Treatment of industrial effluents for neutralization and sulphate removal

Johannes Philippus Maree B.Com, Ph.D.

Thesis submitted in fulfillment of the requirements for the degree Philosophiae Doctor in Chemical Engineering at the Potchefstroom Campus of the North-West University

Promoter: Prof F B Waanders

March 2006

DECLARATION

I, Johannes Philippus Maree, hereby declare before a Commissioner of Oaths:

1. That the publications submitted for the degree Ph.D. (Eng.) at the North West University have not previously been submitted for such a doctoral degree at another university.

2. That this submission takes place with due recognition being given to my copyright in accordance with each case.

SIGNED BEFORE ME

JP Maree

(31 October 2005)

Signed and sworn to before me at Pretoria on 31 October 2005.

NIVASHNEE NARAINDATH
COMMISSIONER OF OATHS
EX OFFICIO
LEGAL ADVISOR
CSIR 395
PRETORIA 0001

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and appreciation to the following persons and institutions who contributed towards the completion of this study:

Prof F B Waanders, Faculty of Engineering, North West University, for his guidance and support.

CSIR, Water Research Commission, Anglo Coal (Landau Colliery) and THRIP (Technological and Human Resources Industrial Program) program of the National Research Foundation for financial support.

My colleagues Dr Johan de Beer, Harma Greben, Marinda de Beer, Deon van Tonder, Gerhard Strobos, Ryneth Nengovhela and Patrick Hlabela, for assistance and support.

Dr Angus Christie and Mr Peter Günther of Anglo Coal, for their support, advice and guidance during projects with Anglo Coal.

Mr Mboneni Muofhe and Ms Etresia du Plessis from the THRIP (Technological and Human Resources Industrial Program) program of the National Research Foundation, for their support.

Mr Leo Pistorius from H Pistorius and Co and Dr Wynand Louw from Aqualime, who are the suppliers of precipitated calcium carbonate. They also assisted with the successful commercialization of the limestone neutralization technology.

Messrs Bill Pullen, Hennie Cronjé and Francois le Roux of Thuthuka Project Managers who assisted with full-scale implementation of the limestone neutralization technology.

My family, Annatjie, Phillip and Evert, my late father and mother, Jannie and Johanna Maree, my mother-in-law, Elsa Kleynhans, and late father-in-law, Prof Evert Kleynhans, for their loyal support.

TABLE OF CONTENTS

GLOSSARY

Acid mine drainage	Acid water, rich in iron, produced when pyrite (FeS_2) is oxidised in water due to the presence of air and iron oxidising bacteria.
Barium sulphate	$BaSO_4$
Barium sulphide	BaS
Calcium carbonate	$CaCO_3$
Dolomite	A sedimentary rock of chemical composition, $CaMg(CO_3)_2$
Fluidised-bed Reactor	A column type reactor, packed with solid material, e.g. limestone, through which a fluid is moved, at a rate, high enough, to expand the volume in the reactor occupied by the solid particles.
Limestone	Sedimentary rock containing predominantly $CaCO_3$.
Slaked lime	$Ca(OH)_2$
Lime or Unslaked lime	CaO

ABBREVIATIONS

AMD	Acid mine drainage
BCL	Botswana Copper Limited
EDR	Electrodialysis
GYPCIX	Gypsum counter current ion exchange
HDS	High density sludge
HRT	Hydraulic Retention Time
MB	Methanogenic bacteria
OSI	Over saturation index
RO	Reverse osmosis
RWQO	Receiving water quality objective
SRB	Sulphate Reducing Bacteria
UASB	Up-flow Anaerobic Sludge Blanket
WLA	Waste load allocation

CHAPTER 1. SUMMARY OF THESIS

1.1 Background

Acid mine water containing sulphate and high concentrations of dissolved heavy metals, including iron(II), can have pH values as low as 2.5. Environmental pollution caused by such effluents are major contributors to the salinisation of receiving water, and may prove toxic to both fauna and flora. Acid, sulphate-rich solutions are produced bacteriologically from pyrite present in waste dumps from mining and metallurgical operations and from spent sulphuric acid used in chemical or metallurgical plants. The following large mine water treatment projects are currently receiving attention in South Africa on a national level:

1. Amanzi Water Project. The Amanzi project deals with the treatment of mine water (potentially 240 Ml/d) for the recovery of potable water and by-products (e.g. gypsum). Participating mines in the project are Randfontein Estates, First Wesgold, Durban Roodepoort Deep, Rand Leases, ERPM and Grootvlei. The pH of these waters varies from 2.8 to 6.0 and the sulphate concentrations from 600 to 3 000 mg/l (SWaMP Steering Committee, 1998).
2. Olifants Forum. Polluted mine water, estimated at a volume of 130 Ml/d, is currently discharged to water courses on the Highveld. The mine water has a pH level between 2 and 4 and contains high sulphate concentrations (> 700 mg/l) (Van Zyl, *et al.*, 2000).

Unless neutralized, such water may not be discharged into water courses. Lime is generally used for neutralization. Neutralization costs could be reduced significantly should lime be replaced with limestone. The cost of limestone is currently R130/t compared to R700/t for lime. Furthermore, increasing pressure is being exerted by the Department of Water Affairs and Forestry to enforce sulphate removal from effluent. Extensive studies have already been carried out by the mining industry to evaluate possible sulphate removal technologies. The high cost of these technologies are considered a major obstacle. Therefore, efforts to develop a cost-effective treatment process for the recovery of re-usable water from sulphate-rich effluents, is of national importance.

1.2 Objectives

The objectives of this investigation were to develop processes whereby acid and/or sulphate-rich water can be treated. The specific aims of the investigation were to:

1. Develop the integrated iron(II)-oxidation and limestone neutralization process where powdered limestone is used for the neutralization of iron(II)-rich acid water in a completely-mixed reactor (Chapters 3 and 4 and Patents 1 - 3).
2. Develop the biological sulphate removal process for treatment of sulphate-rich effluents (Chapters 5 and 6).
3. Develop the barium sulphide process for treatment of sulphate-rich effluents (Chapter 7).
4. Develop a water flow and chemical mass balance model to identify the most cost-effective treatment option for a water network (Chapter 8).

1.3 Findings

The following innovative processes/models were developed for neutralization and sulphate removal from industrial effluents:

1. A limestone handling and dosing system.
2. A limestone neutralization and iron(II)-oxidation process for the removal of free acid, iron and aluminium.
3. A biological sulphate removal stage which includes biological sulphate reduction, H_2S-stripping and aerobic treatment for the removal of residual organic material, and calcium carbonate precipitation. The barium process, which is similar to the biological sulphate removal process, can also be used for sulphate removal.
4. Modeling of a typical water network of a mining operation.

1.3.1 Limestone neutralization

In order to develop the limestone neutralization technology to the stage of full-scale implementation it was necessary to understand its limitations, study its kinetics, develop design criteria for full-scale plants and to protect the intellectual property through patents.

1.3.1.1 The limestone neutralization process.

Limestone was not used previously on a large scale for neutralization of iron(II)-rich acid water. The reasons were:

1. The pH of iron(II)-rich water could not be raised sufficiently with limestone to rapidly allow iron(II) to be oxidized to iron(III). Rapid oxidation of iron(II) occurs only at pH 7 and higher. This can however be achieved with lime, while limestone only raises the pH of iron(II)-rich water to pH 6.
2. The reactivity of limestone is too low to neutralize acid water completely within an acceptably short residence time when stoichiometric dosages are applied.
3. Iron(II) passivates limestone particles due to $Fe(OH)_3$ preferentially precipitating on the surface of the limestone particles, where the pH is the highest.

1.3.1.2 Kinetics of limestone neutralization.

Stumm and Lee (1961) investigated the rate equation for biological iron(II)-oxidation and determined that it is a function of the pH, iron(II) and oxygen concentrations. This rate equation was investigated for the case where limestone was used as the neutralization agent. Special attention was given to the effect of suspended solids concentration on the rate of iron(II)-oxidation.

1.3.1.3 Full-scale implementation of limestone neutralization

For the present investigation a demonstration plant was constructed and evaluated for iron(II)-

oxidation/limestone neutralization (Maree, *et al.*, 2004). A plant with a capacity of 1 Ml/d was constructed at BCL, a nickel and copper mine in Botswana. Ore tailings leachate, with an acid concentration of 10 g/l (as $CaCO_3$), was treated. Limestone, available at a cost of R150/t, was used for neutralization of the acid water. Previously, leachate with a high acid concentration was combined with less acidic streams before it was neutralized with lime. The result of this approach was that a large volume of product water was slightly over-saturated with respect to gypsum, resulting in scaling of pipelines and other equipment. The leachate was neutralized separately from the less acidic streams. The over-saturated fraction was first allowed to crystallize from solution in the fluidized-bed reactor before being combined with the other streams.

The following patents were registered, following the investigation:

1. A patent on the integrated limestone and iron(II)-oxidation process.

2. A patent for a limestone handling and dosing system was registered where powdered precipitated $CaCO_3$ was dumped onto a concrete slab, slurried to constant density with an automatic control, and used for neutralization of the acid water.

3. A patent on an integrated limestone and lime process for the treatment of acid and sulphate-rich effluents. This allows the following:

    - Stage 1: The bulk of the acid is neutralized with limestone while CO_2 is produced and stripped off by aeration.

    - Stage 2: Lime is added to allow precipitation of magnesium and other metals as well as sulphate associated with these metals.

    - Stage 3: The CO_2 that is produced in Stage 1 is used to adjust the high pH of the water from Stage 2 to 8.3. This allows $CaCO_3$ precipitation.

1.3.2 Biological sulphate removal

A biological process was developed whereby sulphate reduction to sulphide and sulphide oxidation to elemental sulphur occur in the same reactor. The following aspects were investigated: the reaction rate of biological sulphate reduction, the effect of various parameters on the reaction rate such as temperature, sulphide and sulphate concentrations and the identification of intermediate products formed.

Pilot scale evaluation of the following stages of the biological sulphate removal process were evaluated:

1. Heating stage. Feed water to the anaerobic stage was first contacted directly with hot coal gas to raise the temperature of the water to 30 °C.
2. Anaerobic stage. A pilot plant with a capacity of 8 m^3/h was operated, using ethanol or sugar as energy source.

3. H_2S-stripping and processing stage. A laboratory unit was operated to evaluate the suitability of the following reactor types for H_2S-stripping and processing: Venturi device and a packed-bed reactor.

1.3.3 Integrated BaS process for sulphate removal

Laboratory studies were carried out to demonstrate that the integrated BaS-process is technically and economically viable for sulphate removal. The BaS process consists of the following stages:

1. Thermal stage where barium sulphate is reduced to barium sulphide at 1050°C, using coal as the reductant.
2. Sulphate removal stage
3. Sulphide stripping and processing stage
4. Softening stage where limestone is precipitated.

1.3.4 Modeling

The water network of a coal mine was audited and simulated by an interactive, steady state model to determine the optimum effluent treatment process configuration. The findings from this investigation were used to optimize the mine's water management strategy. Simulation of the interactions in the water network was used to show the following: (i) Powdered $CaCO_3$ can be used as an alternative to lime for the neutralization of acid water at a cost saving. (ii) The amount of gypsum crystallization that occurred in the primary neutralization and coal processing plants. This information was needed to plan for sludge disposal. (iii) The benefits associated with separate treatment of the most polluted stream versus combined treatment of all streams during mine water treatment. By treating the higher polluted streams separate from the lesser polluted streams, higher salt removal efficiencies are achieved. (iv) The OSI (gypsum over-saturation index) value can be controlled effectively at 1 by treating the feed water to the coal processing, for sulphate removal. The capacity of the sulphate removal plant required was determined as well as the associated capital and running costs.

1.4 Benefits

The treatment approach outlined offers the following benefits: (i) The cheapest alkali, a by-product from the paper industry, can be used for neutralization of the acid and for the removal of the bulk of the sulphate concentration through gypsum crystallization. The more advanced biological process is then used only for removal of the remaining sulphate, to low concentrations. (ii) A robust biological process is used for sulphate removal to produce process water which is non-scaling and suitable for discharge into public streams. (iii) This is an integrated process as CO_2 produced during limestone-neutralization is used for H_2S-stripping in the biological stage. The stripped H_2S-gas is utilized in the limestone-neutralization stage for precipitation of iron as iron sulphide. Iron is also removed as inert $Fe(OH)_3$ together with gypsum in the limestone-neutralization stage, after oxidation.

2. SAMEVATTING VAN DIE VERHANDELING

2.1 Agtergrond

Suur mynwater kan hoë metaal, insluitende yster(II), en sulfaat konsentrasies bevat, en kan pH waardes van laer as 2.5 hê. Omgewingsbesoedeling word veroorsaak deur industriële uitvloeisels wat ryk is aan suur, metale en sulfaat. Hierdie besoedeling dra by tot die versouting van die ontvang strome en mag toksie wees vir beide fauna en flora as gevolg van hoë konsentrasies van swaarmetale en sianied. Suur en sulfaatryke water word bakteriologies geproduseer vanaf piriet in die teenwoordigheid van afval ertshope vanaf mynbou en metallurgiese bedrywe en vanaf gebruikte swaelsuur vanaf chemiese en metallurgiese aanlegte. Die volgende projekte wat te make het met sulfaatryke uitvloeisels geneit tans aandag in Suid Afrika op 'n nasionale vlak aandag geniet:

1. Amanzi water projek. The Amanzi projek handel oor die behandeling van mynwater (na raming 240 Ml/d)vir die herwinning van drinkwater en byprodukte (bv gips). Die volgende myne neem deel aan die projek: Randfontein Estates, First Wesgold, Durban Roodepoort Deep, Rand Leases, ERPM en Grootvlei. Die pH van die waters wissel tussen 2.8 en 6.0 en die sulfaatkonsentrasies tussen 600 en 3 000 mg/l (SwaMP Steering Committee, 1998).
2. Olifantforum. Besoedelde mynwater, met 'n geskatte volume van 130 Ml/d, word in die Hoëveld vrygelaat in publieke strome. Die water bevat lae pH waardes (2 tot 4) en hoë sulfaatkonsentrasies (groter as 700 mg/l) (Van Zyl, *et al.*, 2000).

Suur mynwater moet geneutraliseer word voordat dit in openabare strome gestort kan word. Kalk word normaalweg vir die doel aangewend. Neutralisasiekoste kan aansienlik verminder word indien kalk vervang word deur kalkklip. Die koste van kalkklip beloop R130/t teenoor die R700/t vir kalk. Verder word sterk druk toegepas deur die Departement van Waterwese en Bosbou vir die verwydering van sulfaat uit industriële uitvloeisels. Omvattende studies is alreeds deur die mynbou industrie uitgevoer vir die evaluering van verskillende sulfaatverwyderingstegnologieë. Die hoë koste verbonde aan prosesse wat sulfaat verwyder is 'n groot struikelblok. Dit is daarom van nasionale belang dat 'n koste-effektiewe proses ontwikkel word vir die herwinning van herbruikbare water vanaf sulfaatryke uitvloeisels.

2.2 Oogmerke

Die hoof oogmerke van die studie was om prosesse te ontwikkel vir die behandeling van suur en sulfaatryke uitvloeisels. Spesifieke oogmerke was:

1. Ontwikkel die geintegreerde yster(II)-oksidasie en kalksteenneutralisasieproses waar poeier kalksteen gebruik word vir die neutralisasie van yster(II)-ryke suur water water in a volledige mengreaktor (Hoofstukke 3 en 4 en Patente 1 - 3).
2. Onwikkel die biologiese sulfaatproses vir die behandeling van sulfaatryke uitvloeisels (Hoofstukke 5 en 6).
3. Ontwikkel die bariumsulfiedproses vir die behandeling van sulfaatryke uitvloeisels (Hoofstuk 7).

4. Ontwikkel 'n watervloei en chemiese massa balans model om die mees koste-effektiewe behandelingsopsie te identifiseer.

2.3 Bevindinge

Die volgende prosesse/modelle is ontwikkel vir neutralisasie van en sulfaatverwydering uit industriële uitvloeisels:

1. Die kalksteen hanterings en doseringssiteem.
2. 'n Kalksteen neutralisasie en yster(II)-oksidasieproses vir die verwydering van vry suur, yster(II) en aluminium.
3. 'n Biologiese sulfaatverwyderingsproses wat stadiums vir sulfaatreduksie, H_2S-stroping, aerobiese behandeling vir die verwydering van residuele organiese materiaal en $CaCO_3$-presipitasie insluit. Die bariumproses, wat sekere ooreenkomste het met die biologiese sulfaatproses, kan ook aangewend word vir sulfaatverwydering.
4. Modelering van 'n tipiese waternetwerk van 'n mynbou operasie.

2.3.1 Kalksteenneutralisasie

Die volgende aktiwiteite was nodig om die kalksteentegnologie te ontwikkel tot die stadium van volskaalse toepassing: 'n beter begrip kry vir die beperkinge van kalkklip, die kinetika van $CaCO_3$ neutralisasie bestudeer, ontwikkel ontwerpkriteria vir die die bou van volskaalse aanlegte en om die intellektuele eiendom te beskerm via die registrasie van patente.

2.3.1.1 Die kalksteenneutralisasieproses

Kalksteen was nie van te vore op groot skaal gebruik vir die neutralisasie van yster(II)-ryke suur water nie. Die volgende redes word hiervoor aangevoer:

1. Die pH van yster(II)-ryke water kan nie verhoog word tot die vlak waarby yster(II)-oksidasie vinnig plaasvind nie. 'n pH van 7.2 is nodig vir vinnige yster(II)-oksidasie. Kalk kan die pH maklike tot pH 7.2 en hoër verhoog, terwyl kalkklip die pH net tot 6 kan verhoog.
2. Die reaktiwiteit van kalkklip is te laag vir volledige neutralisasie van suurwater by 'n kort retensietyd en wanneer stoichiometriese dosering toegepas word.
3. Yster(II) veroorsaak skaling van kalkklip deeltjies. Dit is vanweë die feit dat $Fe(OH)_3$ by voorkeur op die oppervlakte van $CaCO_3$ deeltjies presipiteer, die area waar die pH die hoogste is.

2.3.1.2 Kinetika van kalksteenneutralisasie

Stumm en Lee (1961) het die snelheidsvergelyking vir die biologiese okisdasie van yster(II)-oksidasie bepaal en gevind dat dit ,n funksie is van pH, yster(II) en suurstofkonsentrasies. In hierdie studie is die snelheidsvergelyking ondersoek vir die toepassing wat klakklip gebruik was as neutralisasie middel. Spesiale aandag is verleen aan die invloed van gesuspendeerde stowwe

konsentrasie op die tempo van yster(II)-oksidasie.

2.3.1.3 Volskaalse implementering van kalklip neutralisasie

'n Neutralisasie aanleg is gebou vir die evealuasie van yster(II) oksidasie/kalkklip neutralisasie (Maree, *et al.*, 2004). 'n Aanleg met 'n kapasiteit van 1 Ml/d is gebou by BCL, 'n nikkel en kopermyn in Botswana. Loog water met 'n suurheid van 10 g/l, vanaf die afval erts hope is behandel. Kalkklip, wat beskikbaar was teen 'n prys van R150/t, is gebruik vir die neutralisasie van suur water. Voorheen is loogwater met 'n hoë suurinhoud gemeng met minder suur strome voor data dit met klak geneutraliseer was. Hierdie benadering lei daartoe dat 'n groot volume produkwater effens oorversadig is ten opsigte van gips, wat aanleiding tot tot skaling van pyplyne en toerusting. In die voorgestelde projek word loogwater afsonderlik van die minder besoedelde strome geneutraliseer. Die fraksie oorversadigde gips kristalleseer dan eers uit voordat die water gemeng word met ander minder besoedelde strome.

Die volgende patente is geregistreer vanuit bogenoemde werk:

1. 'n Patent op die geintegreerde kalsteen en yster(II)-oksidasieproses.

2. 'n Patent is geregistreer vir die kalksteen hanterings en doseringssisteem waar poeier kalkklip gestoor word op 'n betonblad, geflodder word tot 'n bepaalde digtheid met outomatiese beheer, en gebruik vir die neutralisasie van suurwater.

3. 'n Patent op die geintegreerde kalksteen en kalkprosesvir die behandeling vna suur en sulfaatryke uitvloeisels. Die patent sluit die volgende stappe in:

    - Stadium 1: Die suurinhoud van die water word in hierdie stroom met kalkklip geneutraliseer terwyl CO_2 wat geproduseer word afgestroop word deur belugting.

    - Staadium 2: Kalk word bygevoeg om voorsiening te maak vir die presipitasie van magnesium and ander metals sowel as sulfaat wat geassosieer met met die metale. Die vlak tot waar sulfaat verwyder word is a funksie van die oplosbaarheid van gips in die teenwoordigheid van natrium.

    - Stadium 3: Die CO_2 wat in Stadium 1 geproduseer word , word gebruik om die hoë pH van die stadium 2 se water tot 8.3 te verlaag met die CO_2 wat in stadium 1 geproduseer word. Dit lei tot CaCO3-presipitasie.

