parameter	Acid feed water	Limestone	Lime
pH	1.95	6.03	12.10
SO_4^{2-} (mg/L)	4270	2353	1145
Acidity (mg/L)	5350	-	-
Alkalinity (mg/L)	-	50	940

From Table 1, it is evident that limestone ($CaCO_3$) can be used effectively in the integrated process for neutralisation of acid water (HRT = one hour). The pH of the water was raised from 1.95 to 6.03 in the neutralisation reactor and is given by the following equation:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4.2H_2O + CO_2 + H_2O \quad (2)$$

The stability of the treated water with respect to calcium carbonate is determined by the pH, calcium and alkalinity values of the treated water. The alkalinity of the treated water was 50 mg/R (as $CaCO_3$) owing to the escape of CO_2 from the solution, which can be ascribed to the following reaction:

$$H_2CO_3 \rightarrow H_2O + CO_2 \quad (3)$$

The sulfate concentration in the water has been decreased from 4270 to 2353 mg/L through limestone addition, which is illustrated by Equation 2. After lime treatment the sulfate concentration of the neutralised water has further been reduced to 1145 mg/L. Because of lime addition, the alkalinity of the water has been increased to 940 mg/L at a high pH of 12.10. The plant is in the process of being optimised by adjusting the high pH water to neutral levels by means of CO_2-bubbling. The CO_2 that has being generated during the limestone neutralisation stage can be captured and used in this last stage of the process to adjust the pH. The optimisation part of this technology has been demonstrated on laboratory and on pilot scale by Geldenhuys, Maree, De Beer and Hlabela (2001).

CONCLUDING REMARKS

The following findings were made:

Limestone handling and dosing system

- Limestone can be slurried to a constant density (or concentration) with the limestone handling and dosing system.
- The operation of the limestone handling and dosing system is simple and requires little maintenance.

Neutralisation of acid leachate from the waste dump and in the coal processing plant

- The water quality improved significantly: the pH increased from 1.95 to 12.10; the acidity of 5350 mg/L was replaced with an alkalinity of 940 mg/L (as $CaCO_3$); the sulfate concentration decreased from 4270 mg/L to 1145 mg/L (as SO_4^{2-}).
- Lime was completely replaced by powdered limestone for neutralising the acid mine water.
- In the coal processing plant, the finely suspended $CaCO_3$-particles only dissolve when acid is leached into the water. The suspended $CaCO_3$-concentration in the coal processing plant circuit exceeded 500 mg/L. The fine $CaCO_3$-particles tended to remain in suspension in the thickening stage, which allows recirculation of unused $CaCO_3$ instead of it being discharged with the waste coal.
- The alkali cost is reduced by 55 per cent for neutralisation of the acid leachate.

Sulfate removal from neutralised water through gypsum crystallisation

- The sulfate concentration in the neutralised water has been reduced to below the saturation level of gypsum (ie 1200 mg/L).
- The treated water (high pH) is reused in the process. The pH of the treated water can however be adjusted from high levels (>12) to pH values of 8.50 and below. In order to do so, CO_2, generated during the limestone neutralisation stage, can be used.

REFERENCES

Geldenhuys, A J, Maree, J P, De Beer, M and Hlabela, P, 2001. An integrated limestone/lime process for partial sulphate removal, in *Proceedings Conference on Environmentally Responsible Mining in Southern Africa*, pp 7A14-7A27 (Chamber of Mines of South Africa: Johannesburg).

PAPER 4: Geldenhuys, A.J., Maree, J.P., Fourie, W.J., Bladergroen, B.J. and Tjati, M. Acid mine drainage treated electrolytically for recovery of hydrogen, iron(II) oxidation and sulphur production, *Proceedings 8^{th} International Congress on Mine Water and the Environment*, 19–22 October 2003, Johannesburg, South Africa.

Previously, sugar and ethanol were utilised as energy and carbon sources for sulphate reducing bacteria in the Biological Sulphate Removal Technology, developed by CSIR: Environmentek. With recent increases in the price of ethanol its use was no longer cost-effective and work was initiated aimed at finding an alternative energy source.

Hydrogen was successfully used in the Biological Sulphate Removal Technology as replacement for ethanol and to act as an energy source. The cost of hydrogen purchased in bulk amounts to ca.R25.00/kg while it can be generated electrolytically at a cost of R3.89/kg. This can be achieved by passing an electric current through a series of stainless steel electrodes (type 316), placed in a solution of 3% m/m KOH as electrolyte. The alkaline solution can be replaced by an acidic solution, i.e. acid mine water, resulting in H_2 costing R9.55/kg. Although the cost of generating hydrogen from an acidic solution is significantly higher than from 3% KOH, it can still be done at 38% of the cost of purchasing hydrogen.

The main advantage of generating hydrogen electrolytically, using an acidic medium, is that the oxidation of iron(II) to iron(III) take place in the acid mine water. This is a prerequisite for neutralisation of acid water, containing a high concentration of iron(II), in order to minimise alkali usage. If iron(II) in the water is not oxidised, it will form acid further downstream when passing through the process unchanged.

After acid mine water is treated biologically to remove the sulphates in the water to below 200 mg/ℓ, unwanted and toxic hydrogen sulphide gas is produced as a waste product. By contacting this waste gas stream with a part of the iron(III)-rich stream after electrolytic oxidation, elemental sulphur, a valuable end-product, will be produced.

This paper was peer-reviewed and presented orally by A J Geldenhuys at the 8^{th} International Congress on Mine Water and the Environment (see Appendix B for confirmation on peer-reviewal and editing of the paper by the conference planner for the

IMWA Conference, Mrs Van Niekerk). The paper was also been submitted for publication in Water SA (see Appendix B for confirmation)

Acid mine drainage treated electrolytically for recovery of hydrogen, iron(II) oxidation and sulphur production

A J Geldenhuys, J P Maree, W J Fourie, J J Smit, B J Bladergroen And M Tjati
CSIR, Division of Water, Environment and Forestry Technology,
PO Box 395, Pretoria, 0001, South Africa
Tel: +27 12 841 4178, Fax: +27 12 841 2506,
E-mail: ajgeldenhuys@csir.co.za

KEYWORDS: electrolysis, acid mine drainage (AMD), hydrogen production, electrolytical iron(II) oxidation, sulphur production

ABSTRACT

Sulphate rich waters such as acid mine drainage (AMD) contribute directly to the mineralisation and degradation of receiving waters, which pose a serious environmental threat. Several sulphate removal technologies are in place, amongst which the biological sulphate removal technology. For the treatment of these effluents, expensive organic material (e.g. ethanol or sugar) is used as the energy source. The use of hydrogen as an energy source presents a cheaper alternative for sulphate removal. Hydrogen can be generated at the cathode in an electrolytic cell by treating AMD electrolytically. While generating hydrogen electrolytically, other benefits arised, i.e. the oxidation of iron(II) to iron(III) at the anode and the conversion of hydrogen sulphide gas to elemental sulphur.

Stainless Steel (type 304) plate has been used effectively as electrode material in AMD as electrolyte for generating hydrogen in a cost effective way and at the same time oxidising iron(II) to iron(III). When relatively large quantities of hydrogen is needed for the sulphate reducing bacteria (SRB), nickel (Ni) can be used as electrode material in a KOH (3% mass) solution as electrolyte.

The reason for iron(II) to be oxidised to iron(II) is that it forms acid downstream when passing through the process unchanged. Toxicity due to increased levels of sulphide and un-ionised hydrogen sulphide will not only lead to diminished process performance of the SRB but will also become a health and safety hazard.

1. INTRODUCTION

During industrial effluent treatment, it is often found that pH is the single most important parameter, as low pH waters (below 5.5) can be toxic to plant and fish life. Industrial effluents (acid mine drainage) rich in sulphate, acid and metals are produced when pyrite is oxidised due to exposure to the atmosphere, e.g. in the coal mining industry. Barnes[1] indicated that acid is produced biologically when pyrites in coal waste are oxidised, according to the following reactions:

$$4FeS_2 + 7O_2 + 4H_2O \rightarrow 4FeSO_4 + 4H_2SO_4$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe2(SO_4)_3 + 2H_2O$$

$$2Fe_2(SO_4)_3 + 12H_2O \rightarrow 4Fe(OH)_3 + 6H_2SO_4$$

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4 \qquad [1]$$

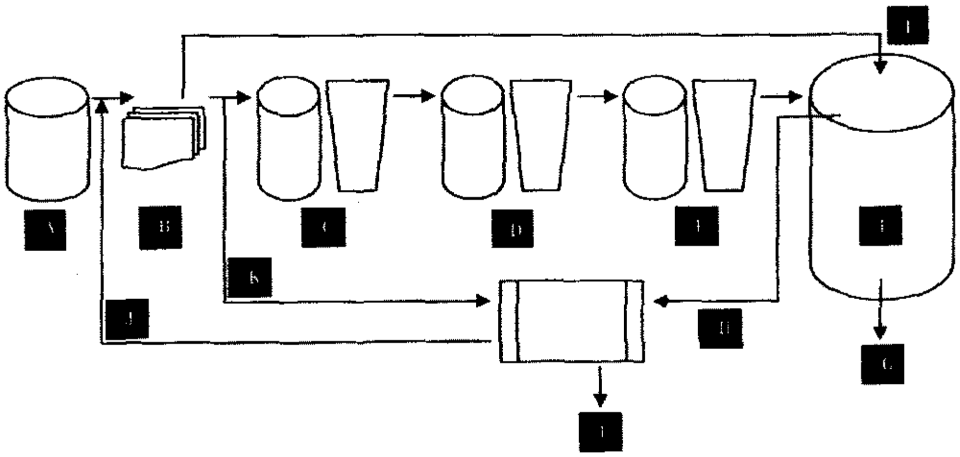
The acid water is formed as a result of bacterial oxidation of pyrites exposed to oxygen and water after or during the mining process. These acid mine waters dissolve high concentrations of metals and can have pH values as low as 1.6. Therefore, it requires treatment prior to discharge into public watercourses.

Assessments of pollution in the Olifants River and its associated surface and geo-hydrological drainage systems, monitored continuously since 1990, identified sulphate, amongst other pollutants, as a consequence of coal mining. Pressure from the legislator is mounting to demand from polluters to enforce the National Water Act to treat acid mine drainage and in particular to reduce sulphate concentrations to a level acceptable to water users. This tendency is experienced globally and is likely to be reflected in a commitment for continuous improvement that companies with ISO 14001 certification will be required to make.

These low pH effluents, rich in sulphate and metals can be treated with the *Integrated Limestone/Lime Process* which was developed by the CSIR. During this treatment, the effluent can be fully neutralised and sulphates can be reduced to the saturation level of gypsum, i.e. 1 200 mg/ℓ. Prior to this process, the iron(II) content in the water should be oxidised to iron(III) before neutralisation of the acid water with limestone. Oxidation will otherwise occur downstream of the neutralisation plant with the formation of acid. Oxidation of the iron(II) also influences the neutralisation rate of AMD greatly, as a $Fe(OH)_3$ coating is formed onto the limestone particles and prevents its dissolution. Magnesium can also be fully removed from the effluent. To further remove sulphates in the effluent to levels lower than 200 mg/ℓ, the Biological Sulphate Removal Process, also developed by CSIR, can be by utilised.

During the Biological Sulphate Removal Process, hydrogen sulphide gas is produced as a by-product that can be completely converted to elemental sulphur. Normally, in bioreactors fed with an influent containing methanol, sulphite, and sulphate, inhibition may result from high concentrations of substrates or possible intermediates and products such as acetate and sulphide. Sulphate reduction results in production of hydrogen sulphide gas (H_2S) and needs to be removed for reasons of health and safety. H_2S become becomes progressively more dangerous as the level of H_2S incurs above toxic limits (70 ppm), becoming lethal at 600 ppm.

The two above-mentioned CSIR processes, combined with the electrolytic process and sulphur production process, as discussed in this paper, are illustrated in Figure 1.



A	Acid mine drainage (AMD) as effluent	*pH 1.6*	*8 400 mg/ℓ SO_4*	*310 mg/ℓ Mg*	*4 245 mg/ℓ Fe(II)*
B	Electrolytic iron(II) oxidation	*pH 1.6*	*8 400 mg/ℓ SO_4*	*310 mg/ℓ Mg*	*279 mg/ℓ Fe(II)*
C	Limestone neutralisation	*pH 6.8*	*1 900 mg/ℓ SO_4*	*290 mg/ℓ Mg*	-
D	Gypsum crystallisation (lime treated)	*pH 13.8*	*1 180 mg/ℓ SO_4*	*0 mg/ℓ Mg*	-
E	CO_2 treatment for $CaCO_3$ precipitation	*pH 8.5*	*1 250 mg/ℓ SO_4*	*0 mg/ℓ Mg*	-
F	Biological Sulphate Removal				
G	Biologically treated water	*pH 8.0*	*< 200 mg/ℓ SO_4*	-	-
H	H_2S gas stripped				
I	H_2S conversion to elemental sulphur				
J	Iron(II) rich water				
K	Iron(III) rich water				
L	Hydrogen gas				

Figure 1. Schematic diagram of combined process of all technologies, as developed by CSIR

The use of hydrogen as energy source in the biological sulphate removal technology has been shown to be successful by several researchers[2,3] and it has been shown that sulphate reducing bacteria has the advantage over methanogenic bacteria when hydrogen is used[4]. Therefore, an alternative option to the use of ethanol or sugar as energy source is the exploitation of the AMD as source of hydrogen for bacterial proliferation. In an earlier attempt of the CSIR, hydrogen was found to be a good source of energy to sulphate reducing bacteria for sulphate removal. A removal rate of 4.42 g SO_4/ℓ.day was achieved at a reactor pH of 7.5 – 8.

Hydrogen is considered to be an ideal future energy carrier because it is a potential energy source and pollution free. The benefits of using hydrogen as energy source to the biological process are:

- Hydrogen can be produced electrolytically to be used as energy source for anaerobic bacteria in a biological sulphate removal process.
- By using hydrogen instead of sugar and ethanol as energy source to these bacteria, no residual organic material is left in the water that requires post-treatment.
- Resulted heat in the electrolytic cell can be utilised to raise the temperature to 30°C which is the optimum temperature for the anaerobic bacteria.

According to Prigent & Martin[5], one of the most promising methods for the production of hydrogen is water electrolysis. Catalyst-activated (platinum group metal oxide) electrodes can be used for e.g. water electrolysis in the presence of an aqueous alkaline electrolyte, or more generally in any electrolysis process operated in aqueous alkaline medium. These electrodes are more particularly adopted to be used as negative electrodes (cathodes) for hydrogen release; they can also be used as positive electrodes (anodes) for oxygen release.

Various catalytic materials for use as electrolytic cell anodes have been proposed. Stainless steel (Ssteel) and nickel plated steel anodes have been most commonly commercially used. Other anode materials which exclude noble metals have been proposed, but it appears that such materials do not improve the overall anode performance in terms of overvoltage savings, material costs and operating life since such prior art anodes have not been accepted to any significant degree. One reason nickel and nickel plated steel catalytic materials have been most commonly used for the electrolysis of water is because of their relatively low costs. Ovshinsky *et al.*[6] found that these materials are resistant to corrosion in hot concentrated caustic solutions and has one of the lowest over voltages among the non-noble metal materials for the oxygen evolution reaction.

The purpose of this investigation was to prove that hydrogen can be generated electrolytically from AMD to be utilised as an alternative energy source for sulphate reducing bacteria. The scope included (1) test work on different electrode/electrolyte combinations, and (2) other benefits that arose from the use of electrolysis to produce hydrogen, i.e. iron(II) oxidation and the conversion of hydrogen sulphide gas to elemental sulphur.

2. MATERIALS AND METHODS

2.1 FEED WATER

The following solutions were tested as electrolytic solutions for the different electrochemical systems: KOH (3% and 30% mass) and AMD as acidic effluent. The chemical composition of the AMD (originated from a Coal Mine near Witbank, Mpumalanga) is listed in Table I. The KOH was a bank reagent from Saarchem.

Table I. Chemical composition of acid mine drainage (AMD)

Parameter	**Acid feed water**
pH	2.48
SO_4^{2-} (mg/ℓ)	9 150
Acidity (mg/ℓ)	10 100
Ca (mg/ℓ)	434
Mg (mg/ℓ)	301
Al (mg/ℓ)	556
Na (mg/ℓ)	22.8

2.2 PROGRAMME FOR BATCH STUDIES IN BEAKERS AND CONTINUOUS STUDIES ON PILOT SCALE

Batch studies were conducted in the laboratory by using various types of materials as electrodes, in the form of plate. In each set-up, the electrolytic solution was recycled and monitored on a 30 minute basis for pH, conductivity, acidity and iron(II) concentration. The electric current, potential and flow rate of gas evolving from the electrodes (anode and cathode) were monitored on the same basis. The weights of the electrodes (anode and cathode) were determined before and after each experiment. The same variables as for batch studies were measured during continuous studies. Parameters that were also varied and tested in order to evaluate additional benefits that resulted from generating hydrogen electrolytically, are current density, pH, iron(II) concentration, Mn concentration and amount of sulphur produced.

2.3 EQUIPMENT AND PROCEDURE

A complete cell with plate metal as electrodes and an *Ionac MA3475* anion selective membrane (nano-filtration membrane) as diaphragm, were used for laboratory scale testing (see Figure 2). The membrane was used to separate the electrodes (anode from cathode) to ensure no contamination of the hydrogen with oxygen, generated at the cathode and anode respectively. Mild steel (Fe), zink (Zn), nickel (Ni) and stainless steel (Ssteel) were used as electrode material. For laboratory tests, the electrodes were 1 dm^2 (10cmx10cm) each while for the pilot scale plant, the electrodes were scaled up by 30 times (70cmx40cm). Both the laboratory and pilot scale cell were constructed of Perspex frames that are bolted together and sealed off with rubber strips and silicon.

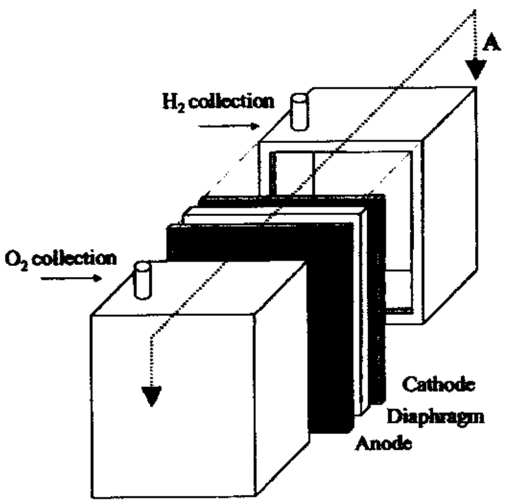
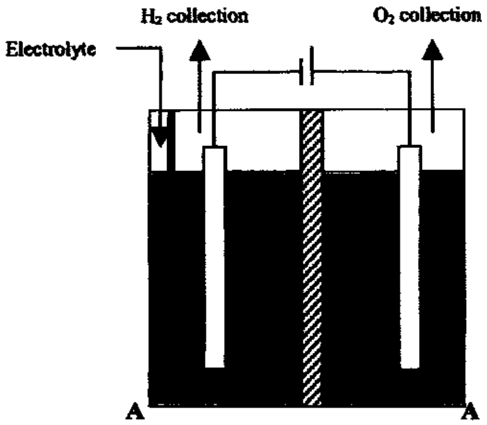


Figure 2. Illustration of electrolytic cell design for the dissociation of water



In each set-up for the laboratory studies, the electrolytic solution was 1.5 litres on both the cathode's and anode's side and was recycled through the electrolytic set-up for the duration of the experiment.

Six combinations of electrodes and electrolytes were grouped into three categories according to their expected outcome. In order to determine the electrochemical efficiency and stability of these combinations for hydrogen production, they were subjected to different analyses. Table II contains the six different electrolytic combinations that were tested.

Table II The six different electrolytic set-ups for testing

Electrode	**Fe plate**	**Zn plate**	**Ni plate**	**Ni plate**	**Ni plate**	**SSteel plate**
Electrolyte	AMD	AMD	KOH (30%)	KOH (3%)	AMD	AMD
Category	A		B		C	

A constant current was applied to the electrodes and the resulting potential between the electrodes, because of the resistance of the electrodes, was measured with 30-minute intervals between measurements. The variables listed in section 2.2 were all measured at these intervals.

2.4 ANALYTICAL

Samples were collected every 30 minutes for analysis. A Hewlett Packard power supply unit (0 - 60 V, 0 – 15 A) was linked to the cell set-up. A conductivity meter (WTW – LF318) was used for measuring conductivity while the power supply unit digitally displayed the electric current and cell potential. Schlumberger flow meters were used for measuring the amount of hydrogen and oxygen gas, generated at the cathodes and anodes respectively.

3. RESULTS AND DISCUSSION

3.1 ELECTROCHEMICAL PROPERTIES OF SIX DIFFERENT SYSTEMS

The volt-amperometric results for the six hydrogen production systems, as tested, are listed in Table III. The amount of hydrogen gas generated was determined on a pure basis (>99%), based on gas chromatographic results from the SABS where the gas samples were analysed for hydrogen purity.

Table III Volt-amperometric results of hydrogen production versus electrode consumption

Electrolytic Combination	**Category**	**$pH_{cathode}$**	**pH_{anode}**	**Current (ampere)**	**Potential (volt)**	**H_2 prod ($\ell.hr^{-1}$)**	**O_2 prod ($\ell.hr^{-1}$)**	**Electrode Consumption ($g.\ell^{-1}H_2$ prod)**	**Membrane**
Fe+AMD	A	3.26	3.26	5	32	2.15	√	2.43	Anionic
Zn+AMD	A	3.13	3.13	5	38	2.33	√	3.53	Anionic
* Ni+30%KOH	B	13.78	13.83	5	3.8	2.43	√	0.00	Anionic
* Ni+3%KOH	B	13.49	13.53	5	6	2.50	√	0.00	Anionic
Ni-plate+AMD	C	3.49	3.49	5	6	4.00	√	0.00	Anionic
Ssteel+AMD	C	2.44	2.45	2	4.3	1.68	√	0.00	Anionic
Ssteel+AMD	C	2.45	2.45	1	3.7	0.72	√	0.00	Anionic

* *KOH concentration not yet optimised for maximum hydrogen production*

In category A, hydrogen was produced at the cathode while the anode started to dissolve due to the anodic reaction. The main reactions are given by:

Anode: $Fe/Zn \rightarrow Fe^{2+}/Zn^{2+} + 2e^-$ [2]
Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ [3]

Although hydrogen was generated at a fairly high rate at the cathode by using Fe/Zn electrodes, the potential became increasingly high due to the decreasing surface area that resulted in a much higher resistance and electrode inhibition by electrode products. For every litre of hydrogen produced, 1.13 gram of Fe or 1.52 gram of Zn is needed. The costly effect of the sacrificial nature of Fe/Zn in AMD will be presented in section 3.4.

In category B, hydrogen was generated at the cathode while oxygen was generated at the anode. Not only was hydrogen produced at a higher rate and at an almost ten times smaller potential, but the electrodes were totally unaffected by the KOH used as electrolyte. The amount of gas production can be increased by increasing the current density. This will, however result in an increase in production cost as the voltage will also increase. The reactions at the anode and cathode can be given as:

Anode: $2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$ [4]
Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ [5]

After 72 hours of running the set-up continuously, the diaphragm developed micro-holes as a result of the caustic nature of the KOH (30%). This phenomenon however abated when a more diluted solution of KOH (3%) was used.

From the volt-amperometric results in category C, fairly high volumes of hydrogen can be generated, using AMD as electrolytic medium. The electrodes (Ni and Stainless Steel) and membrane were totally unaffected by the AMD that was used as electrolytic medium. It has been proved that the higher the current density, the higher is the amount of gas that is generated electrolytically. This also results in an increase in production cost as a result of higher voltages. The membrane was unaffected by the AMD.

3.2 EXTENT OF IRON(II) OXIDATION

One of the main benefits that resulted from the use of electrolysis in order to generate hydrogen economically, was the oxidation of iron(II) at the anode in using stainless steel as electrode material in AMD as electrolytic medium. This means that, while producing hydrogen, iron(II) oxidation as a pre-treatment stage to AMD can be applied. The half-cell reactions for the stainless steel/AMD cell are illustrated by:

Anode $2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$ [6]
Cathode $2H_3O^+ + 2e^- \rightarrow 2H_2 + H_2O$ [7]

Figure 3 illustrates the relevant reactions at the anode and cathode. The oxidation of iron(II) to Fe(III) can be proved by the transparent, ocher coloured AMD that was transformed to a dark brown solution. Precipitates that formed from these solutions, onto the anode, were analysed by means of Mössbauer spectroscopy. Signatures of β-FeOOH (akaganeite) were quite distinct in these spectra and appears to have evolved partially to α-FeOOH (goethite).

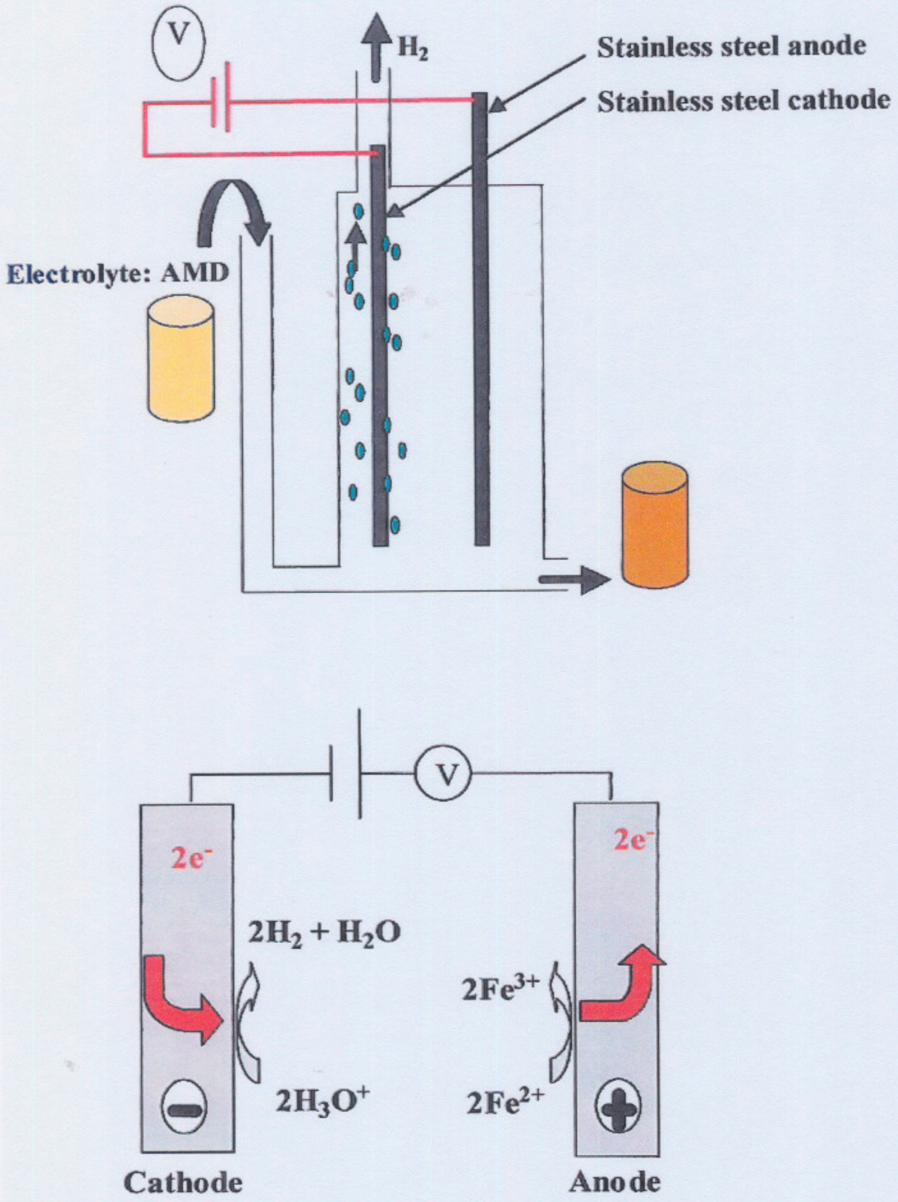


Figure 3. Illustration of electrolytic set-up: stainless steel electrodes in AMD

The oxidation of iron(II) is illustrated in Figure 4 over a period of 55 minutes.

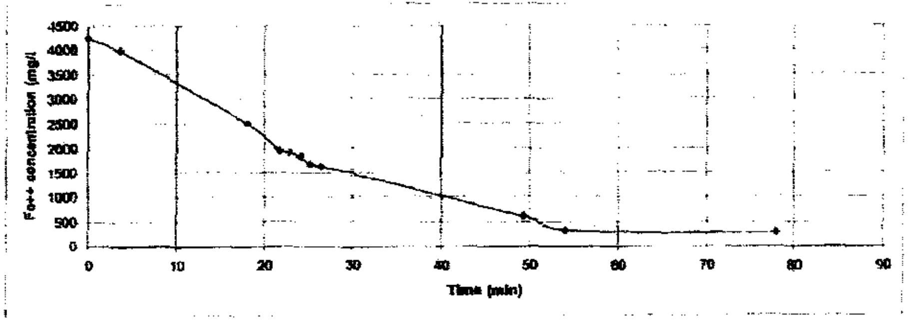


Figure 4. Iron(II) oxidation of AMD using stainless steel electrodes

In the CSIR's integrated limestone/lime process for neutralisation and partial sulphate removal[7], calcium carbonate is used to precipitate iron and sulphates. Due to the fact that iron(II) stays in solution up to a pH of 7, it is beneficial to convert iron(II) to iron(III), which will precipitate at pH 3. As stated earlier, iron(II) also readily coats the carbonate particles which slows down the neutralisation reaction significantly. Calcium carbonate can lift the pH of the solution to around 6 after which calcium oxide is dosed to increase the pH to above 10. As calcium carbonate is much cheaper than calcium oxide, the decreased amount of oxide needed with regards to the oxidised iron(II) incurs a cost benefit. From Figure 4 it is clear that the iron(II) in the water can be oxidised by 50% in 18 minutes' time while it will be fully oxidised after 53 minutes.

An increase in acidity (8 400 mg/ℓ to 11 200 mg/ℓ) resulted from oxidation of the iron(II) (4 245 mg/ℓ iron(II) to 279 mg/ℓ iron(II)). During oxidation, the pH also dropped from 3.10 to 2.65. This drop in pH and increase in acidity can be ascribed to the higher oxidation state of the iron ion (iron(II) to iron(III)). These results are illustrated in Table IV.

Table IV Electrolyte characteristics (stainless steel in AMD)

Time (hours)	pH	Iron(II) (mg/ℓ)	Acidity (mg/ℓ)
0	3.10	4 245	8 400
3	2.97	3 965	8 800
15	2.88	2 513	8 100
18	2.65	1 955	9 700
19	2.79	1 899	10 200
20	2.83	1 843	11 700
21	2.85	1 676	11 200
22	2.86	1 620	11 000
41	2.83	614	11 000
45	2.82	335	11 200
65	2.79	279	11 200

The effect of various other parameters on the rate of oxidation, as illustrated in Figures 5 to 8, have been tested.

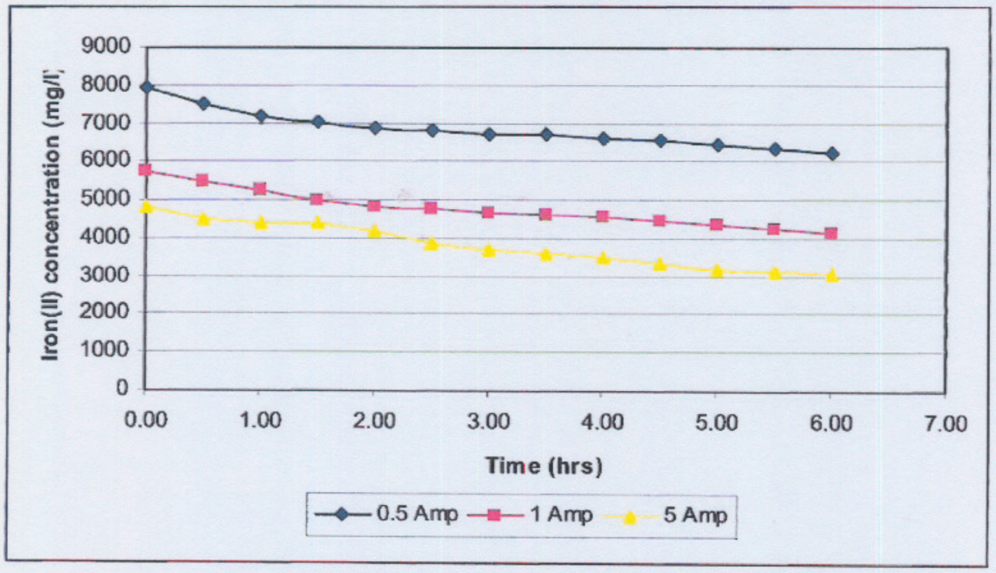


Figure 5. Effect of current density on the rate of iron(II) oxidation

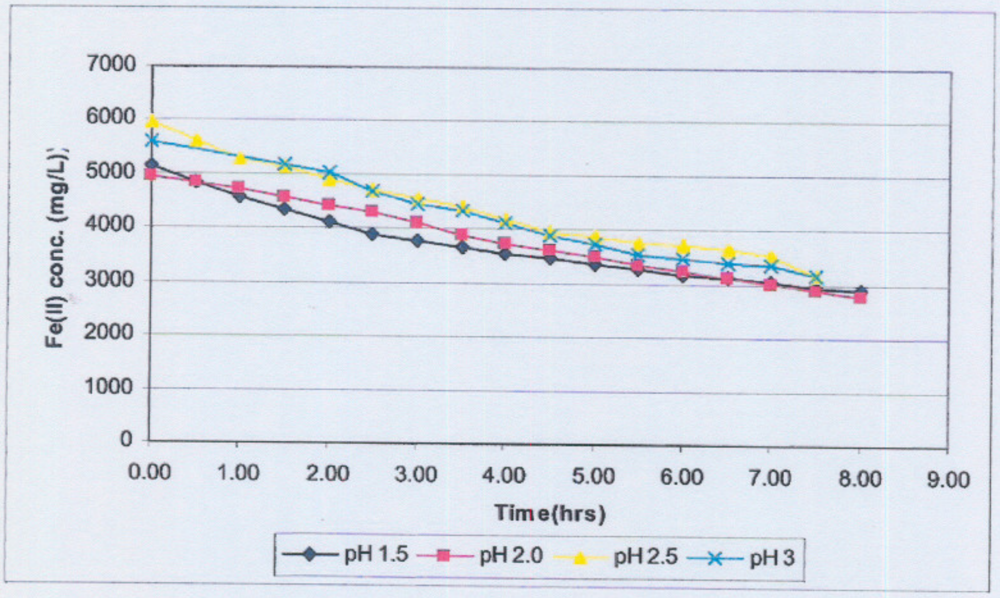


Figure 6. Effect of pH on the rate of iron(II) oxidation

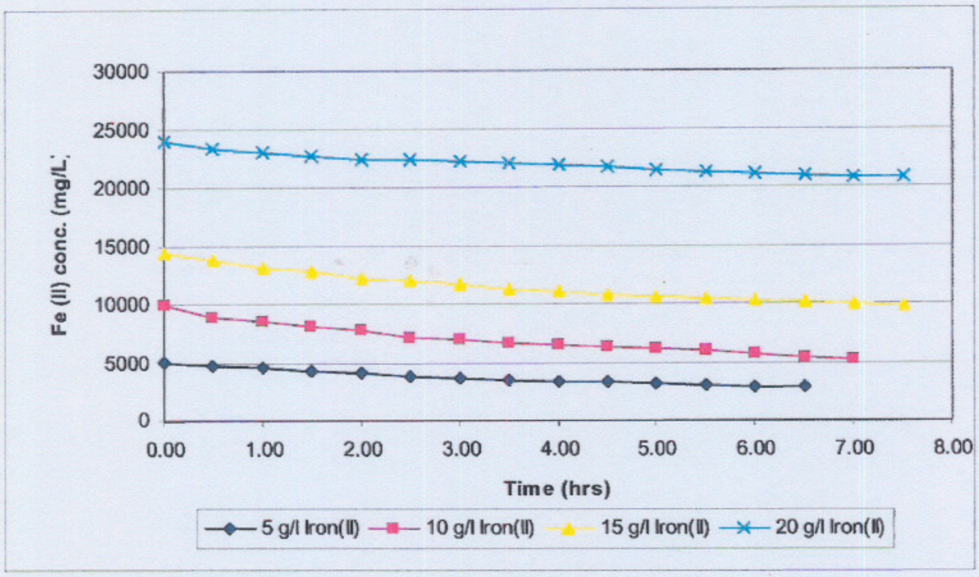


Figure 7. Effect of initial iron(II) concentration on the rate of iron(II) oxidation

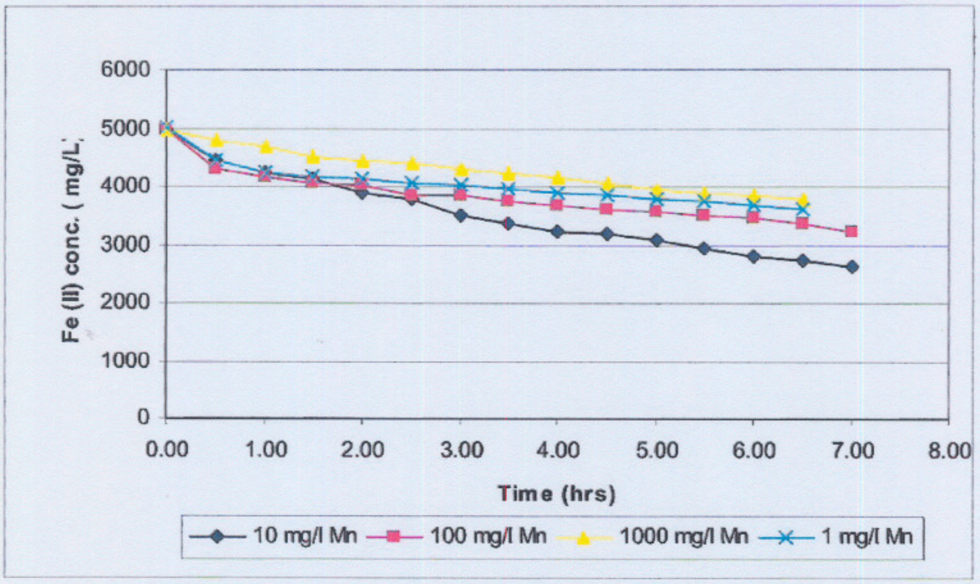


Figure 8. Effect of Mn concentration on the rate of iron(II) oxidation

From Figures 5 to 7, it is clear that the current density, pH and initial Iron(II) concentration had no effect on the rate of oxidation. The Mn concentration in the AMD as electrolytic solution, however reached an optimum at 10 g/ℓ of Mn, resulting in the highest oxidation rate for iron(II).

3.3 CONVERSION OF HYDROGEN SULPHIDE TO ELEMENTAL SULPHUR

The presence of sulphide, produced as a waste product after the Biological Sulphate Removal Process, may affect the sulphate reducing bacteria (SRB) in several ways. Because of its detrimental characteristics, it is forbidden to drain sulphide containing effluents to sewer pipes or surface waters. Since a number of physicochemical methods require large investment and operational costs, e.g. high temperatures, high pressures or special chemicals, the continuing search for more economical methods has led to partly investigating this issue of purifying H_2S.

The oxidation of the iron(II)-rich effluent (AMD) as a pre-treatment stage prior to limestone/lime neutralisation, produced an iron(III)-rich water that can be reduced back to iron(II) by contacting it with the waste product, H_2S of the biologically stage, as illustrated by reactions 8 and 9. The result of reactions 6 and 7, combined with reaction 8, proves the production of sulphur from H_2S gas and illustrated in reaction 9.

$$\begin{array}{ll} H_2S + 2Fe^{3+} \rightarrow S + 2Fe^{2+} + 2H^+ & [8] \\ 2Fe^{2+} + 2H_2O \rightarrow 2Fe^{3+} + H_2 + 2OH^- & \\ \hline H_2S \rightarrow S + H_2 & [9] \end{array}$$

A major advantage of this new process is that a potentially valuable end-product is produced without large cost implications. No additional energy, e.g. pressure or temperature, needs to be applied. The produced iron(II)-rich water can now be recycled back to the oxidation stage for re-use in the production of hydrogen. During an experiment, it has been found that at a specific pH of 2.5, the maximum amount of sulphur can be produced from the H_2S gas, and is illustrated in Photo 1. Table V contains the values for the amount of sulphur, produced per litre of iron(III)-rich water, when contacted with the stripped H_2S gas.

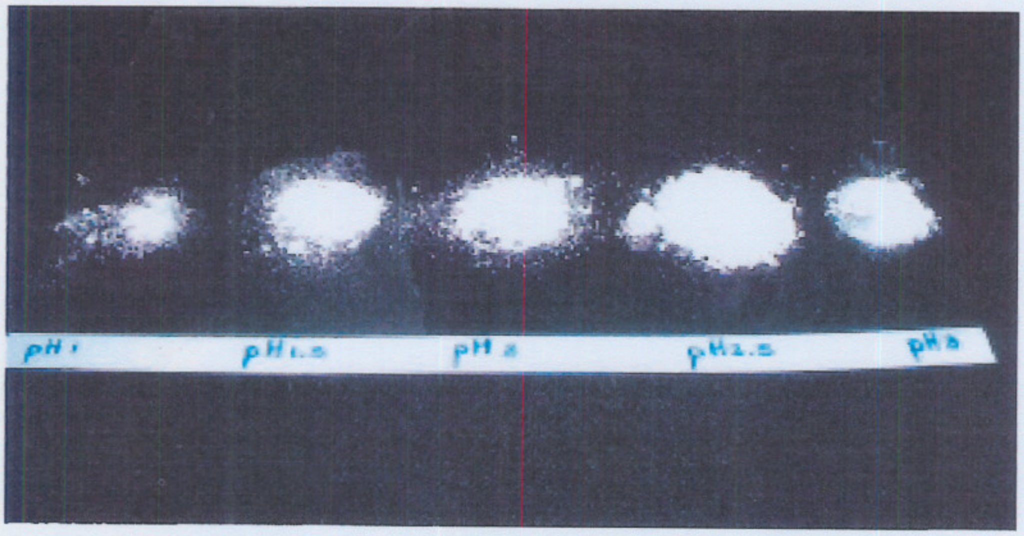


Photo 1 Effect of pH on the amount of sulphur produced when contacting iron(III)-rich water with stripped H_2S gas

Table V Amount of sulphur, produced per litre of iron(III)-rich water, when contacted with the stripped H_2S gas

pH	1.0	1.5	2.0	2.5	3.0
Mass S produced (g)	0.014	0.122	0.217	1.565	0.089

3.4 COST ANALYSIS

No mass lost occurred when stainless steel (Ssteel) electrodes were used, proving that the electrodes are resistant to corrosion. With AMD (which is a waste product) served as electrolyte, the iron content in the AMD served as a reducing agent and therefore limited amount of oxygen was produced. Stainless steel in AMD as electrolytic medium was found to be the cheapest way of generating hydrogen electrolytically and was therefore used as benchmark to calculate the cost efficiency of the other possible electrolytic set-ups. The electrolytic production cost of hydrogen is mainly influenced by the voltage in the electrolytic cell which is directly related to the resistance in the cell set-up, and the cost of electricity. The costing values are listed in Table VI.

Table VI Electrolytic hydrogen production cost

Electrode/Electrolyte	**Cost of H_2 generated (R/kg)**	**Percentage of H_2 cost (Ssteel plate as 100)**
H_2 bought commercially	25.00	207
Fe plate / AMD	138.84	1 159
Zn plate / AMD	151.94	1 268
Ni plate / KOH (30%)	14.57	122
Ni plate / KOH (3%)	22.39	187
Ni plate / AMD (5Amp)	21.20	177
Ssteel plate / AMD (2Amp)	11.98	100
Ssteel plate / AMD (1Amp)	11.98	100

From the cost analysis, as listed in Table V, it can be noted that iron(II) oxidation is an excellent benefit added to the electrolytic production of hydrogen. It will however not produce enough hydrogen as energy source to the sulphate reducing bacteria to remove all the sulphates in the water that needs to be treated biologically. For example, an AMD stream containing 4 580 mg/ℓ iron(II) and 9 150 mg/ℓ SO_4^{-2} (see Table I) would only be able to deliver 0.08 mole/ℓ of hydrogen which is only enough bacterial energy to reduce 2 000 mg/ℓ SO_4^{-2}. The combination of nickel (Ni) electrodes in an electrolytic medium of KOH (30%) will therefore be an economically alternative way of producing extra hydrogen electrolytically to remove sulphate concentrations higher than 2 000 mg/ℓ.

4. CONCLUSIONS

- Hydrogen can be produced electrolytically, 52% cheaper than buying it in bulk commercially. Stainless steel electrodes in acid mine drainage as electrolytic medium were found to be the most cost effective way to generate hydrogen electrolytically. The use of a membrane has the advance that the purity of this hydrogen will be of such a standard that it can be used as energy source to sulphate reducing bacteria in a biological sulphate removal process.
- If higher volumes of hydrogen is needed, it can be generated 42% cheaper than buying it from industry, making use of nickel electrodes in an electrolytic medium of KOH (30%).
- One major benefit in the generation of hydrogen electrolytically by means of stainless steel electrodes in AMD was the oxidation of iron(II) to iron(III). This reaction is beneficial to the down stream processes as iron(II) precipitates at a lower pH than iron(III) and will not form acid further down in the process. During neutralisation, the formation of an $Fe(OH)_3$ layer onto the calcium carbonate particles affects the dissolution rate of the calcium carbonate negatively which will have a direct effect on the rate of neutralisation. It is therefore vital to assure oxidation of iron(II) in AMD as pre-treatment to neutralisation of the effluent by means of limestone and lime.
- After the AMD has been treated biologically to remove the sulphates to below 200 mg/ℓ, unwanted and toxic H_2S gas was produced as waste product. An alternative way of treating this gas economically had been developed by contacting the H_2S gas with part of the iron(III)-rich effluent, resulted from electrolytic oxidation of iron(II) as pre-treatment to neutralisation. This resulted in a low cost and uncomplicated conversion of H_2S gas to a valuable end-product, i.e. elemental sulphur.

REFERENCES

1. Barnes, H.L. & Romberger, S.B. *Chemical aspects of acid mine drainage.* J. WPCF, Vol. 40(3), 1968, pp. 371-384.
2. Du Preez, L.A., Odendaal, J.P., Maree, J.P. and Ponsonby, M. *Biological Removal of Sulphate from Industrial Effluents Using Producer Gas as Energy Source.* Environmental Technology RSA, Vol. 13(9), 1992, p. 875.
3. Van Houten, R.T., Van Spoel, H., Van der Aelst, A.C., Hulshoff Pol, L.W. and Lettinga, G. *Biological sulfate reduction using synthesis gas as energy and carbon source.* Biotechnology and Bioengineering, Vol.50(2), 1996, pp. 136-144.
4. Oude Elferink, S.J., Visser, W.H., Hulshoff, L.W. and Stams, A.J.M. *Sulfate reduction in methanogenic bioreactors.* FEMS Microbiology Reviews, Vol. 15, 1994, pp. 119-136.
5. Prigent, M. & Martin, L. *Activated nickel-containing electrode and its use particularly for water electrolysis.* US Patent 4,363,707: Appl. 18 June 1980: Acc. 14 December 1982.
6. Ovshinsky, S.R., Sapru, K. and Liang, G. *Energy conversion devices.* US Patent 4,537,674: Appl. 19 July 1982: Acc. 27 August 1985.
7. Geldenhuys, A.J., Maree, J.P., De Beer, M. and Hlabela, P. *An integrated limestone/lime process for partial sulphate removal.* Conference on Environmentally Responsible Mining in Southern Africa. September 2001.

PAPER 5: Maree, J.P., De Beer, M., Geldenhuys, A.J., Strobos, G., Greben, H., Judels, C and Dreyer, J. Comparison of the combined limestone/lime and combined limestone/biological sulphate removal process for treatment of acid mine water, *Proceedings 5th Hard Rock Mining Conference: Issues Shaping the Industry*, 7-9 May 2002, Colorado, USA.

In this paper the Combined Limestone/Lime process to treat acid mine water was compared to the Combined Limestone/Biological process for the same purpose.

In the Combined Limestone/Lime process, acid water (Berkeley Pit water), containing iron and aluminium, was neutralised (pH 6) using limestone, followed by lime treatment (pH 12) for complete removal of metals. Sulphates were partially removed through gypsum crystallisation to less than 1 200 mg/ℓ as a result of lime addition. To adjust the high pH of the water, it was contacted with CO_2 (generated during limestone treatment stage) to precipitate $CaCO_3$ that is available for re-use as alkali in the limestone stage. Aeration can be applied in the limestone stage for iron(II) to be oxidised to iron(III) and precipitated as $Fe(OH)_3$. This results in a very stable sludge that cannot form acid because Fe(III) is in its highest oxidation state. A disadvantage of this process is the high volume of sludge that requires disposal.

The same acid water was neutralised with limestone, followed by biological treatment (SRB), using either ethanol or hydrogen as energy source, to produce a sulphide-rich stream. Sulphide is biologically generated from sulphate. This process offers the benefit that the amount of sludge that is generated is much less than for the Combined Limestone/Lime process. Sulphate was only removed to 2 500 mg/ℓ. The sludge generated was unstable as it forms acid when exposed to the leading to the oxidation of sulphide precipitates.

Paper 5 was presented as a poster by J P Maree at the 5th Hard Rock Mining Conference

COMPARISON OF THE COMBINED LIMESTONE/LIME AND COMBINED LIMESTONE/BIOLOGICAL SULPHATE REMOVAL PROCESSES FOR TREATMENT OF ACID MINE WATER

J. P. Maree (presenter), **M. de Beer, A. Geldenhuys, G. Strobos, H Greben, C. Judels and J. Dreyer**
Environmentek
CSIR, Water, Environment and Forestry Technology
P.O. Box 395, Pretoria, 0001, South Africa
Phone: +27-012-841-2285; Fax: +27-012-841-2506; Email address: jmaree@csir.co.za

Waste ore containing pyrites results in leachates of acid water when exposed to the atmosphere and precipitation (as rain). Acid mine water contains high concentrations of dissolved metals (e.g. iron, aluminium, manganese, copper and zinc) and sulphate, and can have pH values as low as 2.0.

The purpose of this investigation was to compare the following two integrated processes for the treatment of acid mine water (e.g. Berkeley Pit water):

- Integrated Limestone/Lime process for partial sulphate removal. In this process the free acid and acid associated with iron and aluminium are neutralized with limestone to pH 6, followed by lime treatment to pH 12 for complete removal of metals (e.g. manganese, zinc, copper and magnesium) and partial removal of sulphate through gypsum crystallization to less than 1,200 mg/l (as SO_4). After sludge separation (through settling or filtration) the pH is adjusted to 8.6 by contacting the lime treated water at pH 12 with CO_2 that is produced in the limestone treatment stage. The $CaCO_3$ precipitates out and is recycled for neutralization of further acid water.

- Integrated Limestone/Biological sulphate removal process. In this process, limestone treatment, as described above, is followed by biological treatment of a side-stream for sulphide production. The sulphide-rich side stream is recycled to the $CaCO_3$ treatment stage for precipitation of the metals as metal sulphides. Sulphide is produced from sulphate through biological treatment using either ethanol or hydrogen as the energy source.

A spreadsheet-based, water flow and chemical mass balance model was developed to determine various parameters (chemical composition of the water after each treatment stage, chemical consumption, size of various reactor units, capital and running cost) for the two treatment options. Laboratory studies were also carried out to determine the chemical composition of the water after various treatment stages and the reaction rates of the slow chemical reactions (biological sulphate reduction, gypsum crystallization and calcium carbonate crystallization).

The following findings were made from modeling, beaker studies in the laboratory and continuous pilot-scale studies in the field:

Integrated Limestone/Lime process:

Sulphate was removed to less than 1,200 mg/l (as SO_4) and complete removal of the metals including magnesium and aluminium was achieved (Table 1). If aeration was applied in the limestone stage, iron(II) was oxidized to iron(III) and precipitated as $Fe(OH)_3$. In this case a stable sludge was produced and cannot form acid water due to further oxidation of the metal. This process produces good quality water. However, large sludge volumes need to be disposed of.

Limestone/Biological sulphate removal:

Sulphate was removed to 2,500 mg/l by gypsum crystallization and complete metal removal (Table 1). Aluminium was precipitated as $Al(OH)_3$ and the other metals as sulphides. Magnesium remained in solution.

This process offers the benefit that less sludge is produced because less sulphate is removed from the water and because metals are precipitated as sulphides and not as hydroxides. The sludge produced, however, is unstable as sulphide precipitates will oxidize and acid will be generated when exposed to atmosphere.

Table 1. Chemical composition of feed and treated water

Parameter	**Feed**	**Treated**			
		Limestone/lime treatment			**Limestone/ H_2S treatment**
		Limestone	**Lime**	**CO_2**	
pH	3.0	6.1	12.0	8.6	6.1
Sulphate (mg/l SO_4)	8 800	3 100	1 200	1 220	1 240
Alkalinity (mg/l $CaCO_3$)	0	0	1 000	100	102
Calcium (mg/l Ca)	524	316	900	548	557
Magnesium (mg/l Mg)	517	400	0.10	0.10	0.10
Iron (mg/l Fe)	1 110	4.0	0.01	0.01	0.01
Aluminium (mg/l Al)	304	0.02	0.02	0.02	0.02
Copper (mg/l Cu)	215	50	0.005	0.005	0.005
Zinc (mg/l Zn)	637	400	0.04	0.04	0.04
Manganese (mg/l Mn)	226	202	0.005	0.005	0.005
Total dissolved solids (mg/l)	11 696	4 473	2 700	1 828	1 859
Temperature (^{0}C)	23	23	23	23	23

PAPER 6: Adlem, C.J.L., Geldenhuys, A.J., Maree, J.P. and Strobos, G.J. Examining the implementation of limestone neutralisation technology in the mining and industrial sector to neutralise acid and reduce sulphate pollution, *Proceedings 5th Annual Industrial Water Management and Treatment Symposium*, 15–16 May 2002, Johannesburg, South Africa.

This paper focussed, in a very practical way, on the implementation of a limestone neutralisation system for AMD, to replace the current lime system that is in place at various mine sites in South Africa. A new limestone handling and dosing system has been developed for dosing powdered limestone instead of lime. Dust problems that are part of the old-fashioned lime treatment technology are avoided when using limestone instead as it has a content of 15% moisture.

A single stage process, the Integrated Limestone/Lime Treatment Process, for the simultaneous oxidation of Fe(II), neutralisation of acid and the crystallisation of gypsum from the treated effluent, has been developed. Where lime is largely replaced with powdered limestone. A small amount of lime is dosed after limestone neutralisation to ensure sulphate removal to below the saturation level of gypsum, i.e. 1 500 mg/ℓ. The reactor is a fluidised bed that runs under high suspended solids conditions with air and acid water being fed to the system.

The limestone-based approach has been shown to effectively compete with lime neutralisation in terms of efficiency (utilisation) and effectiveness (rate of reaction). The benefits are that two aspects of neutralisation technology are successfully combined:

- ✓ Limestone treatment for neutralisation of acid mine water and partial sulphate removal is cost-effective and generates carbon dioxide, and
- ✓ Lime treatment to high pH (>12) reduces sulphate concentrations to below the saturation level of gypsum

Paper 6 was presented orally by C J L Adlem at the 5th Annual Industrial Water Management and Treatment Symposium

Institute for
International
Research
IIR South Africa BV
Incorporated in The Netherlands

Examining the Implementation of Limestone Neutralisation Technology in the Mining and Industrial Sector to Neutralise Acid and Reduce Sulphate Pollution

C J L Adlem, A J Geldenhuys, J P Maree and G J Strobos

Division of Water, Environment and Forestry Technology,

CSIR

P O Box 395, Pretoria 0001

April 2002

INTRODUCTION

The CSIR has developed the biological sulphate removal process (since 1981) and the limestone process since 1991. Both were developed in response to the acid water problem in South Africa.

The purpose of this document is to describe the implementation of the limestone neutralisation based technologies in the mining and industrial sector.

Acid water is a problem at many of South Africa's mines. The water needs treatment, e.g. neutralisation, before releasing it into the environment. Untreated it pollutes water sources, threatening aquatic life and safe human consumption. Re-use of these waters is also not possible without treatment. Most of the ores and coal mined in South Africa contains pyrite. Pyrite oxidises to form sulphuric acid in the presence of water and air. This reaction is often faster due to bacteria that catalyse the oxidation of the Pyrite.

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$

The neutralisation technology has reached the stage of full-scale implementation and the biological sulphate removal technology is currently evaluated for full-scale implementation.

EXTENT OF PROBLEM

To illustrate the kind of problems that need to be addressed by mines with acid water problems some data from a case study at a Witbank coal mine will be discussed. CSIR have been involved with the mine for several years and recently implemented the limestone neutralisation process at the mine.

Column studies carried out on typical coal discard from the mine showed acid was produced consistently at 1140 g/ℓ/week for 23 weeks (Figure 1). It shows that acid water must be handled both as a short term and a long term problem. Many mines and associated industries must handle large volumes of similar water daily.

Looking at a water balance (Table 1) for the coalmine near Witbank one sees the extent of water quality problems caused by pyrite oxidation. Their water circuit receives 17.3 t/d (as $CaCO_3$) acid of which 15.6 tons is from the pyrite in the coal. The sulphate received from the pyrite oxidation process is 16.8 t/d (as SO_4). The water with this load needs to be neutralised to protect equipment pipes etc. as the mine re-uses the water in their circuit. From the neutral water about 4.5t/d of the sulphate crystallises in the coal processing plant. Scaling causes an increase in maintenance and operating costs

One example is the precipitation of gypsum on magnetite particles. A higher fraction of the magnetite is wasted instead of being recovered due to the loss of magnetic properties.

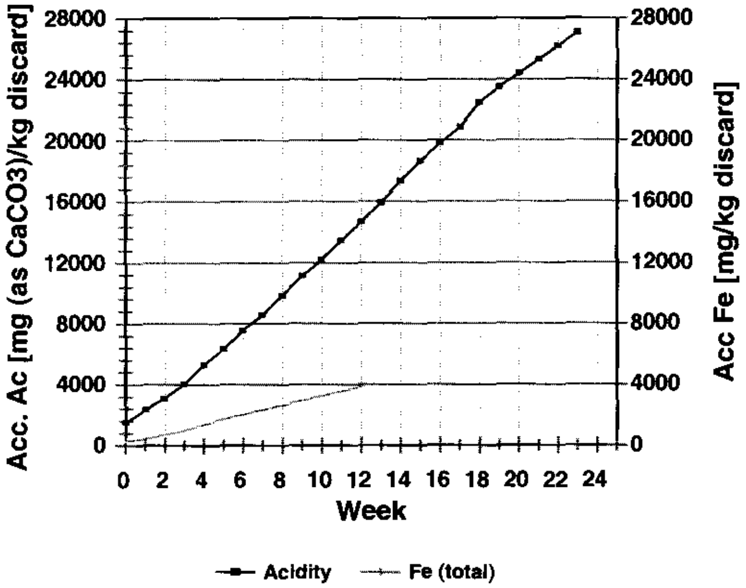


Figure 1. Acid Mine Drainage produced by a typical coal discard.

Table 1. A water balance for a typical coal colliery near Witbank

STAGE	ACID	SO_4
	t/d $CaCO_3$	t/d SO_4
INPUT	17,3	24,1
Inflows	1,7	7,3
Coal	15,6	16,8
Plant	6,0	5,8
Discard	9,6	11,0
OUTPUT	17,3	24,1
Effluents	9,6	16,1
Neutralisation/Crystallisation	7,7	8,0
Neutralisation Plant	1,7	0,2
Coal Processing Plant (CPP)	6,0	4,5
Fines Discard dam	0,0	3,2

The gypsum saturation index (OSI) (Table 2) shows that neutralisation of acid waters formed by pyrite oxidation (sulphuric acid) causes over-saturation with regard to gypsum. As this crystallisation of gypsum is slow it causes scale in the coal processing plant.

Table 2. The gypsum saturation index for a coal colliery near Witbank Colliery

Place	OSI
Neutralisation plant feed	1.02
Neutralisation plant out	1.07
Coal processing plant	1.47
Thickener overflow	1.23
Fines discard dam	0.99

LIMESTONE NEUTRALISATION TECHNOLOGIES

In response to these acid water problems and similar problems in the mining and industrial sector CSIR developed a suite of technologies. The aims of these developments can be summarised as follows:

- Reducing scaling of equipment
- Reducing neutralisation cost
- Treating effluent to meet discharge specifications

Technologies developed were:

- Limestone handling and dosing system
- Limestone neutralisation process
- Integrated process for Fe(II)-oxidation, limestone neutralisation and gypsum crystallisation
- Integrated limestone/lime treatment process
- Biological sulphate removal process

Lime is currently used to neutralise the acid water. It is a fine powder that effectively and efficiently neutralises acid at a fast rate as it is relatively soluble (0.15%) (Maree et al, 1992). Metal hydroxides e.g. iron and aluminium hydroxides precipitate. Sulphate also crystallises as gypsum to a saturation level of about 2000 mg/ℓ dependent on the presence of other metals and salts in the water treatment. Slaking equipment is also known for maintenance costs and problems. The most serious disadvantage of lime is the hazards that operators can be exposed to when handling the chemical.

Lime is more costly than limestone (2 to 4 times). Smaller sludge volumes are produced with limestone than lime. However, in contrast with lime, limestone reacts relatively slowly and inefficiently with acid mine water. Systems developed and implemented before the CSIR process lead to wastage of unutilised limestone.

A new limestone handling and dosing system for dosing powdered limestone instead of lime has been developed by CSIR. Handling it, using the new system, the limestone is wetted as part of the procedure, preventing dust problems often found when handling lime or limestone.

Maree et al (1998) developed a single stage process for the simultaneous oxidation of Fe(II), neutralisation of acid and the crystallisation of gypsum from the effluent treated. The reactor is a fluidised bed that runs under high suspended solids conditions with air and acid water being fed to the system. Sulphate is removed to the saturation levels of gypsum.

Maree et al (1992) showed that a fluidised bed reactor and its entrenched principles can establish a limestone based approach that effectively competes with lime neutralisation, in efficiency (utilisation) and effectiveness (rate of reaction).

The integrated Limestone/Lime Treatment Process, can be used for neutralisation of acid mine water and partial sulphate removal to below the saturation level of gypsum. The benefits of this process are that two aspects of neutralisation technology are combined successfully:

- The cost-effective limestone treatment for neutralisation of acid mine water, and partial sulphate removal, that produces carbon dioxide, and
- lime treatment to high pH (>12), that can reduce sulphate to below gypsum saturation levels.

Limestone Handling and Dosing System

The dosing system is an inclined concrete slab and a slurry tank. The limestone used is stored on the slab. From there, it is washed into the slurry tank with water. A load cell controls the density of the slurry in the slurry tank. The weight is measured while the tank is kept at a constant volume. Low and high weight settings activate and deactivates the spray of the recycled slurry onto the slab (Figure 2). Some optimum operating parameters were found with experimental pilot scale studies:

- Recycle slurry to make-up water ratio of a minimum of 4:1 (Figure 3),
- a slurry density of approximately 14% in the slurry tank, and
- the need for nozzles to slurry the limestone e.g. an open ended pipe.

The load cell was found to be an effective control for the density of the slurry in the slurry tank under continuous operating conditions.

Studies showed that the linear velocity of the water on a 8° slab would be enough to wash off particles on a smooth concrete surface.
The benefits that this system has in comparison to a lime neutralisation plant set-up is:

- No silo for storage required
- Reduced use of lime slaker (where applicable)
- Reduced alkali cost
- $CaCO_3$ safe to handle
- No dust

Using this data a full-scale plant was designed and constructed at the Witbank coal colliery. Within one year from development, the first full-scale plant was constructed last year.

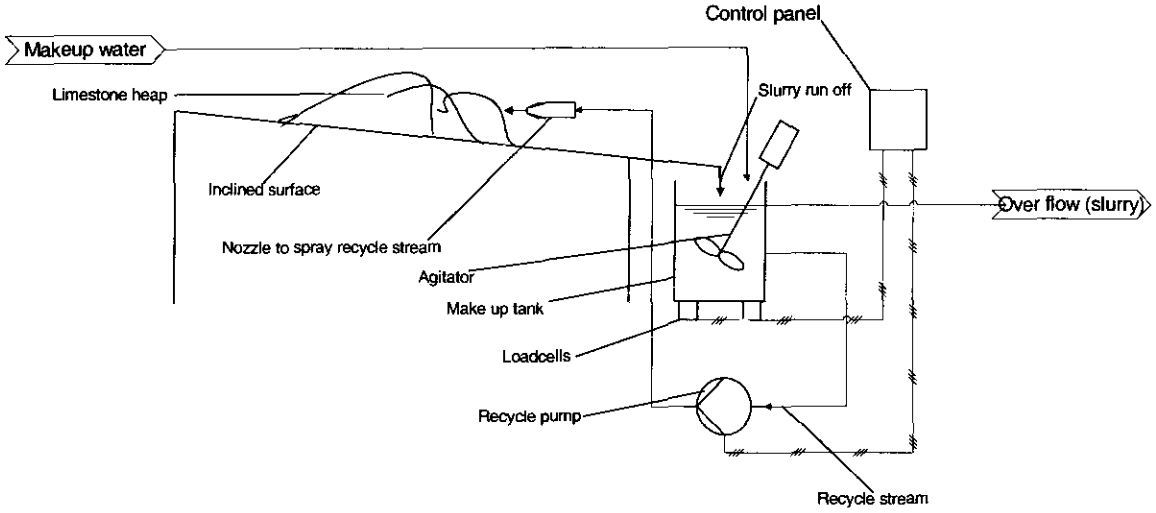


Figure 2 Limestone dosing system

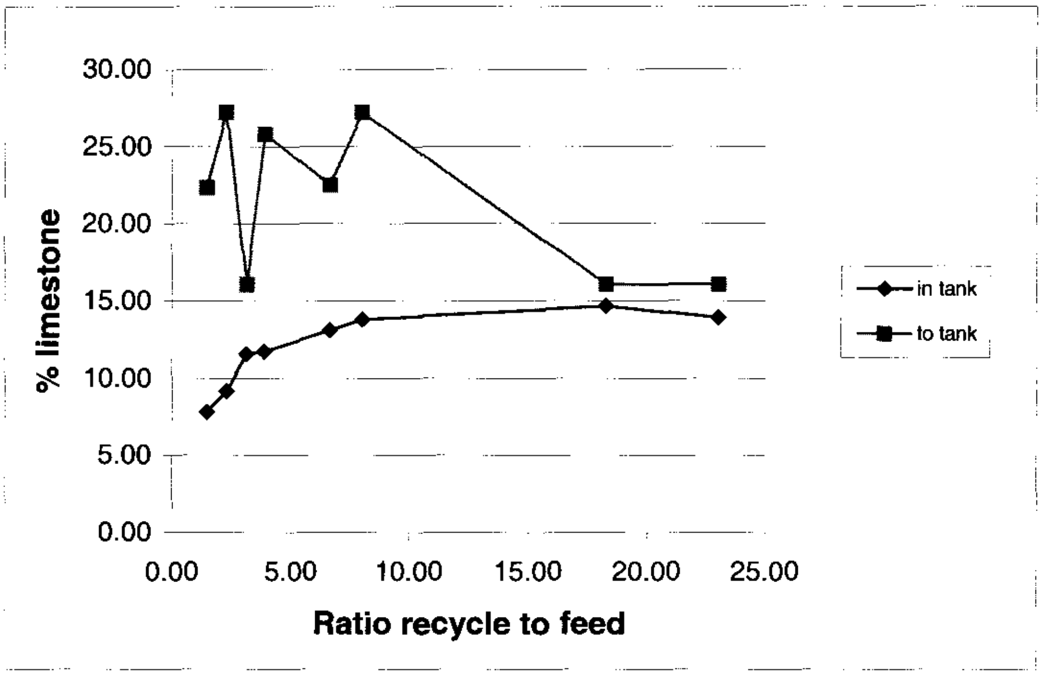


Figure 3 The influence of feed to recycle ratio

Case study/full-scale implementation at Witbank coal colliery

A full-scale makeup and dosing facility

Limestone was shown to be a viable substitute for lime in the neutralisation of acidic waste water (Maree *et al.*, 1996). A limestone by-product from the pulp and paper with a particle size of –6 μm was more reactive than previous limestone products. If aeration was carried out in the same reactor basin iron oxidation could be achieved simultaneously (Maree *et al.*, 1999). It was agreed by S A Coal Estates (SACE) to substitute lime for limestone at a neutralisation plant that treats 4 to 6 Mℓ/day of acid water with an average acidity of 450 mg/ℓ as $CaCO_3$. A Full-scale limestone dosing system was designed to dose limestone slurry to a converted neutralisation plant at the colliery.