2.3.2 Biologiese sulfaatverwydering

'n Biologiese proses is ontwikkel waar die resuksie van sulfaat na sulfied and die oksidasie van sulfied na swael in dieslefde reaktor plaasvind. Die volgende aspekte is ondersoek: die reaksietempo van biologiese sulfaatreduksie, die effek van verskillende parameters op die reaksietempo soos bv temperatuur, sulfied en sulfaatkonsentrasies en die identifikasie van intermediêre produkte wat vorm.

Op loodsskaal is die volgende stadiums van die biologiese sulfaatproses geevalueer:

1. Verhittingsstadium. Voer water na die anaerobiese stadium is direk met met warm steenkoolgas gekontak om die temperatuur van die water tot 30 °C te verhoog.
2. Anaerobiese stadium. 'n Loodsaanleg met 'n kapasiteit van 8 m^3/h, wat etanol of suiker gebruik, is bedryf.
3. H_2S-stroping en prosessering stadium. 'n Laboratoriumeenheid is bedryf om die volgende reaktor tiepes te evalueer: Venturi sisteem en 'n gepakte bedreaktor.

2.3.3 Geintegreerde BaS proses vir sulfaatverwydering

Laboratoriumstudies is uitgevoer om te demonstreer dat die geintegreerde BaS-proses tegnies en ekonomies uitvoerbaar is vir sulfaatverwydering. Die BaS proses bestaan uit die die volgende stadiums:

1. Termiese stdium waar bariumsulfaat by 1050 °Cgereduseer word tot BaS met steenkool as reduseermiddel.
2. Sulfaatverwyderingsstadium
3. Sulfaatstropings en prosesseringsstadium
4. Versagtingsstadium waar kalsiumkarbonaat presipiteer.

2.3.4 Modelering

Die waternetwerk van 'n steenkoolmyn is geondersoek en nageboots deur 'n interaktiewe model ten einde die optimum proseskonfigurasie te indentifiseer vir uitvloeisel behandeling. Die bevindinge van hierdie ondersoek is aangewend te ondersteuning van die strategie wat gevolg moet word in die bestuur van mynwater. Modelering van die interaksies in die waternetwerk is gebruik om die volgende te demonstreer: (i) Poeier $CaCO_3$ kan as alternatief tot kalk gebruik word vir die neutralisasie van suurwater teen verminderde koste. (ii) Die hoeveelheid gips wat kristalliseer in die primêre neutralisie en steen wasaanlegte. Hierdie inligting word benodig vir slykwegdoening. (iii) Voordele verbonde aan die afsonderlike bahandeling van die mees besoedelde strome teenoor die gesamentlike behandeling van verskeie strome van verskillende kwaliteit. Meer soute word verwyder wanneer die mees besoedelde strome afsondelik behandel word. (iv) Die OSI (gips oorversadigingsindeks) waarde kan effektief op 1 beheer word deur behandeling van die voerwater van die steenkoolwasaanleg vir sulfaatverwyderinig. Die kapasiteit van die sulfaatverwyderingsaanleg wat benodig word kan bepaal word sowel as die kapitaal en lopende koste.

2.4 Voordele

Die behandelings proses soos uiteengesit bied die volgende voordele: (i) Die goedkoopste alkalie, 'n byproduk van die papiernywerheid, is gebruik vir die neutralisasie van suurwater en vir gedeeltelike sulfaatverwydering duer gipskristallisasie. Die meer gevorderde biologiese sulfaatproses word slegs gebruik vir die verwydering van die oorblywende sulfaat, tot lae konsentrasies. (ii) 'n Robuste biologiese prose word gebruik vir sulfaatverwydering om proseswater te produseer wat nie-skalend is nie en wat geskik is vir storing in openbare strome.

(iii) Dit is 'n geintegreerde proses omdat CO_2 wat geproduseer word tydens kalksteenneutralisasie, gebruik word vir H_2S-stroping in die biologiese stadium. Die gestroopte H_2S-gas word gebruik vir die presipitasie van yster as ystersulfied in die kalksteenneutralisasie stadium. Yster word ook na oksidasie verwyder as $Fe(OH)_3$ saam met gips.

CHAPTER 2. BACKGROUND

2.1 OCCURRENCE OF ACID WATER

Environmental pollution caused by industrial effluents rich in acid, metals and sulphate, and with pH values of less than 2.5, are major contributors to the salinisation of receiving water, and may prove toxic to both fauna and flora due to the unacceptably high concentrations of heavy metals and cyanide. Unless neutralized, such water may not be discharged into public water courses.

Acid and sulphate-rich solutions are produced by bacterial action on pyrite present in waste ore dumps from mining and metallurgical operations and from spent sulphuric acid used in chemical or metallurgical plants. The following reactions are responsible for pyrite oxidation (Barnes, 1968):

$$4FeS_2 + 14O_2 + 4H_2O \rightarrow 4FeSO_4 + 4H_2SO_4$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$$

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

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

The reactions occur underground during or after mining activities and on the surface in old mine dumps containing pyrite. In underground workings the pumping of mine water reduces the rate at which leaching occurs from exposed surfaces, but when mining operations and pumping cease, the water table returns to its natural level, or to a new level as a result of the mining operations. This flooding of the exposed seams stops the oxidation of iron pyrite, but brings the sulphuric acid and iron sulphates which are the products of the oxidation reactions into solution. The pH of such water may be as low as 1 resulting in further iron dissolution.

When the water finally reaches the surface it may emerge via old adits, emerge as a spring, or simply as seepage through the ground or even through the bed of an existing river or stream. It may be clear, because the underground water is low in oxygen and the iron is in solution as iron(II). As the water becomes aerated - which may occur before it emerges above ground - the iron rapidly oxidises from the ferrous to the ferric state and precipitates as an orange deposit. In shallow mines, or in adits set in higher ground, such cycles may be repeated as the groundwater level fluctuates. In deeper mines connections may exist with underground aquifers. Quite frequently the history and extent of mining is such that neither the hydraulic conditions, nor the chemical state of the water, can be predicted after mining activities have ceased (NRA, 1994).

Increasing pressure is being exerted by the Department of Water Affairs and Forestry to enforce sulphate removal from industrial effluents. Extensive studies have already been carried out by the mining industry to evaluate possible sulphate removal technologies (SWaMP Steering Committee, 1998; Golder, 2004). It is of national importance to develop a treatment process for the recovery of re-usable water from acid and sulphate-rich effluents and in South Africa emphasis is placed on the removal of sulphate from such effluents to minimize salinization of surface water. This is due to the fact that in South Africa with its small rivers, little dilution takes place when industrial effluents are discharged, compared to in North America and Europe with its large rivers. In the USA emphasis is placed on the removal of heavy metals and acidity due to their toxicity. Less emphasis is placed on sulphate removal due to high dilution factors (Mudder, 1995).

2.2 QUANTITY AND QUALITY OF MINE WATER

The mining industry stands to benefit the most from the limestone neutralisation process owing to the large volumes of acid water produced, resulting from natural oxidation of pyrites and from the use of sulphuric acid in uranium refineries. Table 2.1 shows that 196 000 tons of alkali (as $CaCO_3$) is required per year for the neutralization of AMD, while 222 000 tons is required for the neutralisation of acid water from the mining industry as a whole. This indicates that the effluent from metallurgical plants is of less importance than mine water effluent. It is important to note that various industries produce acidic effluents. A summary of these is given in Table 2.2.

Table 2.1 Estimated volume of acid water produced by the mining industry (Maree, 1994).

Source	Area/ Industry	Volume (Ml/d)	[Acid] mg/l $CaCO_3$	Load t/d $CaCO_3$	$CaCO_3$ t/a
AMD	Reef	50	4000	200	86 000
	Witbank	44	4000	176	76 000
	Natal	20	4000	80	34 000
Subtotal		114		456	196 000
Metallurgical plants	Zinc processing	3	20	60	26 000
TOTAL		**117**		**516**	**222 000**

Carbonate content of limestone was assumed to be 85% (as $CaCO_3$).

Table 2.2 Industries that produce acidic effluents (Maree, 1994).

Industry	Source	Acidity Range (as mg/l $CaCO_3$)
Mining	Acid mine drainage	500 - 4 000
	Uranium raffinate	18 000 - 22 000
	Acid plant	2 000 - 4 000
Edible oil	Total effluent	500 - 2 000
	Refinery stream	2 000 - 6 000
Explosives	Total effluent	2 000 - 5 000
Steel	Total effluent	140 000
Metal Finishing	Total effluent	6 000 - 8 000

The gold and coal mining industries, produce acid mine drainage (AMD), both from underground workings and surface water. This occurs when ore tailings containing pyrite and air come into contact with each other. It is estimated that about 240 Ml/d of acid water is produced in the Gauteng area alone (Volman, 1984). The Amanzi project deals with the treatment of mine water (potentially 240 Ml/d) for the recovery of potable water and by-products (e.g. gypsum). Participating mines in the Amanzi project are Randfontein Estates, First Wesgold, Durban Roodepoort Deep, Rand Leases, ERPM and Grootvlei.

Mine water discharged from coal mines in the Upper Olifants River Catchment currently amounts to approximately 44 Ml/d during an average hydrological year (Van Zyl *et al.*, 2000) (Table 2.3). It is expected that this figure will increase to an estimated 130 Ml/d by 2020. The quality of mine water is generally poor with sulphate concentrations between 800 and 3 000 mg/l. It is unacceptable to discharge such poor quality mine water into surface water sources. The current background sulphate load of water in the Upper Olifants River Catchment is estimated at 28.4 t/d (as SO_4) (947 Ml/d @ 30 mg/ℓ SO_4), which is small compared to the estimated 103 t/d sulphate load associated with excess mine water (2 337 mg/l SO_4 @ 44 Ml/d). The above-mentioned figures show that a relatively small volume of excess mine water is responsible for a major contribution to salinity. Excess mine water in the Olifants River Catchment currently amounts, volume wise, to only 4.4% of the total water usage, but contributes 78% of the sulphate load. Thus, by treating the relatively small volume of mine water before it is discharged into the public stream, the quality of the large volume of surface water will be significantly improved.

Table 2.3 Comparison between water volumes and sulphate load of fresh water usage and excess mine water discharges in the Upper Olifants River Catchment (Van Zyl *et al.*, 2000).

Parameter	Fresh Water usage	Mine Water discharge	Total	Fresh water	Mine Water
Volume (Ml/d)	947	44.0	991	95.6%	4.4%
Sulphate concentration (mg/l)	30	2337			
Sulphate load (t/d)	28.4	102.9	131.3	21.6%	78.4%

2.3 EFFECTS OF ACID WATER

The discharge of acid or neutralised water with a high salinity is responsible for, or contributes to, one or more of the following:

2.3.1 Salinisation of surface water. Impairment of the river water quality, because of mine water pollution, may render it unsuitable for industrial, potable or irrigation purposes.

2.3.2 Corrosion and scaling of equipment. When the pH is below 5.5, water can be corrosive to pipelines and equipment. When acid water is neutralized with lime it is often over-saturated with respect to gypsum. This practice results in the scaling of equipment by the unstable water produced, malfunctioning of dosing equipment and settling of particles in pipelines and valves. The latter often causes blockages which may result in under-dosage of lime or limestone, which in turn leads to acid corrosion.

2.3.3 Adverse impacts on aquatic life. Plants and fish are sensitive to water with low pH values. Fish deaths have been reported from the accidental discharge of acid water into public water courses, e.g. Olifants River in 1989 when acid water from abandoned coal mines polluted the river (DWAF, 1996). The impact on aquatic communities may not be immediately obvious, but can have serious environmental consequences. The biological effects include:

- Depletion of numbers of sensitive organisms and reduction in the diversity of the

community within the river corridor;

- Depletion of numbers and reduction in the diversity of the benthic, macro-invertebrates (organisms living on and in the stream bed);
- Loss of spawning gravels for fish reproduction and nursery streams; and
- Fish mortalities, particularly of indigenous salmonid species.

Clear but polluted streams, can have an orange appearance when iron(II) is oxidized. Such discharges make rivers virtually fishless by coating the river bed with precipitating iron hydroxides. Depletion of the numbers and diversity of benthic (bottom dwelling) species occurs because the precipitate has a smothering effect, reducing oxygen concentrations and covering the river bed with iron oxides. This process also reduces the extent of spawning gravels for fish breeding, by occluding the interstices of the gravel with fine sediment, and thereby limiting the availability of nursery streams. The low pH can be directly toxic, causing damage to fish gills. Solubilized metals, not only those contaminated in mine water, but those - such as aluminium, the third most abundant element within the Earth's crust - can dissolve because of the acidic conditions. Such conditions are extremely toxic to fish (NRA, 1994).

2.3.4 Aesthetic impact. The aesthetic impact of ferruginous mine water on rivers and streams, by the presence of a high colouration, immediately reduces the amenity value of an area. A direct consequence of this visual damage is a reduction in the use of a water body for recreational and water sport activities. Again, this reduces the economic and social value of the water resource to the local community.

2.3.5 High treatment cost. Lime is generally used for neutralization of acid mine water. Desalinization of neutralized mine water is not yet applied due to high treatment cost. A number of alternative desalinization treatment technologies were considered when treated mine water had to meet more stringent quality requirements for industrial reuse, discharge to a public stream, drinking or power station cooling water (Van Zyl *et al.*, 2000). Table 2.4 shows a summary of the costs associated with various treatment processes.

Table 2.4 Capital and running cost of various treatment processes (treatment module of 15 Mℓ/d) (Van Zyl *et al.*, 2000).

Treatment Process	SO_4 level in treated water (mg/l)	Capital cost (R million / (Mℓ/d))	Running cost (R/m³)
Limestone neutralization (incl. iron(II) oxidation)	2 500	0.50	0.59
Lime neutralization (pH 8)	1 500	0.53	1.36
Limestone/lime treatment (pH 11) & gypsum crystallisation	1 100	0.88	1.02
Lime treatment (pH 11.5) & gypsum crystallization	1 100	0.57	1.61
Advanced sulphate removal (including neutralization pre-treatment	200	4.0 – 10.0	2.0 – 5.0

2.3.6 Sludge disposal. Legislation requires that sludge from neutralization plants be discharged into lined ponds to prevent metal leachate from polluting ground water. The volume of sludge to be disposed of also influences the cost and processes that produce sludge with a high solids content

would be preferred.

2.4 LEGAL REQUIREMENTS

Neutralisation of acid water is widely applied by industry to meet legislative requirements before discharging the water into the receiving water body.

The legislative requirements for industrial effluent is primarily related to Section 21 of the Water Act (Act 54 of 1956). This requires that any person who uses water for industrial purposes shall purify or otherwise treat such water in accordance with requirements which the minister in consultation with the SABS may prescribe in the Government Gazette. The applicable standards are set out in the General Standard and the Special Standard (Government Gazette, 1984). The relevant criteria for discharge of acidic and sulphate-rich water are given in Table 2.5.

Table 2.5 Criteria set for the discharge of acidic and sulphate-rich effluents into public water courses (Government Gazette, 1984).

Parameter	General Standard	Special Standard
pH	5.5 - 9.5	5.5 - 7.5
Sulphate (mg/l)	no criterion	no criterion
Conductivity (mS/m)	inlet + 75%	250 or inlet + 15%

Before any permit for discharge is granted all efforts should be made to ensure maximum use of water through recycling or alternative uses. One alternative prior to discharge, is to pass the water on to a responsible local authority, body or person who can then either use, treat or purify the water.

According to the Water Act, local authorities who accept industrial effluent have the right to establish criteria as deemed necessary and require such criteria to be met. Table 2.6 gives the general criteria set by various local authorities in three provinces.

Table 2.6 Typical criteria set by local authorities for discharge of acidic and sulphate-rich effluents into sewerage systems in three provinces (Personal Communication).

Province	pH	Sulphate mg/l SO_4	Conductivity mS/m
Gauteng	6 - 10	1 800	500
Western Cape	5.5 - 12	500	-
KwaZulu-Natal	>6	200	300

Current and future approach

In the past the Department of Water Affairs and Forestry only used the uniform effluent approach to control pollution from point sources in South Africa, as required by the relevant sections in the Water Act, 1996. This approach did not achieve the desired results. The Act does, however, also make provision for the more stringent standards to be promulgated or exemptions to be granted.

The current process by which exemptions are granted is through a hierarchical system of application and approval of a permit. For this purpose the applicant must comply with the following:

- Demonstrate that all avenues of pollution prevention through waste minimisation, recycling of effluent and migration prevention have been investigated and applied.

- Perform an impact assessment for the catchment where the discharge is to be made, if, after the first step has been carried out, the effluent still does not meet the uniform effluent standards. Such an impact assessment must ascertain what the requirements of all the users of water from the receiving water body will be, as well as the extent to which the receiving water body will be affected.

- Through acceptable scientific calculations, negotiate specific receiving water quality objectives with the users, and the Department, which may then result in a new acceptable standard for the discharge of effluent. This approach is known as the, "Receiving Water Quality Objectives (RWQO) approach".

The aim of the RWQO approach is to extend and improve in future approaches to ensure the sustained fitness for use of water for all users and to cater for specific South African circumstances. This will eliminate some of the shortcomings of the uniform effluent approach as it will *inter alia* cater for diffuse (non-point) pollution sources and will result in some added benefits, such as the application of the Waste Load Allocation (WLA) concept.

In principle, WLA is the assignment of allowable discharges to a water body in such a way that the water quality objectives for the designated water users are being met. Principles of cost-benefit analysis are used in these assignments. It involves determining the water quality objectives for desirable water uses as described above. To obtain a waste load allocation an understanding of relationships between pollutant loads and water quality, and the use of these to predict the impacts on water quality, are required. The analysis framework also includes economic impacts and socio-political constraints. The Department of Water Affairs has started using WLA investigations to determine allowable discharges from some major industries.

These approaches and requirements will also apply in cases where lime or limestone treatment is applied to acid water before discharge of any effluent.

2.5 TREATMENT OF ACID MINE WATER

Acid water requires treatment for both neutralization and desalinization, where neutralization is required as pre-treatment to desalinization. Various processes have been developed for desalinization and include the following: Biological sulphate removal, SAVMIN, Aqua-K, Reverse Osmosis and Electro dialysis. In biological sulphate removal sulphate is converted to sulphide by sulphate reducing bacteria when an energy source such as sugar, ethanol or hydrogen is provided. The produced sulphide is removed as elemental sulphur. The SAVMIN process is an ion exchange process. Sulphuric acid

and lime is used for regeneration of the cat and anion resins. Aqua-K, Reverse Osmosis and Electro dialysis are all membrane processes. This investigation deals with neutralization and with desalinization associated with gypsum crystallization, biological sulphate removal and the barium process.

Neutralization is generally the first step in treating acid mine water (gold, operational and abandoned coal mines). In Gauteng about 240 Mℓ/d of acid mine water from gold and coal mining industries require treatment. At an acidity of 3 g/ℓ (as $CaCO_3$), a lime (CaO) price of R360/t and a purity of 93% the neutralization cost would amount to R57 million/a. It is, therefore, essential that the most suitable and cost-effective technology be identified or developed. Should limestone be used for the neutralization of acid water the cost could be reduced significantly as shown in Table 2.7.

Passive treatment is also evaluated for treatment of acid and sulphate-rich mining effluents. This method would be suitable to treat water with low acid concentrations with less than 300 mg/l acidity (as $CaCO_3$).

Table 2.7 Price comparison of neutralization alkalis (2001 cost figures; 1 US$ = ZAR9)

Cost	Sodium hydroxide	Hydrated lime	Unhydrated lime	Lime-stone
Cost (ZAR/t)	2000	500	480	110
Cost (c/kl)†	320	74	53.8	22

† Treatment cost for the neutralization of water with an acid content of 2 g/ℓ as $CaCO_3$. Total utilization and 100% purity are assumed.

2.6 LIME TREATMENT PROCESSES

The most suitable technology, to date, for the neutralisation of acid water is lime treatment, where the conventional and High Density Sludge processes are used (Osuchowski, 1992).

2.6.1 Conventional treatment with lime

The flow diagram for the conventional process is shown in Figure 2.1. The main advantage of this process is that sludge with a high density is produced which requires minimum storage area.