The limestone dosing plant has an inclined concrete slab (14.56 x 10.4 m) *with a fall of 5% or 2.8°*, a 10 m^3 makeup tank in an excavated concrete sump to enable the slurry to decant into the tank, a 40 m^3/hr recycle pump and a 1,5 m^3/hr dosing pump. The recycle stream is controlled by pneumatic valves to be directed either onto the slab or back into the tank. Signals from the load cell control the valves. A simple ball valve dose make-up water and controls the level of the tank (Figure 4).

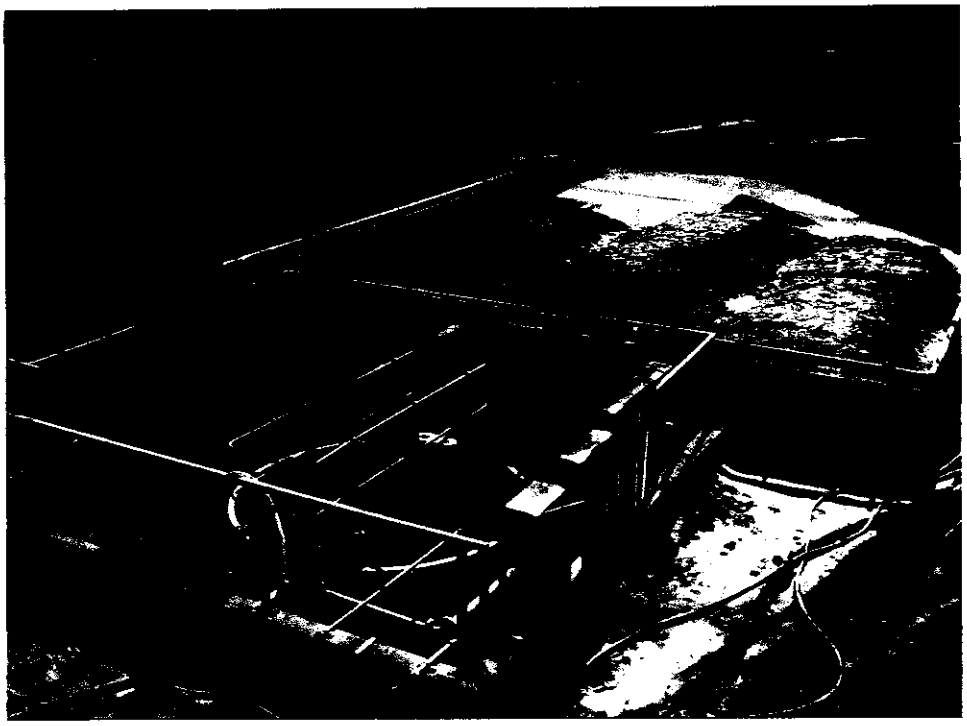


Figure 4 Photo of full scale limestone makeup and dosing plant

A policy of minimal operator intervention is practiced by operating the plant automatically. The utilisation of the plant is currently being expanded to supply limestone to the coal plant where about 1 200 to 1 600 m^3/hr of water, with an acidity of 500 mg/ℓ as $CaCO_3$ have to be neutralised.

Conversion of lime neutralisation plant to an integrated iron(ii) oxidation/limestone neutralisation plant

Limestone effectively replaced lime as neutralisation agent for acid mine water.

The lime neutralisation plant that was converted to a limestone neutralisation plant is briefly described below:

The neutralisation plant consists of three stages, a conditioning tank with a volume of 30 m^3 (3.5 x 3.5 x 2.5m), an aeration tank with a volume of 80m^3 (5.7 x 5.7 x 2.5m) and a clarifier tank (also referred to as a turbo circulator). With a floe of 200 m^3/hr, the retention time 10 minutes in the conditioning tank and 25 minutes in the aeration tank.

Limestone, the feed water and the recycled sludge flows to the conditioning tank. The slurry then overflows into the aeration tank. Here the slurry is aerated so that neutralisation and iron(II) oxidation occurs simultaneously. If lime dosing is necessary, it is dosed in the overflow of the aeration box.

In Figure 5 (Strobos *et al.*, 2001) it can be seen that the pH of the feed was raised from 3 to 6.5 in the treated water during December 2001.

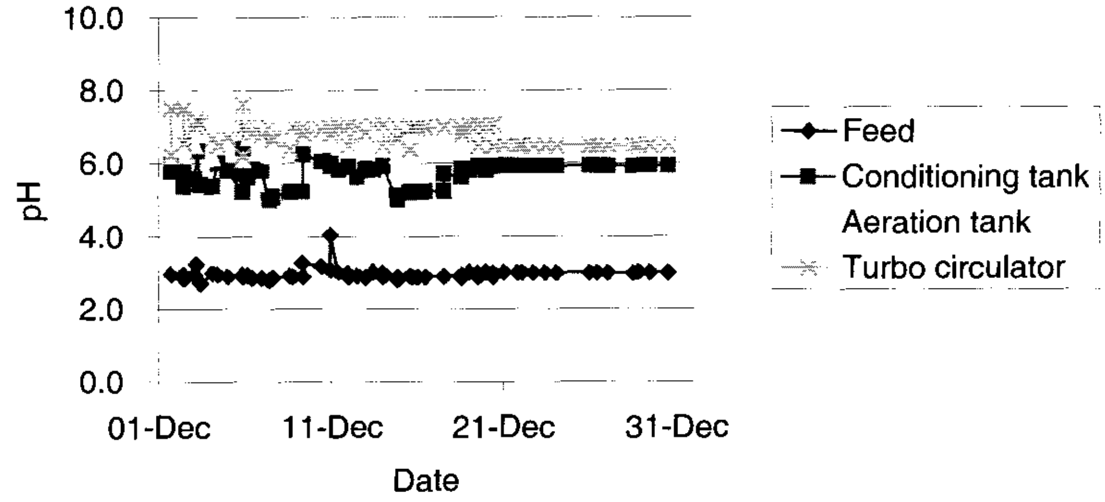


Figure 5 pH of the feed and treated water

Figure 6 shows the acidity for the feed water and the stages of treatment. As expected the acidity was removed from about 450 mg/ℓ to below 50 mg/ℓ.

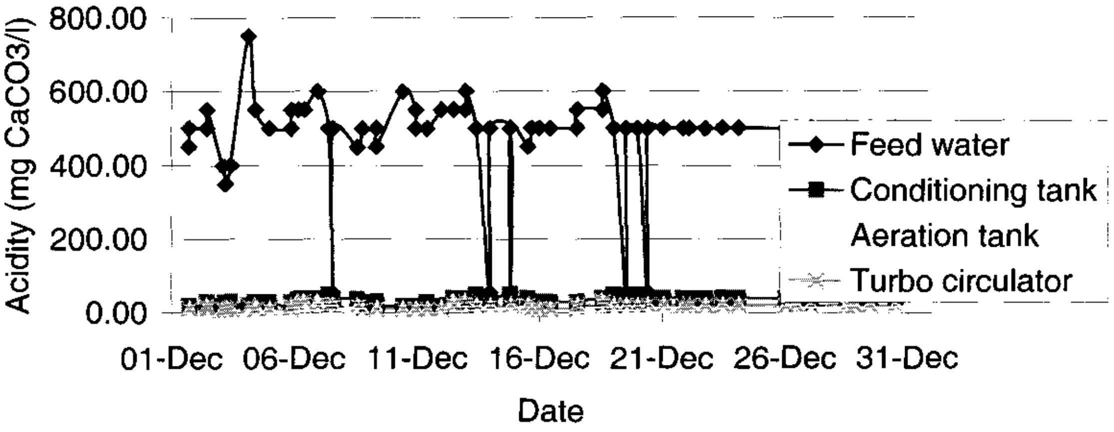


Figure 6 Acidity of the feed and treated water

The results show that free acid and acid associated with metals was removed through this neutralisation process. In contrast lime neutralisation removed less than 25% of the acid associated with metals. Aluminium is also removed from the water, but magnesium and manganese is not removed.

Financial savings due to the introduction of limestone

The Witbank coal colliery saved about R20 000,00 per month by the replacement of lime with limestone at their neutralisation plant. Table 3 shows the relevant data for a six month period. Approximately R120 000,00 was saved due to the introduction of limestone. In contrast to known science before the development of the CSIR's limestone process, comparison of before and after scenarios show that lime is commonly utilised at an efficiency of 60% and limestone at an efficiency of 90% at the neutralisation plant.

Table 3 Calculation of cost saving due to usage of limestone for July to December 2002

Parameter	Theoretical		Current	
	Unslaked lime	**Powder Limestone**	**Unslaked Lime**	**Powder Limestone**
Flow rate (m^3/d)	4037	4037	4037	4037
Acidity (mg/ℓ)	453	453	453	453
Total acid load (t/d CaCO3)	1.8	1.8	1.8	1.8
Molecular mass (g)	56	100	56	100
Utilisation efficiency (%)	60	90		76
Purity (%)	90	75	90	87
Consumption (t/d)	1.9	2.7	0.16	2.9
Price (R/t)	550	112.5	550	112.5
Cost (R/month)	32343	9451	2640	9828
Total alkali cost (R/month)	32343	9451		12468
Saving (R/month)		22892		19876
Cost ratio (relative to unslaked lime)	100	29		39

Fluidised bed limestone neutralisation process

A high limestone concentration and a small particle size favoured the rate of neutralisation, and the reactor configuration (fluidised bed) ensured utilisation efficiencies of almost 85% over a particle size range of 0.3 to 1.7 mm. Powdered limestone of >0.3 mm should be dosed directly to a mixing tank with the acid feed, to prevent the loss of particles that can wash out of a fluidised bed. Iron(III), aluminium(III) and fluoride are effectively removed, while iron(II) retards the neutralisation process. Sulphate is removed to about 2600 mg/ℓ from a typical acid mine water if sufficient gypsum crystals are present. PH increases from about 2.2 to 7.0. As the solubility of limestone reduces to almost nothing at a pH of 7.5, no pH control is necessary for a basic process using limestone alone.

To solve the potential difficulties in treating water containing iron(II), a biological iron oxidation stage has been developed to use with the limestone process where applicable. Bacterial oxidation of iron(II) to iron(III) occur in a separate reactor. Many neutralisation plants are also equipped with aerator type systems to chemically oxidize their effluents. The use of either will be determined by the levels of Fe(II) and the specific needs of the potential user.

The capital costs of a limestone neutralisation and lime neutralisation plant were shown to be similar, making the new limestone process an attractive alternative to lime neutralisation.

Integrated Iron(II)-oxidation and Limestone Neutralisation Process

The technological and kinetic aspects was intensively studied in labscale beaker studies and then upscaled to a pilot plant. It was found that iron(II) oxidation rates is a function of iron(II), hydroxide, oxygen and suspended solids concentrations. The resultant rate equation developed from that of Stumm is given below. Chemical oxidation of iron(II) dominates the reaction at a pH between 4.5 to 5.5.

$-d[Fe]/dt = k[Fe^{2+}].[OH-]^2.P_{O2}$ (Stumm)

$-d[Fe]/dt = k[Fe^{2+}]^{0.5}.[OH^-]^{1.5}.[O_2]^{0.5}.[SS]^{0.5}$ (This investigation)

The reactions occurring in this process are:

$Fe^{2+} + ½O_2 + 2H \rightarrow 2Fe^{3+} + H_2O$

$2Fe^{3+} + 6H_2O \rightarrow 2Fe(OH)_3 + 6H^+$

$6H^+ + 3CaCO_3 \rightarrow 3Ca^{2+} 3CO_2 + 3H_2O$

$3SO_4^{2-} + 3Ca^{2+} \rightarrow 3CaSO_4.2H_2O$

The pilot scale plant could treat 24 ℓ/h of iron(II) rich acid water with a residence time of typically 6.5 h in the fluidised bed reactor. Typical results for the treatment of discard leachate treated in the pilot scale plant is shown in Table 4. The process generated a sludge with a typical concentration of 550 g/ℓ that compares well with the 200 g/ℓ when the High Density Sludge process (a lime neutralisation process) is applied. Disposal of sludge is an important cost parameter for most mines and industries.

Table 4 Water Quality of Discard Leachate treated in the integrated oxidation/neutralisation pilot plant

Parameter	**Feed**	**Treated**
pH	1.8	6.6
Acidity	7 300	100
Iron (II)	2 500	<100
Sulphate	8 342	1 969
Ortho phosphate	2.9	0

The benefits of this process are similar to those mentioned previously and can be summarised as:

- Maximum sulphate removal
- Cheapest alkali
- No pH control
- High density sludge

Case study/full-scale implementation at BCL Ltd (Botswana)

BCL of Botswana approached the CSIR and its implementation partners for the design of an integrated limestone/iron oxidation neutralisation plant. They discharge 300 m^3/h of effluent with sulphate concentrations of > 500 mg/ℓ. In addition, acid seepage occurs at a tailings dump and they have to deal with land deterioration. Another cost is the raw water intake of 300 to 400 m^3/h.

In Figure 7 the schematic diagram for their 50 kℓ/h plant is shown. The plant is currently under construction and is designed to also facilitate oxidation of iron(II) in a pretreatment stage followed by a fluidised bed neutralisation reactor, a crystalliser and a settling tank. The design is deliberately versatile enough to allow two process configurations.

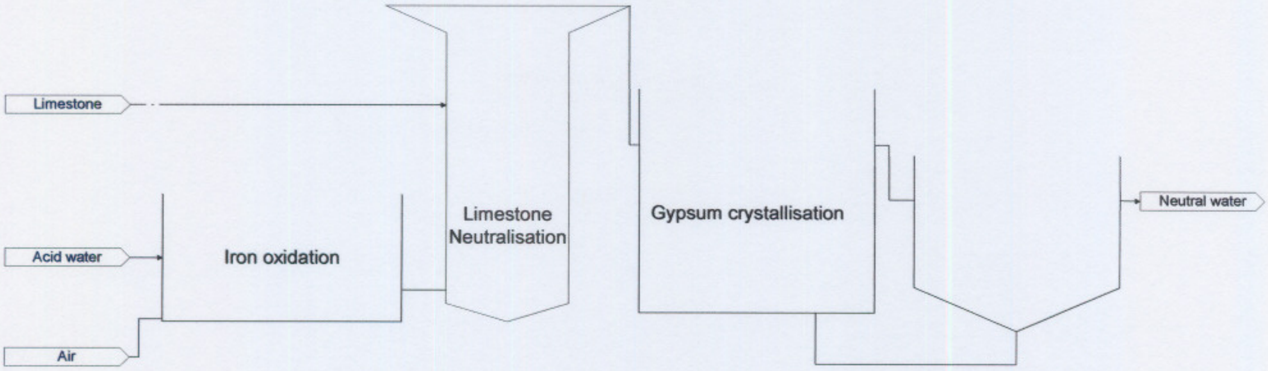


Figure 7. Schematic diagram of the neutralisation/crystallisation plant at BCL

Completion of the plant is expected in July 2002. CSIR will then be involved in the commissioning of the plant.

Integrated limestone/lime treatment process

A pilot scale plant was constructed to evaluate the process described. Waste, powdered limestone ($CaCO_3$) from the paper industry was used in the limestone neutralisation stage of the process and slaked lime ($Ca(OH)_2$) in the gypsum crystallisation stage. Each stage of the process consists of a reactor and clarifier. All sludges produced were recycled back to the respective reactors.

Figure 8 shows the process flow diagram with the water quality of each stage in the treatment process.

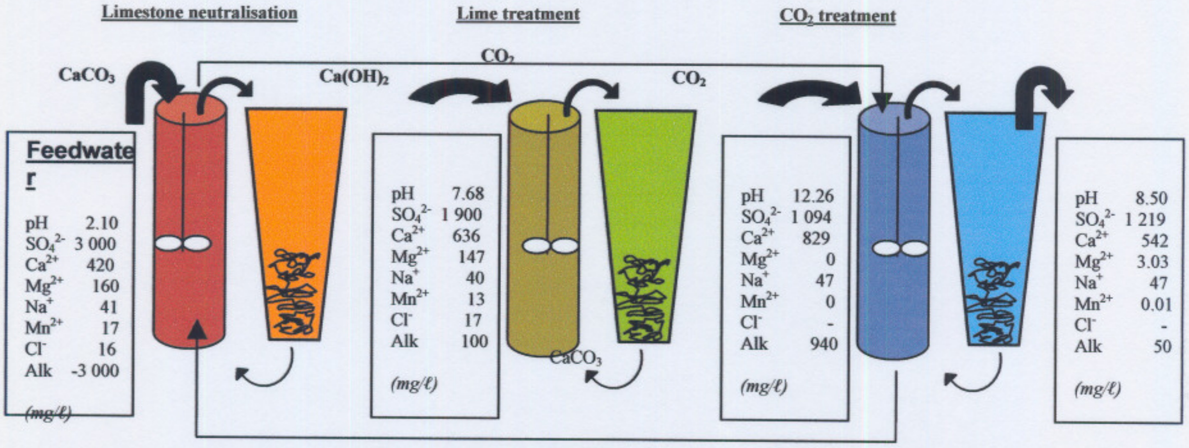


Figure 8: Flow diagram indicating quality of the water before and after treatment in the integrated Limestone/Lime Neutralisation Process

When acid mine water (discard leachate) was treated with limestone, the pH of the water was raised from 2.10 to 7.68 in the neutralisation reactor. Sulphate was reduced from 3 000 to 1 900 mg/ℓ. The decrease of 96.6% in the acidity of the water after limestone neutralisation is a result of the following reaction:

$$CaCO_3 + H_2SO_4 + 2H_2O \rightarrow CaSO_4 + CO_2 + H_2O$$

The stability of the treated water with respect to calcium carbonate is determined by the pH, calcium and alkalinity values of the treated water. The alkalinity of the treated water was 100 mg/ℓ (as $CaCO_3$) owing to the escape of CO_2 from the solution as seen in the following reaction:

$$H_2CO_3 \rightarrow H_2O + CO_2$$

From the results in Figure 8, it can be seen that sulphate in the neutral water can be reduced effectively, with lime treatment during gypsum crystallisation, to levels below the original target of 1200 mg/ℓ SO_4^{2-}, by raising the pH to 12.3. Maximum sulphate removal was achieved by raising the pH to 12 and higher for magnesium precipitation and removal of sulphate associated with magnesium through gypsum crystallisation. The magnesium concentration at pH 7.68 was 140 mg/ℓ while at pH 12.26, the magnesium content dropped to zero, due to magnesium hydroxide precipitation. The calcium concentration increased from 636 to 829 mg/ℓ due to the dissolution of lime ($Ca(OH)_2$) as seen in the following reaction:

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4$$

The pH of the treated water that was under-saturated with respect to gypsum was adjusted, using CO_2 from the neutralisation stage, from 12.26 to 8.50. Due to $CaCO_3$ crystallisation the calcium content was also reduced from 829 to 542 mg/ℓ. A slight increase in the sulphate content was ascribed to some of the gypsum possibly having been washed out to the third stage of the process ($CaCO_3$ precipitation).

Gypsum concentration was found to have a major influence on the rate of sulphate removal during gypsum crystallisation (Figure 9). This concurs with the findings of Maree *et al (1998)*, that the rate of crystallisation is influenced by the concentration of gypsum seed crystals. It can be concluded that the rate of gypsum crystallisation is directly proportional to the surface area of the gypsum.

The higher the concentration of seed crystals the larger the surface area. Therefore, effective removal of suspended and colloidal matter from the overflow of each stage is required and can be achieved by coagulation and flocculation. In order to optimise this process, the settling rates of the sludges produced during the three different stages were increased dramatically. The polymers, PAC6 and 3095 were effectively used as coagulant and flocculant respectively. The addition of these polymers in very low dosages resulted in clear overflow in each of the above stages with very low turbidities.

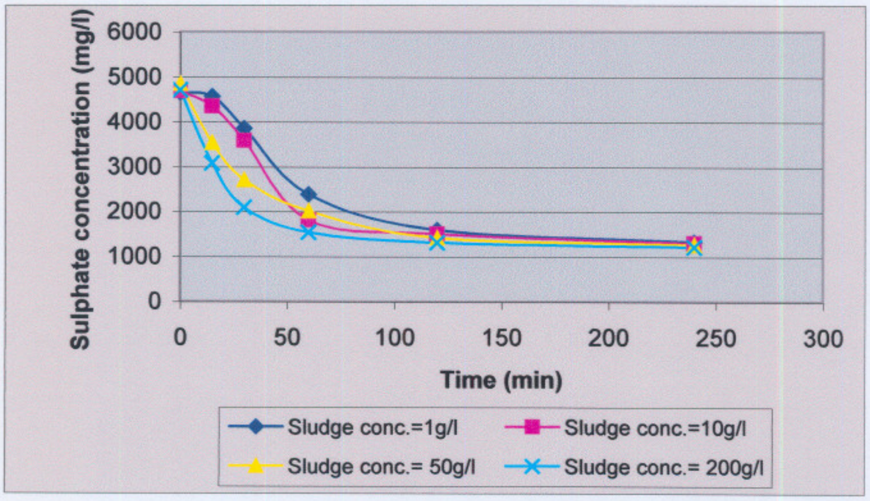


Figure 9: Effect of sludge concentration on rate of gypsum crystallisation at pH 12

The combination of limestone neutralisation with lime treatment for neutralising acid mine water achieves complete magnesium removal and sulphate removal to less than 1 200 mg/ℓ. The primary neutralisation is done using limestone (much cheaper than lime), followed by lime treatment for metal removal and partial sulphate removal. Treatment of the high pH water with CO_2 lowers the pH of the water to near neutral levels while a high quality $CaCO_3$ is produced. It can be recycled to the limestone neutralisation stage. The treated water will be suitable for re-use in the process or discharge into the sewerage network. A comparison of the costs of treating acid mine water with limestone neutralisation, combined with further neutralisation using lime and sulphate removal via gypsum crystallisation is shown in Table 5.

Table 5. Comparison of chemical costs for neutralisation of acid mine water and sulphate removal through gypsum crystallisation in the integrated limestone/lime process or by lime treatment

Chemical process	Minimum sulphate level (mg/ℓ)	Chemical cost (R/t)	Chemical usage (t/t sulphate)	Cost of sulphate removal (R/t sulphate)
Limestone	1 900	120	1.04	124.80
Slaked lime	1 100	675	0.77	519.75

US$1 = ZAR11-65

Using PAC6 (Montan Chemicals) and 3095 (Montan Chemicals) as coagulant and flocculant, respectively, for improved settling of the sludges, produced in the three consecutive steps of the process, amount to 1.10c/m^3 for Stage 1, 2.75c/m^3 for Stage 2 and 4.13c/m^3 for Stage 3.

Case study/ full-scale implementation at TICOR (Natal)

TICOR approached the CSIR for the design of an integrated limestone/lime neutralisation process for their new metal beneficiation plant at Empangeni in Natal. TICOR produces, rutile (TiO_2), titanium (Ti), zircon (Zi) and illminite (TiO_2 plus iron compounds). The plant also produces 80 m^3/h of acid water. This water must be treated to a quality suitable for re-use in the metallurgical process or for discharge into the Empangeni sewage system. Neutral water that is undersaturated with respect to gypsum can be re-used. The sulphate needs to be less than 500 mg/ℓ (as SO_4) for discharge into the sewage system.

The neutralisation plant consists out of the following stages (Figures 10 and 11):

- $CaCO_3$-neutralisation
- Lime treatment and gypsum crystallisation
- Filter press and
- CO_2-treatment for $CaCO_3$-precipitation

Figure 10 $CaCO_3$-neutralisation (right column) and lime treatment/gypsum crystallisation (left column) stages.

Figure 11 CO_2-treatment stage.

Construction and initial commissioning of the plant was finished at July 2001.
The cheapest alkali available for the neutralisation plant is waste limestone from Mondi.

The CSIR is currently cooperating closely with TICOR to fully optimise and commission the plant. Ongoing involvements also led to a decision to upgrade the limestone dosing system to the newly developed limestone handling and dosing system.

Initial results show that pH is controlled effectively at pH 5 and 10 respectively. Sulphate levels of 8000 mg/ℓ is reduced to 2000 mg/ℓ.

CONCLUSIONS

A full-scale limestone dosing system was constructed and commissioned successfully to treat acid water for re-use. Lime was replaced by limestone as neutralisation agent saving the company as much as R120 000 a year (e.g. full-scale plant at Witbank Colliery).

Acid water can be neutralised effectively with limestone. In the fluidised bed, limestone, and integrated limestone and iron oxidation processes, sulphate is removed to the saturation levels of gypsum.

Lime neutralisation plants can be successfully converted to a limestone neutralisation plant (e.g. conversion of the lime plant at the Witbank Colliery).

The integrated limestone/lime process was proven technologically and economically to reduce sulphate of effluents to less than the saturation levels of gypsum producing a water that can be re-use by the mine or industry (e.g. full-scale plant at (TICOR).

The limestone neutralisation technologies developed at the CSIR are proven, effective and cheaper alternatives to lime neutralisation.

REFERENCES

Adlem CJL, Strobos JG AND Maree AJ (2001) Cost effective feeder for neutralisation plants, Internal seed report of the CSIR, March

Maree, JP, de Beer, M, Strydom, WF and Christie, ADM (1998) Limestone neutralisation of acidic effluent, including metal and partial sulphate removal, *IMWA. Proceedings of the 1998 Symposium of IMWA*, Johannesburg, South Africa.

Maree JP, Strydom WF and De Beer M (1999) Integrated iron(II) oxidation and limestone neutralisation of acid water. *Water Sci. Tech.* 39 (10-11) 231-238

Maree JP, Van Tonder GJ, Millard P and Erasmus TC (1996) Pilot-scale neutralisation of underground mine water. *Water Sci. Tech.* 34 (10) 141-149

Strobos JG, Maree JP, Malatji N, De Beer M and Adlem CJL (2001) Progress report No 6-Limestone handling and dosing system. Prepared for: The Mine Manager, December

PAPER 7: Maree, J.P., Hlabela, P., Geldenhuys, A.J., Nengovhela, R., Mbhele, N. and Nevhulaudzi, T. Treatment of mine water for sulphate and metal removal using barium sulphide, *Proceedings Waste Management, Emissions & Recycling in the Metallurgical & Chemical Process Industries*, 18–19 March 2004, Johannesburg, South Africa.

High volumes of mine water are generated in the Gauteng region and also in the Olifants River Catchment in Mpumalanga. Several processes are under consideration to remove sulphate from the water, e.g. the Biological Sulphate Removal Technology, SAVMIN, Etringite, EcoDose, reverse osmosis and electrodialysis. The barium process can also be used and offers the following advantages:

- ✓ Sulphate can be removed to specific values due to the solubility of barium sulphate
- ✓ The soluble barium salt, barium sulphide, can be regenerated from the product, barium sulphate

The specific aims of the work were to:

- ✓ Demonstrate that sulphate can be removed to less that 200 mg/ℓ by means of barium sulphide treatment
- ✓ Determine the optimum process conditions for the following stages:
    - Partial sulphate removal through lime pre-treatment
    - Reduction of barium sulphate to barium sulphide
    - H_2S stripping and processing
- ✓ Estimate the running cost of the process

The process consists of the following stages:

- ✓ Lime pre-treatment for partial sulphate removal
- ✓ Removal of sulphate as barium sulphate to below 200 mg/ℓ by means of barium sulphide treatment
- ✓ H_2S-stripping with CO_2 gas
- ✓ Stripping of CO_2 and crystallisation of $CaCO_3$
- ✓ Regeneration of barium sulphide by heating the barium sulphate, resulting from the process

The following conclusions were drawn from the results, obtained during the investigation:

- ✓ After lime treatment, the sulphate concentration in the water was reduced from 2 800 mg/ℓ to less than 1 200 mg/ℓ due to gypsum crystallisation. Metals were precipitated as metal hydroxides.
- ✓ The sulphate concentration was further reduced to below 200 mg/ℓ after $BaSO_4$-precipitation
- ✓ Sulphide was removed from 333 mg/ℓ to less than 10 mg/ℓ, using CO_2 gas for stripping
- ✓ Due to $CaCO_3$-precipitation after CO_2-stripping with air, of the water following lime treatment, a lowering of the alkalinity resulted, from 1 000 mg/ℓ to 110 mg/ℓ
- ✓ Stripped H_2S gas was contacted with an iron(III)-solution to produce elemental sulphur
- ✓ Following sulphur production, iron(II) was re-oxidised to iron(III) using an electrolytic step
- ✓ For a removal of 2 g/ℓ of sulphate, the running cost of the barium sulphide process amounts to R2.12/m^3

Paper 7 was presented orally by P Hlabela at the Waste Management Symposium for Emissions & Recycling in the Metallurgical & Chemical Process Industries

TREATMENT OF MINE WATER FOR SULPHATE AND METAL REMOVAL USING BARIUM SULPHIDE

J P Maree, P Hlabela, A J Geldenhuys, R Nengovhela, N Mbhele and T Nevhulaudzi

Division of Water, Environment and Forestry Technology, CSIR, P O Box 395, Pretoria, South Africa (email: jmaree@csir.co.za)

ABSTRACT

Mining is a significant contributor to water pollution. Effluents need to be treated for sulphate and metal removal. The barium process can meet these requirements. The purpose of this study was to demonstrate the performance of the integrated barium sulphide process, consisting of the following stages: Sulphate precipitation as barium sulphate using barium sulphide, H_2S-stripping, Crystallization of $CaCO_3$ and recovery of barium sulphide from barium sulphate.

The following conclusions were made from the investigation:

1. *During lime treatment sulphate was removed from 2 800 mg/ℓ down to less than 1 200 mg/ℓ due to gypsum crystallization and metals were precipitated as metal hydroxides).*
2. *During BaS treatment, sulphate was removed down to less than 200 mg/ℓ due to $BaSO_4$-precipitation.*
3. *Sulphide was removed from 333 down to less than 10 mg/ℓ (as S) in the stripping stage, using CO_2 gas for stripping.*
4. *The stripped H_2S-gas was contacted with an iron(III)-solution and converted quantitatively to elemental sulphur.*
5. *The alkalinity of the calcium bicarbonate rich water was reduced from 1 000 to 110 mg/ℓ (as $CaCO_3$) after CO_2-stripping with air due to $CaCO_3$-precipitation.*
6. *Iron(II), after sulphur production, was re-oxidized to iron(III) using an electrolytic step.*
7. *The running cost of the barium sulphide process amounts to R2.12/m^3 for the removal of 2 g/ℓ of sulphate.*

1 INTRODUCTION

Mining is a significant contributor to water pollution, the prime reason being that many geological formations that are mined contain pyrites, which is oxidised to sulphuric acid when exposed to air and water. Mine water also has high concentrations of metals such as magnesium. This water is receiving major attention due to its poor quality and large volumes which impact on the quality of surface water. The volume of mine water generated in Gauteng is estimated at 200 Mℓ/d while in the Olifants River Catchment in Mpumalanga at 50 Mℓ/d. Legislation requires removal of sulphate to less than 500 mg/ℓ. Several processes are currently considered for sulphate removal, e.g. biological sulphate removal process, SAVMIN, Etringite, ecoDose, reverse osmosis and electrodialysis. The barium process can also be used for sulphate removal and offers the following advantages:

- Sulphate can be removed quantitatively to specific values due to the low solubility of barium sulphate.
- The soluble barium salt, barium sulphide, can be recovered from the product, barium sulphate.