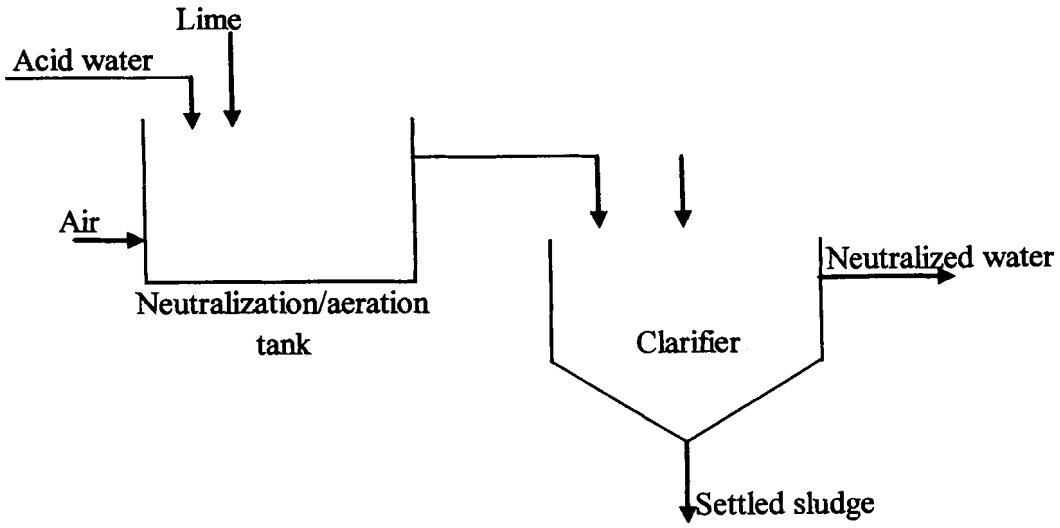


Figure 2.1 The conventional process for acid water neutralisation.

2.6.2 High Density Sludge (HDS) process

The HDS process (Figure 2.2) consists of the following stages:

- pH correction/sludge conditioning stage
- neutralisation/aeration stage, and
- solid/liquid separation stage.

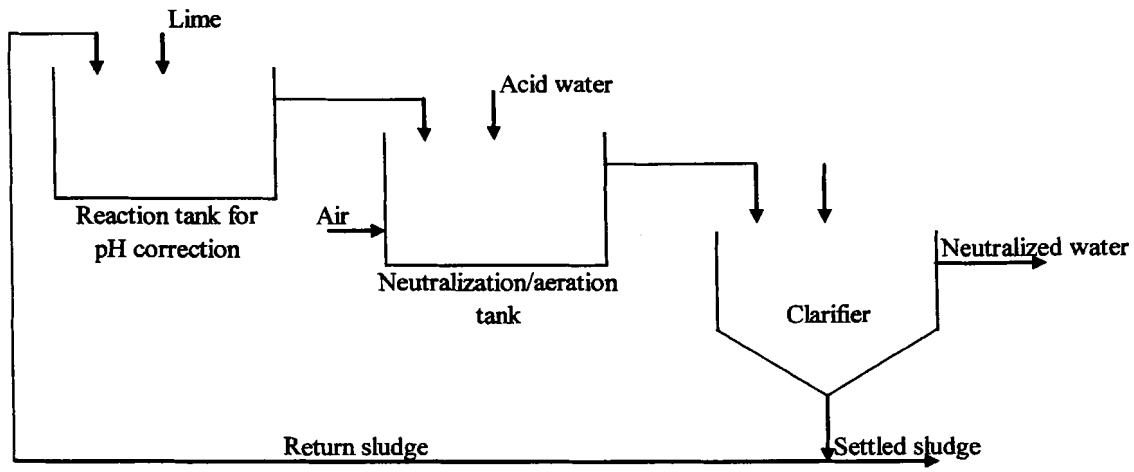


Figure 2.2 The High Density Sludge process for acid water neutralisation.

The pH correction stage consists of a reaction tank for the preparation of a lime solution and a sludge conditioning tank which receives both the recycled settled sludge from the settling tank underflow and the lime solution. The lime dosage in the pH correction stage is such that the pH of the final treated water is pH 8.

The conditioned sludge from the pH correction stage overflows into the neutralisation/aeration tank. This tank serves as a mixer to keep the solids in suspension, to mix the conditioned sludge with the acid mine water entering the tank and for aeration. In this tank ferrous iron is also oxidised to ferric iron.

The neutralised and oxidised effluent overflows to the clarifier where sludge is separated from the liquid. A poly-electrolyte can be dosed to the clarifier to promote flocculation.

The HDS process has the following advantages over the conventional process (Osuchowski, 1992):

- Sludge with a density 10 times higher than that of the conventional process is produced. As a result less demanding sludge drying facilities are required. The capital costs associated with the construction of sludge ponds (including pumping and piping facilities) vary between R1/m^3 and R3/m^3 of sludge handling, and thus the importance of minimum sludge volume becomes evident.
- The sludge settles faster, therefore, a smaller clarifier is required with a saving on the clarifier of approximately 38%.

2.7 LIMESTONE NEUTRALIZATION

To date, only lime, sodium hydroxide and sodium carbonate have generally been used for neutralisation. These chemicals have the disadvantage that they require accurate dosing to prevent under or over dosages, and pH controlled dosing systems tend to be unreliable due to fluctuations in the water flow rate and poor maintenance. The result is that water from low to high pH values (3 to 10, respectively) is pumped through the vertical mine water pipelines, resulting in either corrosion as a result of the low pH, or scale formation (gypsum) as a result of the high calcium concentrations. Since large amounts of lime are required, neutralisation of effluents such as the above is a costly operation.

Various benefits can be achieved by replacing lime with limestone. Limestone is significantly cheaper than lime which results in a cost saving and a simplified process control system is possible in the case of the use of the limestone. No pH-control is required as limestone and dolomite dissolution occurs mainly at pH-values below 7. Since the flow rate of underground mine water may vary by a factor of 10 (Pulles *et al.*, 1994), lime/soda ash systems only function well if their dosing rates are adjusted accordingly. Limestone offers the benefit that it is easy and safe to handle. It is not readily soluble in neutral water and can therefore be stored in the open. Utilization of existing equipment at lime neutralization plants is possible when lime is replaced with limestone. Dolomite can also be used but has disadvantages such as a slower reaction rate compared to limestone and the addition of magnesium to the water.

Notwithstanding these advantages, limestone neutralization has had limited application as a result of low neutralization rates compared to other alkalis and the phenomenon of surface scaling, which inhibits the reaction rate (Maree & Du Plessis, 1993). These limitations have been overcome by developing a fluidized-bed process (Maree & Clayton, 1992), which ensures a high effective limestone concentration in the reactor and counters scale formation by particle attrition. Despite these developments, iron(II) still needs to be oxidized to iron(III) upstream of the neutralization stage or even simultaneously.

2.7.1 Limestone Properties and its Selection

Limestone is composed primarily of $CaCO_3$ or combinations of calcium and magnesium carbonate with varying amounts of impurities, the most common of which are silica and alumina (Boynton, 1966). Since limestone does not have a constant chemical composition, it is important to establish what characteristics are necessary for a good neutralizing agent.

Most limestones are rated by the producers with regard to their $CaCO_3$ or $CaCO_3$ equivalent content.

The higher the $CaCO_3$ content, the greater the alkalinity available and the fewer the impurities. In comparing pure lime and limestone, it should be noted that when both are compared on the same basis, such as $CaCO_3$ equivalent, 1 kg of lime has 1.35 times the alkalinity of 1 kg of limestone.

Several investigators have reported that limestone, that contains magnesium carbonate in appreciable quantities, reacts very slowly (Jacobs, 1947; Hoak *et al.*, 1945; Ford, 1970). Hoak *et al.* (1945) reported that dolomitic limestone's rate of reaction was approximately inversely proportional to the quantity of magnesium carbonate it contained. The dolomite content of limestone often exceeds 2%. Ford (1970) conducted studies with 14 limestones of various compositions by treating both artificial and actual mine drainage and found that, in general, the neutralizing efficiency of limestone increased with higher percentages of $CaCO_3$ and lower percentages of $MgCO_3$, thus, the calcites, $CaCO_3$, were more effective than dolomites or magnesites. Empirically it was established that the efficiency of a limestone can be predicted by the following equation:

Efficiency (%) = CaO + (SA x D)

where: CaO = CaO (as $CaCO_3$) (%)
SA = Surface area (m^2/g)
D = Bulk density (g/mℓ)

A good limestone should have a high neutralizing rate, fast settling sludge, and result in a small volume of sludge, with a high solids content. The following factors should thus be considered in the selection of a limestone:

- High $CaCO_3$ content,
- Low magnesium content,
- Low amounts of impurities and
- Large surface area, i.e. smallest particle size.

After a preliminary screening of the proposed limestones by chemical analysis, a simple laboratory test was recommended. Twice the stoichiometric concentration of limestone, compared to the acidity of the AMD should be dosed. The sample should be mixed by introducing air, and the pH recorded over 5 h. A pH-time plot is then used to evaluate the limestone.

In addition to the reaction rate, the characteristics of the sludge should also be considered. Three characteristics of the sludge are important, i.e.:

- settling rate,
- sludge volume, and
- sludge solids content.

To perform these tests, a sample of the unsettled, neutralized AMD is placed in a 1 000 mℓ graduated cylinder and the depth of the sludge blanket determined periodically over 2 to 12 h. These data are then plotted with the final reading considered as the sludge volume, usually expressed as a percent of the total volume of sample. The supernatant water is then be drained off. The sludge is dried and the percentage of solids calculated.

In addition to the chemical properties of the limestone, the geological history of the stone and its crystal structure play a role in its neutralization ability. The crystal structure has some bearing on the surface area of the limestone particle. Several investigators have shown that the reaction rate is a function of

the particle size (Jacobs, 1947; Hoak *et al.*, 1945; Ford, 1970) with the limit on the fineness of the limestone an economic consideration. Cost of grinding increases at an exponential rate as the resultant particle size decreases. The cheapest small particle size material in mining areas is 'rock dust' of which 60 to 70% passes a 200 mesh. To obtain a smaller size may not be economically viable.

2.7.2 LIMESTONE TREATMENT SYSTEMS

Various limestone treatment systems have been investigated (Hill & Wilmoth, 1971), of which a few will be discussed.

2.7.2.1 **Aerated Limestone Powder Reactor**

Volpicelli *et al.* (1982) showed that effluent from a sugar plant containing sulphuric acid can be neutralized with powdered limestone. Two back-mix reactors were used to perform the operation in order to reduce the required residence time. A single back-mix reactor would have required a long residence time. The first reactor worked at pH 4 under steady state conditions as the dissolution rate of limestone is fast at low pH. The dissolution rate is very slow as the system approaches neutrality. Disadvantages associated with this system were that a long residence time was required unless powdered limestone was dosed, and that dosages, higher than stoichiometrically required, are necessary.

Limestone powder was found to react rapidly with the free acid, ferric and aluminium salts in AMD, but not in ferrous containing AMD (Glover *et al*, 1965). The ferrous containing AMD can only be treated if aeration is applied as it leads to iron(II) being slowly oxidized.

2.7.2.2 **Stationary Limestone Grit Reactor**

Stationary limestone beds can be operated by vertical fluid flow (Figure 2.3) or horizontal fluid flow configurations (Figure 2.4) (Hill & Wilmoth, 1971). These approaches have the advantage that an excess amount of limestone is in contact with the acid water. Losses of limestone can be recovered by a screening or sedimentation device downstream of the limestone bed.

A disadvantage of this approach is that the vertical reactor and the channel block, due to the formation of reaction products such as gypsum or ferric hydroxide on the limestone particles.

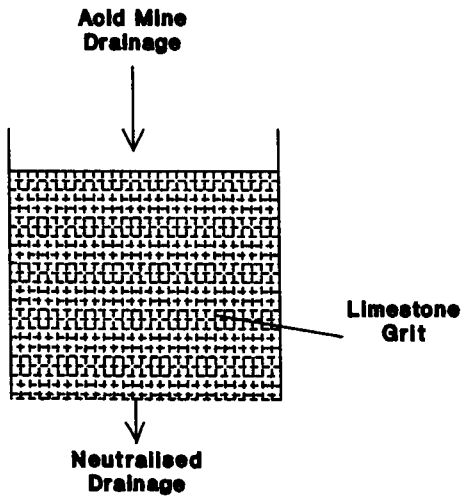


Figure 2.3 Stationary limestone grit reactor with vertical fluid flow.

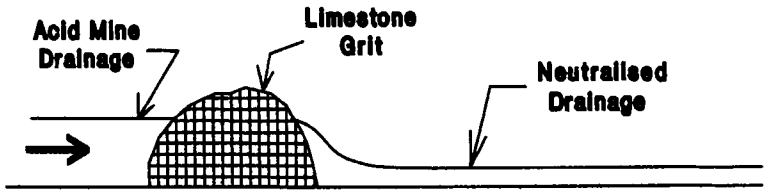


Figure 2.4 Stationary limestone grit reactor with horizontal fluid flow.

2.7.2.3 Stationary Aerated Limestone Grit Reactor

The purpose of stationary aerated grit reactors (Figure 2.5) is to treat ferrous containing acid water (Glover *et al.*, 1965). The reactivity of the limestone bed in these aerated stationary beds fell appreciably after one or two per cent of the limestone had been consumed under continuous flow conditions, but it was possible to restore the activity by up-flow fluid expansion of the beds (Figure 2.6). However, after seven per cent of the limestone had been consumed, a hard, dark-coloured scale formed on the limestone particles and the activity could no longer be restored by up-flow expansion.

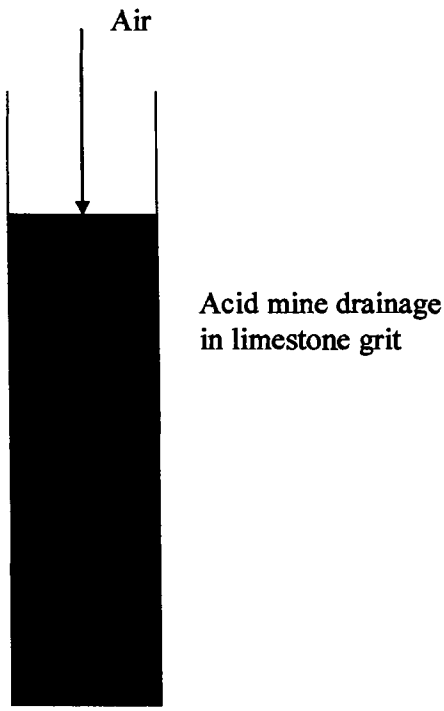


Figure 2.5 Stationary aerated limestone grit reactor.

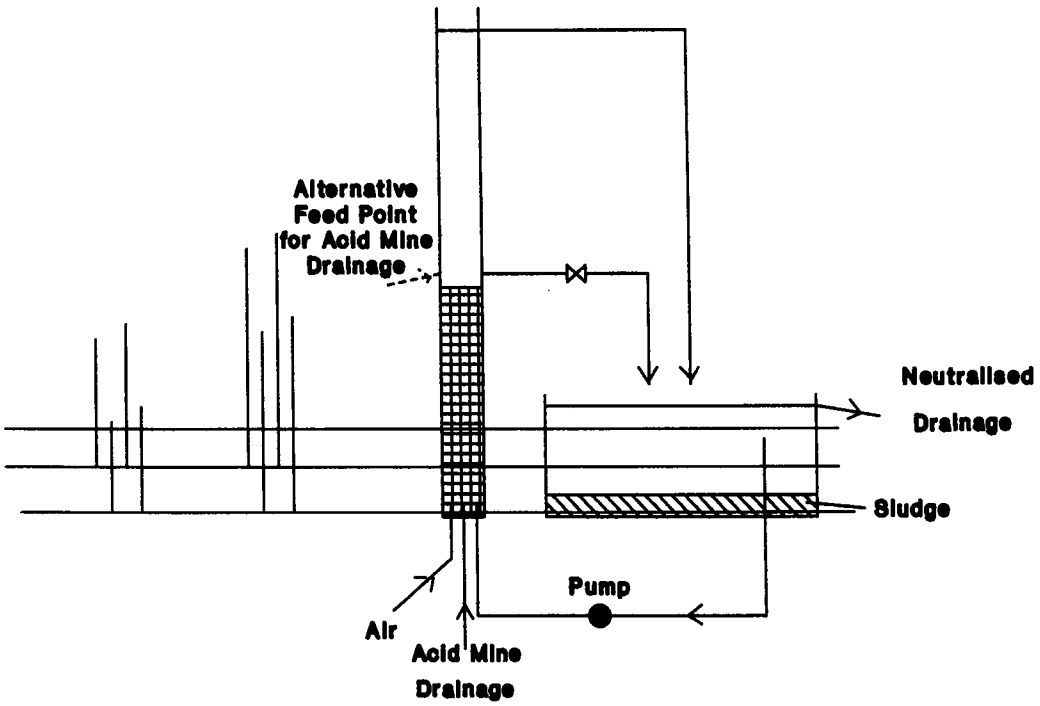


Figure 2.6 Stationary aerated limestone grit reactor with intermittent wash by upflow expansion.

2.7.2.4 Rotating Drum

The U S Bureau of Mines investigated the use of the tube mill for limestone neutralization (Deul & Mihok, 1967; Mihok, *et al.*, 1968; Mihok, 1970). In this process, 8 cm pieces of limestone were fed, together with acid mine water, to a rotating tube mill. The drum had a diameter of 1 m, a length of 8 m, and was rotated at a speed of 25 rpm. The rotation had the effect that the limestone was milled to a powder of less than 400 mesh. Acid water was fed to the drum at a rate of 2.3 Mℓ/d with the retention time of the water in the tube calculated to be 0.25 min. The water that was treated had a pH of 2.8, and contained 36 mg/l iron(II), 324 mg/l iron(III) and 1 700 mg/l acidity (as $CaCO_3$). A schematic diagram of a rotating drum reactor is shown in Figure 2.7.

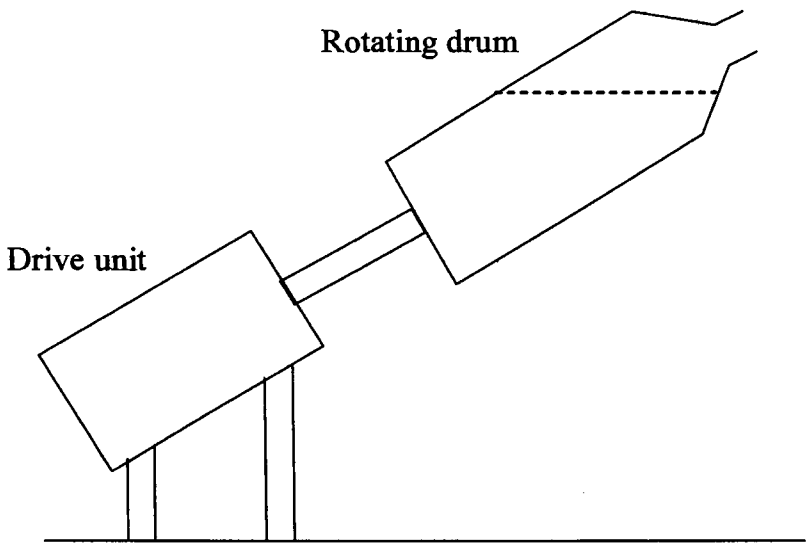


Figure 2.7 Schematic diagram of a rotating drum reactor.

The pH of the water after treatment was 7.4. At the Rochester and Pittsburgh Coal Co.'s Lucerne 3A mine (Coal Age, 1969), acid mine water containing iron was continuously treated in a revolving drum charged with limestone chips. The treated water was fully neutralized and all iron was removed. A drawback of the rotating drum is that limestone is used inefficiently and a large portion of the limestone is washed out with the treated effluent stream.

2.7.2.5 Limestone Lime Treatment

Wilmoth (1974), in concurrent studies, compared the cost advantage associated with the use of limestone-lime treatment versus lime in a completely mixed reactor. As limestone is not effective for the treatment of iron(II)-rich effluents, he proposed a two-stage process where limestone was used in the first stage and lime in the second stage. First, the AMD was treated with limestone to pH 4.0 – 4.5 to take advantage of the pH range where limestone is most effective. The water then passed through a second reactor where lime was applied to raise the pH to the desired level. Benefits associated with this approach were that the iron(II) was removed, the sludge produced had a high density which is characteristic of the limestone process, and a cost reduction of 25% was achieved. Although this two-stage process is more cost effective than the conventional lime neutralization process, it was not adopted generally by the mining industry because it is rather a complex process.

2.7.2.6 Fluidized-bed Neutralization Process

The CSIR has developed a fluidized-bed neutralization process using limestone or dolomite as the neutralizing agent (Maree & Clayton, 1992; Du Plessis & Maree, 1993; Maree & Du Plessis, 1994; Maree, *et al.*, 1996a; Maree, *et al.*, 1996b.). In this process crushed limestone (particle size less than 4 mm) was dosed to a column type reactor. The particles were kept in suspension by controlling the up-flow velocity by means of a recycle pump. In this fluidized-bed limestone process, no accurate control of the dosage was required as limestone only dissolves when the water is under-saturated with respect to $CaCO_3$ which usually occurs at pH below 7.

A limitation of the fluidized-bed process is that acid water rich in iron(II) cannot be treated directly as it passes through the fluidized-bed reactor. When aeration is applied to remove iron(II), it forms ferric hydroxide and limestone particles become coated with a layer of gypsum and ferric hydroxide which prevents further dissolution of the limestone particles.