Kun studied the removal of sulphate with barium carbonate and obtained good results [1]. However, he identified three problem areas, namely, the requirement of a long retention time, high concentrations of soluble barium in the treated water when more barium carbonate is dosed than stoichiometrically required, and the high cost of the barium carbonate. Volman overcame the cost problem by demonstrating that the barium sulphate produced could be reduced efficiently and economically with coal under thermic conditions to produce barium sulphide [2]. This compound can be used directly for the process or converted to barium carbonate. Wilsenach demonstrated the economic viability by calculating the cost of producing barium sulphide from barium sulphate [3].

Trusler *et al.* developed a barium carbonate method in a two-staged fluidised bed reactor system to overcome the other problems identified by Kun, namely, long retention time and the high barium concentration in the treated water [4],[1]. However, the barium carbonate process was found to be unsuitable for water containing metals, as is the case with some mine waters. The barium carbonate crystals became inactive when coated with metal hydroxide precipitates. Maree *et al.* also saw a disadvantage of the barium carbonate process in the separation of barium sulphate and calcium carbonate, which co-precipitate [5].

The purpose of this study was to demonstrate the performance of the integrated barium sulphide process, consisting of the following stages (Figure 1):

- Lime pre-treatment for partial sulphate removal.
- Removal of sulphate as barium sulphate to below 200 mg/ℓ by means of barium sulphide treatment.
- H_2S-stripping with CO_2-gas.
- Stripping of CO_2 and crystallization of $CaCO_3$.
- Production of barium sulphide by heating the barium sulphate produced from the above stage.

The specific aims were to:

- Demonstrate that sulphate can be removed to less than 200 mg/l with barium sulphide treatment.
- Determine optimum conditions for the following process-stages:
  - o Partial sulphate removal through lime pre-treatment.
  - o Reduction of barium sulphate to barium sulphide.
  - o H_2S-stripping and processing.
- Estimate the running cost of the process.

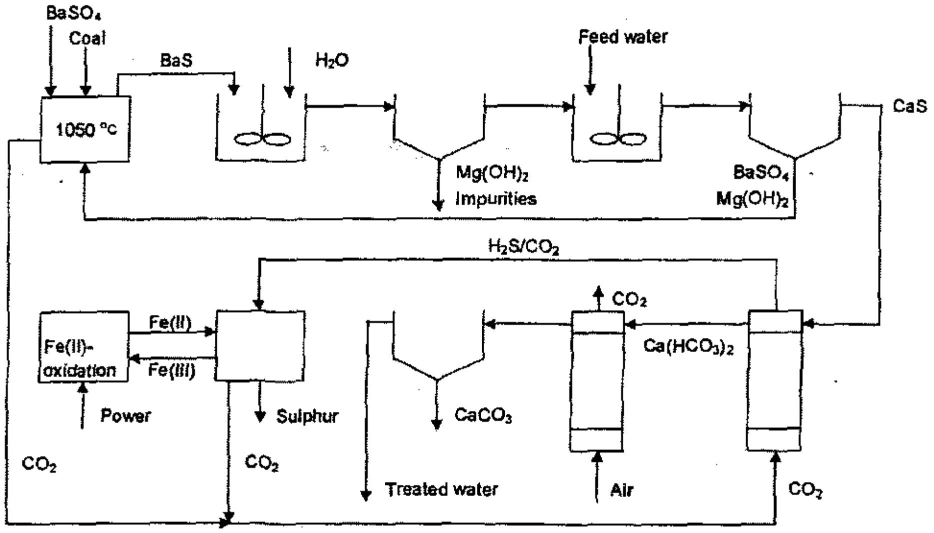


Figure 1: Process flow diagram for the barium sulphide process (pre-treatment with lime not shown).

2 MATERIALS AND METHODS

2.1 Feedstock

Artificial feed water containing 2 500 mg/ℓ sulphate and 292 mg/ℓ magnesium (1.96 g/ℓ $MgSO_4.7H_2O$, and 1.01 mℓ/ℓ H_2SO_4) was used during continuous pilot-scale studies. Lime (supplied by Lime Distributors) and barium sulphide (supplied by G&W Base Minerals) were used for pH adjustment and sulphate removal, respectively.

For H_2S-stripping studies, a synthetic sulphide rich feed water, with sulphide concentrations between 700 to 800 mg/ℓ was used. CO_2 gas (supplied by Afrox) was used for H_2S-stripping. An $Fe_2(SO_4)_3$ solution (11 g/ℓ) as Fe was used for absorption of the stripped H_2S-gas.

During thermic studies, $BaSO_4$ produced during continuous pilot-scale studies and chemically pure $BaSO_4$ were used for BaS recovery studies.

2.2 Equipment

Figure 1 shows the laboratory-scale plant that was used for sulphate removal with barium sulphide. Figures 2 and 3 show the laboratory-scale plant that was used for H_2S-stripping and H_2S-processing to elemental sulphur. Table 1 shows the volume and dimensions of the various reactors depicted in Figures 1, 2 and 3. Photo 1 shows the tube furnace that was used for thermic studies. The tube had a diameter of 40 mm and was 530 mm long.

A packed bed reactor and a venturi system was used for H_2S-stripping and H_2S-absorption into an iron(III)-solution, using configurations A (Figure 2) and B (Figure 3). In configuration A, the sulphide solution was fed continuously to the packed-bed reactor (stripping stage), and allowed to drip down the packing material (25 mm diam. Raschig rings), while H_2S-free CO_2-gas, flowing from bottom to top, was recycled via the H_2S-absorption stage. In the H_2S-absorption stage, H_2S was contacted with an iron(III)-solution *at a pH of 2.5, to* produce elemental sulphur (Reaction 1). The iron(III)-solution was replaced batchwise, as required.

$$H_2S + 2Fe^{3+} \rightarrow S + 2Fe^{2+} + 2H^+ \qquad (1)$$

In configuration B, the sulphide solution was recycled through the venturi system in batch mode, and allowed for H_2S-stripping, by sucking in CO_2-poor gas, hence contacting it with the sulphide-rich water (stripping stage). The stripped H_2S-rich gas was passed through the packed bed-reactor to which the iron(III)-solution was continuously fed for sulphur production.

The packed column consisted of a 0.8-m randomly packed bed, with 25-mm Pall-rings used as packing material. A 240-mm diam. Perspex cylinder (adsorption) was used and Perspex plates were used for support of the packing and to aid in liquid distribution to the column. A Perspex plate with evenly distributed holes was installed at the top of the column to ensure adequate distribution of the liquid feed. The venturi *was used for gas recirculation between the stripping and the absorption stages. A centrifugal pump* (capacity, 1 m^3/h) was used to recycle the iron (III) (configuration 1) or the sulphide (configuration 2) solution via the venturi. Table 1 shows the dimensions of the various units. CO_2 was transferred from a CO_2-cylinder to a CO_2 float tank from where it was pumped at a set flow rate with a peristaltic pump at NTP (normal pressure and temperature) to the H_2S-stripping stage.

Table 1: Volume and dimensions of various reactors.

Item	**Volume (ℓ)**	**Diameter (mm)**	**Height (mm)**
BaS treatment stage			
BaS storage tank	10	235	235
BaS treatment reactor	10	235	235
Clarifier ($BaSO_4$)		*450*	
H_2S-stripping/processing			
Packed bed-reactor packed with 25 mm Pall-rings	39	250	800
Venturi reactor	40	300	800

Photo 1: Tube furnace.

2.3 Experimental Procedure

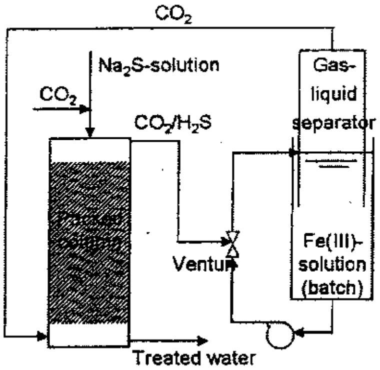
2.3.1 Pre-treatment and BaS-treatment

Continuous studies

- Feed water (2 500 mg/ℓ SO_4; 83 mℓ/min), lime slurry (10%, 3 mℓ/min), barium sulphide slurry (57.7 g/ℓ; 3 mℓ/min) and Flocculant 3095 (3 mℓ/min) were fed to the system shown in Figure 2. Sludge was recycled from the under flow of the two clarifiers to the completely-mixed reactors at a rate of 83 mℓ/min. Sludge was withdrawn periodically to maintain the solids content in the lime treatment reactor at 40 g/ℓ and in the BaS-treatment reactor at 32 g/L

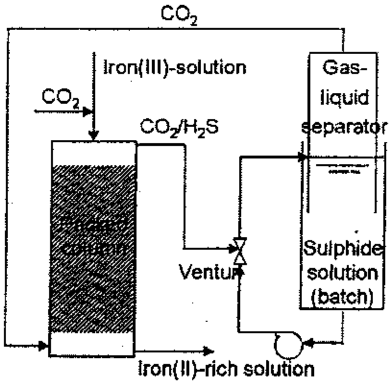
Batch studies

Batch studies were carried out on the barium sulphide treated water for H_2S-stripping and softening. H_2S-stripping was achieved by bubbling CO_2 through while softening was achieved by dosing 5 g/ℓ $CaCO_3$ and stripping CO_2 with air.



Configuration A

Figure 2: H_2S-stripping and processing



Configuration B

Figure 3: H_2S-stripping and processing

H_2S-stripping and processing

In configuration A (NaS fed continuously to the packed bed-reactor and contacted with an iron(III)-solution which was passed through a venturi system in batch mode), Na_2S was contacted with CO_2-gas with varied concentrations and flow rates. Sulphide removal was monitored in the feed water after the feed pipe at the inlet of the packed bed-reactor and the treated water. The iron(II)-concentration was monitored in the iron(III) solution that was handled in batch mode.

In configuration B (an iron(III)-solution was fed to the packed bed-reactor and contacted with stripped H_2S-gas from the venturi system), iron(III) solution was fed at various flow rates. The resulting iron(II) was monitored in the feed and treated streams of the iron(III)-solution. The sulphide concentration was monitored in the sulphide solution that was handled in batch mode.

Thermal studies

$BaSO_4$ (industrial grade and pure $BaSO_4$) and coal were mixed and reacted at elevated temperature in the tube furnace and the muffle furnace for various reaction periods. Solid samples were collected and analyzed for mass loss, sulphide content and ability to remove sulphate.

2.3.2 Experimental program

The following parameters were investigated:

BaS-treatment stage

- Water quality (feed and treated)

H_2S-stripping and processing stage

- Reactor type (packed bed-reactor and venturi system)
- CO_2-concentration (20% to 100%)
- CO_2 : Sulphide ratio

- Feed rate of CO_2 rich stream (0.2 to 1.0 ℓ/min)
- Retention time of sulphide solution (Feed rate of sulphide rich stream (0.5 to 2 ℓ/min))
- Efficiency of sulphide reaction with iron(III)-solution

Thermic studies stage

- C: $BaSO_4$-ratio (2, 2.5 and 3)
- Type of furnace (Tube furnace and Muffle furnace)
- Temperature (1000 °C, 1050 °C and 1100 °C)
- Reaction time (15 min, 30 min, 60 min and 120 min).

2.3.3 *Analytical*

Samples were collected regularly and filtered through Whatman No 1 filter paper. Sulphate, sulphide, alkalinity, calcium, iron(II), mixed liquor suspended solids (MLSS), volatile suspended solids (VSS), acidity and pH determinations were carried out manually according to procedures described in Standard Methods [6] . Calcium was assayed using atomic absorption spectrophotometry. Acidity was determined by titrating the solution to pH 8.3 using NaOH. Sulphide (in the product from thermic studies) was determined by mortaring the product, and analyzing for sulphide with the iodine method in a 0.5 g/100 mℓ BaS solution.

3 RESULTS AND DISCUSSION

3.1 Water Quality

Table 2 shows the chemical composition of the feed water before and after treatment with lime and BaS. It was noted that:

- During pre-treatment sulphate was removed from 2 650 mg/ℓ to 1 250 mg/ℓ. This low sulphate concentration was achieved due to the high calcium concentration as a result of lime addition and the solubility product of gypsum. Magnesium and other metals were completely removed.
- During BaS-treatment, sulphate was removed according to the stoichiometric BaS-dosage (1 000 mg/ℓ).
- During H_2S-stripping with CO_2-gas, sulphide was removed from 320 down to < 20 mg/ℓ (Figure 4).
- During the softening stage, 890 mg/ℓ $CaCO_3$ (993 – 103) precipitated due to CO_2-stripping with air (Figure 5).

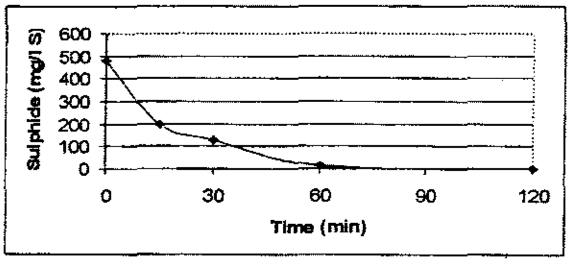


Figure 4: H_2S-stripping with CO_2.

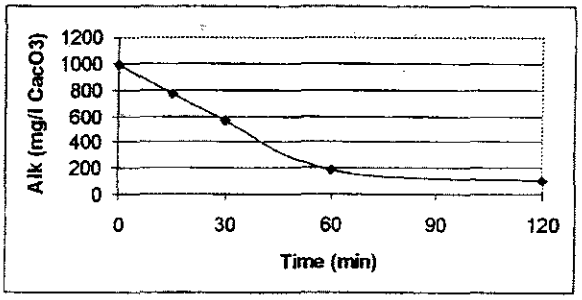


Figure 5: CO_2-stripping with air and $CaCO_3$-precipitation.

Table 2: Chemical composition of feed water and after treatment with BaS.

Parameter	Concentration				
	Feed	Lime	BaS	H_2S-stripping	Softening
$Ca(OH)_2$-dosage (g/ℓ)		1.89			
BaS-dosage (g/ℓ)			1.76		
Gypsum dosage (g/ℓ)		5			
$CaCO_3$ dosage (g/ℓ)					5
Alkalinity addition (g/ℓ)		2554	1041	3595	
pH	1.6	12	11.9	5.7	7.2
Sulphate (mg/ℓ SO_4)	2650	1250	250	255	250
Sulphide (mg/ℓ S)	0	320	<20	<20	<20
Alkalinity (mg/ℓ $CaCO_3$)	-1900	960	2276	993	103
Alkalinity increase (mg/ℓ)		2860	1316	4176	
Calcium (mg/ℓ Ca)	43	950	981	460	139
Magnesium (mg/ℓ Mg)	166.5	<0.1	<0.1	1.70	1.8
Iron (mg/ℓ Fe)	8.53	<0.01	<0.01	<0.01	<0.01
Aluminium (mg/ℓ Al)	9.3	0.14	0.23	0.16	0.19
Manganese (mg/ℓ Mn)	10.6	<0.03	<0.03	<0.03	<0.03
Copper (mg/ℓ Cu)	9	<0.05	0.06	0.06	0.07
Lead (mg/ℓ Pb)	8.9	<0.1	<0.1	<0.1	<0.1
Zinc (mg/ℓ Zn)	16	<0.05	<0.05	<0.05	<0.05
Nickel (mg/ℓ Ni)	11.2	<0.03	<0.03	<0.03	<0.03
Cations (meq/ℓ)	57.28	47.50	40.97	23.00	6.95
Anions (meq/ℓ)	55.21	45.24	50.73	25.17	7.27

3.2 H_2S-Stripping and Processing Stage

Sulphide can be removed through CO_2-stripping from 300 to less than 20 mg/ℓ (Figure 4). In order to obtain engineering design criteria for full-scale implementation, the effects of various parameters on the rate of H_2S-stripping were determined, using configuration A (Figure 2). By feeding a sodium sulphide solution and a CO_2-gas stream, counter current, on a continuous basis through to a packed bed reactor, it was noted that:

- Number of stages. By passing the sulphide solution through two stages in series at a CO_2 feed load/Na_2S feed load of 1.4 g CO_2/g S, sulphide was removed from 834 down to 376 mg/ℓ in stage 1, and to 77 mg/ℓ (as S) in stage 2 (Table 3). By providing a third stage sulphide could have been removed to less than 20 mg/ℓ. The aim, however, with this investigation was to identify optimum process conditions to allow the minimum number of process stages for complete sulphide removal. Sulphide is quantitatively converted to sulphur as indicated by the correspondence between the actual and theoretical values for the ratio: load of iron(II) produced/load of sulphide removed (3.65 versus 3.49). More CO_2 was consumed than theoretically required (1.75 versus 1.38). The higher CO_2 consumption can be ascribed to the partial solubility of both CO_2 and H_2S in the pH range 6 to 7. The theoretical ratios for load of CO_2 consumed/load of sulphide removed (1.38) and load of iron(II) produced/load of sulphide removed (3.49) were calculated from Reactions 2 and 3.

$$H_2S + 2Fe^{3+} \rightarrow S + 2Fe^{2+} + 2H^+ \quad (2)$$
$$2CO_2 + S^{2-} + 2H_2O \rightarrow 2HCO^{3-} + H_2S \quad (3)$$

- Effect of HRT. Table 4 shows the effect of the Na_2S feed rate on the sulphide removal. Better sulphide removal was achieved with increased Na_2S feed rate (lower HRT). An amount of 217 mg/ℓ sulphide was removed at a feed rate of 0.5 ℓ/min (HRT = 59 min), compared to only 154 mg/ℓ at a feed rate of 2 ℓ/min (HRT = 15 min). The results in this experiment were however negative in the sense that the pH of the treated water was higher than 8 (9.0), despite of the fact that the actual value of dCO_2/dNa_2S of 14.53 was higher than the theoretical value of 1.38. The negative result can be ascribed to the fact that CO_2 was not completely utilized due to too little contact time between CO_2 and the Na_2S-solution. In the next experiments this problem was solved by allowing sufficient contact time by passing the Na_2S/CO_2 mixture through a 5 m pipe with a diameter of 20 mm (volume = 6.3 ℓ). At a feed rate of 1 ℓ/min, the hydraulic retention time in the 5 m pipe amounted to 6.3 min.
- Effect of CO_2 flow rate. Table 5 shows the effect of CO_2 flow rate on the sulphide removal at a constant Na_2S flow rate of 1 ℓ/min. By increasing the CO_2 flow rate from 0.19 ℓ/min to 0.83 ℓ/min, the

sulphide removal increased from 342 to 474 mg/ℓ and residual sulphide in solution decreased from 134 to 0 mg/ℓ (as S). The corresponding ratios of CO_2 feed load/Na_2S feed load increased from 0.78 to 3.46. The stoichiometric value required for this ratio is 1.38 (Reaction 3). This demonstrates that complete sulphide removal can be achieved by dosing 2.5 times more CO_2 than stoichiometrically required. Excess CO_2 gas would be available in many applications. During barium treatment, CO_2 is produced at the rotary kiln where barium sulphide is recovered from barium sulphate. With the biological sulphate removal process CO_2-gas is produced by the heating unit. During limestone neutralization of acid water, CO_2 with a high concentration is produced due to dissolution of $CaCO_3$.

- Effect of CO_2-concentration. Table 6 shows the effect of the CO_2 concentration on sulphide removal. By increasing the CO_2 concentration from 20% to 100%, the sulphide removal increased from 278 to 387 mg/ℓ (as S). In this case sulphide was not removed to 0 mg/ℓ as the dCO_2/dNa_2S feed ratio was less than the value of 3.46 as determined above empirically.

- Effect of gas recycle rate. Table 7 shows the effect of the gas recycle rate on the sulphide removal. By increasing the gas recycle rate from 9.1 to 19.6 ℓ/min, the sulphide removal was improved from 304 to 666 mg/ℓ. In this experiment sulphide was also not removed to 0 mg/ℓ as the dCO_2/dNa_2S feed ratio was less than the value of 3.46.

It was demonstrated above that a packed bed-reactor (configuration A) (Figure 2) can be used for sulphide stripping. In this configuration it appeared that the absorption stage, where H_2S-rich gas was contacted with an iron(III) solution in a venturi system, was effective, due to good contact between gas and liquid phase. With the apparent good performance of the venturi system for H_2S absorption, it was decided to evaluate the suitability of the venturi system also for H_2S-stripping. The same equipment that was used for configuration A (Figure 2), was used for configuration B (Figure 3), except that the venturi system was used for sulphide stripping in batch mode, and the packed bed-reactor was used for H_2S-absoption into an iron(III) solution under continuous conditions.

Table 8 and Figure 6 show the effect of iron(III) feed rate on sulphide removal. It was noted that:

- Better sulphide removal was achieved with increased feed rate of iron(III). This can be ascribed to only partial absorption of H_2S at low iron(III) feed rates in the closed circuit of Configuration 2. This is an indication that the packed bed-reactor does not function as well as the venturi system for the absorption of H_2S into an iron(III)-solution.

- The experimental (actual) dFe/dH_2S ratio was similar to the theoretical value of 3.49 (Reaction 2). This result shows that all iron(III) that was introduced to the packed bed reactor was consumed for H_2S-absorption through the reaction:

The results showed that H_2S-stripping and H_2S-absorption is favoured by intensive mixing. Intensive mixing supports mass transfer of H_2S from liquid to gas phase in the case of H_2S-stripping and from gas to liquid phase in the case of H_2S-absorption. It was demonstrated that the venturi device was more efficient than the packed-bed reactor. This could be ascribed to the high pressure (300 kPa) and the high velocity (50 m/sec) of gas and liquid particles. Based on this observation, it is recommended that the Turbulator be used during a scale-up version. The Turbulator exists out of a motor which directly (no gear box) drives a disc via a hollow shaft. The Turbulator allows mixing between the gas and liquid phase by sucking in air through the hollow shaft that rotates at 2000 rpm. The velocity at the outer limit of the disc is 15 m/sec (Dia = 0.15 m; rpm = 2 000).

Table 3: Sulphide removal in two stages in series.

Parameter	State number	
	1	2
CO_2/Na_2S-feed ratio (g CO_2/g S)	0.77	1.40
Na_2S feed rate (ℓ/min)	0.90	0.90
CO_2 feed rate (ℓ/min)	0.29	0.24
CO_2-concentration (%)	100	100
HRT (min)	32.7	32.7
Gas recycle rate (ℓ/min)	22.9	22.9
Sulphide in feed (mg/ℓ S)	834	376
Sulphide after pipe (mg/ℓ S)		
Sulphide in treated water (mg/ℓ S)	434	77
Sulphide removed (mg/ℓ)	400	299
pH in feed	9.05	
pH after pipe		
pH in treated water	7.02	
dCO_2/dNa_2S ratio (g CO_2/g S)		
Theoretical	1.38	1.38
Actual	1.70	1.79
dFe/dH_2S		
Theoretical	3.49	3.49
Actual	3.60	3.70

Table 4: Effect of retention time (Na_2S feed rate) on sulphide removal. NaS inside table change Na_2S

Parameter	Na_2S feed rate (ℓ/min)		
	2.00	1.00	0.50
CO_2/Na_2 feed ratio (g CO_2/g S)	2.77	1.85	1.51
Na_2S feed rate (ℓ/min)	2.00	1.00	0.50
CO_2 feed rate (ℓ/min)	2.09	0.66	0.26
CO_2-concentration (%)	100	100	100
HRT (min)	14.7	29.5	58.9
Gas recycle rate (ℓ/min)	18.1	18.1	18.1
Sulphide in feed (mg/ℓ S)	742.4	704	688
Sulphide after pipe (mg/ℓ S)			
Sulphide in treated water (mg/ℓ S)	588.8	496	470.4
Sulphide removed (mg/ℓ)	153.6	208	217.6
pH in feed	12.18	12.15	12.17
pH after pipe			
pH in treated water	9.00	8.41	8.47
dCO_2/dNa_2S ratio (g CO_2/g S)			
Theoretical	1.38	1.38	1.38
Actual	14.53	7.28	4.25 5.37
dFe/dH_2S			
Theoretical	3.49	3.49	3.49
Actual	1.80	0.98	8.90

Table 5: Effect of the CO_2 feed rate on the sulphide removal.

Parameter	CO_2 feed rate (ℓ/min)		
	0.19	0.40	0.83
CO_2/Na_2 feed ratio (g CO_2/g S)	0.78	1.68	3.46
Na_2S feed rate (ℓ/min)	1	1	1
CO_2-concentration (%)	29.5	29.5	29.5
HRT (min)	100	100	100
Gas recycle rate (ℓ/min)	18.1	18.1	18.1
Sulphide in feed (mg/ℓ S)	476.8	464	473.6
Sulphide after pipe (mg/ℓ S)	378	265	73.6
Sulphide in treated water (mg/ℓ S)	134.4	25.6	0
Sulphide removed (mg/ℓ)	342.4	438.4	473.6
pH in feed	8.40	8.48	8.95
pH after pipe	7.02	6.62	6.38
pH in treated water	7.10	7.06	6.54
dCO_2/dNa_2S ratio (g CO_2/g S)			
Theoretical	1.38	1.38	1.38
Actual	1.02	1.77	3.46
dFe/dH_2S			
Theoretical	3.49	3.49	3.49
Actual	0.88	1.13	1.91

Table 6: Effect of CO_2-concentration on sulphide removal.

Parameter	CO_2-concentration (%)		
	20	53	100
CO_2/Na_2 feed ratio (g CO_2/g S)	1.37	1.61	1.46
Na_2S feed rate (ℓ/min)	1	1	1
HRT (min)	29.5	29.5	29.5
CO_2 feed rate (ℓ/min)	0.51	0.56	0.49
Air feed rate (ℓ/min)	2	0.5	0
Gas recycle rate (ℓ/min)	18.1	18.1	18.1
Sulphide in feed (mg/ℓ S)	739.2	678.4	665.6
Sulphide after pipe (mg/ℓ S)	640	538	486
Sulphide in treated water (mg/ℓ S)	460.8	393.6	278.4
Sulphide removed (mg/ℓ)	278.4	284.8	387.2
pH in feed	9.54	12.30	12.34
pH after pipe	8.62	8.22	7.36
pH in treated water	8.12	8.03	7.97
dCO_2/dNa_2S ratio (g CO_2/g S)			
Theoretical	1.38	1.38	1.38
Actual	3.94	3.86	2.53
dFe/dH_2S			
Theoretical	3.49	3.49	3.49

Table 7: Effect of gas recirculation rate on sulphide removal.

Parameter	CO_2-concentration (%)		
	19.63	13.09	9.06
CO_2/Na_2 feed ratio (g CO_2/g S)	0.78	1.34	1.17
Na_2S feed rate (ℓ/min)	1	1	1
CO_2 feed rate (ℓ/min)	0.26	0.48	0.41
C_2 concentration (%)	100	100	100
HRT (min)	29.5	29.5	29.5
Gas recycle rate (ℓ/min)	19.6	13.1	9.1
Sulphide in feed (mg/ℓ S)	665.6	697.6	681.6
Sulphide after pipe (mg/ℓ S)	666	374	
Sulphide in treated water (mg/ℓ S)	0	371.2	377.6
Sulphide removed (mg/ℓ)	665.6	326.4	304
pH in feed	12.10	12.30	12.34
pH after pipe	7.55	7.55	7.36
pH in treated water	7.81	7.64	7.97
dCO_2/dNa_2S ratio (g CO_2/g S)			
Theoretical	1.38	1.38	1.38
Actual	1.19	2.88	2.70
dFe/dH_2S			
Theoretical	3.49	3.49	3.49
Actual	1.76	2.23	3.73

Table 8: Effect of the iron(III) flow rate on the sulphide removal.

Parameter	Fe^{3+}-feed rate (ℓ/min)			
	1.00	1.00	3.00	4.00
CO_2/Na_2S feed ratio (g CO_2/g S)	Batch	Batch	Batch	Batch
Na_2S feed rate (ℓ/min)	Batch	Batch	Batch	Batch
HRT (min)	Batch	Batch	Batch	Batch
Gas recycle rate (ℓ/min)	18.1	18.1	18.1	18.1
Time (min)	Sulphide (mg/ℓ S)			
0	816	1056	704	784
15	768	944	560	720
30	688	880	432	416
45	592	816	336	224
60	432	768	224	32
75	320	672	96	
90		480	94	
Time (min)	Sulphide removed (mg/ℓ S)			
0	0	0	0	0
15	48	112	144	64
30	128	176	272	368
45	224	240	368	560
60	384	288	480	752
75	496	384	608	
90		576	640	
Time (min)	pH			
0	11.35	12.13	12.84	12.98
15	10.19	11.79	10.04	11.16
30	8.44	10.24	8.03	8.34
45	7.65	8.93	7.04	7.70
60	7.41	8.05	7.23	7.30
75	7.23	7.83	7.13	
90		7.74	7.08	
dCO_2/dNa_2S ratio (g CO_2/g S)				
Theoretical	1.38	1.38	1.38	1.38
Actual	8.40	8.06	8.02	7.99
dFe/dH_2S				
Theoretical	3.49	3.49	3.49	3.49
Actual	2.87	3.49	8.15	3.12

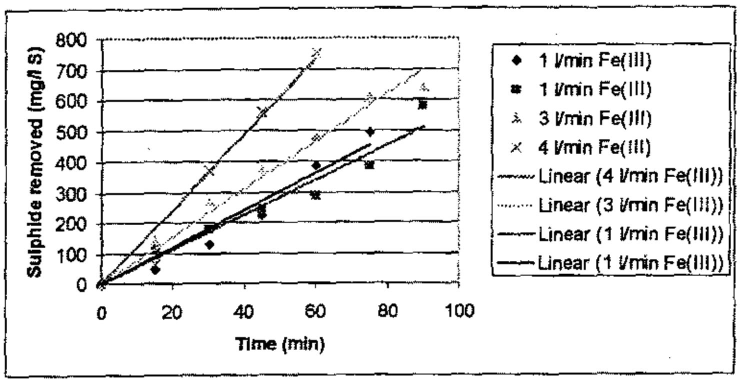


Figure 6: Effect of iron(III) flow rate on the sulphide removal.

3.3 Thermal Studies

Table 9 shows the effect of various parameters on the BaS yield during the thermic conversion of $BaSO_4$ to BaS. It is noted that:

- The conversion efficiency reduce with time when a Muffle furnace was used (Exp 1). This is ascribed to the large volume of air surrounding the reaction vessel. Initially $BaSO_4$ is converted to BaS due to reducing conditions created by the conversion of coal to CO and CO_2. When the carbon is exhausted, the BaS produced is contacted with oxygen at the high temperature which allows oxidation of BaS to $BaSO_4$. Therefore, all further studies (Experiments 2 to 8) were carried out in a tube furnace. The air was also purged with nitrogen to eliminate oxidation conditions.
- A short reaction time of 15 min is sufficient to obtain a high yield of BaS at a temperature of 1050 °C (Exp 2). Figure 7.a shows the conversion of $BaSO_4$ to BaS as a function of time.
- The reaction starts at a temperature of 900 °C and reaches an optimum at 1050 °C (Exp 3 and Figure 7.b).
- The minimum $C/BaSO_4$ mole ratio required for complete reduction is 2 which indicates that the reaction is as follows (Exp 4 and Figure 7.c:
  $2C + BaSO_4 \rightarrow 2CO_2 + BaS$
- Both activated carbon and coal can be used for $BaSO_4$ reduction (Expts 5 and 6). Slightly better values are achieved with activated carbon than with coal which could be ascribed to impurities (e.g. FeS) in coal.
- Both analytical grade and industrial grade $BaSO_4$ provided good yields of BaS (Exp 7).
- $Mg(OH)_2$ does not interfere with the reduction reaction of $BaSO_4$ to BaS (Exp 8).

The methods used for conversion measurements (mass loss, sulpide and sulphate precipitation) compares well. The sulphide values were lower than the mass loss values and can be ascribed to sulphide losses during the dissolution stage. Such losses are confirmed by a sulphide odor that was picked up. The product was also tested for the ability to remove sulphate (Exp 5). Although the sulphate method is not as accurate as the other methods, a value of the same order was achieved.

3.4 Running Cost

The running cost of the barium sulphide process amounts to R2.12/m^3 for the removal of 2 g/ℓ of sulphate (Table 10). This and the cost of water (R2/m^3) and by-products, sulphur (R0.30/m^3) and calcium carbonate (R3.33/m^3).

4 CONCLUSIONS

The following conclusions were made from the investigation:

1. During lime treatment sulphate was removed from 2 800 mg/ℓ down to less than 1 200 mg/ℓ due to gypsum crystallization and metals were precipitated as metal hydroxides).

2. During BaS treatment, sulphate was removed down to less than 200 mg/ℓ due to $BaSO_4$-precipitation.
3. Sulphide was removed from 333 down to less than 10 mg/ℓ (as S) in the stripping stage, using CO_2 gas for stripping.
4. The stripped H_2S-gas was contacted with an iron(III)-solution and converted quantitatively to elemental sulphur.
5. The alkalinity of the calcium bicarbonate rich water was reduced from 1 000 to 110 mg/ℓ (as $CaCO_3$) after CO_2-stripping with air due to $CaCO_3$-precipitation.
6. Iron(II), after sulphur production, was re-oxidized to iron(III) using an electrolytic step.
7. The running cost of the barium sulphide process amounts to R2.12/m^3 for the removal of 2 g/ℓ of sulphate.