A three-stage neutralization process consisting of a biological iron(II) oxidation stage, limestone neutralization in a fluidized-bed reactor and gypsum crystallisation was evaluated for treatment of discard leachate (Maree, 1994). Laboratory studies and on-site pilot plant studies at the Navigation Section of Landau Colliery over the period January 1995 to March 1997 showed that:

- Complete neutralization of discard leachate containing 10 g/ℓ acid (as $CaCO_3$) and 4 000 mg/ℓ iron(II) (as Fe) can be achieved in a limestone neutralization, fluidized-bed reactor, provided that iron(II) is oxidized beforehand.
- Iron(II) can be oxidized biologically to iron(III) at low pH-values. The rate of iron(II) oxidation is related to the surface area of the support medium. With plastic medium (specific surface area of 200 m^2/m^3 a residence time of 18 h is required for water containing 4 g/ℓ iron(II) (as Fe).
- Sulphate can be reduced from 18 000 mg/ℓ (as SO_4) to less than 2 500 mg/ℓ by gypsum crystallization in a contact reactor when 300 mg/ℓ magnesium (as Mg) is present. With a fluidized-bed contactor, a residence time of 2 h is required.

2.7.2.7 Need for further studies on limestone neutralization

A disadvantage of the three-stage process (where biological iron(II)-oxidation is applied in the first stage, limestone neutralization with crushed limestone in the second stage and gypsum crystallization in the third stage) is unacceptably high capital cost. This is due to the long residence time of 18 h required for iron(II) oxidation. The purpose of this investigation was to develop a single stage process where three reactions take place simultaneously. The three reactions are: iron(II)-oxidation, limestone neutralization and gypsum crystallization. The process consists of a neutralisation reactor and a clarifier.

2.8 SULPHATE REMOVAL

Several processes can be considered for sulphate removal, e.g. biological sulphate removal, SAVMIN (etringite), reverse osmosis, and electrodialysis. In biological sulphate removal sulphate is converted to sulphide by sulphate reducing bacteria when an energy source such as sugar, ethanol or hydrogen is provided. The produced sulphide is removed as elemental sulphur. The SAVMIN process is an ion exchange process. Sulphuric acid and lime is used for regeneration of the cat and anion resins. Aqua-K, Reverse Osmosis and Electro dialysis are all membrane processes. Both the biological sulphate removal and the barium sulphide processes were investigated with the aim to make it suitable for treatment of sulphate-rich effluents during full-scale applications.

2.8.1 Biological sulphate removal process

Biological treatment can be used to treat industrial effluents to achieve, in addition to sulphate removal, 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 $CaCO_3$ 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 been 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 (1985) showed that sulphate could be removed in an anaerobic packed-bed reactor using sucrose, pulp mill effluent or molasses as a carbon and energy source. Metals like nickel, cadmium and lead were completely removed due to precipitation of metal sulphides. Maree and Hill (1989) showed that a three-stage process could be applied for sulphate removal, using molasses as the carbon and energy source in an anaerobic packed-bed reactor. 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.* (1991) showed that when molasses is used as a carbon and energy source it can either be utilised in the fermented or unfermented form. 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, it was concluded that by running two anaerobic sulphate removal reactors in series, sucrose could be fermented to lactate in the first reactor and via acetate to CO_2 in the second reactor. Du Preez *et al.* (1992) were the first to demonstrate that producer gas (mixture of H_2, CO and CO_2) can be used as a carbon and energy source for biological sulphate reduction. CO and H_2 were utilised as the carbon and energy source respectively. Visser (1995) investigated the competition between sulphate-reducing

bacteria (SRB) and methanogenic bacteria (MB) for acetate as the carbon and energy source in an Up-flow Anaerobic Sludge Blanket (UASB) reactor. He found that at pH values less than 7.5, SRB and MB are equally affected by the presence of H_2S, while at higher pH values SRB out-compete MB. Van Houten (1996) 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 the carbon and energy source and pumice or basalt particles used to support bacterial growth in a fluidised-bed reactor. The sulphate reduction rate was not inhibited at H_2S-concentrations less than 450 mg/ℓ (as S).

2.8.2 Barium sulphide process

Barium can also be used for sulphate removal and has certain advantages such as that the sulphate can be removed to specific values due to the low solubility of barium sulphate; and the soluble barium salt, barium sulphide, can be recovered from the barium sulphate.

Kun (1972) studied the removal of sulphate with barium carbonate ($BaCO_3$) and obtained good results. However, he identified three problems: a long retention time requirement, high concentrations of soluble barium in the treated water when more $BaCO_3$ is dosed than stoichiometrically required, and the high cost of the $BaCO_3$. Volman (1984), Maree (1989) and Maree *et al.*(1989) overcame the cost problem by demonstrating that barium sulphate ($BaSO_4$) could be reduced efficiently and economically with coal under thermic conditions to produce barium sulphide (BaS). This compound can be used directly for the process or converted to $BaCO_3$. Wilsenach (1986) demonstrated its economic viability by calculating the cost of producing BaS from $BaSO_4$. Trusler *et al.* (1988) developed a $BaCO_3$ method using a two-stage, fluidised bed reactor system to overcome the other problems identified by Kun (1972), namely, long retention time and the high barium concentration in the treated water. However, the $BaCO_3$ became inactive when coated with metal hydroxide precipitates, which made it unsuitable for most mine water. Maree *et al.* (1989) also noted a problem in separating $BaSO_4$ and $CaCO_3$, which co-precipitate.

2.8.3 Need for further studies on sulphate removal

Previous studies described the stages for sulphate removal. In the case of the biological sulphate removal process the rate for sulphate reduction with various energy sources were described. In the case of the barium process much attention was given to the removal of sulphate when soluble barium salts (e.g. BaS) were added to the water. The reduction of $BaSO_4$ to BaS was also documented. In this investigation the focus was on the integrated processes, which include the following stages: (i) sulphate removal with either BaS addition in case of the barium process or ethanol addition as energy source in case of the biological process, (ii) sulphide stripping using CO_2-gas, sulphur production by contacting the stripped H2S-gas with iron(III) in solution and (iv) thermal stage for the reduction of barium sulphate to barium sulphide in the case of the barium process.

2.9 AIMS OF INVESTIGATION

The objectives of this investigation were to develop processes whereby acid and/or sulphate-rich water can be treated. The specific aims of the investigation were to:

1. Develop the integrated iron(II)-oxidation and limestone neutralization process where powdered limestone is used for the neutralization of iron(II)-rich acid water in a fluidized-bed reactor (Chapters 3 and 4 and Patents 1 - 3).
2. Develop the biological sulphate removal process for treatment of sulphate-rich effluents (Chapters 5 and 6).

3. Develop the barium sulphide process for treatment of sulphate-rich effluents (Chapter 7).
4. Develop a water flow and chemical mass balance model to identify the most cost-effective treatment option for a water network (Chapter 8).

2.10 REFERENCES

Act 54 (1956) Statutes of the Republic of South Africa (1956) Water Act, Act 54 of 1956

Barnes, HL and Romberger SB (1968) Chemical aspects of acid mine drainage. Journal WPCF 40(3): 371 - 384.

Boynton RS (1966) Chemistry and Technology of Lime and Limestone, John Wiley, New York.

COAL AGE, (1969) **75**, (2), 112-114.

Deul M and Mihok EA (1967) Mine water research - Neutralization, US Bureau of Mines, Report of Investigations 6987.

Du Plessis P and Maree JP (1994) Neutralization of acid water in the chemical industry with limestone, Wat Sci Tech 29(8): 93 - 104.

Du Preez LA, Odendaal JP, Maree JP and Ponsonby M (1992) Biological removal of sulphate from industrial effluents using producer gas as energy source, Env Technol 13: 875 - 882.

DWAF (1996) South African water quality guidelines. Volume 7: Aquatic ecosystems. Pretoria.

Ford CT (1970) Selection of limestones as neutralising agents for coal-mine water, Third Symposium on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pennsylvania, May, 27 - 51.

Glover HG, Hunt J, and Kenyon WG (1965) Process for the bacteriological oxidation of ferrous salts in acid solution, U S Patent 3,218,252, November.

Government Gazette (1984)18 May, No 9225

Golder (2004) Evaluation of new and emerging mine water teatment technologies, Coaltech Report (WMB4431/2582/2/P.

Hill RD and Wilmoth RC (1971) Limestone treatment of acid mine drainage, Society of Mining Engineers, AIME, Transactions 250: 162 - 166.

Hoak RD, Lewis CJ and Hodge WW (1945) Treatment of spent pickling liquors with limestone and lime, Ind. and Eng. Chem. 36(6).

Jacobs HL (1947) Acid neutralization, Chemical Engineering Process 43(5).

Kun LE (1972) A report on the reduction of the sulphate content of acid mine drainage by precipitation with barium carbonate. Internal report, Anglo American Research Laboratories, Project D/3/W/1

Maree JP and Strydom, WF (1985) Biological sulphate removal from a packed bed reactor, Water Res 19(9): 1101 - 1106.

Maree JP (1989) Treatment of water (BaS process), Republic of South Africa (Patent No. 90/1889), 28 November), Canada (Patent No: 2 012 266 8) and United States of America (Patent No. 5,035,807).

Maree JP and Hill E (1989) Biological removal of sulphate from industrial effluents and concomitant production of sulphur, Wat. Sci. Technol. 21, 265 - 276.

Maree JP, Bosman DJ, Jenkins GR (1989) Chemical removal of sulphate, calcium and heavy metals from mining and power station effluents. Proc, 1st Biennial Conf of the Water Inst of Southern Africa, Cape Town

Maree JP, Hulse G, Dods D and Schutte CE (1991) Pilot plant studies on biological sulphate removal from industrial effluent, Wat Sci Technol 23, 1293 - 1300.

Maree JP and Clayton JA (1992) United States Patent. 20 October 1992. Patent Number: 5156746.

Maree JP and du Plessis P (1993) Neutralization of acid mine water with calcium carbonate. Proc. IAWQ Conf. on Pre-treatment of Industrial Wastewaters, Athens, 399 - 411

Maree JP (1994) Neutralization of acidic effluents with limestone, Water Research Commission Report No 355/1/94.

Maree JP and Du Plessis P (1994) Neutralization of acid mine water with calcium carbonate, Wat. Sci. Technol. 29(9), 285 - 296.

Maree JP, Van Tonder GJ, Millard P and Erasmus C (1996a) Pilot scale neutralization of underground mine water. Wat Sci Tech 34(10): 141 - 149.

Maree JP, Van Tonder GJ, Millard P and Erasmus C (1996b) Underground neutralization of mine water with limestone. Water Sewage and Effluent 16(3): 21 -23.

Maree JP, Hagger MJ, Strobos G, Hlabela P, Cronjé H, Van Niekerk A, Wurster A, Nengovhela R and Waanders FB (2004) Design Criteria for Limestone Neutralization at a Nickel Mine, Mine Water and the Environment 23(3), 152 - 156.

Mihok EA, Deul M, Chamberlain CE and Selmeczi JG (1968) Mine water research - The limestone neutralization process, US Bureau of Mines, Report of Investigations 7191.

Mihok EA (1970) Mine water research - Plant design and cost estimates for limestone treatment, US Bureau of Mines, Report of Investigations 7368.

Mudder T (1995) Personal Communication

NRA (National River Authorities) (1994) Abandoned mines and the water environment, Water Quality Series No 14, 10.

Osuchowski R (1992) Advanced treatment of acid mine water. Technology SA, April, 9 - 11.

Pulles W (1994) Underground settling in South African gold mines, Chemical Technology,

July/August, 5-7. September, 587 - 597.

Trusler GE, Edwards RI, Brouckaert CJ, Buckley CA (1988) The chemical removal of sulphates. Proc, 5th National Meeting of the S.A. Institution of Chemical Engineers, Pretoria, W3-0 – W3-11

Stumm W and Lee GF (1961) Oxygenation of ferrous iron. Industrial and Engineering Chemistry, 53(2), 143 - 146.

SWaMP Steering Committee (1998) An Integrated Strategy Water Management Plan (SwaMP) for the Gauteng Gold Mines (Version 3), January.

Van Houten RT (1996) Biological sulphate reduction with synthesis gas, Ph.D. Thesis, University of Wageningen, p.39.

Van Zyl HC, Maree JP, Van Niekerk AM, Van Tonder GJ and Naidoo C (2000) Collection, treatment and re-use of mine water in the Olifants River Catchment, SAIMM 101(1): 41 - 46.

Visser A (1995) The anaerobic treatment of sulphate containing waste water, Ph.D. Thesis, University of Wageningen, p.67.

Volman, R (1984) Die gebruik van bariumsulfied om sulfate uit suur industrieëleuitvloeisels te verwyder. M.Sc. tesis (Chemiese Ingenenieurswese), Universiteit van Stellenbosch, 5.

Volpicelli G, Caprio V, and Santoro L (1982) Development of a process for neutralising acid waste water by powdered limestone, Env Technol Lett 6: 97 - 102.

Wilmoth RC (1974) Limestone and limestone-lime neutralization of acid mine drainage, National Environmental Research Centre, EPA, Cincinnati, Report No. EPA-670/2-74-051.

Wilsnach IT (1986) Cost estimate for barium sulphate reduction. Internal report, Div of Water Technology, CSIR, Project 620/2616/6

CHAPTER 3. NEUTRALIZING COAL MINE EFFLUENT WITH LIMESTONE TO DECREASE METALS AND SULPHATE CONCENTRATIONS

Maree JP, de Beer M, Strydom WF, Christie ADM and Waanders FB (2004) Neutralizing Coal Mine Effluent with Limestone to Decrease Metals and Sulphate Concentrations, Mine Water and the Environment, 23(2), 81 – 86.

Summary

This paper describes a novel process for the neutralisation of acid water produced during coal mining and processing. The leachate from a waste coal dump was neutralised with limestone for the removal of iron, aluminium, and sulphate. Specific aspects studied were the process configuration, the rates of iron oxidation, limestone neutralisation and gypsum crystallisation, the chemical composition of the effluents before and after treatment, the efficiency of limestone utilisation, and the sludge solids content.

The acid content was reduced from 12 000 to 300 mg/L (as $CaCO_3$), sulphate from 15 000 to 2 600 mg/L (as SO_4), iron from 5 000 to 10 mg/L (as Fe), aluminium from 100 to 5 mg/L (as Al), while the pH increases from 2.2 to 7.0. Reaction times of 2.0 and 4.5 h were required under continuous and batch operations, respectively, for the removal of 4 g/L iron(II) (as Fe). The iron oxidation rate equation is a function of the Fe(II), hydroxide, oxygen and suspended solids (SS) concentrations. The optimum SS concentration for iron oxidation in a fluidised-bed reactor was found to be 190 g/L. Up-flow velocity had no influence on the rate of iron oxidation in the range 5 to 45 m/h. Sludge with a high solids content of 55% (m/v) was produced. This is high compared to the typical 20% achieved with the high density sludge process using lime. Neutralisation costs can be reduced significantly with the integrated iron oxidation and limestone neutralisation process as limestone is cheaper than lime, and a high-solids- content sludge is produced.

Mine Water and the Environment (2004) 23: 81–86 © IMWA Springer-Verlag 2004

Technical Article

Neutralizing Coal Mine Effluent with Limestone to Decrease Metals and Sulphate Concentrations

J. P. Maree[1], M. de Beer[1], W. F. Strydom[1], A. D. M. Christie[2] and F. B. Waanders[3]

[1]Div of Water, Environment and Forestry Technology, CSIR, PO Box 395, Pretoria, 0001, South Africa; [2]SA Coal Estates, PO Box 2851, Witbank, 1035, South Africa; [3]Director, School of Chemical and Minerals Engineering, North West University (Potchefstroom campus), Potchefstroom, 2531, South Africa; corresponding author's e-mail: jmaree@csir.co.za

Abstract. This paper describes pilot scale tests of a novel process for the neutralisation of acidic mine water. Leachate from a waste coal dump was neutralised with limestone, and iron, aluminium, and sulphate were removed. Specific aspects studied were: the process configuration; the rates of iron oxidation, limestone neutralisation, and gypsum crystallisation; the chemical composition of the effluents before and after treatment; the efficiency of limestone utilisation; and the sludge solids content. The acidity was decreased from 12,000 to 300 mg/L (as $CaCO_3$), sulphate from 15,000 to 2,600 mg/L, iron from 5,000 to 10 mg/L, aluminium from 100 to 5 mg/L, while the pH increased from 2.2 to 7.0. Reaction times of 2.0 and 4.5 h were required under continuous and batch operations respectively for the removal of 4 g/L Fe(II). The iron oxidation rate was found to be a function of the Fe (II), hydroxide, oxygen, and suspended solids (SS) concentrations. The optimum SS concentration for iron oxidation in a fluidised-bed reactor was 190 g/L. Up-flow velocity had no influence on the rate of iron oxidation in the range 5 to 45 m/h. Sludge with a high solids content of 55% (m/v) was produced. This is high compared to the typical 20% achieved with the high density sludge process using lime. It was determined that neutralisation costs could be reduced significantly with an integrated iron oxidation and limestone neutralisation process because limestone is less expensive than lime, and a high-solids-content sludge is produced. Full scale implementation followed this study.

Key Words: Acid mine drainage; iron oxidation; limestone neutralization

Introduction

Coal mining and fertiliser manufacturing are examples of industrial operations that can give rise to severe acid pollution of the environment unless the water is appropriately treated. Water with a pH below 5.5 can be toxic to plant and fish life and corrosive to pipelines and equipment. Disposal of sludge from neutralisation of such effluents is costly, though the volume of sludge can be reduced by increasing the solids concentration. Currently, acid water at most mine sites in arid areas is neutralised with lime and then re-used. Apart from its dependence on lime, which is costly, this practice results in the scaling of equipment, malfunctioning of dosing equipment, and settling of particles in pipelines and valves. The latter often causes blockages, which result in under-dosage, which in turn leads to acid corrosion. In contrast, limestone is relatively cheap and readily available, process control is simplified (no pH-control is required as limestone dissolution essentially occurs at pH values below 7), and material wastage through over-dosage is minimised. Also limestone is non-hazardous and easy to store. Raw material can be stockpiled in the open as $CaCO_3$ is not readily soluble in neutral water.

The fluidised-bed limestone neutralisation process has been developed to neutralise free acid and remove Fe (II) and Al (III) concomitantly (Maree et al. 1992; du Plessis and Maree 1994; Maree and du Plessis 1994; Maree 1994; Maree et al. 1996a,b). Previous studies showed that:

- Complete neutralisation of discard leachate containing (10 g/L acid (as $CaCO_3$) and 4,000 mg/L Fe (II)) can be achieved in a limestone neutralisation fluidised-bed reactor, provided that the Fe is oxidised beforehand (Maree et al. 1998).
- Fe (II) can be oxidised biologically to Fe(III). The rate of iron oxidation is related to the surface area of the support medium. With plastic medium (specific surface area 200 m^2/m^3), a residence time of 18 h is required for water containing 4 g/L Fe (II) (Maree et al. 1998).
- Magnesium keeps the equivalent amount of sulphate in solution. When 300 mg/L magnesium (as Mg) is present, SO_4 can be reduced from 18 000 mg/L to about 2 700 mg/L by gypsum crystallisation; at 0 mg/L Mg, SO_4 can be reduced to 1 500 mg/L. With a fluidised-bed contactor, a residence time of 2 h is needed.

Treatment of Fe(II)-rich water with limestone conventionally requires a multiple-stage neutralisation system. The expected capital cost of such a system is unacceptably high due to the long residence time required for iron oxidation. An integrated iron oxidation and limestone neutralisation process was developed to overcome this disadvantage. The process consists of a neutralisation reactor and a clarifier. Discard leachate is treated in an aerated sludge reactor into which limestone powder (100% < 200 μm) is dosed to a level slightly in excess of stoichiometrical requirements. Iron

oxidation is achieved within 2 h when the plant is operated in sequential batch mode and within 5 h under continuous conditions. Gypsum crystallises to an over-saturation index less than 1.1. The clarifier is required to return sludge to the neutralisation reactor to maintain a minimum concentration of suspended solids.

The objectives of this investigation were to determine the quality of treated water and sludge solids content when discard leachate is neutralised with the integrated iron oxidation and limestone neutralisation process, and to obtain design criteria for full-scale implementation.

Materials and Methods

A synthetic solution, similar to leachate from a waste coal dump, was used as feed water. The solution contained 4,000 mg/L Fe(II), 40 mg/L P, 20 mg/L Mg, 30 mg/L N, 8,900 mg/L SO_4 and 9,200 mg/L acidity (as $CaCO_3$). Crushed limestone, mined near Rustenburg, South Africa, and sodium hydroxide were used for neutralisation. In later studies, calcium carbonate powder (100% < 300 μm and 80% < 75 μm), a by-product from the paper industry, was used.