Table 9: Effect of various parameters on the thermic conversion of $BaSO_4$ to BaS

Exp No.	Parameter	Value	Conversion (%)			Experimental conditions					
			Mass loss	Sulphide analysis	Sulphate precipitation	Time min	Temp °C	$C/BaSO_4$	Carbon	$Mg(OH)_2/BaSO_4$	Furnace
1	Time (min)	15	75.3			15	1050	Coal	Pure	0	Muffle
		30	63.8			30	1050	Coal	Pure	0	Muffle
		60	60.6			60	1050	Coal	Pure	0	Muffle
2	Time (min)	2	1.1	0		2	1050	Activated	Industrial	0	Tube
		4	37.5	35.5		4	1050	Activated	Industrial	0	Tube
		5	75.6	74.4		5	1050	Activated	Industrial	0	Tube
		15	101	96.3		15	1050	Activated	Industrial	0	Tube
		20	99.6	94.6		20	1050	Activated	Industrial	0	Tube
3	Temperature (°C)	900	5			20	900	Activated	Industrial	0	Tube
		950	54.7	50.7		20	950	Activated	Industrial	0	Tube
		1000	81.6	79.4		20	1000	Activated	Industrial	0	Tube
		1050	90.4	86.5		20	1050	Activated	Industrial	0	Tube
		1100	107.4	96.3		20	1100	Activated	Industrial	0	Tube
4	$C/BaSO_4$-mole ratio	1	45.5	40.1		20	1050	Activated	Industrial	0	Tube
		2	82.1	77.7		20	1050	Activated	Industrial	0	Tube
		3	89.3	82.8		20	1050	Activated	Industrial	0	Tube
5	Carbon	Activated	101.6	94.6		30	1050	Activated	Industrial	0	Tube
		Coal	94.6	93	90	30	1050	Coal	Industrial	0	Tube
6	Carbon	Activated	89.3	82.8		20	1050	Activated	Industrial	0	Tube
		Coal	84.4	79.4		20	1050	Coal	Industrial	0	Tube
7	Barium	Pure	107.1	99.7		30	1050	Activated	Pure	0	Tube
		Industrial	101.6	94.6		30	1050	Activated	Industrial	0	Tube
8	$Mg(OH)_2/BaSO_4$	0	89.3	86.2		20	1050	Activated	Industrial	0	Tube
		0.7	93.2	78.4		20	1050	Activated	Industrial	0.7	Tube
		1.7	97.6	76		20	1050	Activated	Industrial	1.7	Tube
		4.3	96.9			20	1050	Activated	Industrial	4.3	Tube

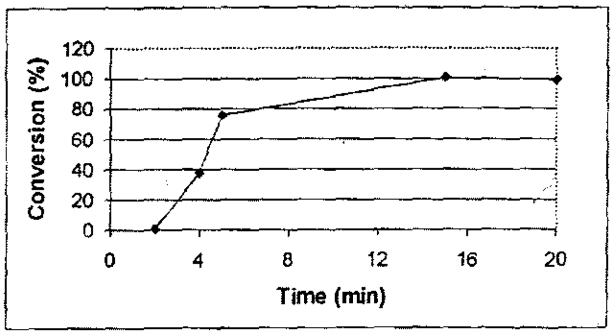
Table 10: Running cost of the barium sulphide process.

Item		Cost/ (Rm^3)
Feed sulphate (mg/ℓ)	2200.00	
Treated sulphate (mg/ℓ)	200.00	
$BaSO_4$ production (kg/m^3)	5.22	
Barium losses (%)	5.00	
$BaSO_4$ purity (%)	93.00	
$BaSO_4$ required (kg/m^3)	0.26	
$BaSO_4$ price (R/t)	2630.00	
$BaSO_4$ cost (R/m^3)		0.69
Carbon content of coal (%)	70.00	
C:$BaSO_4$-ratio	3.00	
Coal required (kg/m^3)	1.07	
Coal price (R/t)	150.00	
Coal cost (R/m^3)		0.16
Iron (II) oxidation (kg.m^3)	2.33	
Energy requirement:		
$BaSO_4$ reduction (MJ/kg)	2.03	
Iron(II) oxidation (kW/kg Fe)	1.07	
Energy requirement (kW/m^3)		
$BaSO_4$ reduction	2.94	
$Mg(OH)_2$		
Iron(II) oxidation	2.50	
Electricity cost (R/kWh)	0.16	
Energy cost (R/m^3)		
Kiln		0.47
Iron(II) oxidation		0.40
Electrical drives, pumps, etc		0.20
Labour		0.20
TOTAL RUNNING COST		2.12
Products		**Value (R/m^3)**
Water value		2.00
Sulphur	0.60	
Sulphur yield (%)	90	
Price (R/t)	500.00	
Sulphur value (R/m^3)		0.30
$CaCO_3$ (kg/m^3)	1.67	
$CaCO_3$ yield (%)	80	
Price (R/t)	2000.00	
$CaCO_3$ value (R/m^3)		3.33
TOTAL VALUE OF BY-PRODUCT		5.63

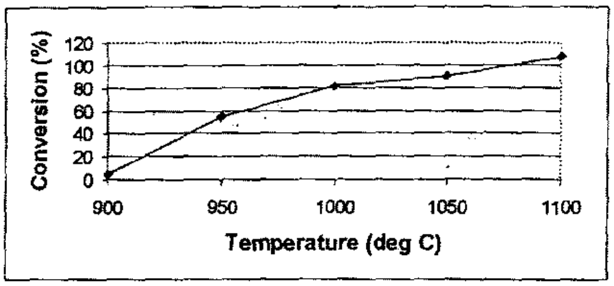
5 ACKNOWLEDGEMENTS

Sincere thanks are due to the following organizations for their financial and logistical support of the research reported in this paper:

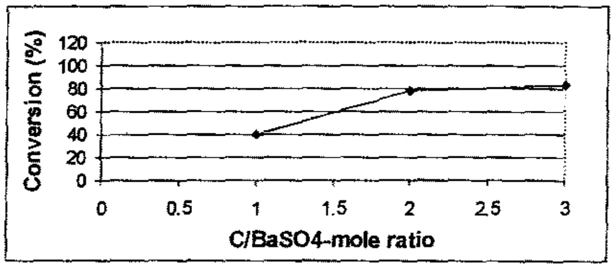
- **Anglo Coal (Navigation Section of Landau Colliery)**, who provided the necessary infrastructure at the mine and general assistance.
- **The National Research Foundation (NRF)** who provided funding through their Technology and Human Resources for Industry Programme (THRIP) for CSIR projects on neutralization and sulphate removal.
- **The CSIR** who provided substantial financial support for the research programme.



a. Time



b. Temperature



c. C/$BaSO_4$-mole ratio

Figure 7: Effect of various parameters on the conversion of $BaSO_4$ to BaS.

6. REFERENCES

[1] Kun, L.E. "A report on the reduction of the sulphate content of acid mine drainage by precipitation with barium carbonate". Internal report of Anglo American Research Laboratories, Project No. D/3/W/1, (1972).

[2] Volman, R., "The use of barium sulphide to remove sulphate from industrial effluents." Thesis presented for the degree M.Sc. (Chem. Eng), University of Stellenbosch, (1984).

[3] Wilsnach, I.T. "Cost estimate for barium sulphate reduction." Internal report of the Division of Water Technology, CSIR, Project No 620/2616/6, (1986).

[4] Trusler, G.E., Edwards, R.I., Brouckaert, C.J. and Buckley, C.A., "The chemical removal of sulphates." Proceedings of the 5th National Meeting of the S.A. Institution of Chemical Engineers, Pretoria, W3-0 – W3-11, (1988).

[5] J.P. Maree, J.P., Bosman, D.J. and Jenkins, G.R. "Chemical removal of sulphate, calcium and heavy metals from mining and power station effluents." Proceedings of the first biennial Conference of the Water Institute of Southern Africa, Cape Town, March, (1989).

[6] APHA,. *Standard Methods for the Examination of Water and Wastewater.* Twelfth Edition, American Public Health Association, New York, (1985)

PAPER 8: Maree, J.P., Netshidaulu, I., Strobos, G., Nengovhela, R. and Geldenhuys, A.J. Integrated process for biological sulphate removal and sulphur recovery, *Proceedings WISA 2003 – Biennial Conference & Exhibition,* 2–6 May 2004, Cape Town, South Africa.

The Biological Sulphate Removal Process has been used to remove sulphates in industrial effluents, rich in acid, sulphate and metals, to less than 200 mg/ℓ. Previously, ethanol was employed as energy and carbon source. Because of an unexpected increase in the price of ethanol, it became imperative to explore the possibility of finding an alternative source of energy and carbon for the sulphate reducing bacteria (SRB).

In this paper, the specific aims were to investigate:

- ✓ The energy utilisation efficiency when feed water is contacted directly with hot coal gas (SRB thrive between 30 - 35^{0}C)
- ✓ The rate of sulphate removal in the anaerobic reactor
- ✓ The effect of reactor type, CO_2-feed rate, CO_2/H_2S-ratio and the efficiency of H_2S-stripping
- ✓ The cost of electrolytic hydrogen generation (to replace ethanol as energy source)

From the investigation the following conclusions were made:

- ✓ The Biological Sulphate Removal Process allows sulphates to be removed from industrial effluents to below 200 mg/ℓ, using ethanol as the carbon and energy source
- ✓ With the use of a venturi system, H_2S can be stripped to a concentration below 20 mg/ℓ (as S) with CO_2. A number of aspects influenced the efficiency of H_2S-stripping, namely, H_2S feed rate, CO_2-concentration, CO_2/H_2S load ratio and absorption efficiency of H_2S in an iron(III) solution
- ✓ Hydrogen is a cost-effective energy source for the SRB (R1.53/kg of sulphate removed)

Paper 8 was presented orally by J P Maree at the WISA 2003 – Biennial Conference & Exhibition

INTEGRATED PROCESS FOR BIOLOGICAL SULPHATE REMOVAL AND SULPHUR RECOVERY

J.P. Maree, I. Netshidaulu, G. Strobos, R. Nengovhela and A.J. Geldenhuys

Division of Water, Environment and Forestry Technology, CSIR, PO Box 395, Pretoria, 0001, South Africa
Tel: (012) 841 2285. Fax: (012) 841 2506. E-mail: jmaree@csir.co.za

ABSTRACT

Industrial effluents rich in sulphate, acid and metals are produced when sulphuric acid is used as a raw material, and when pyrites is oxidised due to exposure to the atmosphere, e.g. in the mining industry. Biological sulphate removal can be used to treat industrial effluents to achieve, in addition to sulphate, metal removal and neutralisation. Sulphate can be removed as elemental sulphur via sulphide as an intermediate product when an energy source is provided. The biological sulphate removal process has developed over the past 15 years to the stage where it can compete successfully with other sulphate removal technologies for full-scale treatment of mine and other industrial effluents. The aim of this investigation was to demonstrate the performance of the integrated process consisting out of hydrogen generation, sulphate reduction with hydrogen as energy source, H_2S-stripping and stabilization stages.

The following conclusions were made from this investigation:

- *The biological sulphate removal process can be used for removal of sulphate to less than 200 mg/l using ethanol as the carbon and energy source.*
- *H_2S can be stripped to below 20 mg/l (as S) with CO_2 by using a venturi as a stripping device. The efficiency of H_2S-stripping is influenced by H_2S feed rate, CO_2-concentration, CO_2/H_2S load ratio and absorption efficiency of H_2S in iron(III).*
- *Hydrogen is the most cost-effective energy source. The cost of hydrogen amounts to R1.53/m^3 per g/l of sulphate removed (R1.53/kg SO_4 removed).*

INTRODUCTION

Industrial effluents rich in sulphate, acid and metals are produced when sulphuric acid is used as a raw material, and when pyrites is oxidised due to exposure to the atmosphere, e.g. in the mining industry. Acid mine waters contain high concentrations of dissolved metals and sulphate, and can have pH values as low as 2.5. Acidic industrial effluents require treatment prior to discharge into sewage networks or into public watercourses. In water-rich countries the main causes of concern are the low pH and metal content of acidic effluents. Salinity is not a problem due to dilution with surplus capacity of surface water. In water-poor countries, e.g. South Africa, the high salinity associated with acidic industrial effluents is an additional concern.

Biological sulphate removal can be used to treat industrial effluents to achieve, in addition to sulphate, metal removal and neutralisation. Sulphate can be removed as elemental sulphur via sulphide as an intermediate product when an energy source is provided. Desalination is achieved by effecting calcium carbonate crystallisation after sulphate removal. Metals are completely removed by precipitation as sulphides. Alkalinity is generated in quantities stoichiometrically equivalent to the amount of sulphate removed, which allows direct treatment of acid water.

The biological sulphate removal process has developed over the past 15 years to the stage where it can compete successfully with other sulphate removal technologies for full-scale treatment of mine and other industrial effluents. Maree and Strydom showed that sulphate can be removed in an anaerobic packed-bed reactor using sucrose, pulp mill effluent or molasses as carbon and energy source (1). Metals like nickel, cadmium and lead were completely removed due to precipitation of metal sulphides. Maree and Hill showed that a three-stage process can be applied for sulphate removal, using molasses as carbon and energy source in an anaerobic packed-bed reactor (2). Sulphide can be stripped with a mixture of CO_2/N_2 from the effluent of the anaerobic reactor in a H_2S-stripping stage and residual COD and $CaCO_3$ can be removed in an aerobic final treatment stage. Maree et al. showed that when molasses is used as carbon and energy source it can either be utilised in the fermented or unfermented form (3). When molasses is allowed to ferment, acetic acid is the main carbon and energy source for the sulphate reducing bacteria. When molasses is kept sterile in the storage tank, sucrose is the main carbon and energy source with acetic acid as the metabolic end-product. With this information in mind it was concluded that by running two anaerobic sulphate removal reactors in series, sucrose can be fermented to lactate in the first reactor and via acetate to CO_2 in the second reactor. Du Preez et al. were the first to demonstrate that producer gas (mixture of H_2, CO and CO_2) can be used as carbon and energy source for biological sulphate reduction (4). H_2 and CO were utilised as energy and carbon sources, respectively. Visser investigated the competition between sulphate reducing bacteria (SRB) and methanogenic bacteria (MB) for acetate as energy and carbon source in an upflow Anaerobic Sludge Blanket (UASB) reactor (5). He found that at pH values less than 7.5, SRB's and MB's are equally affected by the presence of H_2S, while at higher pH values SRB's out-compete MB's. Van Houten showed that sulphate can be reduced to H_2S at a rate of 30 g SO_4/(l.d) when H_2/CO_2 is used as carbon and energy source and employing pumice or basalt particles to support bacterial growth in a fluidised-bed reactor (6). He found that the pH should be between 6.5-8.0; the temperature should be between 20 - 35°C; the H_2S concentration should be less than 450 mg/l; the system should be completely anaerobic; the biomass should be immobilized and the retention of the active biomass should be high; the gas should be in the ratio: H_2:CO_2, 80%:20%; the hydrogen mass transfer should be maximized; there should be a high gas hold-up (through the system recycle) and there should be a low bubble diameter (small gas bubbles). Geldenhuys et al. demonstrated that hydrogen can be generated on-site to provide it cost-effectively (7). Eloff at al. showed that a venturi device can be used to introduce hydrogen gas into the system as the energy source, while geotextile (a coarse, fibrous material, used in road construction) can be used as a support material for SRB growth (8).

The aim of this investigation was to demonstrate the performance of the integrated process consisting out of a heating unit, anaerobic reactor for sulphate reduction, H_2S-stripping and stabilization stages (Figure 1). The following reactions take place in the various stages:

$$\begin{array}{lcl}
4H_2 + SO_4^{2-} + CO_2 + Ca^{2+} & \rightarrow & HS^- + HCO_3^- + 3H_2O + Ca^{2+} \\
M^{2+} + HS^- & \rightarrow & MS + H^+ \\
HS^- + CO_2 + H_2O & \rightarrow & H_2S + HCO_3^- \\
H_2S + 2Fe^{3+} & \rightarrow & S + 2Fe^{2+} + 2H^+ \\
2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ & \rightarrow & 2Fe^{3+} + H_2O \\
2HCO_3^- + Ca^{2+} & \rightarrow & CaCO_3 + CO_2 + H_2O \\
\hdashline
4H_2 + SO_4^{2-} + CO_2 + Ca^{2+} + \tfrac{1}{2}O_2 & \rightarrow & CaCO_3 + S + 4H_2O \qquad [1]
\end{array}$$

The following specific aims were investigated:

- The energy utilization efficiency when feed water is contacted directly with hot coal gas.
- Determination of the sulphate removal rate in the anaerobic reactor.
- The effect of reactor type, CO_2-feed rate, CO_2/H_2S-ratio and the efficiency of H_2S-stripping.
- The cost of electrolytic hydrogen generation.

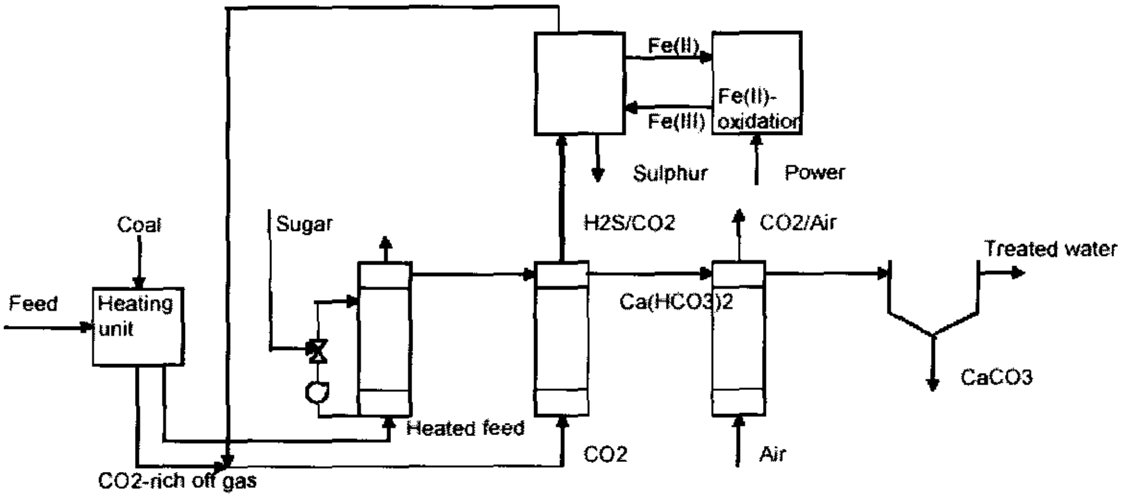


Figure 1. Process flow diagram of integrated biological sulphate removal process (CSIRosure process).

MATERIALS AND METHODS

Feedstock

The various stages of the process as shown in Figure 1 were operated in parallel using different feed waters.

The biological sulphate removal stage was fed with effluent from a lime neutralization plant at a rate of 8 to 16 m^3/h (hydraulic retention time of 10.3 to 5.2 h), while 0.1 to 0.2 g sugar/l mine water, 0.7 to 1.0 ml ethanol B (75 % ethanol, 25 % propanol)/l mine water were added as the carbon and energy source. Ammonium sulphate (25 mg/l (as N)) and phosphoric acid (5 mg/l (as P)) were added to maintain the COD:N:P ratio at 1000:7:2. No trace elements, except for 3 mg/l iron(II), were added, as the mine feed water contains all trace elements which are required by sulphate reducing bacteria.

For H_2S-stripping studies a synthetic sulphide rich water was used as feed water containing a sulphide concentration between 700 to 800 mg/l. CO_2 gas (supplied by Affox) was used for H_2S-stripping. An iron solution (11 g $Fe_2(SO_4)_3$/l (as Fe)) was used for absorption of the stripped H_2S-gas.

The heating unit was fed with peas (25 mm coal).

Equipment

Anaerobic stage. The anaerobic stage (Photograph 2) was evaluated on-site. The anaerobic reactor consists of a completely mixed reactor (dia. = 4 m, height = 8 m, volume = 105.5 m^3) with a cone in the top of the reactor to allow for sludge separation (9). The feed-rate to the anaerobic reactor was 8 to 16 m^3/h and 0.3 m^3/h to the H_2S-stripping stage. The reactor contents were stirred with a side entry stirrer positioned at the bottom of the reactor (260 rpm) and additional mixing was provided by a recycle pump (35 m^3/h). The feed inlet pipe entered the reactor at the top from where it fed to the bottom. The reactor was inoculated with 10 m^3 anaerobic digester sludge from Daspoort Sewage Works Pretoria on 6 May 2000. The temperature was approximately 17^{0}C.

Heating unit. The heating unit consists out of the following items: coal bunker, speed control spiral feeder (100 kg/h), heating unit and fan and water spray reactor where feed water is sprayed through 3/8 inch spiral jet nozzles while hot air is flowing upwards. (Photo 2).

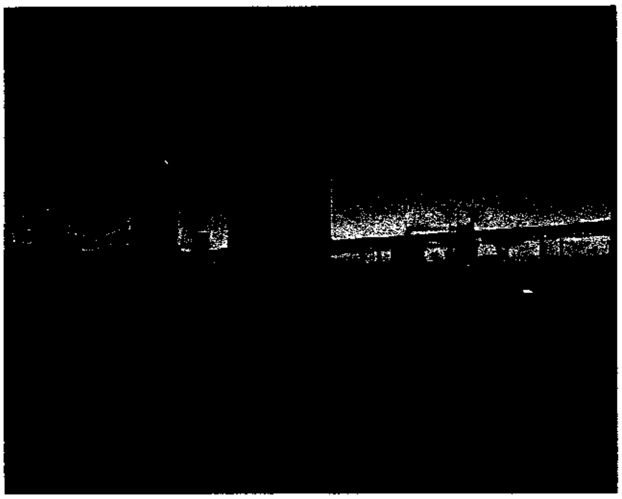


Photo 1. Anaerobic stage of biological sulphate removal process.

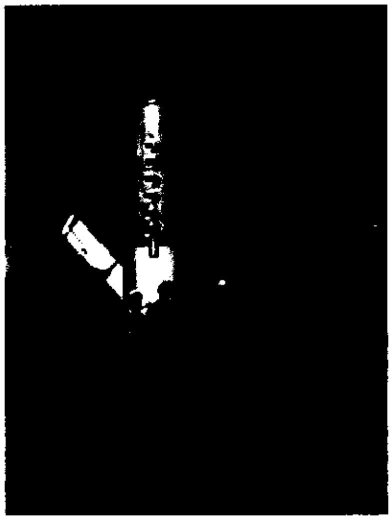


Photo 2. Heating unit.

H_2S-stripping and processing. Figures 2 and 3 show the laboratory-scale plant that was used for H_2S-stripping and processing to elemental sulphur. Table 1 shows the volume and dimensions of the various reactors.

A packed bed reactor and a venturi system was used for H_2S-stripping and H_2S-absorption into an iron(III)-solution, using two different configurations. In configuration A (Figure 2), the sulphide solution was fed continuously to the packed-bed reactor (stripping stage), and allowed to drip down the packing material (25 mm dia. Pall-rings), while H_2S-free CO_2-gas, flowing from bottom to top, was recycled via the H_2S-absorption stage. In the H_2S-absorption stage, H_2S was contacted with an iron(III)-solution at a pH of 2.5, to produce elemental sulphur (Reaction 2). The iron(III)-solution was replaced on a batch basis.

$$H_2S + 2Fe^{3+} \rightarrow S + 2Fe^{2+} + 2H^+ \qquad [2]$$

In configuration B (Figure 3), the sulphide solution was recycled through the venturi system in batch mode, and allowed for H_2S-stripping, by sucking in CO_2-poor gas, hence contacting it with the sulphide-rich water (stripping stage). The stripped H_2S-rich gas was passed through the packed bed-reactor reactor to which the iron(III)-solution was continuously fed for sulphur production.

The packed column consisted of a 0.8-m randomly packed bed, with 25-mm Pall-rings used as packing material. A 250-mm Perspex cylinder (adsorption) was used and Perspex plates were used for support of the packing and to aid in liquid distribution to the column. A Perspex plate with evenly distributed holes was installed at the top of the column to ensure adequate distribution of the liquid feed. The venturi was used for gas recirculation between the stripping and the absorption stages. A centrifugal pump was used (capacity of 1m^3/h) to recycle the iron (III) (configuration 1) or the sulphide (configuration 2) solution via the venturi. CO_2 was transferred from a CO_2-cylinder to a CO_2 float tank from where it was pumped at a set flow rate with a peristaltic pump at NTP (normal pressure and temperature) to the H_2S-stripping stage.

Experimental Procedure

Anaerobic Reactor and Heating Unit

A volume of 12 m^3/h of feed water was passed through the heating unit of which 4 to 8 m3/h was fed to the anaerobic reactor and the balance was returned to the feed water pond. The performance of the various stages (sulphate reduction and H_2S-stripping) were evaluated by determining the chemical composition and temperature of the feed and treated water and the temperature of the in and off gasses during continuous operation.

H_2S-Stripping and Processing

In configuration A (fed Na_2S continuously to the packed bed-reactor and contact the stripped H_2S-gas with an iron(III)-solution which is passed through a venturi system in batch mode) Na_2S was contacted with CO_2-rich gas, while sulphide removal was monitored in packed-bed reactor. The iron(II)-concentration was monitored in the iron solution (that was handled in batch mode).

In configuration B (fed iron(III)-solution to the packed bed-reactor and contact it with stripped H_2S-gas from the venturi system) and iron(III)-rich solution was fed at various flow rates. Iron(II) was monitored in the feed and treated streams of the iron(III)-solution. The sulphide concentration was monitored in the sulphide solution that was handled in batch mode.

Experimental Program

The following parameters were investigated:

Anaerobic stage. Hydraulic retention time (5 h, 10h, 15 h).

H_2S-stripping and processing stage. Reactor type (packed bed-reactor and venturi system), CO_2-concentration (20% to 100%). CO_2: Sulphide ratio, Feed rate of CO_2 rich stream (0.2 to 1.0 l/min). Retention time of sulphide solution (Feed rate of sulphide rich stream (0.5 to 2 l/min)). Efficiency of sulphide reaction with iron(III)-solution.

Analytical

Samples were collected regularly and filtered through Whatman No 1 filter paper. Sulphate, sulphide, alkalinity, calcium, iron(II), mixed liquor suspended solids (MLSS), volatile suspended solids (VSS), acidity and pH determinations were carried out manually according to procedures described in Standard Methods (10). Calcium was analysed using atomic absorption spectrophotometry. Acidity was determined by titrating the solution to pH 8.3 using NaOH. The COD samples were pre-treated with a few drops of H_2SO_4 and N_2 to strip off H_2S gas.

Table 1. Volume and dimensions of various reactors.

Item	Volume (l)	Diameter (mm)	Height (mm)
Anaerobic	100000	4000	8000
H_2S-stripping/processing			
Packed bed-reactor packed with 25 mm Pall-rings	39	250	800
Venturi reactor	40	300	800

RESULTS AND DISCUSSION

Sulphate Removal

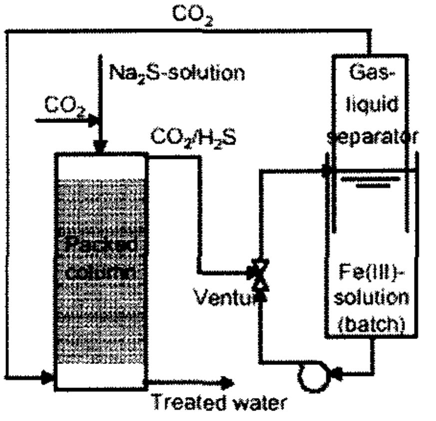
The feed rate of the reactor varied between 8 and 16 m^3/h, during the period from 1 September 2000 to 26 June 2001, which corresponded with a hydraulic retention time of 5.2 to 10.3 h, respectively. Table 2 shows the chemical composition of the feed and treated water.

It was noted that:

- Sulphate was removed consistently down to 200 mg/l. This was achieved when sufficient carbon and energy source was provided.
- Ethanol was completely utilized for either sulphate reduction or acetate production as indicated by measurement of ethanol and fatty acids. Almost no formate and propionate were formed during sulphate reduction.
- The sulphide concentration in the effluent is stoichiometrically equivalent to the sulphate concentration. The high sulphide concentrations measured in the anaerobic reactor indicated that the sulphate-reducing bacteria can achieve high sulphate reduction rates despite the high sulphide concentrations. This is contrary to the findings of McCartney and Oleskiewicz (11)

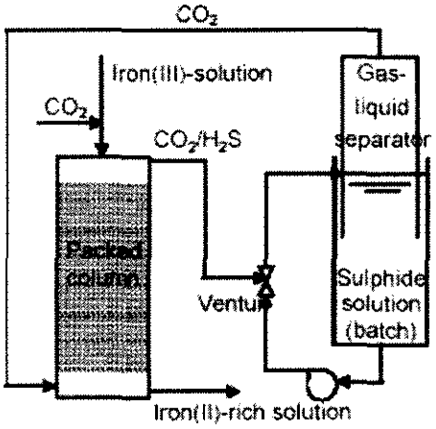
who found that sulphate reduction is inhibited by sulphide concentrations higher than 300 mg/l (as S).

- The sulphate removal rate increased to 12 g SO_4/(l.d) at a temperature of approximately 20°C, at an HRT of 6 h. This rate may improve still further by increasing the temperature of the feed water. Good sulphate removal rates were achieved despite the fact that the most simple and cost-effective reactor type was used. By integrating a completely-mixed reactor with a settler, positioned in the top of the reactor for sludge separation, the capital cost was reduced without compromising on the residence time. Sulphate removal could still be achieved within 6 hours.
- An $Alk_{produced}/SO_{4removed}$-ratio = 1.0 was measured, which corresponds well with the theoretical ratio of 1.04 (Reaction 3). Alkalinity values as high as 2000 mg/l were measured with an equal reduction in the sulphate content.
- The biomass distribution was uniform, bottom to top, in the reactor. During the start-up period more sludge occurred in the lower part of the reactor due to the presence of heavy chemicals and gypsum. The biomass concentration increased from 2 500 mg/l on 1 September 2000 to 10 000 mg/l where it stabilized. The specific biomass production was calculated to be 0.02 g biomass/g $SO_{4removed}$.



Configuration A

Figure 2. H_2S-stripping and processing.



Configuration B

Figure 3. H_2S-stripping and processing.

Table 2. Chemical composition of feed and treated water during Biological sulphate reduction.

Parameter	Feed	Treated
pH	7.2	7.7
Sulphate (mg/l SO4)	2 203	198
Sulphide (mg/l S)	0	606
Alkalinity (mg/l CaCO3)	60	2 065
Ethanol (mg/l)	690	0
Acetate (mg/l)	0	218
Formate (mg/l)	0	5
Propionate (mg/l)	0	0
Volatile suspended solids (mg/l)	0	9 000
Mixed liquor suspended solids (mg/l)	0	13 000

Figure 4 shows the percentage sulphate removal and the COD_{feed}/SO_{4feed}-ratio with time. It was noted that sulphate removal increased from between 30 % and 50 % during the period before 18 October 2000 to above 75% after 18 October 2000 (Figure 4. Sulphate line). The improved sulphate removal with time could be ascribed to the increased value for the COD_{feed}/SO_{4feed}-ratio with time (Figure 4, COD_{feed}/SO_{4feed} line). Before 18 October 2000, this value was lower than the theoretical value of 0.67 (Reaction 4). Thereafter this value increased to between 1 and 1.2.

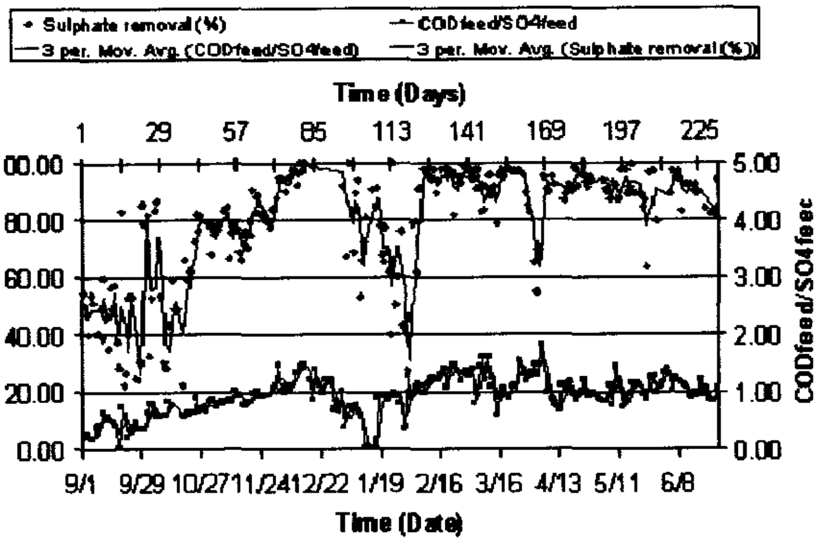


Figure 4. Percentage sulphate removal during the period 1 September to 26 June 2001 compared with the ratio of CODfeed to SO4feed.

$$2C + SO_4^{2-} + 2H_2O \rightarrow 2HCO_3^- + H_2S \text{ or} \quad [3]$$

$$2CH_3CH_2OH + SO_4^{2-} \rightarrow 2CH_3COOH + S^{2-} + 2H_2O \quad [4]$$

The utilization efficiency of the energy source (ethanol and sugar) and its cost are calculated in Table 3.

Table 3. Comparison between measured and calculated COD values.

Parameter	Energy source			
	Sugar	Ethanol B		Total
		Ethanol	Propanol	
Dosage (g/l)	0.1	0.72		0.10
Purity(%)	100	75	25.00	
Dosage (g/l)	0.1	0.54	0.18	0.82
COD value (g O_2/g)	1.12	2.09	2.40	
COD (g O_2/l) (calculated)	0.11	1.13	0.43	1.67
COD (g O_2/l) (measured)				1.75
Sulphate equivalent (g SO_4/l)				2.51
Sulphate removed (g SO_4/l)				2.00
COD utilization efficiency(%)				80
Carbon source price (R/t)	2384	2750		
Carbon source cost (R/m^3)	0.24	1.98		2.22

It was noted that:

- At a dosage of 0.1 g/l sugar and 0.72 g/l ethanol B (75 % ethanol + 25 % propanol), 2.0 g/l sulphate was removed. This represented a utilization efficiency of 75%.
- The measured COD value of 1.75 g/l (as O_2) agreed well with the calculated value of 1.78 g/l (as O_2).
- The energy source cost associated with the removal of 2.0 kg/m^3 sulphate amounted to R2.22/m^3. This cost could be reduced further should by partial replacement of ethanol and sugar with carbon monoxide. Carbon monoxide could be recovered when coal off-gas is used for heating of feed water.

Heating of Feed Water

The plant was operated at a flow rate of 9 m^3/hr and an average water inlet temperature of 15°C. The feed water was effectively heated from 15 °C to 30 °C. Heat transfer from the gas to the water was more than 99% effective. The exit temperature of the gas was approximately equal to the inlet temperature of the water. The heat transfer from the coal to the water was approximately 75 to 90 %. Heat losses was due to incomplete combustion of coal and disposal of hot ash. Figure 5 shows the total heat transfer efficiency in the period August to September 2003.

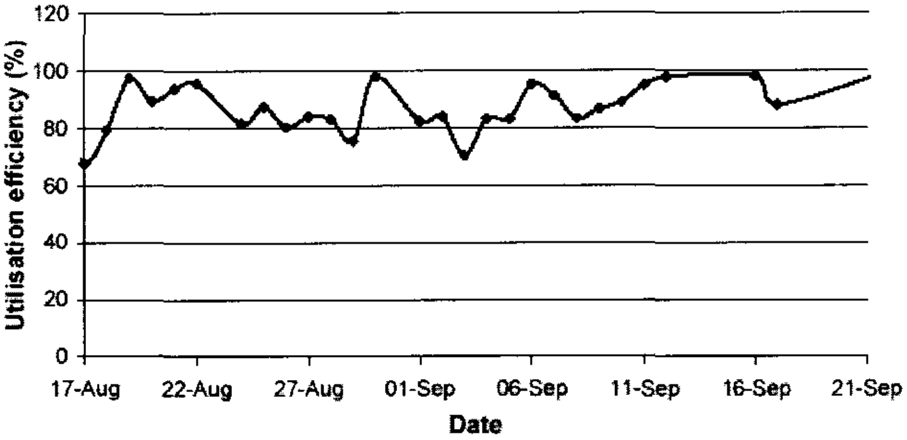


Figure 5. Total heat transfer efficiency in the period 17 August to 20 September 2003.

Table 4 gives a summary of the energy balance over the direct contact heat exchanger column. It can be seen that the spray column is a very effective configuration to establish heat transfer. Due to back mixing the column allows complete heat transfer between the water and the gas (12).

Table 4. Energy balance over the direct contact heat exchanger column.

Parameter	Value
Feed rate (m^3/h)	9
Temperature increase (°C)	11
Gas temperature inside furnace (°C)	365
Temperature of exit gas (°C)	17
Coal feed (kg/h)	17
Energy load feed (kJ/h)	470400
Energy absorbed (kJ/h)	426995
Efficiency (%)	89

H_2S-Stripping and Processing Stage

Sulphide can be removed through CO_2-stripping from 300 to less than 20 mg/l (see Figure 6 and Maree (13) for a more detailed discussion on H2S-processing and stripping). In order to obtain engineering design criteria for full-scale implementation, the effect of various parameters on the rate of H_2S-stripping was determined, using configuration A (Figure 2).

By feeding a sodium sulphide solution and a CO_2-gas stream counter current on a continuous basis through to a packed bed reactor, it was noted that:

- Number of stages. By passing the sulphide solution through two stages in series at a CO_2 feed load/Na_2S feed load of 1.4 g CO_2/g S, sulphide was removed from 834 to 376 mg/l in stage 1, and to 77 m/l (as S) in stage 2 (Table 5). By providing a third stage, sulphide could have been removed to less than 20 mg/l. The aim, however, with this investigation is to identify optimum process conditions to allow the minimum number of process stages needed for complete sulphide removal. Sulphide is quantitatively converted to sulphur as indicated by the correspondence between the actual and theoretical values for the ratio: load of iron(II) produced/load of sulphide removed (3.65 versus 3.49). More CO_2 was consumed than theoretically required (1.75 versus 1.38). The higher CO_2 consumption can be ascribed to the partial solubility of both CO_2 and H_2S in the pH range 6 to 7. The theoretical ratios for load of CO_2 consumed/load of sulphide removed (1.38) and load of iron(II) produced/load of sulphide removed (3.49) is calculated from Reactions 5 and 6.

$$2CO_2 + S^{2-} + 2H_2O \rightarrow 2HCO_3^- + H_2S \quad [5]$$

$$H_2S + 2Fe^{3+} \rightarrow S + 2Fe^{2+} + 2H^+ \quad [6]$$

- Effect of HRT. An amount of 217 mg/l sulphide was removed at a feed rate of 0.5 l/min (HRT = 59 min), compared to only 154 mg/l at a feed rate of 2 l/min (HRT = 15 min).
- Effect of CO_2 flow rate. By increasing the CO_2 flow rate from 0.19 l/min to 0.83 l/min, the sulphide removal increased from 342 to 474 mg/l and residual sulphide in solution decreased from 134 to 0 mg/l (as S). The corresponding ratios of CO_2 feed load/Na_2S feed load increased from 0.78 to 3.46. The stoichiometric value required for this ratio is 1.38 (Reaction 5). This demonstrates that complete sulphide removal can be achieved by dosing 2.5 times more CO_2 than stoichiometrically required. Excess CO_2 gas would be available in many applications. With the biological sulphate removal process CO_2-gas is produced by the heating unit. During limestone neutralization of acid water, CO_2 with a high concentration is produced due to dissolution of $CaCO_3$.
- Effect of CO_2-concentration. By increasing the CO_2 concentration from 20% to 100%, the sulphide removal increased from 278 to 387 mg/l (as S). In this case sulphide was not removed to 0 mg/l as the CO_2/Na_2S feed ratio was less than the value of 3.46 as determined above empirically.
- Effect of gas recycle rate. By increasing the gas recycle rate from 9.1 to 19.6 l/min, the sulphide removal was improved from 304 to 666 mg/l. In this experiment sulphide was also not removed to 0 mg/l as the CO_2/Na_2S feed ratio was less than the value of 3.46.

It was demonstrated above that a packed bed-reactor (configuration A) (Figure 2) can be used for sulphide stripping. In this configuration it appeared that the absorption stage, where H_2S-rich gas was contacted with an iron(III) solution in a venturi system, was effective, due to good contact between gas and liquid phase. With the apparent good performance of the venturi system for H_2S absorption, it was decided to evaluate the suitability of the venture system also for H_2S-stripping. The same equipment that was used for configuration A (Figure 3), was used for configuration B (Figure 3), except that the venture system was used for sulphide stripping in batch mode, and the packed bed-reactor was used for H_2S-absoption into an iron(III) solution under continuous conditions.

Figure 6 show the effect of iron(III) feed rate on sulphide removal. It is noted that:

- Better sulphide removal was achieved with increased feed rate of iron(III). This can be ascribed to only partial absorption of H_2S at low iron(III) feed rates in the closed circuit of Configuration 2. This is an indication that the packed bed-reactor does not function as well as the venturi system for the absorption of H_2S into an iron(III)-solution.
- The obtained experimental (actual) dFe/dH_2S ratio was similar to the theoretical value of 3.49 (Reaction 6). This result shows that all iron(III) that was introduced to the packed bed reactor was consumed for H_2S-absorption through 6.

The obtained results showed that H_2S-stripping and H_2S-absorption is favoured by intensive mixing. Intensive mixing supports mass transfer of H_2S from liquid to gas phase in the case of H_2S-stripping and from gas to liquid phase in the case of H_2S-absorption. It was demonstrated that the venturi device was more efficient than the packed-bed reactor. This could be ascribed to the high pressure (300 kPa) and the high velocity (50 m/sec) of gas and liquid particles. Based on this observation, it is recommended that the Turbulator be used during a scale-up version. The Turbulator exists out of a motor which directly (no gear box) drives a disc via a hollow shaft. The Turbulator allows mixing between the gas and liquid phase by sucking in air through the hollow shaft that rotates at 2000 rpm. The velocity at the outer limit of the disc is 15 m/sec (Dia = 0.15 m; rpm = 2 000).

Table 5. Sulphide removal in two stages in series.

Parameter	Stage number	
	1	2
CO_2/Na_2S feed ratio (g CO_2/g S)	0.77	1.40
Na_2S feed rate (l/min)	0.90	0.90
CO_2 feed rate (l/min)	0.29	0.24
CO_2-concentration (%)	100	100
HRT(min)	32.7	32.7
Gas recycle rate (l/min)	22.9	22.9
Sulphide in feed (mg/l S)	834	376
Sulphide after pipe (mg/l S)		
Sulphide in treated water (mg/l S)	434	77
Sulphide removed (mg/l)	400	299
pH in feed	9.05	
pH after pipe		
pH in treated water	7.02	
dCO_2/dNa_2S ratio (g CO_2/g S)		
Teoretical	1.38	1.38
Actual	1.70	1.79
dFe/dH_2S		
Teoretical	3.49	3.49
Actual	3.60	3.70

Running Cost

The energy source is the highest cost item of the CSIRosure process. Geldenhuys et al. investigated the electrolytic production of hydrogen and founded that hydrogen can be generated electrolytically at a cost of R14.57/kg H_2 (14) The cost for various energy sources for removing 2 g SO4/l are compared in Table 6. It is noticed that electrolytic generated hydrogen compares favorable with other energy sources, such as ethanol, propanol and sugar.

Table 6. Cost comparison of various energy sources for biological sulphate removal.

Item	Product			
	Sugar	**Ethanol**	**Propanol**	**H2**
Sulphate removed (g/l SO4)	1000.00	1000.00	1000.00	1000.00
Carbon source/SO4 mole ratio	0.17	0.67	0.44	4.00
Mol mass (g)	342.00	46.00	60.00	2.00
Carbon source required (g/g SO4)	0.59	0.32	0.28	0.08
Efficiency (%)	70.00	70.00	70.00	80.00
Purity (%)	99.30	95.00	100.00	99.00
Carbon source required (kg/kl)	0.85	0.48	0.40	0.11
Carbon source cost (R/kl)	4.20	2.37	1.70	1.53

Note: Date of prices - January 2004.

CONCLUSIONS

The following conclusions can be made from this investigation:

- The biological sulphate removal process can be used for removal of sulphate to less than 200 mg/l using ethanol as the carbon and energy source.

- H_2S can be stripped to below 20 mg/l (as S) with CO_2 by using a venturi as a stripping device. The efficiency of H_2S-stripping is influenced by H_2S feed rate, CO_2-concentration, CO_2/H_2S load ratio and aborption efficiency of H_2S in iron(III).
- Hydrogen is the most cost-effective energy source. The cost of hydrogen amounts to R1.53/m^3 if 1 g/l of sulphate is removed (R1.53/kg SO_4 removed).

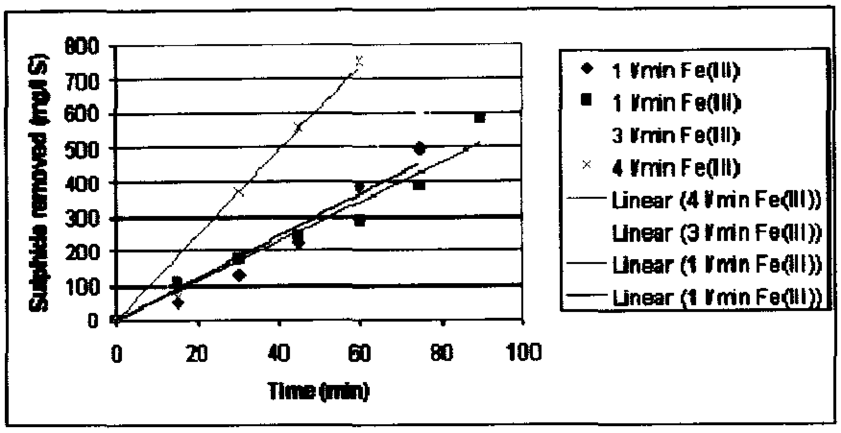


Figure 6. Effect of iron(III) flow rate on sulphide removal.

ACKNOWLEDGEMENTS

Sincere thanks are due to the following organizations for their financial and logistical support of the research reported in this paper:

- *Anglo Coal (Navigation Section of Landau Colliery)* who provided financial support, the necessary infrastructure at the mine and general assistance.
- *The National Research Foundation (NRF)* who provided funding through their Technology and Human Resources for Industry Program (THRIP) for CSIR projects on neutralization and sulphate removal.
- *The CSIR* who provided substantial financial support for the research program.

REFERENCES

1. Maree, J.P. and Strydom, W.F., "Biological sulphate removal from a packed bed reactor", Water Research, 19(9), pp 1101-1106, (1985).
2. Maree, J.P. and Hill, E., "Biological removal of sulphate from industrial effluents and concomitant production of sulphur", Water Sci. Technol., 21, pp 265-276, (1989).
3. Maree, J.P. Hulse, G. Dods, D. and Schutte, C.E., "Pilot plant studies on biological sulphate removal from industrial effluent", Wat. Sci. Tech., 23, pp. 1293-1300, (1991).
4. du Preez, L.A. Odendaal, J.P. Maree, J.P. and Ponsonby, M., "Biological removal of sulphate from indusrial effluents using producer gas as energy source", Env. Techn., 13, 875-882, (1992).
5. Visser, A., "The anaerobic treatment of sulphate containing wastewater". Phd thesis Agricultural University Wageningen, The Netherlands, (1995).
6. Van Houten, R. T., "Biological sulphate reduction with synthesis gas". Ph.D. thesis, Wageningen Agricultural University, Wageningen, The Netherlands, (1996).
7. Geldenhuys, A.J., Maree, J.P., de Beer, M. and Hlabela, P., "An integrated limestone/lime process for partial sulphate removal", The Journal of The South African Institute of Mining and Metallurgy, July/August, (2003).
8. Eloff, E. Greben H.A. Maree, J.P. Radebe, B.V. and Gomes, R.E., "Biological Sulphate Removal Using Hydrogen As The Energy Source", Proceedings of the 8th International Mine Water Association (IMWA) Congress, Johannesburg, 20 -25 Oct., (2003).
9. Maree, J P, Strobos, G, Greben, H, Günther, P and Christie A D M, Biological treatment of mine water using ethanol as energy source, Conference on Environmentally Responsible Mining in South Africa, Muldersdrift, South Africa, 25 – 28 September, (2001).

10. APHA, "Standard Methods for the Examination of Water and Wastewater". Twelfth Edition, American Public Health Association, New York. (1985).
11. McCartney, D. M. and Oleszkiewicz, J.A., Competition between methanogens and sulphate reducers: effect of COD:sulphate ratio and acclimation, Wat. Environ. Res., 65, 655-664, (1993).
12. Plass S.B, Jacobs H.R. and Boem R.F. Operational characteristics of a spray column type direct contact preheater, Heat Transfer-San Diego, Vol. 75 pp 227-234, (1979).
13. Maree, J.P., Hlabela, P., Geldenhuys, G.J., Mbhele, N. and Nevhilaudzi, T., "Treatment of mine water for sulphate and metal removal using barium sulphide", Waste Management, Emissions and Recycling in the Metallurgical and Chemical Process Industries Conference, Mintek Conference Centre, Randburg, 18-19 March, (2004).
14. Geldenhuys, A.J., Maree, J.P., Fourie, W.J., Smit, J.J., Bladergroen, B. and Tjati, M., "Acid Mine Drainage Treated Electrolytically for Recovery of Hydrogen, Iron(II) Oxidation and Sulphur Production". Proceedings of the 8 th International Mine Water Association (IMWA) Congress, Johannesburg, 20 -25 Oct., (2003).

CONCLUDING DISCUSSION

Acid mine drainage is the term used in this thesis to define drainage that occurs as a result of natural oxidation of sulphide minerals contained in rock and exposed to air and water. The principal ingredients in the acid mine drainage process are reactive sulphide minerals, oxygen and water. The oxidation reactions are often accelerated by biological activity. The chemical and biological reactions yield low pH water that has the potential to mobilise any heavy metals contained in the rock.

Acid mine drainage, besides sulphate, contains high concentrations of dissolved heavy metals, including iron(II) and sulphate, and can have pH values as low as 1.9. Since water and oxygen are essential components to form a strongly acidic solution, exclusion of one or the other will prevent this reaction from occurring. However, much larger quantities of oxygen are needed compared to water. Unless neutralised, such waters can have a detrimental impact on water quality in the environment, e.g. public water courses. The objective of acid mine drainage treatment is, therefore, the elimination of acidity and precipitation of heavy metals.

- *Neutralisation of acid mine drainage.*

The most common acid consuming mineral is calcium carbonate (calcite), the major constituent of limestone. Although several minerals are capable of removing acidity, including carbonates of iron and magnesium and hydroxides of iron and aluminium, a limited number will increase the pH from relatively low values, such as 1.9, to an acceptable, approximately neutral level. Whether the drainage from a mine is acidic depends on a number of factors and site-specific conditions. The most important factors are probably the balance between sulphide and neutralising minerals and their relative reactivities. The rate at which neutralisation occurs, is dependent on a number of physical and chemical factors. An important consideration is the susceptibility of carbonates to the forming of surface coatings of precipitates, such as gypsum and iron salts. These can cause "blinding" of the carbonate and result in a decrease in reaction rates.

Previously lime was used for neutralisation. Replacing lime with limestone, the cost of neutralisation could be reduced significantly. Table 3 compares the cost of neutralisation with limestone, slaked- and unslaked lime.

Table 3 Cost comparison between limestone ($CaCO_3$), unslaked lime (CaO) and slaked lime ($Ca(OH)_2$ as neutralisers of AMD

Parameter	**Limestone**	**Unslaked lime**	**Slaked lime**
Flow (Mℓ/day)	75	75	75
pH after treatment	7.00	7.00	7.00
Acidity (mg/ℓ $CaCO_3$)	683.04	683.04	683.04
Purity	69.00	85.00	85.00
Utilisation efficiency (%)	90.00	90.00	90.00
Dosage (kg/m^3)	1.10	0.50	0.66
Usage (ton/day)	82.49	37.50	49.55
Price (R/ton)	150.00	652.23	900.00
Treatment cost (R/month)	376 165	743 542	1 355 786
Cost ratio	0.51	1.00	1.82

Other benefits of using limestone instead of lime for neutralisation are:

- Limestone is a by-product from the local paper industry
- Fluctuations in the flow of underground water do not affect the neutralisation process as the acid feed water is diluted by bleeding it into the recycle stream which passes through a fluidised bed containing excess limestone
- Limestone is easy and safe to handle and dust-free. It can be stored on an elevated slab of concrete and eliminates the need for silos or other expensive storage facilities as it already contains 15% moisture.

With the limestone neutralisation process, the pH of the bulk of an acid stream can almost be neutralised (pH 6.8) with powdered limestone in a fluidised bed reactor. A small amount of lime is added for rapid iron(II) oxidation at pH 7 and higher. Acidity can be reduced from 16 000 g/ℓ to almost zero, as $CaCO_3$. Free acid and acid associated with Fe(III)) will be completely removed and sulphate concentration lowered from 16 800 mg/ℓ to 1 900 mg/ℓ. A retention time of 1 hour is sufficient to achieve these results.

The rate of neutralisation depends mainly on the type and particle size of the limestone. The chemical composition of both the acid water and limestone also play a role. The presence of iron(II), aluminium or magnesium in the acid water decreases the rate of neutralisation. The same rule applies to the concentration of magnesium in the limestone being used.

- *Iron(II)-oxidation*

Feed water containing iron(II) concentrations in excess of 50 mg/ℓ impaired the dissolution process, due to scaling, also known as blinding, of the limestone particles with ferric hydroxide and gypsum. It is essential that iron(II) is converted to iron(III) as a pre-treatment stage to the neutralisation of iron(II)-rich acid water with limestone. Iron(II) causes scaling as the oxidation rate increases with increasing pH values. Therefore, most of the reaction occurs on the surface of the limestone particles where the pH is higher than in the bulk of the water.

Iron(II) in the acid feed water can be oxidised either mechanically (aeration), chemically, biologically or electrolytically. For both chemical and biological iron(II)-oxidation, it has been shown by Maree *et al.* (1997, 1998) that the rate of oxidation depends on the surface area of the support medium and the suspended solids concentration. However, in this work, iron(II) was oxidised electrolytically. This was done while generating hydrogen in an electrolytic cell for utilisation as energy source for sulphate reducing bacteria in the biological process. Oxidation rates as high as 110 g Fe/(ℓ.day) were measured when performing the electrolytic generation of hydrogen with acid mine drainage (pH 1.9) as electrolytic medium and stainless steel (type 316) as electrode material. These results compared well with the rates of 80 and 66 g Fe/(ℓ.day) for biological and chemical iron(II)-oxidation, respectively, as reported earlier by Maree *et al.* (1997, 1998).

These results were achieved at a current density of 1 ampére/dm^2 and a potential of 4 volts and using asbestos plate (4mm thickness) as diaphragm to avoid contamination of the hydrogen with oxygen. Hydrogen was generated at the cathodes and oxygen at the anodes, according to the following reactions:

$$2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^- \qquad [12]$$

$$2H_3O^+ + 2e^- \rightarrow 2H_2 + H_2O \qquad [13]$$

It has been demonstrated that hydrogen can be generated electrolytically at a cost of 16% (R3.89/kg of hydrogen) of the cost of purchasing hydrogen in bulk from industry (R25.00/kg). Cost figures for generating hydrogen electrolytically are listed in Table 4.

Table 4 Cost comparison for various electrolytic hydrogen generation systems

Electrode material	Electrolytic solution	Diaphragm material	Production cost (R/kg)
Fe plate	AMD	Anionic selective	138.84
Zn plate	AMD	Anionic selective	151.94
Stainless Steel	KOH (30%)	Anionic selective	14.57
Stainless Steel	KOH (3%)	Anionic selective	22.39
Stainless Steel	AMD (5 ampére)	None	21.20
Stainless Steel	AMD (5 ampére)	None	11.98
Stainless Steel	AMD (5 ampére)	None	9.55
Stainless Steel	KOH (3%)	Asbestos	3.89
Commercially available in bulk	-	-	25.00

It was concluded that iron(II) oxidation is an excellent benefit added to the electrolytic production of hydrogen from AMD. This process can therefore be applied upstream of the neutralisation stage of acid mine drainage. Due to the fact that iron(II) remains in solution up to pH7, it is beneficial to convert iron(II) to iron(III), which will precipitate at pH 3 and coat the carbonate particles which slowing down the neutralisation reaction significantly.

- *Gypsum crystallisation and $CaCO_3$ precipitation*

The primary product of acid mine drainage neutralisation using either limestone or lime is gypsum ($CaSO_4.2H_2O$), produced largely as a precipitate. Gypsum commonly forms scale in tanks and piping which then require periodic acid treatment and mechanical removal. Proper design can reduce the severity of some scaling problems. Heavy metal ions hydrolyse and precipitate as their respective hydroxides during neutralisation and any ferrous ion present in the slurry is oxidised to ferric iron and precipitated as ferric hydroxide.

After neutralisation, sulphate concentration in water can be further effectively lowered with lime treatment to 1 200 mg/ℓ by raising the pH to 12 and higher.

This is well below the saturation level of gypsum (1 500 mg/ℓ) and no scaling of pipelines will occur at a retention time of 2.7 hours. Magnesium was also fully removed as a result of the high pH. During gypsum crystallisation, the gypsum concentration was found to have a major influence on the rate of sulphate removal. It was concluded that the rate of gypsum crystallisation is directly proportional to the surface area of the gypsum crystals.

Water, under-saturated with respect to gypsum, can be produced by adjusting the pH with CO_2 from the high levels of 12 and higher to pH8.5 where $CaCO_3$ has a low solubility. At this stage of the process, the treated water is suitable for re-use in a plant or for irrigation purposes.

Sludges resulting from the various stages contain gypsum, heavy metal hydroxides and heavy metal sulphides. Polymeric substances, PAC6 and Type 3095, were successfully introduced to the process as coagulant and flocculant, respectively. The solids were recycled from the clarifier underflow to the feed, upstream of polymer addition, to build a high density sludge. Dosing these polymers in very small quantities to the various sludges, generated during the process, their settling rates were significantly increased. These properties are important in providing clarifiers of suitable size after each stage.

- *Electrolytic hydrogen generation*

Several sulphate removal technologies are in place, amongst others the Biological Sulphate Removal Technology. For the treatment of these effluents, expensive organic material (e.g. ethanol or sugar) is used as the carbon and energy source for the SRB. The use of hydrogen as energy source provides a cheaper alternative for sulphate removal. Toxicity due to increased levels of sulphide and un-ionised hydrogen sulphide will not only lead to a diminished process performance of the SRB but will also become a health and safety hazard.

Stainless steel (type 316) plates have been used effectively as electrode material with AMD as electrolyte for generating hydrogen in a cost-effective way. While generating hydrogen at the cathode, other benefits such as the oxidation of iron(II) to iron(III) at the anode and the conversion of hydrogen sulphide gas to elemental sulphur in a down-stream stage also occur. After the iron(II)-rich acid water was treated electrolytically, oxidation resulted in an iron(III)-rich product which is the feed stream to the limestone neutralisation stage. Part of this iron(III)-rich stream can be contacted with the waste H_2S gas from the biological process and elemental sulphur will be produced. Thus, the waste product of the Biological Sulphate Removal Technology can be converted into a valuable product, elemental sulphur. The need for a membrane (diaphragm) is eliminated as no oxygen is generated at the anode.

Hydrogen can also be generated using stainless steel (type 316) as electrode material in a high pH environment (3% KOH). Asbestos has been successfully utilised as membrane to prevent mixing of hydrogen and oxygen, generated at the cathode and anode, respectively. When comparing the cost of hydrogen purchased at R25.00 per kilogram, huge cost savings can be achieved by generating on site for use as energy source for the SRB. Pure hydrogen can be generated electrolytically at a cost of R9.55 per kilogram from AMD or R3.89 from a 3% KOH solution.

- *Barium sulphide process*

After the lime- and CO_2 treatment stages, the water can be further treated with a *Reverse Osmosis (RO) Process* developed by The Chamber of Mines or the *Biological Sulphate Removal Process* developed by the CSIR (Maree, *et al.*, 1987; Maree & Hill, 1989) in order to be released into a river system (sulphate concentration required: <200 mg/ℓ) or to be treated to a level similar to that of municipal water. These processes are relatively expensive and therefore other means of desalination should be considered. Another promising process to treat sulphate-rich waters entails the chemical removal of sulphate by means of soluble barium salts such as barium sulphide and is illustrated in the following reaction:

$$CaSO_4 + BaS \rightarrow BaSO_4 + CaS \qquad [14]$$

The barium sulphide process is attractive for large scale application for the following reasons:

- ✓ Acid waters can be treated directly with barium sulphide
- ✓ The process removes ammonia, magnesium, manganese and other heavy meals due to the high pH achieved prior to the softening stage
- ✓ By-products like sulphur and NaHS can be produced from the H_2S generated in the process and $CaCO_3$ from the softening stage
- ✓ $BaSO_4$ can be converted to BaS on-site by heating to 1 050°C and re-used

- Closing assertion

Several full-scale plants, as listed previously in this thesis, have been constructed over the past four years in South Africa, containing one or more of the above mentioned stages of the technology developed by CSIR: Environmentek. The *Limestone Handling and Dosing System* and the *CSIR Density Meter* were specifically designed by CSIR: Environmentek to add value to their chemical treatment technology. Because of the essential mechanical design of these two developments, they are not discussed in this thesis. Their significance for the treatment of acid mine water can, however, not be over-emphasized as they have a vital role in the successful treatment of acid mine water by means of the technology. The Limestone Handling and Dosing System and CSIR Density Meter are depicted in the following two photographs (Photos 1&2). The author was personally involved in the design, construction, testing and industrial application of these two developments. Continuous improvements have been effected to both systems in order to achieve optimum performance.

Successful treatment depends on the selection of an appropriate technology for a task, as well as its correct implementation. pH adjustment, lowering metal loads and meeting specific discharge standards can require vastly different approaches requiring significantly different technologies depending on the aim and purpose. For most sites, successful treatment technologies will require site-specific installation and implementation to achieve maximum benefit. Correctly selected treatment systems that are poorly installed or operated can be as ineffective as inappropriately chosen treatment systems.

It is evident that, regardless of emerging technologies, pH control with cost-effective neutralisation agents will remain the most widely used and the most economical approach to both passive and active acid mine water treatment.

Active treatment using calcium compounds, particularly limestone, is likely to remain the prime choice for neutralising acid mine water due to their non-proprietary nature, widespread availability, ease of application and cost effectiveness.

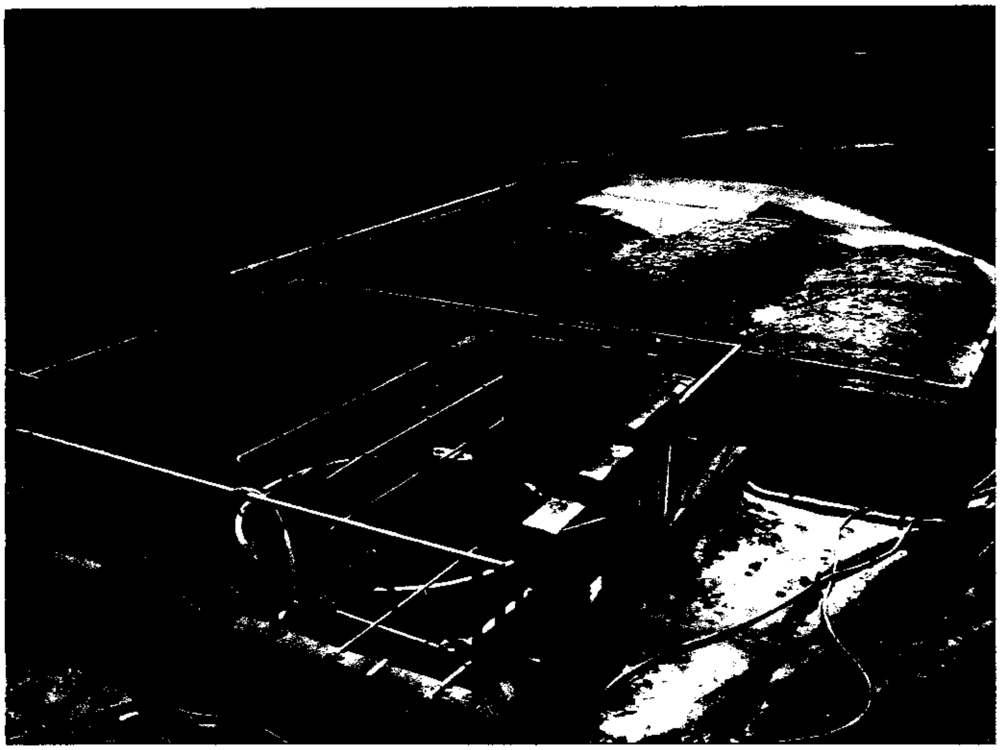


Photo 1 Limestone Handling and Dosing System developed by CSIR Environmentek. Evident from this photograph is the powdered limestone stored onto concrete slab, slurried with water spraying system to flow into yellow slurry make-up tank in sump.

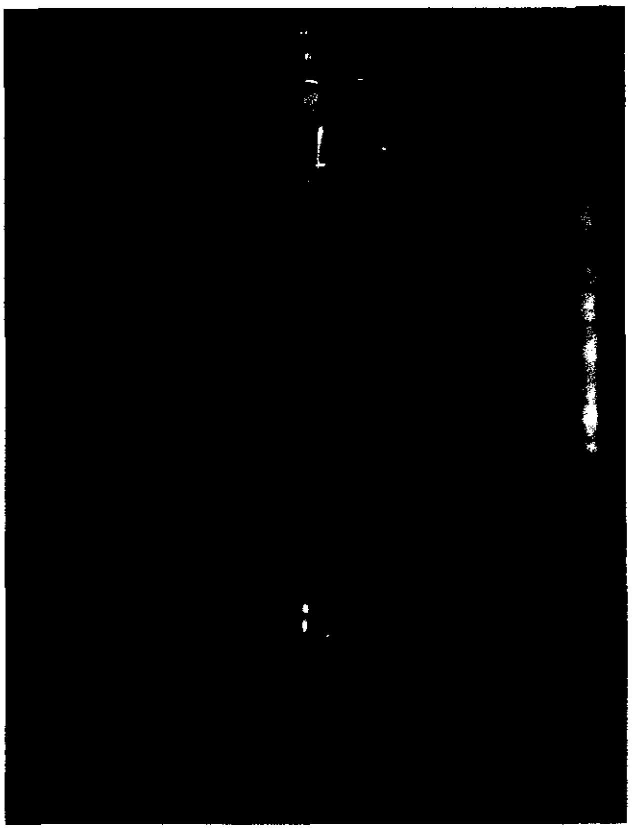


Photo 2 Density Meter developed by CSIR Environmentek

ACKNOWLEDGEMENTS

I would like to express my gratitude to God who cares, loves and guides me and gives me the opportunity to glorify His name in what I do.