Batch studies were conducted in 0.5, 1.0, 2.0, and 5.0 L beakers at atmospheric pressure to determine the rate of iron oxidation and neutralisation. The specific surface areas of the beakers were 58.1, 46.2, 36.8, and 27.3 m^2/m^3 respectively. The following steps were followed:

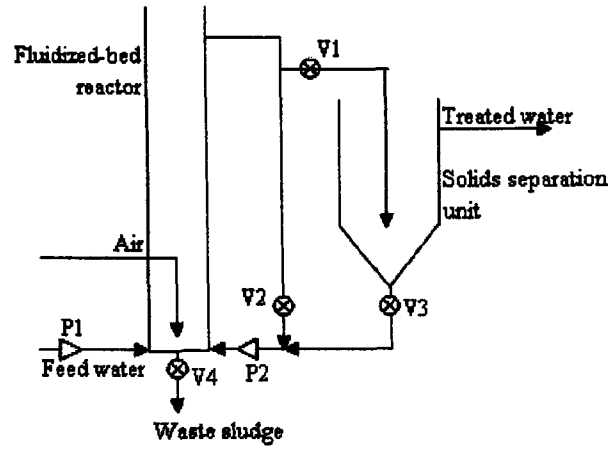
- Each batch test was started by mixing the treated contents from the previous batch with the synthetic feed, in a ratio varying from 1:1 to 1:4. An excess amount of $CaCO_3$ (20% to 40%) was applied over the amount required to ensure complete iron oxidation and precipitation of the iron(III) as $Fe(OH)_3$. NaOH additions were made as required to maintain the pH at a specific value when the influence of pH was determined.
- The reactor contents were aerated continuously. Filtered samples were taken regularly and analysed for iron(II), oxygen, acidity, sulphate and pH.
- Aeration was stopped when the iron was completely oxidised, whereafter the appropriate amount of the Fe(III)-containing mixture was replaced with a fresh Fe(II) solution. First, solids was allowed to settle, whereafter the clear water was decanted and replaced with fresh iron(II)-rich water.
- Aeration was restarted and the procedure described above repeated.

Batch and Continuous Studies on Pilot Scale

A pilot plant (Figure 1, Table 1), consisting of a fluidised-bed reactor and a sludge separator, was used for a fluidised-bed consisting of slimes/limestone/gypsum during batch studies, and through both the fluidised-bed reactor and the sludge separator during continuous studies. The purpose of the sludge separator during continuous operation was to prevent wash-out of support medium in an uncontrolled manner. Compressed air was used for iron oxidation.

Table 1. Dimensions of pilot plant

Parameter	Value	
	Fluidised bed	Solids separation
Feed rate (L/h)	24	
Recycle rate (L/h)	200	
Diameter (m)	0.20	0.53
Water height (m)	4.99	0.35
Specific surface area (m^2/m^3)	20.2	-
Up-flow velocity (m/h)	6.37	0.91
Residence time (h)	6.53	3.22



P1 - Feed pump; P2 - Recycle pump; V1, V2, V3 & V4 - Valves

Figure 1. Schematic diagram of integrated iron oxidation/limestone neutralisation pilot plant

Analytical

Samples were collected regularly and filtered through Whatman No 1 filter paper. Sulphate, acidity, and pH determinations were carried out manually according to procedures described in Standard Methods (APHA 1985), and Fe (II) as described in Vogel (1989). Calcium was analysed by atomic absorption spectrophotometry. Acidity was determined by titrating the solution to pH 8.3 using NaOH.

Results and Discussion

Water Quality

Limestone can be used in the integrated process for treatment of acid water. Table 2 shows the results when synthetic discard leachate was treated with limestone. The water was neutralised effectively and sulphate was reduced from 8,342 to 1,969 mg/L.

Table 2. Chemical composition of feed and treated water (in mg/L where applicable) when synthetic discard leachate was treated with limestone

Parameter	Feed (Synthetic discard leachate)	Treated (Limestone)
pH	1.8	6.6
Acidity (as $CaCO_3$)	7 300	100
Sulphate	8 342	1 969
Orthophosphate (as P)	2.9	0.0
Chloride	27	30
Iron(II)	2 500	56
Total iron	2 500	56
Aluminium	6.8	7.3
Manganese	15.7	21.8
Magnesium	35	45
Calcium	40	682
Sodium	25.2	29.5

Kinetics

Stumm and Lee (1961) determined the following relationship between the iron oxidation rate and pH in the absence of microorganisms for clear solutions:

$$-d[Fe(II)]/dt = k[Fe(II)][OH^-]^2 P(O_2) \quad (1)$$

where: $-d[Fe(II)]/dt$ = rate of iron oxidation; k = reaction rate constant; [Fe(II)] = iron(II) concentration (moles/L); $[OH^-]$ = hydroxide concentration (moles/L); and $P(O_2)$ = partial pressure of oxygen (mm Hg).

Most iron oxidation occurs either at pH levels less than 4, when catalysed by bacterial activity, or at pH values greater than 6, through chemical oxidation. Maree et al. (1997) showed that the rate of chemical iron oxidation is also catalysed by suspended solids, which can lower the pH where the rate of chemical oxidation is fast enough for practical application from 6.5 to 5.0. The integrated iron oxidation and limestone neutralisation process is based on this finding, as limestone can raise the pH of Fe(II)-rich water to between 5 and 6. Volumetric iron oxidation rates exceeding 100 g/(L·d) were achieved when artificial acid mine water was treated with powdered limestone and pure oxygen in a sludge contact reactor. Neutralisation and partial sulphate removal were achieved as well.

The relative importance of various factors in terms of their influence on the rate of iron oxidation was determined by a series of controlled tests in which the dependence of the rate on one variable at a time was determined. In the pH range 5 to 6, which is of importance from the point of view of limestone neutralisation, the iron oxidation rate was assumed to have the following functional form:

$$-d[Fe^{2+}]/dt = k.[Fe^{2+}]^{n1}.[O_2]^{n2}.[OH^-]^{n3}.[RSA]^{n4}.[SS]^{n5}.M^{n6} \quad (2)$$

where: $-d[Fe^{2+}]/dt$ or R = rate of iron oxidation; k = reaction rate constant; $[Fe^{2+}]$ = iron(II) concentration (moles/L); $[O_2]$ = oxygen concentration (moles/L); $[OH^-]$ = hydroxide concentration (moles/L); RSA = reactor surface area (m^2/m^3); [SS] = suspended solids concentration (g/L); and M = mixing intensity (rpm).

By varying the value of only one parameter in a series of experiments, say $[Fe^{2+}]$, equation 2 can be written as:

$$-\partial[Fe^{2+}]/\partial t = K.[Fe^{2+}]^{n1} \text{ or } \log(-\partial[Fe^{2+}]/\partial t) = \log K + n_1 \log[Fe^{2+}] \quad (3)$$

where: $K = k.[O_2]^{n2}.[OH]^{n3}.[RSA]^{n4}.[SS]^{n5}.M^{n6}$

The contribution, n_1, of Fe (II) to the overall reaction rate was determined from the slope of the graph obtained by plotting log R versus log $[Fe^{2+}]$. From pH, log R was plotted against log$[OH^-]$ ($[OH^-] = 10^{pH-14}$). The data in Table 3 show that the rate of iron oxidation is of order 0.42 (≈ 0.5), 1.41 (≈ 1.5), 0.51 (≈ 0.5), 0.37 (≈ 0.5) and 0.43 (≈ 0.5) relative to Fe^{2+}, OH^-, O_2 and SS concentrations, and mixing intensity (M), respectively. The findings suggest that the rate equation proposed by Stumm and Lee (1961) for clear solutions should be modified for suspensions to:

$$-d[Fe^{2+}]/dt = k.[Fe^{2+}]^{½}.[OH^-]^{1.5}.[O_2]^{½}.[SS]^{½}.M^{½} \quad (4)$$

The significance of this finding is that the rate of Fe (II) is not only determined by hydroxide-, Fe (II), and oxygen concentrations, but also by the SS concentration.

Table 3 also indicates that the rate of iron oxidation in suspensions with high concentrations of SS in the pH range 4.5 to 5.5 is dominated by chemical oxidation. This was concluded from studies where experiments were carried out on sterilised and unsterilised suspensions respectively (Table 3, Experiments 1 and 2). This finding contradicts Maree et al. (1997), where chemical iron oxidation was studied using a clear solution (the only solids present was that which precipitated from solution during iron oxidation and neutralisation) and was compared with biological iron oxidation where solids were present from the start of the experiment (medium to support bacterial growth). The slower oxidation rates determined for chemical iron oxidation at pH values between 5 and 5.5 should be ascribed to lower SS concentrations and not to the absence of bacterial activity.

In a previous investigation, Maree et al. (1997) determined that the rate of iron oxidation in the pH range 4.5 to 6 was influenced by the reactor surface area (RSA). It was pointed out that this behaviour is in line with the behaviour of iron oxidation in the pH range 2 to 3 where the rate is directly proportional to the square root of the medium specific surface area (Maree et al. 1998). The current investigation, however, shows that chemical iron oxidation in the pH range 4.5 to 6 is not influenced by the medium-specific surface area, but by the mixing intensity, M. In the previous investigation,

Table 3. Effect of various factors on the kinetics of iron oxidation, as measured in nine experiments

Variable	Value	Rate g Fe/(L.d)	Log C	log R	Rxn order
pH (no	4.50	22.56	-9.50	1.35	1.33
bacteria)	5.00	90.22	-9.00	1.95	
	5.25	229.20	-8.75	2.36	
	5.50	462.44	-8.50	2.67	
pH	4.50	18.40	-9.50	1.26	1.41
(with	5.00	93.48	-9.00	1.97	
bacteria)	5.25	233.24	-8.75	2.37	
	5.50	454.39	-8.50	2.66	
Fe(II)	0.30	21.72	-0.52	1.34	0.42
(g/L)	1.00	41.24	0.00	1.62	
	3.00	82.04	0.48	1.91	
	10.00	88.46	1.00	1.95	
SS	0.00	30.36		1.48	0.37
(g/L)	4.70	42.93	0.67	1.63	
	12.00	53.15	1.08	1.73	
	49.30	66.07	1.69	1.82	
	75.20	129.25	1.88	2.11	
	152.00	155.75	2.18	2.19	
	328.10	136.34	2.52	2.13	
O_2 (air)	0.10	18.16	-1.00	1.26	0.51
(mg/L)	0.50	30.41	-0.30	1.48	
	2.00	92.79	0.30	1.97	
	5.00	113.93	0.70	2.06	
Stirring	20	50.83	1.30	1.71	0.43
(rpm)	150	120.25	2.18	2.08	
Stirring	50	80.09	1.70	1.90	0.41
(pure O_2)	150	136.92	2.18	2.14	
(rpm)	300	163.73	2.48	2.21	
RSA	58.12	100.18	1.76	2.00	1.25
(m^2/m^3)	46.13	94.06	1.66	1.97	
	36.61	84.64	1.56	1.93	
	26.98	37.57	1.43	1.57	
Temp.			1/T		E (kcal/
(^{0}C)	5.0	13.56	0.00265	1.13	mole)
	11.0	26.99	0.00261	1.43	21.55
	18.7	48.77	0.00256	1.69	
	25.0	81.94	0.00252	1.91	
	37.0	128.64	0.00244	2.11	
	45.0	147.30	0.00240	2.17	

• the values of RSA and M were varied simultaneously, as beakers of different sizes were used to provide different RSA values (see Table 3, Experiment 8 for the relationship between RSA and beaker volume). Unfortunately, the mixing intensity decreases when larger beakers are used if the stirring rate is not adjusted accordingly (Table 3, Experiments 6 and 7). The iron oxidation rate increases with increased mixing intensity.

The Arrhenius equation $\log k = \log A - E/(2.303RT)$ can be used to estimate the value of the reaction rate k at other temperatures. The amounts E, R, and log A have the values 21.55 kcal/mole (activation energy), 13.70 (a constant) and 1.987 cal $mole^{-1}$ $degree^{-1}$ (gas constant) respectively (Table 3, Exp 9). A linear relationship was obtained over the range 5 to 25 ^{0}C. It is expected that the linear relationship will fail at higher temperatures as optimum reaction rates are often achieved at 37 ^{0}C.

Design Criteria for Continuous Operation

Oxygen versus Air

The iron oxidation rate increases with increased oxygen concentrations (Table 4). For a specific oxygen concentration (0.2 mg/L), reaction rates are similar for pure oxygen and air (between 44.9 and 65.8 g Fe/(L.d)). Although high iron oxidation rates can be achieved by using pure oxygen, air is a more suitable oxidant for full-scale application due to safety reasons. Typical values for various parameters: Fe(II) = 2.8 to 4.7 g/L; $CaCO_3$ = 10 g/L; pH = 4.8 to 6.0; O_2 = 1 to 24 mg/L; SS = 94 to 291 g/L; temperature = 23 to 28 ^{0} C; bacteria only present in experiments 1 and 2; stirring rate = 150 rpm; reactor volume = 0.5 to 4 l.

Suspended Solids Concentration

The optimum SS concentration for iron oxidation in the fluidised-bed reactor of the integrated process was 190 g/L (Table 5). The decrease in the iron oxidation rate for SS concentrations greater than 190 g/L can possibly be ascribed to decreased oxygen transfer. It is expected that the optimum level of 190 g/L can be increased when pure oxygen is used and/or when the mixing intensity is increased. The reaction order with respect to suspended solids (over the range 0 to 190 g/L) is 0.50.

Up-flow Velocity

Up-flow velocity has no influence on the rate of iron oxidation in the range 5 to 45 m/h.

Table 4. Effect of oxygen concentration on the rate of iron oxidation

Parameter	Oxygen concentration (mg/L O_2)						
	0.11	0.20	0.20 (air)	0.20	0.27	5.7	10
Iron oxidation rate (g Fe/(L d)	22.8	44.9	59.0	65.8	86.4	183	163
Reaction time (h)	>>4	2.25	2.00	>1.75	1.75	1.0	0.75
Order				0.37			

Note: data collected during batch operation of pilot plant; conditions: pH = 5.9; suspended solids in recycle stream = 240 to 360 g/L; initial iron(II) concentration = 3.2 to 6.3 g/L; initial acidity = 8.8 to 12.0 g/L (as $CaCO_3$); temperature = 15.0- 20.0 ^{0}C

Table 5. Effect of suspended solids on the rate of iron oxidation

Parameter	Suspended solids (g/L)					
	41.1	91.2	95.6	190	277	462
Iron oxidation rate (g Fe/ L·d)	28.7	38.6	47.7	61.9	42.3	32.3
Order			0.50			

Note: data collected during batch operation of pilot plant; conditions: pH of feed = 5.0; excess alkali dosage = 41%; initial sulphate concentration = 5.7 to 12.2 g/L; initial Fe(II) concentration = 2.4 to 5.6 g/L; initial acidity = 4.2 to 9.2 g/L (as $CaCO_3$); temperature = 14.5 to 17.5 °C.

Residence Time and Mode of Operation

A shorter reaction time is required during batch operation than in continuous operation. For the removal of 4 g/L iron(II) (as Fe), reaction times of 2.0 and 4.5 h are required for continuous and batch operations respectively (Figure 2). The shorter reaction time required during batch operations can be explained by the iron oxidation rate equation:

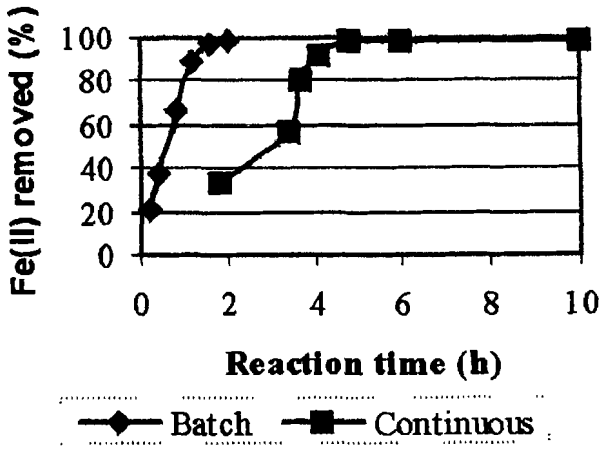
$$-d[Fe^{2+}]/dt = k.[Fe^{2+}]^{½}.[OH^-]^{1.5}.[O_2]^{½}.[SS]^{½}.M^{½} \quad (5)$$

The values for O_2 and SS are the same for batch and continuous operations. The O_2 level is controlled at a specific concentration (e.g., 2 mg/L) while the SS concentration is kept high (e.g., 150 g/L). During continuous operation sludge would be withdrawn continuously to maintain a specific level. During batch operation, the suspended solids will increase during the course of each batch operation. The increase would, however, be small compared to the initial concentrations. The values of Fe^{2+} and OH^- during batch operation are, except for the values at the end of the batch experiment, higher than those measured during continuous operation. As the order of the latter parameters are greater than 0, the reaction rate increases with increased values for the parameters mentioned.

Sequential Batch Mode Operation

Sequential batch mode operation versus continuous operation of the integrated iron oxidation and limestone neutralisation process offers the benefits of a faster reaction rate and better lime utilisation. The reaction rate is faster due to a greater driving force as a result of high Fe (II) concentration in solution, except for the final period of the reaction. Limestone utilisation is better as unused limestone can be contacted with acid feed water while final treated water can be contacted with fresh limestone for maximum neutralisation.

Figure 3 shows the behaviour of the most important parameters for a typical batch operation. Note that Fe (II) was removed during consecutive batch operations in less than 2 h at an average rate of 35 g Fe/(L.d) at a temperature = 24 0C and SS = 250 g/L. The pH was raised from 5.3 to 6.1 or higher while acidity was removed from 5.6 g/L (as CaCO3) to 0.3. Sulphate was removed from 6.6 to 2.2 g/L (as SO4) due to gypsum crystallisation.



Note: data collected during batch operation of pilot plant; conditions: pH of feed = 2.4; excess alkali dosage = 2 to 20 %; initial sulphate concentration = 6.2 to 8.3 g/L; initial Fe(II) concentration = 2.4 to 4.2 g/L; initial acidity = 6.89 g/L (as $CaCO_3$); oxygen = 0.2 mg/L O_2; suspended solids = 200 to 400 g/L; temperature = 15 to 22 °C.

Figure 2. Comparison between batch and continuous operation during iron oxidation

Sludge Characteristics

Table 6 shows the suspended solids content of the sludge in the fluidised-bed reactor at different dilutions (1, 2, 5, 10, and 20 times) before and after settling, as well as the settling rate at each dilution. The settling rate increases from 0.07 to 2 m/h as the dilution factor increases from 1 to 20. A low sludge settling rate (0.07 m/h) would therefore be expected in the fluidised-bed reactor where the sludge solids content is high (200 to 300 g/L), and a high sludge settling rate (2 m/h) in the sludge separation stage where the solids content is low (less than 10 g/L). The sludge concentration can be controlled by withdrawing sludge from the bottom of the fluidised-bed reactor, where the solids content would be at a maximum. One of the major benefits of the integrated iron oxidation and limestone neutralisation process is that a high-solids-content sludge is produced (up to 550 g/L). The high solids concentration was possible due to the column reactor which supports gypsum crystallization onto existing gypsum particles. This compares well with the typical 200 g/L solids content that can be achieved with the high density sludge process.

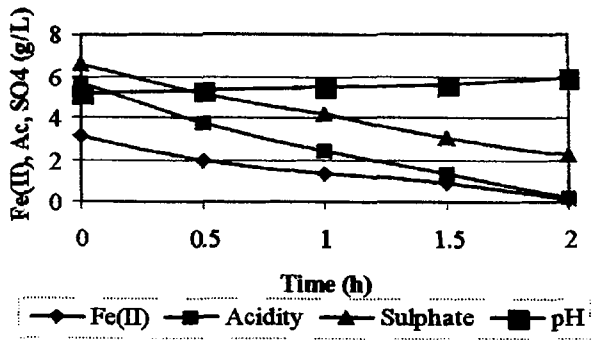


Figure 3. Behaviour of various parameters during batch operation of the integrated iron oxidation and limestone neutralisation process

Table 6. Suspended solids content of the sludge at different dilutions (1, 2, 5, 10, and 20 times) before and after settling, as well as the settling rate at each dilution

Parameter	Dilution				
	1x	2x	5x	10x	20x
Suspended solids before settling (g/L)	619	595	165	59	16
Settling rate (m/h)	0.07	0.10	0.37	0.88	2.00

General

In this process, powdered $CaCO_3$ is used as alkali to allow iron oxidation, neutralization of free acid, and gypsum crystallization to take place in the same reactor. It was shown that Fe (II) can be oxidised at pH 6, using only $CaCO_3$ and not lime; this aspect has been patented (Maree 1997). Previously, lime was used to raise the pH to 7.2, at which pH the iron-oxidation rate is fast. The results of this pilot plant study led to its full-scale application; full-scale plants using calcium carbonate powder for neutralization of acidic streams have now been constructed at the following sites in southern Africa: Ticor (Empangeni), BCL (Botswana), S A Coal Estates (Witbank) and Zincor (Springs).

Conclusions

The following conclusions were reached:

1. The integrated iron oxidation and limestone neutralisation process can be used for the removal of acidity, iron, aluminium (to less than 2 mg/L, as Al) and sulphate (to a level of 2,500 mg/L, as SO_4). All reactions take place simultaneously.

2. Sludge with a solids content of more than 50% can be produced with the integrated process.

3. For water containing 3 g/L Fe (II), a reaction time of 2 h is required when the process is operated in a sequencing batch mode; 5 h is required when it is operated on a continuous basis.

References

APHA (1985) Standard Methods for the Examination of Water and Wastewater Treatment. 12th Edit, American Public Health Assoc, NY

du Plessis P, Maree JP (1994) Neutralisation of acid water in the chemical industry with limestone. Wat Sci Tech 29(8): 93-104

Maree JP, du Plessis P, van der Walt CJ (1992) Treatment of acidic effluents with limestone instead of lime. Wat Sci Tech 26(1-2): 345-355

Maree JP (1994) Neutralisation of acidic effluents with limestone. WRC Report No 355/1/94

Maree JP, du Plessis P (1994) Neutralisation of acid mine water with caclium carbonate. Wat Sci Tech 29(9): 285-296

Maree JP, Van Tonder GJ, Millard P, Erasmus C (1996a) Pilot scale neutralisation of underground mine water. Proc, Biennial IAWQ Conf, Singapore, 23 - 26 June

Maree JP, Dafana D, Mbonjani D, Van Tonder GJ, Millard P (1996b) Development of a limestone process to neutralise acid effluents originates from a phosphate fertilizer manufacturer. Proc, Biennial WISA Conf, Vol1, Port Elizabeth, 20 - 23 May 1996, p 1-10

Maree JP (1997) Patent, Integrated iron(II) oxidation and limestone neutralisation. Patent numbers: Republic of South Africa (98/5777); Australia (732237), USA (6,419,834), Canada (2,294,058 – pending), Europe (98932321.7 – pending)

Maree JP, Strydom WF, de Beer, M (1997) Integrated iron(II) oxidation and limestone neutralisation of acid mine water, Proc, International Assoc on Water Quality (IAWQ), Specialised Conf on Chemical Process Industries and Environmental Management, Cape Town, SA, 6 - 10 Sept

Maree JP, Dingemans DR, van Tonder GJ, Mtimkulu S (1998) Biological iron(II) oxidation as pre-treatment to limestone neutralisation of acid water. Proc, Conf of the International Assoc on Water Quality (IAWQ), Vancouver, Canada, 21 - 26 June

Stumm W, Lee GF (1961) Oxygenation of Ferrous Iron. Industrial and Engineering Chemistry 53(2): 143 - 146

Vogel AI (1989) Textbook of Quantitative Chemical Analysis. 5th edit, John Wiley and Sons, NY, 368 p

Submitted 28 Feb. 2004; Accepted June 06, 2004

CHAPTER 4. DESIGN CRITERIA FOR LIMESTONE NEUTRALIZATION AT A NICKEL MINE

Maree JP, Hagger MJ, Strobos G, Hlabela P, Cronjé H, Van Niekerk A, Wurster A, Nengovhela R and Waanders FB (2004) Design Criteria for Limestone Neutralization at a Nickel Mine, Mine Water and the Environment 23(3), 152 – 156.

Summary

Design criteria were developed for the construction of a full-scale limestone neutralization plant to treat leachate from the waste rock of a nickel mine, using data from laboratory studies, pilot-scale studies, and operation of a full-scale limestone handling and dosing facility. We learned that: limestone powder can be slurried to a constant slurry density of 60 g/L; Fe (II) can be oxidised at low pH (2.5) at a rate of 16.1 g/(L/d) using geotextile as a medium; and that the integrated Fe(II)-oxidation and limestone neutralization process allows neutralization, Fe(II)-oxidation, and gypsum crystallization to take place at the same time, provided that the solids concentration is high (greater than 30 g/L). A full-scale plant with a capacity of 50 m^3/h was designed and constructed. The plant consists of the following stages: biological Fe(II)-oxidation, a fluidised-bed limestone neutralization reactor, a complete-mix gypsum crystallization reactor, and a clarifier.

Mine Water and the Environment (2004) 23: 152–156 © IMWA Springer-Verlag 2004

Technical Communication

Design Criteria for Limestone Neutralization at a Nickel Mine

J. P. Maree[1], M. J. Hagger[2], G. Strobos[1], P. Hlabela[1], H. Cronjé[3], A. van Niekerk[4], A. Wurster[4], R. Nengovhela[1], and F. B. Waanders[5]

[1]CSIR, Water, Environment, and Forestry Technology, PO Box 395, Pretoria, 0001, South Africa; [2]BCL, PO Box 3, Selebi Phikwe, Republic of Botswana; [3]Thuthuka Project Managers, Midrand, PO Box 6013, Halfway House, 1685, South Africa; [4]Golder Assoc Africa, PO Box 6001, Halfway House, 1685, South Africa; [5]Director, School of Chemical and Minerals Engineering, North West Univ, Potchefstroom, 2531, South Africa; corresponding author's e-mail: jmaree@csir.co.za

Abstract. Design criteria were developed for the construction of a full-scale limestone neutralization plant to treat leachate from the waste rock of a nickel mine, using data from laboratory studies, pilot-scale studies, and operation of a full-scale limestone handling and dosing facility. We learned that: limestone powder can be slurried to a constant slurry density of 60 g/L; Fe (II) can be oxidised at low pH (2.5) at a rate of 16.1 g/(L/d) using geotextile as a medium; and that the integrated Fe (II)-oxidation and limestone neutralization process allows neutralization, Fe (II)-oxidation, and gypsum crystallization to take place at the same time, provided that the solids concentration is high (greater than 30 g/L). A full-scale plant with a capacity of 50 m^3/h was designed and constructed. The plant consists of the following stages: biological Fe (II)-oxidation, a fluidised-bed limestone neutralization reactor, a complete-mix gypsum crystallization reactor, and a clarifier.

Key words: Calcium carbonate; discard leachate; gypsum crystallization; limestone

Introduction

When pyritic waste rock is exposed to oxygen and water in the presence of iron-oxidising bacteria, a leachate that contains high concentrations of acid, sulphate, and metals can result. BCL Limited, a copper-nickel mine in Botswana, mines and processes 450 t/d of ore, and experiences such a problem. The operations consist of underground mining, concentration of the copper and nickel by 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 the surface where the combined stream of 350 m^3/h is neutralised.

The used water streams are recycled to the mill return water sump (MRWS), which is used to supply the concentrator circuit 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; 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 as backfill underground, 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 (acidity = 235 mg/L as $CaCO_3$) and 60 m^3/h of tailings dump seepage (acidity = 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 corrosion in the smelter cooling jackets, so raw water is imported from a local dam.

BCL has 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 to 400 m^3/h is expensive.

A modelling exercise was carried out during 1999 to audit and simulate the water network of BCL to identify the optimum water management strategy (van Tonder et al. 2000). It was found that discard leachate could be neutralized with limestone to minimise chemical cost and that this treatment should occur before the water mixes with less polluted streams to maximize sulphate removal through gypsum crystallization and precipitation. This should reduce gypsum scaling in the metallurgical plant.

The purpose of this study was to analyze reported data on laboratory studies, pilot-scale studies, and full-scale experience from the Navigation Section of

Landau Colliery (Maree et al. 1998; Nengovhela at al. 2002; Strobos et al. 2002), and determine the most suitable effluent treatment configuration for neutralization of discard leachate at BCL. An integrated process was investigated, consisting of: $CaCO_3$ handling and dosing, neutralization with $CaCO_3$, and gypsum crystallization to achieve partial sulphate removal. Based on this analysis, we developed design criteria for the construction of a plant to treat 50 m^3/h of leachate.

Materials and Methods

Feedstock

Powdered $CaCO_3$, a by-product of the paper industry, was used to neutralize the acid water. It contained 25% moisture and 10% impurities (dry mass), which was mainly silica. Coal discard leachate or a synthetic solution of similar chemical composition was used as feed water for studies on iron oxidation at low pH and $CaCO_3$ neutralization.

Equipment

The $CaCO_3$ handling and dosing system (Navigation Section of Landau Colliery, near Witbank, South Africa) was the first full-scale plant of its kind. It has a capacity of 23 t/d $CaCO_3$. The plant consists of:

- A sloped concrete slab 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 float valve in the slurry tank maintains the water level at a specific height.
- Slurried $CaCO_3$ (from the slurry tank) or clear water is pumped onto the $CaCO_3$ dump so as to maintain a constant $CaCO_3$ concentration. A side-stream from the delivery side of the recycle pump is passed through a density meter, which controls the $CaCO_3$ concentration of a fixed slurry volume, based on the mass, which is continually measured with a load cell. Based on the measurement, a water jet is automatically directed on to the $CaCO_3$ dump when the slurry density is below a set value or onto a clean section of the slab when the density is equal to or above the set slurry density. The slurried $CaCO_3$ is returned by gravity via the sloped concrete slab back to the slurry tank.
- A transfer pump feeds slurried $CaCO_3$ to the neutralization reactor.

Iron oxidation at low pH was studied in the laboratory under batch conditions. The solutions in the beaker reactors were stirred continuously and aerated with compressed air through diffusers (porosity no. 2, 210 x 8mm (OD)). The air to the container reactors and box reactors was distributed through small holes punched into a perspex pipe situated at the bottom of the reactor. Various support media (discussed later) were evaluated to identify the most suitable medium for iron oxidation at low pH.

The $CaCO_3$ neutralization stage consisted of a fluidised-bed reactor with a sludge separator. The $CaCO_3$-neutralization stage was a continuous laboratory-scale plant. The dimensions are indicated in Table 1. Compressed air was used for iron oxidation when powdered $CaCO_3$ was used for neutralization.

Experimental Methods

Iron oxidation and $CaCO_3$ neutralization was evaluated by determining the chemical composition of the feed and treated water during batch experiments and during continuous operation. Batch studies were carried out in beakers at atmospheric pressure to determine the rate of biological iron oxidation. The following steps were followed:

- Water in the reactor was replaced with new feed water. The same support medium was used repeatedly during consecutive batch runs. During the first run, the reactor was inoculated by adding 5% coal discard leachate from Navigation Mine to the water in the beaker.
- Samples were taken at different intervals, filtered and analysed for Fe (II) concentration and pH (at the beginning and end of the experiment). The run was stopped when all of the Fe (II) was removed.
- The procedure was repeated for several iterations until the rate of iron oxidation had stabilized.

Analytical Methods

Samples were collected regularly and filtered through Whatman No 1 filter paper. Sulphate, sulphide, alkalinity, calcium, Fe (II), mixed liquor suspended solids, volatile suspended solids, acidity, and pH were determined manually using procedures described in Standard Methods (APHA 1985). Calcium was analysed using atomic absorption spectrophotometry. Acidity was determined by titrating the solution to pH 8.3 using NaOH.

Table 1. Dimensions of the $CaCO_3$ neutralization pilot plant

Parameter	Fluidised bed	Solids separation
Feed rate (L/h)	24	
Recycle rate (L/h)	200	
Diameter (m)	0.20	0.53
Water height (m)	4.99	0.35
Specific surface area (m^2/m^3)	20.2	-
Up-flow velocity (m/h)	6.37	0.91
Residence time (h)	6.53	3.22

Results and Discussion

$CaCO_3$ Handling and Dosing System

Waste $CaCO_3$ from the paper industry has been used in the primary neutralization plant at Navigation since July 2001 (Figure 1). During the first 12 months of operation, when only the primary neutralization plant was served, the limestone throughput was limited to 2.5 t/d. Since July 2002, the throughput was increased to 20 t/d as limestone was also used to neutralize acid leached from the coal processing plant. During operation of the limestone plant at a high through-put of 20 t/d, it was learned that the following operational guidelines need to be followed to allow smooth operation (Strobos et al. 2002):

- Stones need to be separated from the limestone to prevent blockages in the slurry pipelines and in the nozzles.
- Limestone slurry on the slab must completely run off into the slurry tank, so no obstacles (e.g. sieves) should be positioned on the slab to separate stones from the fine particles; such obstacles place a limit on the slurry density. A slurry density of only 1.09 was achieved with sieves on the slab while a density of 1.5 was achieved after installation of a rotating sieve to remove stones and ash particles from the slurry.
- The density of the limestone slurry needs to be continuously monitored and controlled. A density meter (already discussed) was developed for this purpose.

Iron Oxidation at Low pH

Figure 2 shows the rate of Fe (II) removal at low pH with brown geotextile as medium (Nengovhela et al. 2002). Note that the rate of iron oxidation stabilised after 14 repeated batch studies as bacterial growth increased to the point where further growth was controlled by the dissolved oxygen, the available surface area of the geotextile, and the temperature. A maximum rate of 16.1 g Fe/(L.d) was determined for iron oxidation with geotextile as medium. This is significantly higher than achieved with other support media (after 8 repeated batch studies) (Table 2). Du Preez and Maree (1994) showed that the rate of iron oxidation is related to the surface area of the medium.

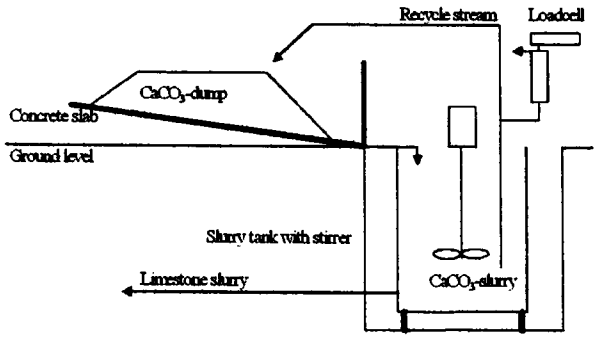


Figure 1. Schematic diagram of limestone handling and dosing system

Neutralization, Iron Oxidation, and Gypsum Crystallization at Neutral pH

Limestone can be used in an integrated process for treatment of acid water (Maree 1997; Maree et al. 1998) as an alternative to other options (Hill and Wilmoth 1971). In this process, powdered $CaCO_3$ is used for neutralization, facilitating precipitation of Fe^{3+} and Al^{3+}, and gypsum crystallization, in the same reactor. The novelty of this development lies in the fact that conditions were identified where Fe (II) can be oxidised at pH 5.5 by the addition of $CaCO_3$. Previously, lime was used to raise the pH to 7.2 where the rate of iron oxidation is rapid. Table 3 shows the results obtained when synthetic discard leachate was treated with limestone. The water was neutralised effectively and sulphate was reduced from 8 342 to 1 969 mg/L. This shows that partial sulphate removal can be achieved by using the cheapest alkali. In the absence of sodium and magnesium, sulphate can be removed to 1 500 mg/L. This was still higher than the target of 500 mg/L. Limestone neutralization, therefore, can be applied effectively as pre-treatment to further treatment for sulphate removal to less than 500 mg/L. It was possible to achieve complete iron oxidation using only $CaCO_3$ as the neutralization agent.

It was determined that the rate of iron oxidation is not only influenced by the Fe (II), hydroxide and oxygen concentrations, as suggested by Stumm and Lee (1961), but also by the suspended solids concentration, as suggested by Maree et al. (1998). In order to achieve complete iron oxidation, sufficient reaction time was allowed for gypsum crystallization to reach its saturation level (2 h). Aeration and sludge recirculation were applied to maintain a suspended solids concentration at 50 g/L.

Design of a Full-scale Plant

The information discussed above was used for the design of the BCL plant with a capacity of 50 m^3/d. The design was required to be flexible so that either crushed limestone, limestone powder, or a mixture of both could be used, depending on the availability of limestone and the Fe (II) concentration of the feed water. The process consists of the following stages (Figure 2):

- $CaCO_3$ handling and dosing
- Biological iron oxidation; initially "red lake" water with a low Fe (II) concentration will be used as feed water. Red lake water is leachate from the waste

dump and contains only 100 mg/L Fe (II) due to natural oxidation during storage. Leachate from the waste dump will be fed later directly to the neutralization plant and the red lake will be used for storage of waste. This reactor is designed to treat a small stream of waste dump leachate water to obtain design criteria for treatment of the total stream.

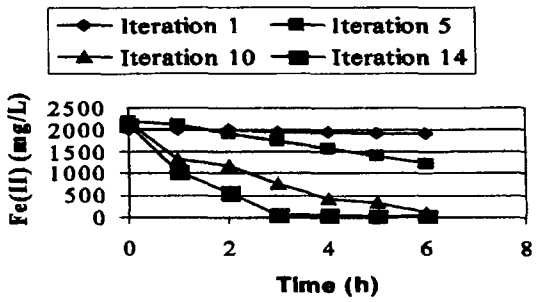


Figure 2. Effect of repeated runs (iteration) on the rate of iron oxidation using brown geotextile

Table 2. Comparison between support media (pH=2.5; after 8 repeated batch studies)

Support medium	Iron oxidation rate (g Fe/(L.d))
Control	1.44
Rings (100g/L)	1.68
Pellets (100g/L)	2.64
Discard (100g/L)	2.88
Sand (100g/L)	4.32
Anthracite (100g/L)	4.49
Activated carbon (100 g/L)	5.16
White geotextile (100 g/L)	6.25
Brown geotextile (100 g/L)	6.34
Grey geotextile (100 g/L)	6.98

Table 3. Chemical composition of feed (synthetic discard leachate) and $CaCO_3$ treated water

Parameter	Feed	Treated
pH	1.8	6.6
Acidity (mg/L $CaCO_3$)	7 300	100
Sulphate (mg/L SO_4)	8 342	1 969
Ortho phosphate (mg/L P)	2.9	0.0
Chloride (mg/L Cl)	27	30
Iron(II) (mg/L Fe)	2 500	<56
Total iron (mg/L Fe)	2 500	<56

- Fluidised-bed reactor for neutralization of acid water with crushed limestone. No aeration is provided in this reactor as crushed limestone particles get scaled with gypsum and ferric hydroxide in the presence of aeration.
- Complete-mix reactor and thickener for limestone neutralization with powder $CaCO_3$, iron oxidation and gypsum crystallization.

Table 4 shows the dimensions of the various stages of the plant, which has been operating since November 2002. The approach offers the following benefits:

- The least expensive alkali, crushed limestone, is used for neutralization of the acid.
- The bulk of the sulphate concentration is removed by gypsum crystallization.

Scaling in the metallurgical plant is reduced due to separate treatment of discard leachate to the level of gypsum saturation. Table 5 shows results collected during commissioning of the plant when red lake water (Fe (II) concentration = 100 mg/L) was used as feed water. Acidity was reduced from 2 100 to 50 mg/L (as $CaCO_3$), the pH was raised from 1.9 to 6.6, and the Fe (II) was lowered from 100 mg/L to <20 mg/L.

Conclusions

It was determined that powdered $CaCO_3$ can be slurried to a constant density and used to treat acid water high in Fe (II). A treatment plant was constructed to treat 50 m^3/d at the BCL nickel mine, using either limestone powder or crushed limestone; it has been successfully operating since November, 2002.

Table 5. Chemical composition of feed and treated water

Parameter	Feed	Treated
Flow rate (m^3/h)	50	50
pH	1.9	6.6
Acidity (mg/L $CaCO_3$)	2 100	50
Iron(II) (mg/L Fe)	100	<20

Table 4. Dimensions of the various stages of the integrated limestone neutralization process

PARAMETER	Iron oxidation	Limestone neutralization		Gypsum crystallization	Solids separation
		Column	Cone		
Flowrate (m^3/h)	50.0	50.0	50.0	50.0	50.0
Length (m)	3.2	9.3	2.4	10.0	15.0
Width (m)	3.2			5.0	5.0
Diameter (top) (m)		1.9	4.6		
Diameter (bottom) (m)		1.9	1.9		
Height (m)	4.0	9.3	2.4	4.0	3.4
Area (m^2)	10.0	2.7	16.6	50.6	75.0
Volume (m^3)	40.0	25.0	39.6	202.5	255.0
HRT (h)	0.8	0.5	0.8	4.1	3.8
Up-flow velocity (m/h)		18.6	3.0		0.7

Acknowledgements

Sincere thanks are due to the following organisations for their financial and logistical support:

- BCL provided financial support, the necessary infrastructure at the mine, and general assistance.
- National Research Foundation (NRF) provided funding through their Technology and Human Resources for Industry Programme (THRIP) for CSIR projects on neutralisation and sulphate removal.
- CSIR provided substantial financial support for the research programme.
- Golder Associates Africa did the detailed engineering design for the full-scale plant.
- Thuthuka Project Managers did project management for the full-scale plant.
- Anglo Coal (Navigation Section of Landau Colliery); experience obtained in the operation of the first full-scale limestone handling and dosing system and neutralization of acid mine water with powder $CaCO_3$ at Navigation was used for the design of the full-scale plant at BCL.
- Water Research Commission provided financial support during the conceptual stage of development of the technology.