I wish to direct a special thank to my dear parents for their love and loyal support in good and bad times and always being there to assist me. I love you.

Thanks are due to the following people and institutions who were involved in this project. Without them this work would not have been possible:

- CSIR: Environmentek for the facilities to construct and run the laboratory and pilot scale units
- National Research Foundation (NRF) for financing the research during the past four years
- Dr J P Maree for his guidance and support as study leader and co-promotor
- Prof F.B. Waanders (School for Chemical & Minerals Engineering, North-West University) for acting as promotor
- Colleagues at CSIR and University of the Western Cape that were involved in the projects and provided very valuable assistance

BIBLIOGRAPHY

References in this section are only applicable to the Literature Overview. Each paper has an independent bibliography.

ALPERN B., NAHUYS J. and MARTINEZ L. 1984. Mineral Matter in Ashy and Non-washable Coals – Its Influence on Chemical Properties. *Comun. Serv. Geol. Portugal*, Vol. 70, No. 2, p. 299.

DAVIS A., 1981. Sulfur in coal: Earth and Mineral Sciences, Pennsylvania State University, University Park, Vol. 51, No. 2, pp. 13-21.

EHRLICH H.L. 1990. Geomicrobiology (2nd Edition): New York, Marcel Dekker Inc., 646 p.

FALCON L.M. & FALCON R.M.S., 1987. The Petrographic Composition of Southern African coals in relation to friability, hardness, and abrasive indices. *J.S. Afr. Inst. Min. Metall*, Vol. 87, No. 10, pp. 323-336.

FALCON R.M.S., 1988. The Characteristics of Southern African Coals. *J.S. Afr. Inst. Min. Metall.*, Vol. 88, No. 5, p 145.

FALCON R.M.S. & SNYMAN C.P., 1986. An Introduction to Coal Petrography: Atlas of Petrographic Constituents in the Bituminous Coals of Southern Africa. pp. 3-4, 19.

GOVERNMENT GAZETTE (PARLIAMENT OF THE REPUBLIC OF SOUTH AFRICA). 1998. *National Water Act*. Vol. 398, No. 36, 200 p.

GRAINGER L. & GIBSON J., 1981. Coal Utilization: Technology, Economics and Policy. pp 1-8.

HAWKINS J.W., 1984. Iron disulfide characteristics of the Wayneburg, Redstone, and Pittsburgh coals in West Viginia and Pennsylvania. Morgantown, W.V., University of West Viginia, M.S. thesis, 195 p.

KLEINMAN R.L.P., CRERAR D.A. and PACELLI R.R. 1981. Biochemistry of acid mine drainage and a method to control acid formation. *Mining Engineering*, Vol. 33, pp. 300-303.

KUYUCAK N. 1998. Mining, the Environment and the Treatment of Mine Effluents. *Int. J. Environ. Poll.*, Vol. 10, No's. 2/3.

KUYUCAK N., LINDVALL M., SERRANO J.A.R. and OLIVA A.F. 1999. Implementation Of A High Density Sludge HDS Treatment Process At The Boliden Apirsa Mine Site, *Clean Technologies – Wastewater Treatment Symposium*, Seville, Spain.

KUYUCAK N. & SHEREMATA T. 1995. Lime Neutralisation Process for treating Acid Waters. U.S. Patent: 5.427.691.

MAREE J.P., STRYDOM W.F. and DE BEER M. 1997. Integrated Iron(II) Oxidation and Limestone Neutralisation of Acid Mine Water, *Proc. International Association on Water Quality (IAWQ), Specialised Conference on Chemical Process Industries and Environmental Management*, Cape Town, South Africa.

MAREE J.P., DINGEMANS D., VAN TONDER G.J. and MTIMKULU S. 1998. Biological Iron(II) Oxidation as Pre-Treatment to Limestone Neutralisation of Acid Water, *Proc. International Association on Water Quality (IAWQ) 19th Biennial International Conference, Vancouver, Canada.*

MEND Report. 1994. Status of Chemical Treatment and Sludge Management, CANMET, NRCAn, Canada.

NEVEAL R.C. 1981. Coal Structure and Coal Science: Overview and Recommendations. *Coal structure ACS*, p. 1.

OTT A.N. 1986. Estimating iron and aluminium content of acid mine discharge from a north central Pennsylvania coal field by use of acidity titration curves. *U.S. Geological Survey Water Research Inv.* Report 84-4335, 25 p.

PAYNE D.A. & YATES T.E. 1970. The effects of magnesium on acidity determinations. *3rd Symposium on Coal Mine Drainage Research, National Coal Ass./Bituminous Coal Research*, Inc., Pittsburgh, Pa., pp. 200-223.

ROSE A.W. & CRAVOTTA C.A. III, 1998. Geochemistry of coal mine drainage. in Brady, K.B.C., Smith, M.W. and Schueck, J., eds. Coal mine drainage pollution prevention in Pennsylvania: Harrisburg, Pa, Pennsylvania Department of Environmental Protection, 5600-BK-DEP2256 8/98, pp. 1.1–1.22

SANDERS D, 1996. Coal Characterisation in Marketing - an Elementary Approach. *Workshop on Coal Characterisation - for Existing & Emerging Technologies*, CRC for Black Coal Utilisation, Newcastle, Australia.

STACH E., MACKOWSKY M.T.H., TEICHMULLER M., TAYLOR G.H., CHANDRA D. and TEICHMULLER R., 1982. Stach's Textbook of Coal Petrology. (3rd Revised and enlarged edition). Gebrüder Borntraeger, Berlin.

STUMM W. & MORGAN J.J., 1981. Aquatic chemistry. Wiley Interscience, 470 p.

TEMPLE K.L. & DELCHAMPS, E.W., 1953. Autotrophic bacteria and the formation of acid in bituminous coal mines. *Appl. Microbiol.*, Vol. 1, pp. 255-258.

VAN TONDER, G.J., THERON, D.J. and MAREE, J.P. 2000. Cost optimisation of the water management strategy by steady-state modelling of the water network of a copper/nickel mine and processing plant, Proc. of the WISA 2000 Conference, Sun City, South Africa, 28 May-1 June.

WARD C.R., 2002. Analysis and significance of mineral matter in coal seams. *Int. J. Coal. Geol.*, Vol. 50, pp. 135-168.

ZINCK J.M. & GRIFFITHS W.F. 2000. An Assessment of HDS-Type Treatment Process – Efficiency and Environmental Impact. *ICARD 2000*, Vol. II, pp. 1 027-1 035.

APPENDIX A LIST OF ADDITIONAL PAPERS AND POSTERS

POSTER 1: Poster to Paper 1

Geldenhuys,A.J., Maree, J.P., de Beer, M. and Hlabela, P. 2003. An integrated limestone/lime process for partial sulphate removal, The *J. South African Institute of Mining and Metallurgy*, **103**(6), 345 – 353.

ACID MINE WATER TREATMENT

An integrated limestone/lime treatment process for neutralisation of AMD and partial sulphate removal

A J Geldenhuys, J P Maree, M de Beer & P Hlabela
Environmentek, Waterprogramme, CSIR, Pretoria, South Africa
ajgeldenhuys@csir.co.za +27 12 841 4178

Why?

Mining in South Africa makes a marked and visual impact on the environment because most of our geological formations contain pyrite. Pyrite is oxidised to H_2SO_4 when exposed to air and water.

The scarcity of water in South Africa is exacerbated by pollution of the surface- and ground-water resources. Typical pollutants of the aquatic environment include industrial effluents and acid mine drainage(AMD).

Limestone neutralisation (Stage 1)

- AMD effectively neutralised
- SO_4^{2-} removal to 1 900mg/ℓ
- Flocculant 3095

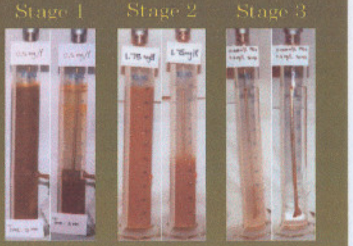
Lime treatment (Stage 2)

- Gypsum crystallisation (pH>12)
- Crystallisation rate ∝ gypsum conc.
- SO_4^{2-} removal to 1 100mg/ℓ
- Total Mg removal – $Mg(OH)_2$
- Flocculant 3095

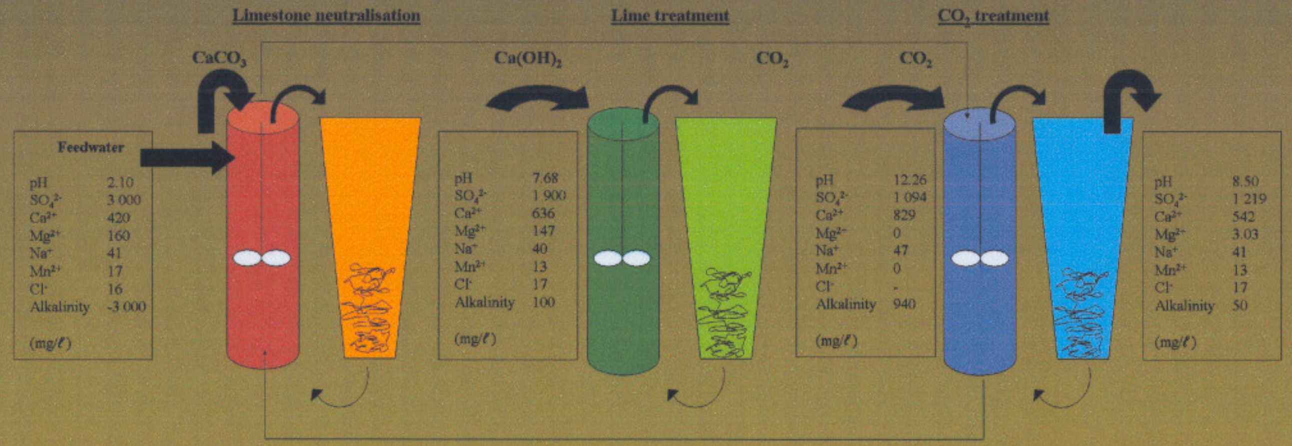
$CaCO_3$ precipitation (Stage 3)

- pH reduction – CO_2
- $CaCO_3$ precipitation
- Coagulant PAC6
  Flocculant 3095

Effect of coagulant addition



Water quality of various stages



Feedwater	
pH	2.10
SO_4^{2-}	3 000
Ca^{2+}	420
Mg^{2+}	160
Na^+	41
Mn^{2+}	17
Cl^-	16
Alkalinity	-3 000
(mg/ℓ)	

pH	7.68
SO_4^{2-}	1 900
Ca^{2+}	636
Mg^{2+}	147
Na^+	40
Mn^{2+}	13
Cl^-	17
Alkalinity	100
(mg/ℓ)	

pH	12.26
SO_4^{2-}	1 094
Ca^{2+}	829
Mg^{2-}	0
Na^+	47
Mn^{2+}	0
Cl^-	-
Alkalinity	940
(mg/ℓ)	

pH	8.50
SO_4^{2-}	1 219
Ca^{2+}	542
Mg^{2+}	3.03
Na^+	41
Mn^{2+}	13
Cl^-	17
Alkalinity	50
(mg/ℓ)	


$CaCO_3$ handling and dosing system


$CaCO_3$ and lime treatment stage


CO_2 treatment stage

Conclusions

- SO_4^{2-} reduced to below 1 100mg/ℓ
- Treated water is under-saturated with respect to gypsum – 300mg/ℓ
- Cost of SO_4^{2-} removal = R0.27/kg SO_4^{2-}

CSIR

Division of Water, Environment & Forestry Technology SA

The scarcity of water in South Africa is exacerbated by pollution of the surface- and ground-water sources. Typical pollutants are industrial effluents, mainly acid water. Ticor SA produces zirkon, rutile and illminite (TiO_2 plus iron compounds) from mining sand dunes at the Natal Coastal Region in South Africa. The plant produces 85m³/hr of acid water which need to be treated for re-use in the metallurgical process or to a higher quality, suitable for discharge into the Empangeni sewage system (2 200mg/ℓ SO_4).

EFFLUENT TREATMENT

Neutralisation and Partial Sulphate Removal of Acid Leachate in a Heavy Minerals Processing Plant with Limestone and Lime

A J Geldenhuys, J P Maree, G Strobos, N Smit' & B Buthelezi'
CSIR, Environmentek, Waterprogramme, P O Box 395, 0001, Pretoria, South Africa
'Ticor SA, Empangeni, South Africa
ajgeldenhuys@csir.co.za +27 12 841 4178

CSIR ENVIRONMENTEK
Your Technology Partner

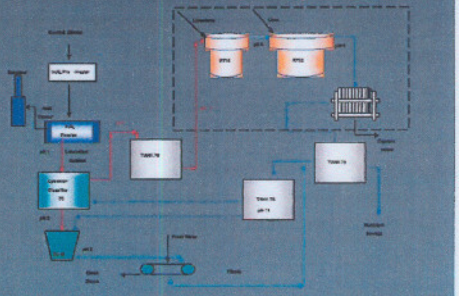
What's different?

Limestone can be used for the complete neutralisation of acidic effluent. Savings of 360000 AUD per annum can be achieved by substituting lime with limestone.

Background & Introduction

Mineral particles must be leached effectively, using sulphuric acid, to dissolve the Fe_2O_3 surface coating, (Fe on Zr = 0.2% before leaching and <0.06% after). The acid water from leaching circuits must be neutralised, clarified and re-used in the leaching circuits. A portion of the process water must be blend to municipal sewage to prevent build up of soluble ions. This stream must have a sulphate content of less than 2 200mg/ℓ.

Water treatment circuits - Results



The technology consists of two configurations:

Configuration A:

1 Limestone handling and dosing system
2 Primary neutralisation stage
pH 1 + Limestone → pH 6 (2 200 mg/ℓ SO_4)
3 Secondary neutralisation stage (optional)
pH 6 + Hydrated lime → pH 11 (1 150 mg/ℓ SO_4)
4 The gypsum slurry is filtered, the filtrate is recycled back to the leaching circuits
Sulphate precipitation during limestone neutralisation is adequate for process requirements (2 200mg/ℓ SO_4)

Configuration B:

1 The same set-up as in Configuration A except that no lime is used and aeration is applied after primary neutralisation stage

Parameter	pH	Sulphate (mg/ℓ)	Acidity (mg/ℓ)	Alkalinity (mg/ℓ)
Acid water	1.82	5 131	5 556	-
Primary Reactor	6.10	2 317	840	464
Secondary Reactor	11.00	1 150	29	386

Parameter	pH	Sulphate (mg/λ)	Acidity (mg/λ)	Alkalinity (mg/λ)
Acid water	1.79	5 210	5 550	-
Primary Reactor	6.50	2 200	821	440

Conclusions

- Aeration of the water after the primary neutralisation stage results in CO_2 removal and therefore lime can be completely replaced by powdered limestone for neutralising the acid mine water
- Sulphates can be reduced to 2 200mg/ℓ for re-use in the plant or to discharge the water into the sewage system
- Alkali savings of 360 000 AUD per annum can be made on replacing lime with limestone
- The quality of the effluent can be controlled and the build-up of ions in the water be avoided

THE SUSTAINABILITY OF BIOLOGICALLY TREATED COPPER MINE EFFLUENT SUITABLE FOR IRRIGATION

Botswana RST Group
BCL LIMITED
(Incorporated in the Republic of Botswana)

H Greben[1], A J Geldenhuys[1], J P Maree[1] and M Hagger[2]
[1]CSIR, Environmentek, Waterprogramme, P O Box 395, Pretoria 0001, South Africa
[2]BCL, P.O.Box 3, Selebi Phikwe, Republic of Botswana

CSIR ENVIRONMENTEK
Your Technology Partner

Background

Botswana is a country in Africa, situated northwest of South Africa. Due to the limited annual rainfall, it is a (semi) arid country.

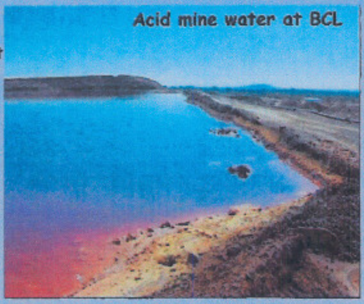
BCL is a copper/nickel mine located in Botswana (Selibi Pikwe), which generates a mine effluent high in metals (Fe, Zn, Cu, Ni and Mn), SO_4^{2-} (2 000 - 2 500 mg/ℓ) and acidity.

Map of Southern Africa (incl. Botswana)

The main stream of the produced AMD is treated applying the biological Fe(II) oxidation method followed by limestone neutralisation technology, as developed by the CSIR

Aim of study

To biologically treat 7Mℓ/day of the produced AMD to remove the sulphate, acidity and metals through metal sulphide precipitation to render it suitable for irrigation of a citrus plantation.



Acid mine water at BCL

Material and Methods

Feed

Mine effluent: SO_4: 1 500-2 200 mg/ℓ, COD = 1 500 mg/ℓ

Macro ($NH_3 + PO_4$) and micro nutrients were added.

HRT: 24-12hrs

Reactor System

Single -stage completely mixed reactor system (Figure 1)

Biomass

Obtained from Pilot Biological Sulphate removal Plant at Navigation, Anglo Coal, Witbank, South Africa.

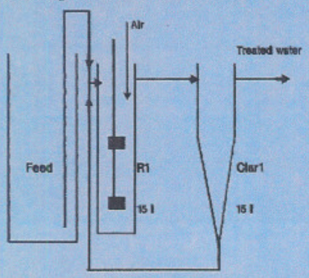


Figure 1. Completely mixed single stage reactor

Results

Process stability (Figure 1)

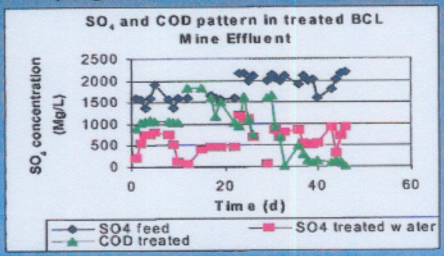


Figure 1. Process Stability of reactor system

Sulphate removal, COD utilization and sulphide production (Table 1)

Table 1. The chemical composition of feed and treated water

DETERMINAND	UNIT	PERIOD			
		1	2	3	4
Feed rate	ℓ/d	15	30	30	15
HRT	hr	24	12	12	24
Feed					
pH	unit	6.5	5.12	4.31	4.32
Sulphate	mg/ℓ	1 600	1 600	2 100	2 250
COD	mg/ℓ	1 727	1 727	1 742	1 602
Alkalinity	mg/ℓ	130	130	100	120
Treated					
pH	unit	6.72	6.10	7.00	7.55
Sulphate	mg/ℓ	550	375	1 138	627
COD	mg/ℓ	1 019	1 657	1 099	488
Alkalinity	mg/ℓ	903	1 477	1 305	1 766
Sulphide	mg/ℓ	140	268	229	260

Metal Removal (Table 2)

Table 2. The metal concentration in the feed and treated water

METAL	UNIT	FEED		TREATED WATER			
PERIOD		1	2	1	2	3	4
Nickel	mg/ℓ	5.86	5.50	0.15	0.17	0.14	0.61
Zinc	mg/ℓ	1.25	38.00	0.03	0.03	0.03	0.03
Manganese	mg/ℓ	0.97	0.99	0.97	1.20	0.17	0.06
Copper	mg/ℓ	0.01	0.05	0.03	0.03	0.03	0.03

Discussion

Sulphate removal/COD consumption

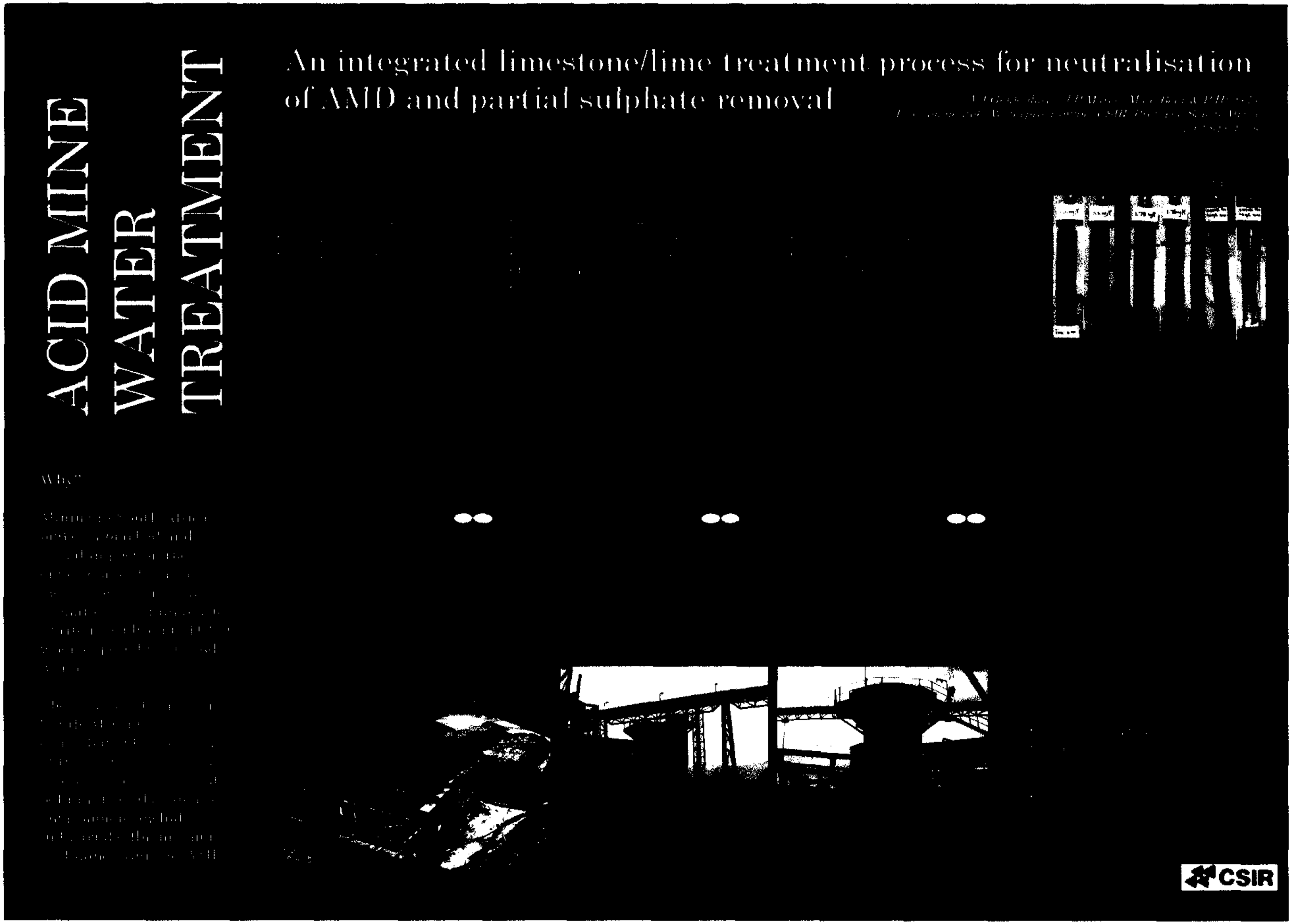
The results show that during the second period the sulphate was removed to concentrations <400 mg/ℓ, at which time the HRT was ½ day. During the last two periods, it was noticed that the COD concentration decreased in the reactor, resulting in less sulphate removal. This COD consumption was ascribed to the presence of increased metal concentration in the feed (BCL water), which was as high as 5 mg/ℓ for Ni and 38 mg/ℓ for Zn. The metals acted as trace minerals for the Methanogens, there by out-competing the Sulphate Reducing Bacteria.

Metal removal

All metals were removed to concentrations <1 mg/ℓ, except for Mn during first two periods. When the reactor pH increased, the Mn was removed as well.

Conclusions

1. Good sulphate reduction
2. Metal removal due to metal-sulphide precipitation
3. Initially COD utilisation by Sulphate Reducing Bacteria
4. Increased metal conc. in feedwater stimulated the methanogens
5. Water after treatment suitable for irrigation



ACID MINE WATER TREATMENT

An integrated limestone/lime treatment process for neutralisation of AMD and partial sulphate removal

Why?

POSTER 2: Poster to Paper 3

Geldenhuys, A.J., Maree, J.P., Strobos, G., Smit, N. and Buthelezi, B. Neutralisation and partial sulphate removal of acid leachate in a heavy minerals plant with limestone and lime, *Proceedings 6th International Conference on Acid Rock Drainage*, 12–18 July 2003, Ciarns, Australia.

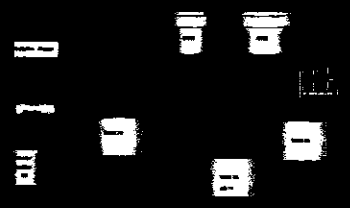
Neutralisation and Partial Sulphate Removal of Acid Leachate in a Heavy Minerals Processing Plant with Limestone and Lime

CSIR
ENVIRONMENTEK
Your Technology Partner

[illegible]

Background / Introduction

[illegible]



Parameter	pH	Sulphate (mg/ℓ)	Acidity (mg/ℓ)	Alkalinity (mg/ℓ)
Acid water	1.82	5 131	5 556	-
Primary Reactor	6.10	2 317	840	464
Secondary Reactor	11.00	1 159	29	386

Parameter	pH	Sulphate (mg/λ)	Acidity (mg/λ)	Alkalinity (mg/λ)
Acid water	1.79	5 210	5 550	-
Primary Reactor	6.50	2 200	821	440

Conclusions

PAPER 9: Greben, H., Geldenhuys, A., Maree, J., Strobos, G. and Hagger, M. The sustainability of biologically treated nickel/copper mine effluent suitable for irrigation, *Proceedings 6th International Conference on Acid Rock Drainage*, 12 – 18 July 2003, Cairns, Australia.

This paper focussed on the treatment of effluent from a copper mine in Botswana. Because Botswana is an arid country, it needs to treat the water either for re-use or for discharge into a river system. The results of this study showed that the effluent could be treated to a quality suitable for agriculture, i.e. for irrigation of newly planted citrus orchards. It has been shown by the Faculty of Agriculture at the University of Pretoria, that acid water that has been neutralised from pH 2.2 to 7.5, can be utilised for irrigation of citrus trees.

The water discharged by this mine contains heavy metals that, when treated with the Biological Sulphate Removal Technology, the resultant H_2S precipitates these as sulphides. This way the metals present in the effluent as well as the sulphides are removed. A single stage, completely mixed reactor was used with a clarifier to trap sludge that formed. All metals, except for magnesium, were removed after the biological treatment. The sulphates in the effluent were reduced to sulphide. Results indicated that an increase in metal concentration, especially zinc, in the feed water, stimulated the enzymatic activities of the methanogenic bacteria. Good sulphate reduction was also observed when 1 mℓ ethanol /ℓ of feed water was added with a COD/SO_4 ratio of 1.

Paper 9 was presented as a poster by A J Geldenhuys at the 6th International Conference on Acid Rock Drainage

The Sustainability of Biologically Treated Nickel/Copper Mine Effluent Suitable for Irrigation

H Greben[1], A Geldenhuis[1], J Maree[1] and M Hagger[2]

ABSTRACT

Disposal of mine water is a worldwide problem occurring in the coal and gold as well in the metal ore mining areas. Since southern Africa is a (semi) arid region, mining effluents should be treated to qualities such that they can be used for agricultural purposes or that they can be discharged in river system. Studies have shown that partly treated acid mine water can be used for irrigation. A copper mine in Botswana plans to use 5 Mℓ/d of treated mine effluent for the irrigation of agricultural product. The results of this study showed that when applying the biological sulfate removal technology the produced sulfide precipitated the metals in the mine effluent, such as nickel, Zn and Mn, to metal sulfide (MeS).

INTRODUCTION

The economy in Southern Africa derives a significant proportion of its income from mining industries. Due to its nature, scope and extent, the mining industry contributes to the pollution of surface and ground water, especially through the production of salts and metals. Disposal of mine water is a worldwide problem occurring in the coal and gold as well in the metal ore mining areas. Southern Africa has a low percentage of arable land, due to the variable rainfall. Therefore, mining effluents should be treated to qualities such that they can be re-used for agricultural purposes or that they can be discharged in river system. Studies carried out by the Department of Agriculture at the University of Pretoria have shown that treated acid mine water, eg through neutralisation, there by improving the pH from about 2.2 to 7.5, can be used for irrigation (Jovanovic *et al*, 2002).

BCL, a nickel/copper mine in Botswana, plans to use 5 Mℓ/d of treated mine effluent for the irrigation of agricultural product (citrus fruit). This mine effluent, containing heavy metals, needs to be treated in order to make it suitable for irrigation. When the biological sulfate removal technology is applied, the produced sulfide can precipitate certain metals to metal sulfide (MeS), thus removing the metals present in the mine effluent, as well as the produced sulfide. The objective of this study focused on metal removal from this mine water, applying the biological sulfate removal technology, using the single stage completely mixed reactor.

MATERIALS AND METHODS

Feedstock

The reactor received BCL mine effluent as feed water, of which the sulfate concentration varied from 1500 to 2200 mg/ℓ. Ethanol (1 mℓ / ℓ)(COD ≈1500 mg/ℓ) was added as the energy source, resulting in a COD/SO_4 ratio of approximately 0.67 - 1. The feed was supplemented with macronutrients: 75 mg/ℓ ammonia-N and 15 mg/ℓ phosphate-P. Although the BCL mine water contained metals, micronutrients were added as well (100 µg / ℓ Fe, 210 µg / ℓ Co, 0.28 µg / ℓ Mn, 0.44 µg / ℓ V, 0.25 µg / ℓ Ni, 0.48 µg / ℓ Zn, 0.40 µg / ℓ Mo, 0.18 µg / ℓ B, 0.37 µg / ℓ Cu).

Single-stage completely mixed reactor

The completely mixed reactor system comprised of a reactor (volume 15 ℓ) and a clarifier (volume 15 ℓ) (Figure 1). Both reactor and clarifier were open to the atmosphere so that air could diffuse into the reactor system. The operational temperature was maintained at 20 - 22°C. A sludge recycle was in place from the bottom of the clarifier to the top of the reactor. The return sludge flow rate was maintained at 4× the feed flow rate.

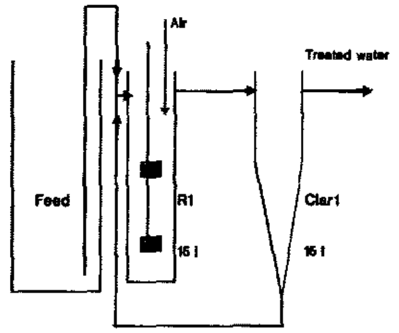


FIG 1 - Completely mixed reactor.

Biomass

The reactor was inoculated with anaerobic sludge, obtained from the sulfate removing Demonstration Plant (Witbank, South Africa).

Analytical

Manual determinations of sulfate, sulfide, alkalinity, chemical oxygen demand (COD), pH and metals were carried out according to analytical procedures as described in Standard Methods (APHA, 1985). With the exception of the feed COD and sulfide, all analyses were carried out on filtered samples. The COD samples were pre-treated with a few drops of H_2SO_4 and N_2 (to eliminate S^{2-} contribution).

Experimental

The BCL experiment was divided in four experimental periods, which were determined by the feed rate and the sulfate concentration in the feed water. The experimental periods are depicted in Table 1.

RESULTS AND DISCUSSION

Feed metal concentration

The concentration of the four most prominent metals in the two different feed samples is given in Table 2. It can be seen from Table 2 that the metals concentration in the two separate composite samples, obtained from the mine, differed. The copper concentration in the second feed sample was 10× as high as in the first feed sample and the zinc concentration increased from just over 1 mg/ℓ to 38 mg/ℓ.

---

[1] Division for Water, Environment and Forestry, CSIR, PO Box 395, Pretoria 0001, South Africa.

[2] BCL, PO Box 3, Selebi Phikwe, Republic of Botswana.

TABLE 1

Experimental periods and conditions when executing the sulfate and nickel removal BCL project.

Period	Days	Feed rate (ℓ/d)	HRT (h)	SO_4 conc feed (mg/ℓ)
1	1 - 12	15	24	1600
2	13 - 23	30	12	1600
3	24 - 29	30	12	2100
4	30 - 46	15	24	2250

TABLE 2

The metal concentration in the feed.