References

APHA, (1985) Standard Methods for the Examination of Water and Wastewater. 12th Edit, American Public Health Assoc, NY

du Preez LA, Maree JP (1994) Pilot-scale biological sulphate removal utilizing producer gas as energy source. Proc, 7th International Symp on Anaerobic Digestion, Cape Town, SA, 23-27 January 1994

Hill RD, Wilmoth RC (1971) Limestone treatment of acid mine drainage. Society of Mining Engineers, Transactions 250: 162 - 166

Maree JP, de Beer M, Strydom WF, Christie ADM (1998) Limestone neutralisation of acidic effluent, including metal and partial sulphate removal. Proc, International Mine Water Assoc Symp, Johannesburg, SA, 6-13 Sept, p 449-460

Maree JP (1997) Integrated iron oxidation and limestone neutralization, Republic of South Africa (Patent No. 98/5777), Australia (Patent No 732237), USA (Patent No – 6,419,834), Canada (2 294 058 - Pending), Europe (9932321.7- Pending)

Nengovhela NR, de Beer M, Greben HA, Maree JP, Strydom CA (2002) Iron (II) oxidation to support limestone neutralization in acid mine water. Proc, Wisa Conf, Durban, SA, 19-23 May 2002

Strobos G, Maree JP, Adlem C, Melatchi N, Christie A, Günther P (2002) A cost effective limestone makeup and dosing system. Proc, Wisa Conf, Durban SA, 19-23 May 2002

Stumm W, Lee GF (1961) Oxygenation of ferrous iron. Ind Eng Chem, 53(2): 143 - 146

van Tonder GJ, Theron DJ, Maree JP (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, WISA Conf, Sun City, SA, 28 May-1 June 2000

Received February 28,2004; revised July 10, 2004; accepted July 24, 2004

CHAPTER 5. TREATMENT OF ACID LEACHATE FROM COAL DISCARD USING CALCIUM CARBONATE AND BIOLOGICAL SULPHATE REMOVAL

Maree J P, Strobos G, Greben H, Netshidaulu E, Steyn E, Christie A, Günther P and Waanders FB (2004) Treatment of Acid Leachate from Coal Discard using Calcium Carbonate and Biological Sulphate Removal, Mine Water and the Environment 23(3), 144 - 151.

Summary

An integrated approach is proposed for treating acidic coal discard leachate, consisting of limestone handling and dosing, limestone-neutralization, and biological sulphate removal. It was found that: powdered limestone can be slurried to a constant density and used to neutralize acid water, remove Fe (II), Fe (III), and Al, and partially remove the sulphate (to saturation level); biological sulphate removal can be used to lower the sulphate to less than 200 mg/L using ethanol as the carbon and energy source; CO_2 produced during $CaCO_3$ treatment can be used for H_2S-stripping and; H_2S gas recovered in the sulphate removal stage can be used for iron removal as FeS.

Mine Water and the Environment (2004) 23: 144–151 © IMWA Springer-Verlag 2004

Technical Article

Treatment of Acid Leachate from Coal Discard using Calcium Carbonate and Biological Sulphate Removal

J. P. Maree[1], G. Strobos[1], H. Greben[1], E. Netshidaulu[1], E. Steyn[1], A. Christie[2], P. Günther[2], and F. B. Waanders[3]

[1]CSIR, Water, Environment and Forestry Technology, P O Box 395, Pretoria, 0001, South Africa; [2]S A Coal Estate, Anglo Coal, P O Box 2851, Witbank, 1035, South Africa; [3]Director: School of Chemical and Minerals Engineering, North West University (Potchefstroom campus), Potchefstroom, 2531, South Africa (e-mail: jmaree@csir.co.za)

Abstract. An integrated approach is proposed for treating acidic coal discard leachate, consisting of $CaCO_3$ handling and dosing, $CaCO_3$-neutralization, and biological sulphate removal. It was found that: powdered $CaCO_3$ can be slurried to a constant density and used to neutralize the acid water, remove Fe (II), Fe (III), and Al, and partially remove the sulphate (to saturation level); biological sulphate removal can be used to lower the sulphate to less than 200 mg/L using ethanol as the carbon and energy source; CO_2 produced during calcium carbonate treatment can be used for H_2S-stripping and; H_2S gas recovered in the sulphate removal stage can be used for iron removal.

Key words: Biological sulphate reduction; calcium carbonate; coal discard leachate; CSIR; ethanol; gypsum precipitation; iron oxidation; limestone; sulphide removal

Introduction

Since 1996, extensive research and development work has been carried out at the Navigation Section of Landau Colliery near Witbank to address problems associated with the leachate from raw coal and coal discard, including the high cost of neutralisation, the high maintenance cost in the coal processing and lime neutralization plants due to acid corrosion and scaling of equipment, and the desalination of the effluent water that is discharged into public streams.

Water is used in the coal processing plant to separate coal from waste, to grade the coal into different particle size fractions, and for dust suppression. Water leaving the processing plant contains slimes (fine coal), which are settled in a thickener. The slurried slimes are pumped to the centre of a waste dump; coarse coal discard is transported on a belt conveyor and placed around the perimeter to contain the slimes. Decanted water is returned via the penstock to the coal processing plant. Some of this water seeps through the discard dump and, together with rainwater, is collected in cut-off trenches at the base of the dump. The seepage is stored in a toe dam. A portion of the toe dam water is combined with the penstock water and other slightly polluted water prior to treatment in a primary liming plant.

In this operation, 20 000 ton per day (t/d) of raw coal is mined to produce 15 500 t/d of final product, 3 000 t/d of coal discard, and 1 500 t/d of slimes (fine coal). The dump has an area of 72.5 ha (25.6 ha under slimes and 46.9 ha under discard) and a height of 12 m. The dump contains an estimated 2.4 million tons of slimes and 4.3 million tons of discard, with the latter containing 2% pyrite (as S). The discard is responsible for most of the pollution. A number of studies have been conducted at this site since 1996 to characterize the nature and extent of pollution. The key findings were:

- Chemical leaching studies showed that 0.33 g of acid (as $CaCO_3$) is leached from each kg of coal.
- The rate of biological oxidation of pyrite under laboratory conditions was determined to be 148 mg of acid (as $CaCO_3$)/(kg·d).
- Modelling of the water network indicated that 24.1 t/d of sulphate enters the water network: 7.3 t/d originates from the feed water, 5.8 t/d from the raw coal and 11 t/d from the coal discard. Sulphate leaves the system through gypsum precipitation (11 t/d during toe seep water neutralization, 0.2 t/d in the primary neutralization plant, 4.5 t/d in the coal processing plant, and 3.2 t/d in the penstock) or with the seepage (5.1 t/d). A portion of the sulphate crystallizes out in the coal processing plant as scale on equipment, such as spirals, sieves, and pipelines, as well as on magnetite used in the separation process.
- Electron microscope studies have shown that needle-like gypsum crystals develop on the magnetite particles and interfere with the recovery of magnetite at the magnetic separators.
- The gypsum over-saturation index (OSI – values shown in brackets) indicates the likelihood of gypsum scaling (Maree et al. 2004b). The water in the coal processing plant (1.47), the thickener overflow (1.23), and the neutralization plant (1.07) are oversaturated with respect to gypsum; the return water from the penstock has an OSI of 0.99. The latter value reflects gypsum crystallization that has taken place.
- The cost of neutralization could be reduced from R0.57/m^3 (1 US$ = SA R6.50, June 2004) to R0.16/m^3 by replacing unslaked lime (utilization efficiency = 60%,

purity = 90%, price = R550/t) with powdered $CaCO_3$ (utilization efficiency = 90%, purity = 75%, price = R110/t) (Maree et al. 2004a).

- Modelling showed that the capital cost associated with neutralization and gypsum crystallization of 40 m^3/h discard leachate with an acidity of 11.5 g/L, could be reduced from R10.3 million to R3.0 million by treating streams with high pollution loads separately from streams with low pollution loads. The total volume of the less polluted streams is 3 ML/d. Only slightly lower gypsum removal is achieved this way, 8.9 t/d versus 9.5 t/d (Maree et al. 2004b).
- A modelling exercise showed that 30% of the over-saturated fraction in the primary neutralization plant and 60% in the coal processing plant crystallizes out as gypsum (Maree et al. 2004b).
- A flow of 210 m^3/h needs to be treated for the removal of sulphate to 350 mg/L in order to obtain an OSI value of 0.98 (less than 1) in the coal processing plant. A biological sulphate removal plant with this capacity has an estimated capital cost of R11.6 million (R2.3 million/(ML/d)) and a running cost of R2.54/m^3 (Maree et al. 2004b).

Approach

As a result of these investigations and observations, an integrated process was proposed for the treatment of the site's coal discard leachate, consisting of the following stages (Figure 1):

- $CaCO_3$ handling and dosing system
- $CaCO_3$-neutralization, which includes iron oxidation and precipitation, and neutralization
- Heating unit (not shown in Figure 1)
- Biological sulphate removal, which includes biological sulphate reduction, H_2S-stripping, aerobic treatment for removal of residual organic material, and $CaCO_3$-precipitation.

This approach offers the following benefits:

- The cheapest alkali, a by-product from the paper industry, is used for neutralization of the acid and for the removal of the bulk of the sulphate concentration through gypsum crystallization. The more advanced biological process is then used only for removal of the remaining sulphate, to low concentrations.

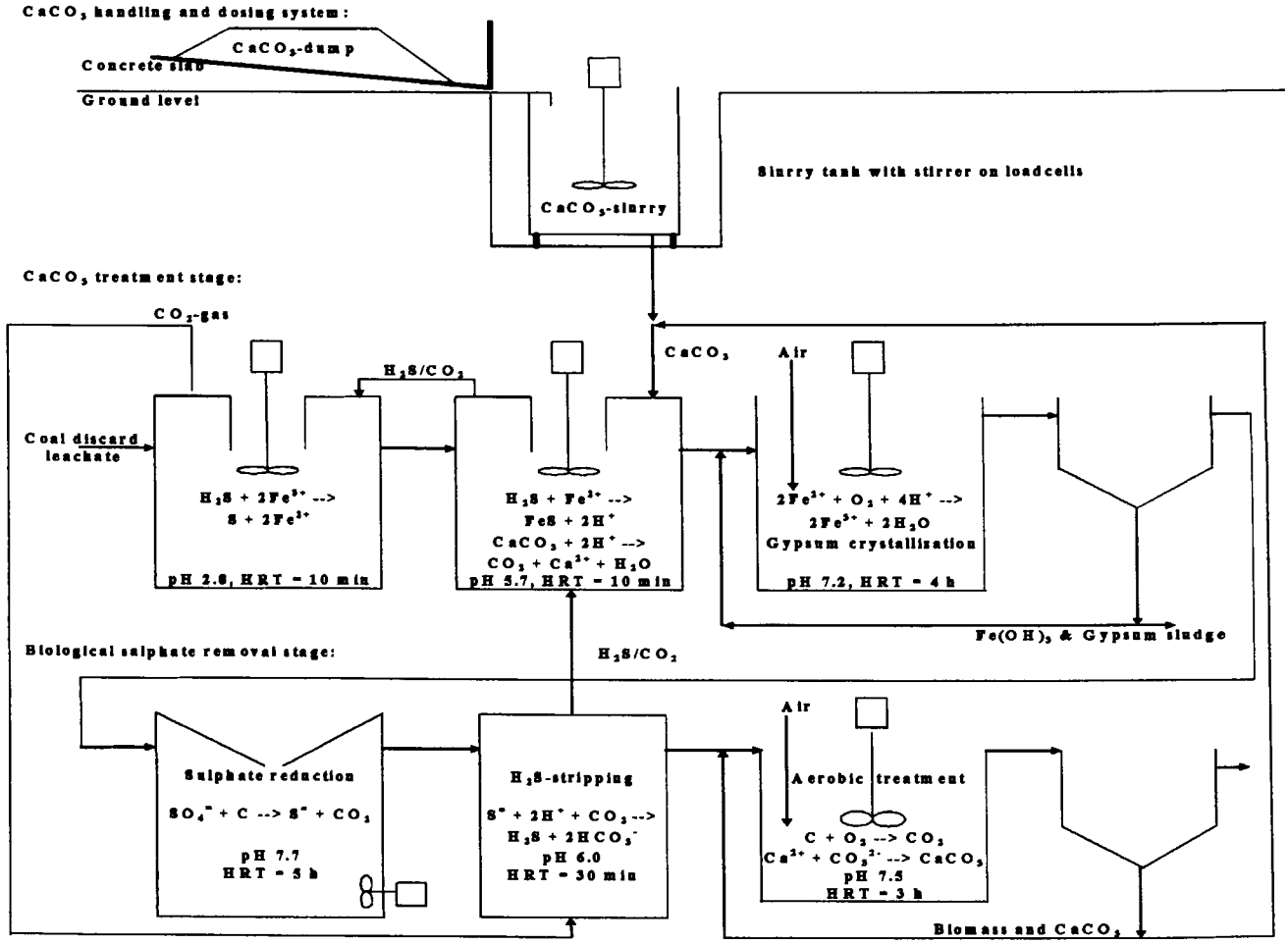


Figure 1. Process flow diagram for the treatment of coal discard leachate

- A robust biological process is used for sulphate removal to produce water suitable for use as process water that is non-scaling and suitable for discharge into public streams.
- This is an integrated process as CO_2 produced during $CaCO_3$-neutralization is used for H_2S-stripping in the biological stage. The stripped H_2S-gas is transported to the $CaCO_3$-neutralization stage for precipitation of iron as iron sulphide, followed by iron oxidation and precipitation of inert $Fe(OH)_3$ and gypsum in the $CaCO_3$-neutralization stage.

This paper addresses:

- Performance of the full-scale $CaCO_3$ handling and dosing system.
- Pilot-plant evaluation of $CaCO_3$ neutralization of the acid leachate.
- The energy utilization efficiency when feed water is contacted directly with hot coal gas.
- Pilot-plant evaluation of a biological sulphate removal plant with a capacity of 400 m^3/day.

Materials and Methods

Analytical

Samples were filtered through Whatman #1 filter paper. Sulphate, sulphide, alkalinity, calcium, Fe (II), mixed liquor suspended solids, volatile suspended solids, acidity, and pH determinations were carried out manually according to procedures described in Standard Methods (American Public Health Association 1985). Calcium was analysed using atomic absorption spectrophotometry. Acidity was determined by titrating the solution to pH 8.3 using NaOH. The samples being analyzed for chemical oxygen demand (COD) were pre-treated with a few drops of H_2SO_4 and N_2 to strip off H_2S gas.

Feedstock

Powdered $CaCO_3$, a by-product from the paper industry, was used for neutralization of acid water. It contained 25% moisture and 10% impurities (dry mass), which was mainly silica. Coal discard leachate or a synthetic solution of similar chemical composition was used as water for the $CaCO_3$ neutralization stage. 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 Fe (II), were added, as the mine feed water contains all trace elements required by sulphate-reducing bacteria. The heating unit was fed with 25 mm coal.

Equipment

The four stages of the integrated process were studied separately.

The *$CaCO_3$ - handling and dosing system* (Figure 2) was evaluated on the first full-scale plant of its kind. It has a capacity of 23 t/d $CaCO_3$. The plant has a sloped concrete slab onto which $CaCO_3$ powder is dumped and stored. The $CaCO_3$ powder is slurried with a water jet and collected in a slurry tank by gravity flow. A ball valve in the slurry tank maintains the water level at a specific height.

- A recycle slurry pump that withdraws $CaCO_3$ of higher density from the slurry tank or clear water through a water jet onto the $CaCO_3$ dump to maintain a constant $CaCO_3$ concentration. 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.
- A transfer pump, feeding slurried $CaCO_3$ to the neutralization reactor.

The *$CaCO_3$ neutralization stage* consists of a fluidised-bed reactor and a sludge separator (Table 1). Compressed air was used for iron oxidation.

The *heating unit stage* consists of: coal bunker, a speed control spiral feeder (100 kg/h), a heating unit, and a fan and water spray reactor where feed water is sprayed through 3/8 inch (1 cm) spiral jet nozzles while hot air is flowing upwards (Figure 3).

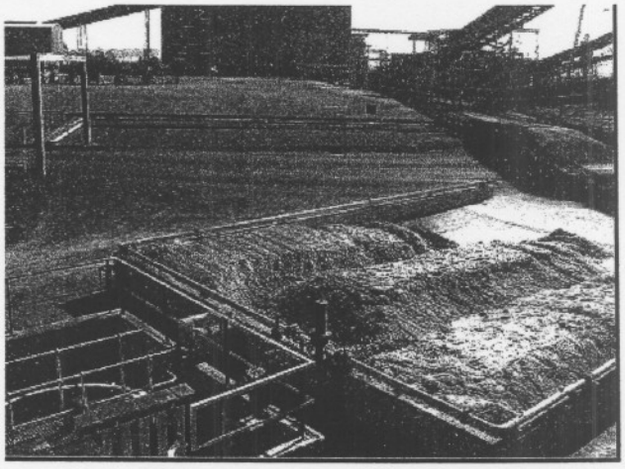


Figure 2. Limestone handling and dosing system

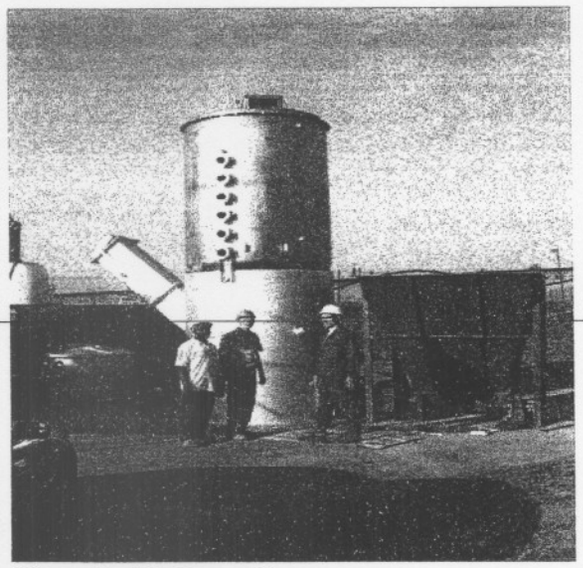


Figure 3. Heating unit

For the *biological sulphate reduction stage,* only the anaerobic (Figure 4) and H_2S-stripping sub-stages were evaluated on-site, as the other processes, e.g. Fe (II) precipitation with H_2S and the aerobic treatment for removal of residual organic material and $CaCO_3$ precipitation were known. The latter were therefore only tested in the laboratory. The anaerobic reactor consists of a completely mixed reactor (diam. = 4 m, height = 8 m, volume = 105.5 m^3) with a cone in the top of the reactor to allow for sludge separation (Maree et al. 2001).

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 ^0C.

Table 2 shows the dimensions of the two reactors operated in series used for sulphide stripping. Silica stones were used as the medium in Reactor 1, while Rashig rings were used in Reactor 2. In Reactor 1, the medium was submersed, while water trickled over the medium in Reactor 2.

Experimental

The performance of the various stages ($CaCO_3$ neutralization, sulphate reduction, and H_2S-stripping) was evaluated by determining the chemical composition of the feed and treated water during continuous operation.

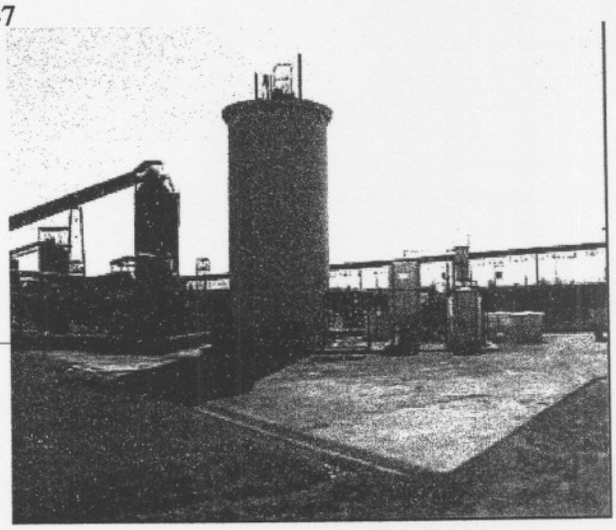


Figure 4. Anaerobic stage of biological sulphate removal

Table 1. Dimensions of $CaCO_3$ neutralization pilot plant

Parameter	Value	
	Fluidised bed	Solids separation
Feed rate (L/h)	24	24
Recycle rate (L/h)	200	200
Diameter (m)	0.20	0.53
Water height (m)	4.99	0.35
Specific surface area (m^2/m^3)	20.2	-
Up-flow velocity (m/h)	6.37	0.91
Residence time (h)	6.53	3.22

Table 2. Dimensions of H_2S-stripping reactors

Parameter	Value	
	Reactor 1	Reactor 2
Diameter (m)	0.50	0.19
Height (m)	0.50	2.20
Medium height (m)	0.37	2.00
Medium	Silica stone	Rashig rings
Medium description	Submersed	Trickling
Empty volume (m^3)	0.098	0.062
Medium volume (m^3)	0.073	0.057
Feed rate (L/min)	5.00	5.00
CO_2 feed rate (L/min)	1 to 2	1 to 2
HRT (min)	19.6	12.5

Results and Discussion

$CaCO_3$ handling and dosing system

Acidic water was neutralized effectively when powdered $CaCO_3$ was used (see schematic section of dosing system in Figure 1). The pH was raised from 2.9 to 6.5, acidity was reduced from 650 to 50 mg/L and iron(II) from 110 to less than 28 mg/L when 20% excess $CaCO_3$ was dosed. Initially problems were experienced with blocked feed and recycle pipelines as a result of grit and stone in the $CaCO_3$. The recycle

pipeline problem was solved by installation of a sieve in the slurry tank opposite to the inlet of the recycle pipe. Grit and stones were prevented from entering the feed line by installation of a grit separator. This unit consists of a pipe (diameter = 450 mm, length = 1.2 m) positioned vertically in the reactor with its upper end above the water level. The inlet of the feed pipe was moved from the bottom of the slurry tank to inside this pipe at a level of 800 mm below water level. This arrangement ensured that the up-flow velocity in the unit was high enough (20 m/h) to keep the fine $CaCO_3$ particles in suspension but low enough to allow settlement of all unwanted larger particles (coal, sand, grit and stones) before reaching the inlet of the feed line.