Metal conc (mg/ℓ)	Feed 1	Feed 2
Cu	0.01	0.05
Mn	0.97	0.99
Ni	5.86	5.50
Zn	1.25	38.00

Process stability

Figure 2 shows the sulfate concentration in the feed and treated water, as well as the COD of the treated water over a period of 46 days in the reactor. It was observed that sulfate was almost totally removed from the feed water after ten days to 50 mg/ℓ (as SO_4). The initial feed rate was 15 ℓ/d, which was doubled, after day 10. From then on, the sulfate was reduced to a consistent 450 mg/ℓ in the treated water. When the sulfate concentration in a new batch of feed water increased to values of and over 2000 mg/ℓ, the sulfate concentration in the treated water increased to 1150 mg/ℓ. Due to the low pH value of the feed water, the reactor pH was low. When the reactor pH was increased and the reactor was operated in a batch mode (days 27 - 29), the sulfate was reduced to 50 mg/ℓ. A new feed batch was introduced to the reactor on day 30. The feed rate was kept at 30 ℓ/d, resulting in a HRT of 12 h. However, the feed rate was reduced to 15 ℓ/d on day 31, with the aim to reduce the sulfate concentration to values lower than 200 mg/ℓ. The reactor pH was strictly monitored from day 30 onwards and when decreased to values lower than pH of 7.5, a solution of concentrated $NaHCO_3$ was added to the reactor. Although the reactor was closely monitored from day 30 onwards, the sulfate concentration in the reactor did not decrease to the required values lower than 500 mg/ℓ, until it was observed that the reactor COD concentration had decreased dramatically. When on day 43, additional ethanol was added to the reactor, the SO_4 concentration in the reactor was as low as 77 mg/ℓ. It can be observed from Figure 2 that the COD value decreased from the average value of about 1750 mg/ℓ, to a concentration less than 100 mg/ℓ. This observation can possibly be ascribed to the metal concentration in the reactor. It has been reported that methanogenesis is stimulated by the addition of micronutrients, especially the trace metals such as iron, cobalt and nickel (Speece, 1996). It can be hypothesised that the methanogens were stimulated and competed with the SRB for the available COD, due to the elevated nickel concentration in the reactor. From the data in Table 2, it can be noted that nickel was present in the feed at concentrations of 5 - 6 mg/ℓ and that the zinc concentration in the feed varied from 1 - 38 mg/ℓ.

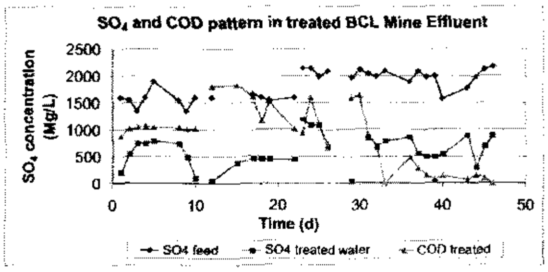


FIG 2 - The SO_4 and COD concentration in the treated BCL mine water.

Sulfate reduction rates, COD utilisation and volatile suspended solids (VSS)

The results of the sulfate removal and sulfide production together with the sulfate reduction rates are given in Table 3, while the metal removal is given in Table 4.

When observing the results of the volumetric sulfate reduction rates treating the BCL mine water during the four experimental periods, the rates varied from 1.05, to 2.45, to 1.92 and 1.62 g SO_4 (ℓ/d), during periods 1, 2, 3 and 4, respectively. The highest sulfate reduction rate (2.45 g SO_4 (ℓ/d)) was obtained during the second experimental period. During this period, the feed rate was 30 ℓ/d, the average feed sulfate concentration was 1600 mg/ℓ and the reactor SO_4 concentration was an average of 375 mg/ℓ. The COD to the reactor was added in the form of ethanol (1 mℓ/ℓ), which resulted in a reactor COD concentration of about 1700 mg/ℓ. The COD utilisation for the sulfate reduction can be expressed as the $COD_{utilised}/SO_{4\,reduced}$ ratio. This ratio as indicated in Table 3 varied during the four different periods. During the first period, the COD/SO_4 ratio was 0.67, which corresponded with the theoretical $COD_{utilised}/SO_{4\,reduced}$ ratio, during the second period however this experimental ratio was very low (0.06), for which no explanation can be given. During the third period, the experimental ratio (1.06) was higher than the theoretical ratio, which can be explained by the increased activity of the methanogens. During the fourth period, the experimental ratio (0.69) was similar to the theoretical period. During this period on two occasions, additional COD was added to the reactor to stimulate further SO_4 reduction, although the feed COD/SO_4 ratio at 0.71 should have been adequate, if indeed only the SRB had utilised the available COD. It can therefore be assumed that competition for the available COD with the methanogens occurred.

As can be seen from Table 3, the VSS concentration throughout the four experimental periods remained more or less constant. The overall VSS concentration increased with ten per cent from about 3000 to 3300 mg/ℓ during the total experimental period of 46 days.

Sulfate reduced, sulfide produced and metal sulfide precipitation

It can be seen from Table 3 that during all four experimental periods, the experimental $sulfide_{produced}/sulfate_{reduced}$ ratio (0.13, 0.22, 0.24 and 0.16) was lower than the theoretical ratio of 0.33. This can be ascribed to the fact that part of the produced sulfide was used to precipitate the metals present in the BCL mine water. In addition, part of the formed sulfide oxidised, because of the occurrence of the sulfide oxidising bacteria (present when sulfide together with some air is available). The Cu, Ni and Zn concentration in the treated water was less than 1 mg/ℓ, during the first periods, while the Mn concentration did not decrease. However, during periods 3 and 4, the Mn concentration in the treated water was reduced to 0.17 and 0.06 mg/ℓ, which might be pH related as the reactor pH was higher at 7.00 and 7.55, respectively. When the zinc concentration in the feed was as high

TABLE 3

Sulfate removal and sulfide production treating the BCL mine effluent.

Determinand	**Unit**	**Period**				**Theoretical ratio**
Period		**1**	**2**	**3**	**4**	
Feed rate	ℓ/d	15	30	30	15	
HRT	h	24	12	12	24	
Feed						
pH	units	6.5	5.12	4.31	4.32	
Sulfate	mg/ℓ	1600	1600	2100	2250	
COD	mg/ℓ	1727	1727	1742	1602	
Alkalinity	mg/ℓ	130	130	100	120	
Treated						
pH	unit	6.72	6.10	7.00	7.55	
Sulfate	mg/ℓ	550	375	1138	627	
COD	mg/ℓ	1019	1657	1099	488	
Alkalinity	mg/ℓ	903	1477	1305	1766	
Sulfide	mg/ℓ	140	268	229	260	
VSS	mg/ℓ	2943	2952	3652	3331	
Ratios						
S/SO_4		0.13	0.22	0.24	0.16	0.33
COD/SO_4		0.67	0.06	1.06	0.69	0.67
Removal rates						
Volumetric SO_4 removal rate		1.05	2.45	1.92	1.62	
Spec. SO_4 removal rate		0.35	0.9	0.52	0.49	

TABLE 4

The metal removal pattern treating the BCL mine water.

Metal	**Feed 1**	**Feed 2**	**Period 1**	**Period 2**	**Period 3**	**Period 4**
Nickel	5.86	5.5	0.15	0.17	0.14	0.61
Zinc	1.25	38	0.03	0.03	0.03	0.03
Manganese	0.97	0.99	0.97	1.20	0.17	0.06
Copper	0.01	0.05	0.03	0.03	0.03	0.03

as 38 mg/ℓ, no zinc was analysed in the treated water, indicating that the produced sulfide was used to precipitate the zinc. During the fourth period, the nickel concentration in the treated water was higher (0.6 mg/ℓ) than in the previous three periods. This result cannot be pH related as with increasing pH, the solubility of Ni decreases (Bhattacharrya *et al*, 1981). The residual sulfide in that period was high enough at 260 mg/ℓ to precipitate the available nickel. Therefore, no immediate explanation can be provided for the Ni concentration increase during period 4.

Metals as trace elements

Trace elements are present in low concentrations in rocks, soils, water and in the atmosphere. Some trace elements, such as cobalt, copper, zinc, iron and nickel are (micro-) nutrients. Trace metals play a structural role in various enzymes, which are the cell's catalysts (Brock *et al*, 1997). The activity of biomass is dependent upon a host of factors, but in the case of trace metals, the lack of only one can severely limit the overall process. Especially iron, cobalt, nickel and zinc have been shown to be stimulatory to the methanogens, degrading acetate (Speece, 1996). In the second mine water sample as obtained from BCL, the zinc concentration in the feed was as high as 38 mg/ℓ. From Figure 2, it can be observed that from about day 30, the COD concentration decreased rapidly in the reactor. This occurrence coincided with the feeding of the second mine water sample, containing a higher zinc concentration than the previous mine (feed) water. It can be assumed that a correlation exists between the higher zinc concentration in the feed water and the total COD degradation in the reactor. On two occasions, during period 4, ethanol was added directly to the reactor in order to investigate whether sulfate reduction could be observed when additional COD was added to the reactor. During period 4, the nickel concentration in the treated water was higher than in the previous periods, which together with Zn is a trace element instrumental for acetate degradation in the bioreactor (Speece, 1996). He described the importance of three trace elements, being nickel, iron and cobalt. When these three trace elements were directly injected into the reactor, acetate utilisation rates could be observed immediately, as could the gas production. In the case of treating BCL mine water, nickel was present in the water, thus it might be possible that the elevated nickel (and likely the zinc) concentration played an important role in the enzyme activity of the methanogens, thus enabling the methanogens to use the available COD. It can be assumed that the methanogens were able to obtain and use the metals for their metabolism, and thus that the methanogens out-competed the SRB for the use of the available COD, which adversely affected the sulfate reduction.

CONCLUSIONS

The results of this study indicated that all metals in the BCL mine water were removed after the biological sulfate reduction to sulfide production. Because the experimental produced $\text{sulfide}_{\text{produced}}/\text{sulfate}_{\text{reduced}}$ ratios (0.13,0.22, 0.24 and 0.16) were lower than the theoretical ratio of 0.33, it can be assumed that the produced sulfide precipitated the metals in the feed water to metal sulfides (MeS). Good sulfate reduction was observed in period 2, resulting in a SO_4 removal rate of 2.5 g SO_4 (g.ℓ). Due to the sulfate concentration increase in the feed water, while the ethanol concentration remained the same, the feed COD/sulfate ratio was <1 during periods 3 and 4. This might explain why the sulfate reduction during those periods was not as efficient as throughout period 2. The lower sulfate reduction can possibly be ascribed to the competition of the SRB and the methanogens for the available COD. The results seem to indicate that the increased feed Zn and Ni concentration stimulated the enzymatic activities of the methanogens, thereby degrading the available COD.

REFERENCES

APHA, 1985. *Standard Methods for the Examination of Water and Wastewater*, 16th Edition, (American Public Health Association: Washington DC).

Bhattacharry, D, Jumawan, A B, Sun, G, Sund-Hagelberg, C and Schwitzebel, K, 1981. Precipitation of heavy metals with sodium sulfide: bench scale and full-scale results, *AIChE Symposium Series 77*, pp 31-38 (American Institute of Chemical Engineers: New York).

Brock, T D, Madigan, M T, Martinko, J M and Parker, J, 1997. *Biology of Microorganisms*, Eighth Edition (Prentice-Hall, Inc).

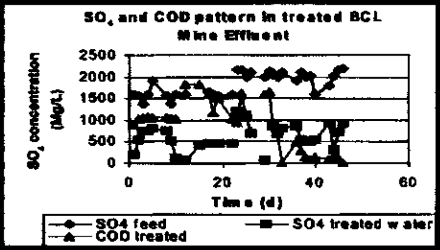
Jovanovic *et al*, 2002. Commercial production of crops irrigated with gypsiferous mine water, *Water SA*, 28(4):413-423.

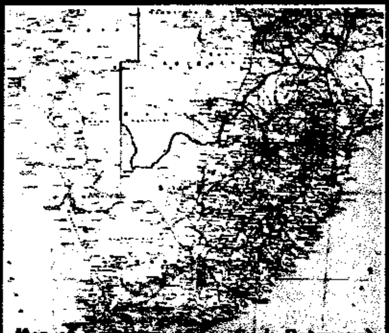
Speece, R E, 1996. *Anaerobic Biotechnology for Industrial Wastewaters*, (Archae Press: Nashville).

THE SUSTAINABILITY OF BIOLOGICALLY TREATED COPPER MINE EFFLUENT SUITABLE FOR IRRIGATION

Botswana RST Group
BCL LIMITED
(Incorporated in the Republic of Botswana)

CSIR
ENVIRONMENTEK
Your Technology Partner





Map of Southern Africa (incl. Botswana)

APPENDIX B LIST OF CONFIRMATIONS

WATER RESEARCH COMMISSION
E-mail: ingridb@wrc.org.za

Private Bag X03
Gezina
0031 SOUTH AFRICA

WEBSITE: http://www.wrc.org.za

TEL: (012) 330-0340
FAX: (012) 331-2565
International code +2712

Enquiries:

Telephone:

Your Reference

Our Reference
K3/6/1734

1 March 2004

Mr AJ Geldenhuys
PO Box 72531
LYNNWOOD RIDGE
0040

Dear Mr Geldenhuys

ACID MINE DRAINAGE TREATED ELECTROLYTICALLY FOR RECOVERY OF HYDROGEN, IRON(II) OXIDATION AND SULPHUR PRODUCTION by AJ Geldenhuys, JP Maree, WJ Fourie, JJ Smit, BJ Bladergroen M Tjati

Thank you very much for your E-mail letter of 1 March 2004 enclosing the above paper to be considered for publication in *Water SA*. The paper will be referred to referees and I shall again communicate with you as soon as I have received the reports.

Yours sincerely

IG Buchan
Editor: *Water SA*
for CHIEF EXECUTIVE OFFICER

Street Address: 491 18th Ave, Rietfontein, Pretoria

Geldenhuys,Andre

From:	imwa@shaftsinkers.co.za
Sent:	04 August 2004 09:49
To:	Geldenhuys,Andre
Subject:	Enquiry

Dear Mr Geldenhuys

Many thanks for your email regarding your paper which you presented at the IMWA Congress last October in Johannesburg.

I can confirm to you that your paper titled "Electrolytic Treatment of Acid Mine Drainage for Hydrogen Production" was reviewed and edited by Mr Don Armstrong, an Honorary President of the Executive Council of The International Mine Water Association and one of four paper editors for the IMWA 2003 Congress.

Should you require further assistance please do not hesitate to contact me.

For your information the official website for the International Mine Water Association is www.imwa.de should you need to include this.

Kind regards

Mimi van Niekerk

CSIR
ENVIRONMENTEK

Water Environment and Forestry Technology

P O Box 395
Pretoria 0001
South Africa
Tel. +27 12 8412285
Cell. 082 465 3547
Fax. +27 12 8412506
5 August 2004

Beste Andre en Prof Waanders

Ek gee graag hiermee stemming dat Andre Geldenhuys die ondergenoemde publikasies vir sy tesis mag gebruik.

PAPER 1: Geldenhuys,A.J., Maree, J.P., de Beer, M. and Hlabela, P. 2003. An integrated limestone/lime process for partial sulphate removal, The J. South African Institute of Mining and Metallurgy, 103(6), 345 - 353.

PAPER 2: Geldenhuys, A.J. & Maree, J.P. Synthetic organic polymers (PAC6 and 3095) as coagulants/flocculants for optimisation of an integrated limestone/lime neutralisation process for partial sulphate removal, Proceedings 5th Annual Industrial Water Management and Treatment Symposium, 15-16 May 2002, Johannesburg, South Africa.

PAPER 3: Geldenhuys, A.J., Maree, J.P., Strobos, G., Smit, N. and Buthelezi, B. Neutralisation and partial sulphate removal of acid leachate in a heavy minerals plant with limestone and lime, Proceedings 6th International Conference on Acid Rock Drainage, 12-18 July 2003, Ciarns, Australia.

PAPER 4: Geldenhuys, A.J., Maree, J.P., Fourie, W.J., Bladergroen, B.J. and Tjati, M. Acid mine drainage treated electrolytically for recovery of hydrogen, iron(II) oxidation and sulphur production, Proceedings 8th International Congress on Mine Water and the Environment, 19-22 October 2003, Johannesburg, South Africa.

PAPER 5: Maree, J.P., de Beer, M., Geldenhuys, A.J., Strobos, G., Greben, H., Judels, C. and Dreyer, J. Comparison of the combined limestone/lime and combined limestone/biological sulphate removal process for treatment of acid mine water, Proceedings Hard Rock Mining Conference: Issues Shaping the Industry, 7-9 May 2002, Colorado, USA.

PAPER 6: Adlem, C.J.L., Geldenhuys, A.J., Maree, J.P. and Strobos, G.J. Examining the implementation of limestone neutralisation technology in the mining and industrial sector to neutralise acid and reduce sulphate pollution, Proceedings 5th Annual Industrial Water Management and Treatment Symposium, 15-16 May 2002, Johannesburg, South Africa.

PAPER 7: Greben, H., Geldenhuys, A., Maree, J., Strobos, G. and Hagger, M. The sustainability of biologically treated nickel/copper mine effluent suitable for irrigation, Proceedings 6th International Conference on Acid Rock Drainage, 12 - 18 July 2003, Ciarns, Australia.

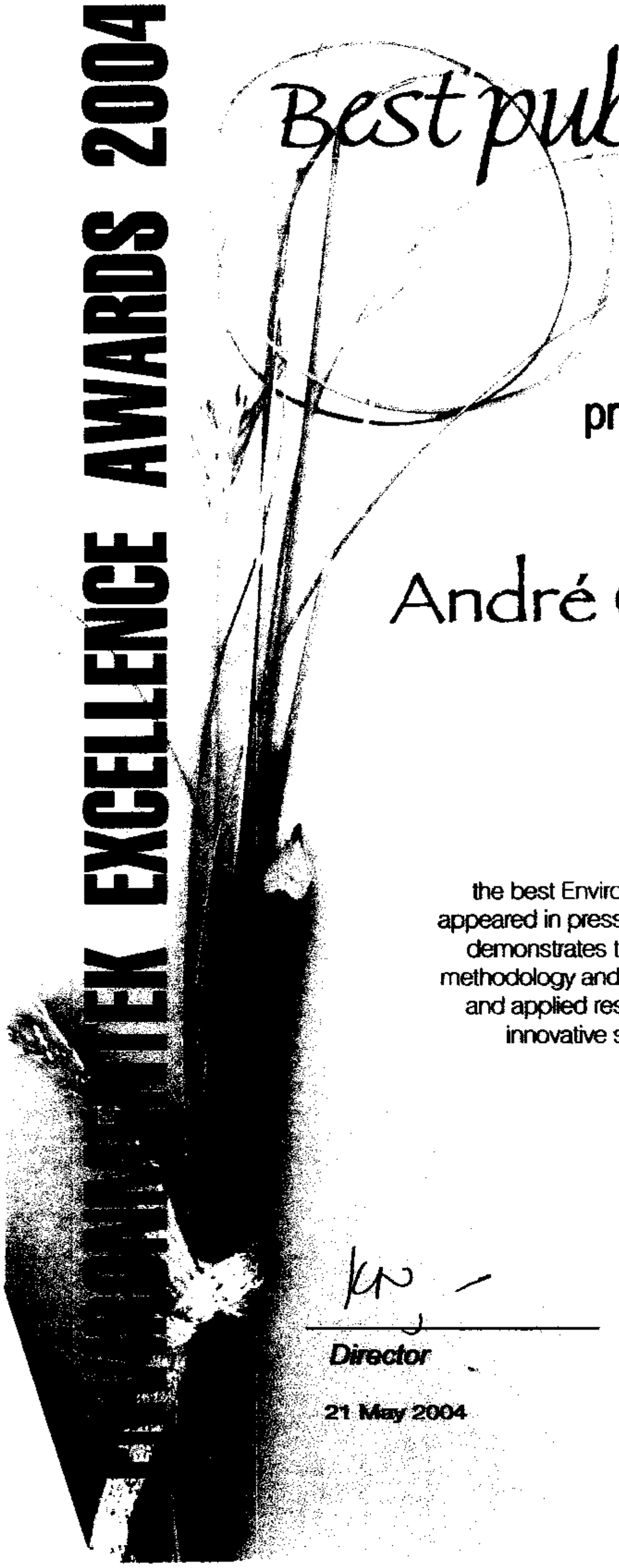
PAPER 9: Maree, J.P., Netshidaulu, I., Strobos, G., Nengovhela, R. and Geldenhuys, A.J. Integrated process for biological sulphate removal and sulphur recovery. Proceedings WISA 2003 - Biennial Conference & Exhibition, 2-6 May 2004, Cape Town, South Africa.

Beste groete

JPmaree

J P Maree
Besigheidsareabestuurder

TEK EXCELLENCE AWARDS 2004



Best publication Award

presented to

André Geldenhuys

for

the best Environmentek research publication that appeared in press in the 2003 calendar year. The paper demonstrates the application of a sound research methodology and is an excellent example of how basic and applied research can be combined to identify innovative solutions to complex problems.

Director

21 May 2004

CSIR
ENVIRONMENTEK

Geldenhuys,Andre

From:	Esther Eloff [EEloff@csir.co.za]
Sent:	31 May 2004 08:55
To:	Andre.Geldenhuys@afrox.boc.com
Subject:	Fwd: One of our most prestigious awards!!!!!

best pub award
citation 2003_....

>>> Rose Clark 31/05/2004 08:51:34 >>>
Hi everyone

many of you attended the 3 events in each major centre celebrating the success of our top achievers over the past 3 weeks. Given for the strong call for having the citations short and sweet, we were not able to give you all the full set of information regarding citations etc for all candidates at each event. An abbreviated version was presented at the functions to ensure that interest was maintained throughout the evening.

Attached is the full set of information on one of our most prestigious awards - the best Publication award.

Please take the time to read this and acknowledge the fantastic work of your colleagues in this arena. Also many thanks to Inge Kotze for co-ordinating the 22 volunteer reviewers, Bob Scholes for programming the algorithms, and David Le Maitre, Dirk Roux and Alex Weaver for doing the final adjudication.

I will also be asking Mandi to ensure that the full list of award winners, with photos and full citations to be made available on our own website so that you can all celebrate their fantastic achievements in style and full detail!

Thanks to our awards review panel for adjudicating all your motivations (Brian van Wilgen, Shamilla Pillay, Vasna Ramasar, Stephan Woodborne, Tanya du Toit and Pat Manders).

I am sure you will all join me in thanking Mandi Titi for organising 3 great events and Khungeka for sponsoring them.

Kind rgds
Rose

Rose Clark
841 4707 (tel)
841 2734 (fax)

ENVIRONMENTEK'S BEST PUBLICATION AWARD FOR 2003.

The annual award for the best scientific publication by an Environmentek staff member is arguably the premier award made to any staff member on an annual basis. The award is intended to show the importance that the management team places on quality research, which in turn underpins our effectiveness as a science-based organization. We also hope that an award of this type will encourage the production of more high-quality publications by providing a substantial incentive. This seems to be working because Environmentek produced 33 scientific publications in 2002 and 54 in 2003, more than 40% of the total produced by the CSIR.

The award for the best publication of the year is in the form of a grant for the researcher or researchers involved to travel to a destination of their choice, worldwide, to pursue further research or studies, attend a conference, or to build networks in their research field, subject to the approval of a costed proposal. The option of a single, large award indicates the importance that is attached to this aspect of our business, and although there can only be one winner, even though there are often many deserving cases.

Environmentek's Research Committee has run an evaluation process that has resulted in the selection of the 2003/04 winning publication. The first step was to examine all the publications on the database, or submitted by the authors, and selected a shortlist of 42 publications. The short-listed publications were shared out among 20 reviewers and rated based on:

- the quality and innovativeness of the work;
- its relevance to Environmentek's mission and impact,
- the standing of the journal or book and
- the relative contribution by CSIR authors.

This process resulted in a shortlist of six outstanding publications from which a team of three adjudicators had to select the final one. The final six papers were as follows:

Cave. L., Beekman, H. and Weaver, J. (2003). Impacts of climate change on groundwater recharge estimation. In: Groundwater recharge estimation in southern Africa (eds Y Xu and H Beekman), pp 189-197. UNESCO IHP Series No. 64, UNESCO, Paris.

Geldenhuys, A.J., Maree, J.P., De Beer, M. and Hlabalela, P. (2003). An integrated limestone/lime process for partial sulphate removal. The Journal of the South African Institute of Mining and Metallurgy July/August 2003, pp 1-9.

Gelderblom, C.M.. Van Wilgen, B.W., Nel, J.L., Sandwith, T., Botha, M. and Hauck, M. (2003). Turning strategy into action: implementing a conservation action plan in the Cape Floristic Region. Biological Conservation 112: 291-297.

McConnachie, A.J., De Wit, M.P., Hill, M.P. and Byrne, M.J. (2003). Economic evaluation of the successful biological control of *Azolla filiculoides* in South Africa. Biological Control.

Schoemann, J.J. and Steyn, A. (2003). Nitrate removal with reverse osmosis in a rural area in South Africa. Desalination 155:15-26.

Scholes, R.J., Bond, W.J. and Eckhardt, H. (2003). Vegetation dynamics in the Kruger ecosystem. In: The Kruger experience: ecology and management of savanna heterogeneity (eds JT Du Toit, KH Rodgers and HC Biggs), pp 242-262.

The chapter by Lisa Cave and her colleagues is a well-written and thorough assessment of the implications of climate change for the use of groundwater as a resource. The UNESCO handbook series gets wide exposure and the book will be used and consulted by many geohydrologists in southern Africa and elsewhere. The analysis uses a simple model based on earlier work by one of the authors. The significant implications of even a small decline in rainfall for groundwater recharge, and for the communities dependent on groundwater, are explained clearly and simply. The shortcomings and assumptions in the model and in the climate change model information used in the model are described clearly. This chapter is based on a presentation given at a local workshop conference and publication in this form will give it much wider exposure.

The paper by Geldenhuys and his co-workers deals with a key aspect of the innovative research being done by Jannie Maree and his team to address the severe acid pollution problems being created by the mining industry. The paper demonstrates the application of a sound research methodology and is an excellent example of how basic and applied research can be combined to identify solutions to genuine problems. It also demonstrates the full cycle of innovation from idea to application. The process it describes reduces the high sulphate concentrations in coal mine water to acceptable levels and simultaneously reduces magnesium levels. A key feature of the process is that by-products can be re-used in the process so that it needs much lower inputs of the basic resources. The process includes the use of polymers to flocculate out suspended and colloidal material and obtain water that has low turbidity levels. The cost reductions with this new process are about 69% compared with the previously accepted methods which also produced greater quantities of waste and required lime which requires more energy to produce than limestone. The paper was produced in a local society journal but one that is very relevant because the society has many members in the mining industry.

Caroline and co-worker's paper describes the result of a lot of work which led to the successful Cape Action Plan for the Environment, a strategic approach to conservation of the unique vegetation Cape Floral Region. The successful completion of this project involved working with a wide range of participants and stakeholders and getting them to collaborate. This manner is in which this was done and the quality of the final products was recognised by, among others Kathy McKinnon of the funding agency (GEF/World Bank) and promoted as a model for similar projects elsewhere in the world. The strategic plan provided the basis for securing very large amounts of money that have revitalised ecological research. It also set the stage for a number of other conservation planning initiatives and for further involvement of CSIR staff in these initiatives. Much of the attention has focused on but this would be of little used without the model for its implementation provided by the CAPE project.

Martin De Wit is the second author of this paper but a key contributor because the reason for the research was to provide a scientifically acceptable assessment of the economic benefits of biocontrol of a major weed species. *Azolla filiculoides* is a very successful invader of aquatic systems, particularly of slow flowing rivers and dams with nutrient-enriched water. It reduces water quality and can develop such thick mats on the surface that sheep have mistaken it for grass, walked into dams and drowned (all we like sheep....). The analysis confirms that the quantifiable financial benefits which could be quantified in hard cash outweighed the costs with ratios of 2.5:1 or more. The savings (Net Present Value) came to about R7300 per ha or about R1.3 billion nationally. An important issue raised by this work is who should pay for this type of research? Currently the government pays and other sectors benefit but the government could potentially put this money to other uses. Maybe a fund is needed that could be sustained by the beneficiaries? An interesting issue that deserves further research.

Schoenman and Steyn's paper is on work done to reduce the high nitrate and salinity levels which are often found in rural water supplies based on groundwater. These high levels create severe health problems for people who often do not have the resources needed to deal with the problems that arise. High nitrates can stunt the development of young babies, especially if they are on a poor diet. The reverse osmosis (RO) technology that was used is not easy to maintain so the project was aimed at demonstrating that it could work and deliver measurable benefits when operated by a typical rural community. The RO system was successfully operated and maintained by the community and produced very good quality water. The concentrated by-products could be used for stock watering. The capital and operational costs of the RO system came to about R3.00 per m^3, about R0.08 per person per day for the 25 l basic human requirement. The costs can be reduced by blending it with unpurified water while maintaining acceptable nitrate and salinity levels. An assessment of the value of the benefits to human health and well-being would be a valuable extension of this work. The work was innovative, targets a key issue for many rural communities and provides a workable solution.

Bob Scholes and co-authors have compiled a through and useful review of the findings of local and international research into the dynamics of savanna vegetation. They document some interesting contrasts between savannas in different parts of the world and how these tropical ecosystems differ from the temperate that have led to most of the generalisations about plant ecology. The various driving factors in savanna are reviewed, focusing on water availability, the direct and indirect impacts of large plant eaters – megaherbivores – and fires. Fires have dramatic impacts on vegetation – it seems that without fires the wetter parts of South Africa would not have the highveld grasslands and savannas that are the source of most of our tourism income. The chapter contains a good example of a synthesis of a lot of information to show how savannas are shaped by multiple, interacting factors.

The selection of the final winners was not easy, it was a very, very close contest. All the papers are outstanding and some hard thought and iterations were required before the final winners were chosen. We would like to congratulate all of the authors of the above papers for making the final shortlist from which we were ultimately forced to choose just one. We urge and encourage our young scientists to make the time to read these papers and learn from them.

Our choice for the winners goes to Andre Geldenhuys and his co authors – congratulations and well done!

PO Box 38083
Garsfontein East
0060
Tel 012 993 2787
Mobile 072 482 3592
carlssonfam@absamail.co.za

Professor FB Waanders
Department of Chemical Engineering
University if the North West
(Potchefstroom Campus)

Ph.D. Thesis: Mr A.J. Geldenhuys

This is to certify that, at his request, I have read and edited the manuscript of the thesis by Mr. A.J. Geldenhuys titled, *Water Treatment Technologies for Removal of Acid, Sulphate and Metals.*

The editing process was aimed at the use of language and comprised corrections and suggestions for improvement. I was also involved in editing some of the publications on which the thesis is based and I am familiar with the work described.

F.H.H. Carlsson MSc PhD (Natal)

20 March 2005

CSIR

Water Environment and
Forestry Technology

P O Box 395
Pretoria 0001
South Africa
Tel. +27 12 8412285
Cell. 082 465 3547
Fax. +27 12 8412506
21 January 2005

Dear Andre and Prof Waanders

We hereby give our authorisation that Andre Geldenhuys may use the following publications for the purpose of his thesis:

PAPER 1: Geldenhuys,A.J., Maree, J.P., de Beer, M. and Hlabela, P. 2003. An integrated limestone/lime process for partial sulphate removal, The J. South African Institute of Mining and Metallurgy, 103(6), 345 - 353.

PAPER 2: Geldenhuys, A.J. & Maree, J.P. Synthetic organic polymers (PAC6 and 3095) as coagulants/flocculants for optimisation of an integrated limestone/lime neutralisation process for partial sulphate removal, Proceedings 5th Annual Industrial Water Management and Treatment Symposium, 15-16 May 2002, Johannesburg, South Africa.

PAPER 3: Geldenhuys, A.J., Maree, J.P., Strobos, G., Smit, N. and Buthelezi, B. Neutralisation and partial sulphate removal of acid leachate in a heavy minerals plant with limestone and lime, Proceedings 6th International Conference on Acid Rock Drainage, 12-18 July 2003, Ciarns, Australia.

PAPER 4: Geldenhuys, A.J., Maree, J.P., Fourie, W.J., Bladergroen, B.J. and Tjati, M. Acid mine drainage treated electrolytically for recovery of hydrogen, iron(II) oxidation and sulphur production, Proceedings 8th International Congress on Mine Water and the Environment, 19-22 October 2003, Johannesburg, South Africa.

PAPER 5: Maree, J.P., de Beer, M., Geldenhuys, A.J., Strobos, G., Greben, H., Judels, C. and Dreyer, J. Comparison of the combined limestone/lime and combined limestone/biological sulphate removal process for treatment of acid mine water, Proceedings Hard Rock Mining Conference: Issues Shaping the Industry, 7-9 May 2002, Colorado, USA.

PAPER 6: Adlem, C.J.L., Geldenhuys, A.J., Maree, J.P. and Strobos, G.J. Examining the implementation of limestone neutralisation technology in the mining and industrial sector to neutralise acid and reduce sulphate pollution, Proceedings 5th Annual Industrial Water Management and Treatment Symposium, 15-16 May 2002, Johannesburg, South Africa.

PAPER 7: Greben, H., Geldenhuys, A., Maree, J., Strobos, G. and Hagger, M. The sustainability of biologically treated nickel/copper mine effluent suitable for irrigation, Proceedings 6th International Conference on Acid Rock Drainage, 12 - 18 July 2003, Ciarns, Australia.

PAPER 9: Maree, J.P., Netshidaulu, I., Strobos, G., Nengovhela, R. and Geldenhuys, A.J. Integrated process for biological sulphate removal and sulphur recovery, Proceedings WISA 2003 - Biennial Conference & Exhibition, 2-6 May 2004, Cape Town, South Africa.

Kind regards

M de Beer ....
G Strobos ....
P Hlabela ....

W Fourie ....
M Tjati ....
C Judels ....
J Dreyer ....
C Adlem ....
R Nengovhela .....NNengovhela.....................
H Greben ....
I Netshidaulu ....
J Maree ....