$CaCO_3$ neutralization of coal discard leachate

Limestone can be used in the integrated process for treatment of acid water. Table 3 shows the results obtained when synthetic discard leachate was treated with limestone (Maree et al. 2004c). The water was neutralised effectively and sulphate was reduced from 8 342 to 1 969 mg/L (as SO_4). It was possible to achieve complete Fe (II) oxidation by using only $CaCO_3$ as the neutralization agent. This differs from the standard approach where the pH is raised to 7.2 with lime where the rate of Fe (II) oxidation is fast. By using $CaCO_3$, the pH of the water remains at 6 while Fe (II) is oxidised.

In this investigation, it was determined that the rate of Fe (II) oxidation is not only influenced by the Fe (II), hydroxide, and oxygen concentrations as suggested by Stumm and Lee (1961), but also by the suspended solids concentration, as suggested by Maree et al. (1998). In order to achieve complete Fe (II) oxidation, sufficient reaction time was allowed for gypsum crystallization to reach its saturation level (2 h). Aeration and sludge recirculation maintained a suspended solids concentration at 50 g/L.

Table 3. Chemical composition of feed (synthetic discard leachate) and $CaCO_3$ treated water.

Parameter	Feed	Treated
pH	1.8	6.6
Acidity (mg/L $CacO_3$)	7 300	100
Sulphate (mg/L SO_4)	8 342	1 969
Ortho phosphate (mg/L P)	2.9	0.0
Chloride (mg/L Cl)	27	30
Fe (II) (mg/L Fe)	2 500	<56
Total iron (mg/L Fe)	2 500	<56

Table 4. Chemical composition of feed and treated water during biological sulphate reduction

Parameter	Feed	Treated
pH	7.2	7.7
Sulphate (mg/L SO_4)	2 203	198
Sulphide (mg/L S)	0	606
Alkalinity (mg/L $CaCO_3$)	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
SO_4 reduction rate (mg SO_4/(L·d)	12.0	12.0

Biological sulphate removal

The feed rate of the reactor varied between 8 and 16 m^3/h, during a period of 300 days of continuous operation, which corresponded with a hydraulic retention time of 5.2 to 10.3 h, respectively. Table 4 shows the chemical composition of the feed and treated water.

It was noted that:

- Sulphate was removed consistently down to 200 mg/L 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 was 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 (1993) 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, and 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. This was achieved by installation of a settler in the top of the completely-mixed reactor to allow sludge separation. This design allowed for reduced capital cost 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 (Reactions 2 or 3). Alkalinity values as high as 2000 mg/L were measured with an equal reduction in the sulphate content.

$$2CH_3CH_2OH + SO_4^{2-} \rightarrow 2CH_3COOH + S^{2-} + 2H_2O \quad (2)$$

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

- 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 at the start of the period to 10 000 mg/L where it stabilized. The specific biomass production was calculated to be 0.02 g biomass/g $SO_{4removed}$.

Figure 5 shows the percentage sulphate removal and the COD_{feed}/SO_{4feed}-ratio with time. Sulphate removal increased from between 30 % and 50 % during the period before day 48 to above 75% after day 48 (Figure 2, sulphate line). The improved sulphate removal with time can be ascribed to the increased value for the COD_{feed}/SO_{4feed}-ratio with time (Figure 2, COD_{feed}/SO_{4feed} line). Before day 48, this value was lower than the theoretical value of 0.67 (Reactions 2 or 3: $2C \equiv 2O_2 \equiv 1\ SO_4$; 24 g C ≡ 64 g O_2 ≡ 96 g SO_4). Thereafter, this value increased to between 0.8 and 1.2 (except for the period around day 135 when the ethanol feed pump failed).

The utilization efficiency of the energy source (ethanol and sugar) and its cost are calculated in Table 5.

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 were due to incomplete combustion of coal and disposal of hot ash. Figure 6 shows the total heat transfer efficiency in the period August to September 2003.

Table 6 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.

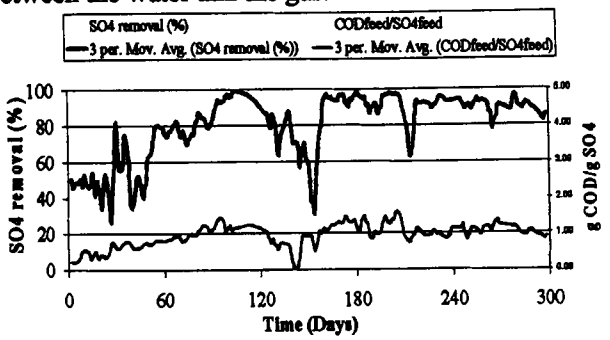


Figure 5. Percentage sulphate removal over a period of 9 months, compared with the ratio of the chemical oxygen demand of the influent water (COD_{feed}) to the SO_{4feed}

Table 5. Comparison between measured and calculated chemical oxygen demand (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
SO_4 equivalent (g/L)				2.51
SO_4 removed (g/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

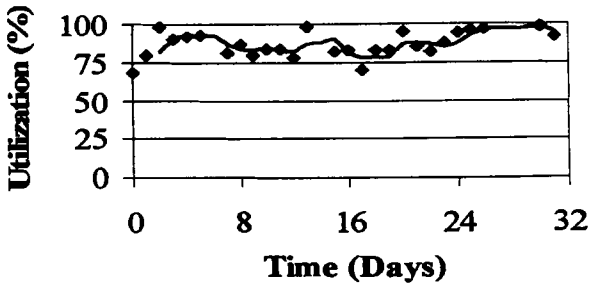


Figure 6. Total heat transfer efficiency in the period 17 August to 20 September 2003

Table 6. 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

Table 7. Determination of the flow rate ratio of CO_2-gas to H_2S-rich water required for complete H_2S-stripping, with water fed at 5 L/min, CO_2 fed at 1 L/min, and H_2S set at 364 mg/L S and at 80 mg/L S after Reactor 1

Parameter	Exp No			
	1	2	3	4
HRT (min): Reactor 1	19.6	19.6	19.6	19.6
Reactor 2	12.5	12.5	12.5	12.5
H_2S after Reactor 2	0	62	8	0
CO_2 into Reactor 2 (L/min)		0.1	0.3	0.5
CO_2 feed (mmol/min)	44.6	49.1	58.0	67.0
H_2S removed	8.9	9.4	11.1	11.4
CO_2/H_2S-ratio	5.03	5.20	5.22	5.89

Sulphide removal

Sulphide can be removed through direct conversion of sulphide to sulphur in the anaerobic reactor by controlled oxygenation or by H_2S-stripping downstream of the anaerobic reactor. The disadvantage of the former option is that sulphur needs to be separated from the water in order to prevent back oxidation to sulphate. Care should be taken to avoid any introduction of air into the process as this will result in sulphide oxidation. Another attractive technology is removal of sulphide by stripping with CO_2-gas. This is a feasible option, provided that CO_2-gas is available (e.g. gas from the aerobic stage or CO_2-gas produced during limestone neutralization of acid water or from coal when the feed water is heated).

Table 7 shows that sulphide is removed effectively from the effluent of the anaerobically treated water by passing it through two stripping units in series. Sulphide can be reduced from 364 mg/L (as S) down to 0 mg/L when the molar ratio of CO_2-gas to sulphide in solution exceeds 5.9.

Aerobic treatment

Laboratory studies showed that the residual organic material in the effluent from the H_2S stripping stage can be removed to less than 30 mg/L (as O_2).

H_2S processing

H_2S-gas recovered from the anaerobic stage can be processed effectively by contacting it with discard leachate that is rich in Fe (II) and Fe (III). Table 8 shows the effect obtained when H_2S is contacted with untreated discard leachate at pH 2.8 and with $CaCO_3$ treated leachate at pH 5.7. It is noted that at a low pH of 2.8, the Fe (II) concentration increases as a result of sulphur production (Reaction 4), while at a pH of 5.7, it decreases due to FeS precipitation (Reaction 5).

Table 8. Treatment of H_2S-rich gas with iron-rich discard leachate

Condition	Iron(II) (mg/L)	
Discard leachate	Feed	Treated
Low pH (2.8)	4 189	7 316
Neutral pH	3 910	1 229

By passing H_2S gas through discard leachate at low pH followed by discard leachate at pH 5.7, as suggested in Figure 1, sulphur and FeS, respectively, are formed as products from H_2S. The S and FeS and residual Fe (II) in the discard leachate, are oxidised to Fe (III) and H_2SO_4 in the Fe (II)/gypsum crystallization reactor to form inert products, namely, ferric hydroxide and gypsum, after neutralization with $CaCO_3$.

$$H_2S + 2Fe^{3+} \rightarrow S + 2Fe^{2+} + 2H^+ \quad (4)$$

$$H_2S + Fe^{2+} \rightarrow FeS + 2H^+ \quad (5)$$

This approach offers the following benefits:

- Small reactor vessels are required as the reactions are fast.
- Only inert sludges are produced, namely ferric hydroxide and gypsum. The mass of sludge is low. By treating 3 Ml/d of sulphate rich water for the removal of 1 500 mg/L sulphate, the gypsum production amounts to 8.1 t/d. This is insignificant when compared to the coal waste production of 4 500 t/d.
- Sufficient Fe (II) and Fe (III) are available in the discard leachate for processing of the H_2S (6.0 t/d iron (as SO_4) while only 4.5 t/d iron (as SO_4) is required.

Conclusions

1. Calcium carbonate powder can be slurried to a constant density and used to treat acid water, despite elevated levels of Fe (II). The water can be completely neutralized, precipitating (Fe (II), Fe (III) and aluminium), and lowering sulfate concentrations (to saturation level).

2. 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. Feed water to the biological stage can be contacted directly with hot coal gas to increase the temperature to 25 °C.

3. CO_2 produced during calcium carbonate treatment can be used for H_2S-stripping and H_2S gas recovered in the sulphate removal stage can be used for iron removal.

Acknowledgements

We sincerely thank the following organisations for their financial and logistical support of the research reported in this paper:

• Anglo Coal (Navigation Section of Landau Colliery), which provided financial support, the necessary infrastructure at the mine, and general assistance.

• The National Research Foundation, which provided funding through their Technology and Human Resources for Industry Programme for CSIR projects on neutralisation and sulphate removal.

• The CSIR who provided substantial financial support for the research programme.

References

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

Maree JP, de Beer M, Strydom WF, Christie ADM (1998) Limestone neutralisation of acidic effluent, including metal and partial sulphate removal. Proc, International Mine Water Assoc Symp, Johannesburg, South Africa, 6 - 13 Sept, p 449-460

Maree, JP, Strobos, G, Greben, H, Günther, P and Christie ADM (2001) Biological treatment of mine water using ethanol as energy source. Conf on Environmentally Responsible Mining in South Africa, Muldersdrift, South Africa, 25 – 28 Sept

Maree JP, de Beer M, Strydom WF, Christie ADM, Waanders FB (2004a) Neutralizing coal mine efluent with limestone to decrease metals and sulphate concentrations. Mine Water and the Environment 23(2): 81-86

Maree JP, Günther P, Strobos G, Waanders FB (2004b) Optimization of effluent treatment at a coal mine by process modelling. Mine Water and the Environment 23(2): 87-90

Maree JP, Hagger MJ, Strobos G, Hlabela, P, Cronje H, van Niekerk A, Wurster, Nengovhela R, and Waanders FB (2004c) Neutralization of acid leachate at a nickel mine with limestone. Mine Water and the Environment (in this issue)

McCartney DM, Oleszkiewicz JA (1993) Competition between methanogens and sulphate reducers: effect of COD: sulphate ratio and acclimation. Wat Environ Res 65: 655-664

Stumm W, Lee GF (1961) Oxygenation of ferrous iron. Ind Eng Che 53(2): 143 – 146

Received June 17, 2004; accepted September 4, 2004

CHAPTER 6. TREATMENT OF ACID AND SULPHATE-RICH EFFLUENTS IN AN INTEGRATED BIOLOGICAL/CHEMICAL PROCESS

Maree J P, Greben H and De Beer M (2004) Treatment of acid and sulphate-rich effluents in an integrated biological/chemical process, Water SA 30(2): 183-189.

Summary

A novel chemical/biological process is described in which sulphate and sulphide were removed simultaneously during biological treatment. Partial sulphate removal was achieved during chemical pre-treatment. In the biological stage sulphate was reduced to sulphide in a complete-mixed reactor through addition of sucrose or ethanol as carbon and energy source. Sulphide was oxidized by allowing oxygen to enter the system in a controlled way.

The experimental investigation of the process showed that sulphate and sulphide can be removed simultaneously due to co-existence of sulphate-reducing bacteria and sulphur oxidising bacteria. The volumetric sulphate reduction rate in a completely-mixed reactor, with sucrose as carbon and energy source, amounted to 12.4 g SO_4/(ℓ.d). The rate of biological sulphate removal was found to be directly related to the square roots of sulphate, COD and VSS concentrations, respectively, and inversely proportional to sulphide concentration. The practical value of simultaneous sulphate and sulphide removal is that only one stage is required for removal of both sulphate and sulphide; a conventional completely-mixed reactor can be used, and sulphate can be removed in a consistent way to below 200 mg/ℓ (as SO_4) due to the stability of the process.

By combining the biological stage with limestone-neutralization and/or lime pre-treatment, the chemical cost was reduced. Sulphate, associated with the over-saturated fraction after treatment with limestone or lime, was removed through gypsum crystallization. In the integrated sulphate removal process (Limestone-neutralization, lime treatment and biological stages), sulphate was removed from 9 200 mg/ℓ (typical sulphate concentration of coal discard leachate) to 2 410 mg/ℓ, 1 230 mg/ℓ and 205 mg/ℓ (as SO_4) in the various stages, respectively. The chemical cost with the integrated process amounts to R2.94/m^3, versus R12.44/m^3 when all the sulphate is removed with the biological stage only. Similarly, the cost for treating magnesium sulphate-rich mine water amounts to R1.92/m^3 for the integrated process, versus R3.11/m^3 for biological treatment only.

Treatment of acid and sulphate-rich effluents in an integrated biological/chemical process

JP Maree, HA Greben* and M de Beer
Division of Water, Environment and Forestry Technology, CSIR, PO Box 395, Pretoria 0001, South Africa

Abstract

A novel chemical/biological process is described in which sulphate and sulphide are removed simultaneously during biological treatment. Partial sulphate removal is achieved during chemical pre-treatment. In the biological stage sulphate is reduced to sulphide in a complete-mixed reactor through addition of sucrose or ethanol as a carbon and energy source. Sulphide is oxidised by allowing oxygen to enter the system in a controlled way. The experimental investigation of the process showed that sulphate and sulphide could be removed simultaneously due to co-existence of sulphate-reducing bacteria and sulphur oxidising bacteria. The volumetric sulphate reduction rate in a complete-mixed reactor, with sucrose as an organic carbon and energy source, amounts to 12.4 g SO_4/(ℓ.d). The rate of biological sulphate removal was found to be directly related to the square root of sulphate, COD and VSS concentrations respectively, and inversely proportional to sulphide concentration. The practical value of simultaneous sulphate and sulphide removal is that only one stage is required for removal of both sulphate and sulphide; a conventional complete-mixed reactor can be used; and sulphate can be removed in a consistent way to below 200 mg/ℓ (as SO_4) due to the stability of the process.

By combining the biological stage with $CaCO_3$-neutralisation and/or lime pre-treatment, the chemical cost can be reduced. Sulphate, associated with the over-saturated fraction after treatment with $CaCO_3$ or lime, can be removed through gypsum crystallisation. In the integrated sulphate removal process ($CaCO_3$-neutralisation, lime treatment and biological stages), sulphate can be removed from 9 200 mg/ℓ (typical sulphate concentration of coal discard leachate) to 2410 mg/ℓ, 1 230 mg/ℓ and 205 mg/ℓ (as SO_4) in the various stages respectively. The chemical cost with the integrated process amounts to R2.94/m³, versus R12.44/m³ when all the sulphate is removed using the biological stage only. Similarly, the cost for treating magnesium sulphate-rich mine water amounts to R1.92/m³ for the integrated process, versus R3.11/m³ for biological treatment only.

Keywords: acid mine water; ethanol; kinetics; sulphate reduction; sulphide oxidation; sucrose

Introduction

Industrial effluents rich in sulphate, acid and metals are produced when sulphuric acid is used as a raw material, and when pyrites are oxidised due to exposure to the atmosphere, e.g. in the mining industry. 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 semi-arid countries like 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 removal, 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 been 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 (1985) showed that sulphate could be removed in an anaerobic packed-bed reactor using sucrose, pulp mill effluent or molasses as a carbon and energy source. Metals like nickel, cadmium and lead were completely removed due to precipitation of metal sulphides. Maree and Hill (1989) showed that a three-stage process could be applied for sulphate removal, using molasses as the carbon and energy source in an anaerobic packed-bed reactor. Sulphide can be stripped with a mixture of CO_2/N_2 from the effluent of the anaerobic reactor in an H_2S-stripping stage, and residual COD and $CaCO_3$ can be removed in an aerobic final treatment stage. Maree et al. (1991) showed that when molasses is used as a carbon and energy source it could either be utilised in the fermented or unfermented form. 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, it was concluded that by running two anaerobic sulphate removal reactors in series, sucrose could be fermented to lactate in the first reactor and, via acetate, to CO_2 in the second reactor. Du Preez et al. (1992) were the first to demonstrate that producer gas (mixture of H_2, CO and CO_2) can be used as a carbon and energy source for biological sulphate reduction. Both H_2 and CO were utilised as the carbon and energy source. Visser (1995) investigated the competition between sulphate-reducing bacteria (SRB) and methanogenic bacteria (MB) for acetate as the carbon and energy source in an up-flow anaerobic sludge blanket (UASB) reactor. He found that at pH values less

* To whom all correspondence should be addressed.
☎+2712 841-2278; fax:012 841 3954 ; e-mail: HGreben@csir.co.za
Received 20 November 2003; accepted in revised form 23 February 2004.

than 7.5, SRB and MBs are equally affected by the presence of H_2S, while at higher pH values SRB out-compete MB. Van Houten (1996) showed that sulphate could be reduced to H_2S at a rate of 30 g SO_4/(ℓ.d) when H_2/CO_2 is used as the carbon and energy source and pumice or basalt particles are used to support bacterial growth in a fluidised-bed reactor. The sulphate reduction rate was not inhibited at H_2S-concentrations less than 450 mg/ℓ (as S).

The aim of this investigation was to further improve the biological sulphate removal process by achieving simultaneous removal of sulphate and its product, sulphide. Specific aims of the investigations were to demonstrate the symbiosis between SRB and sulphide oxidising bacteria (SOB) and to determine the kinetics of simultaneous sulphate and sulphide removal.

Materials and methods

Two experimental set-ups were operated in parallel. One system comprised a complete-mixed reactor (15 ℓ) and a clarifier (15 ℓ), while the other system comprised a column reactor (20 ℓ) and a clarifier (15 ℓ). The reactors and the clarifiers were open to the atmosphere to allow air contact. Sulphate-rich water (1 500 mg/ℓ $CaSO_4$ as SO_4) was fed to both systems. This water was supplemented with sucrose and/or ethanol as the carbon and energy source, and with the macro-nutrients (75 mg/ℓ ammonia-N and 15 mg/ℓ ortho-phosphate-P). The following micro-nutrients (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) were added as well. The reactors were inoculated with anaerobic sludge obtained from a sewage treatment plant. Sludge was recycled from the bottom of the clarifier to the complete-mixed reactor, or from the bottom to the top of the column reactor, at a rate of 50 ℓ/d. The performance of the systems was monitored by operating the two systems in either continuous or batch mode. During continuous operation, water was fed at a rate between 20 and 100 ℓ/d. Batch studies were carried out as follows: Feed water to the system was stopped, recycle pumps were stopped and sludge was allowed to settle. Clear water was decanted and replaced with fresh feedstock, where-after the recycle pumps were started again. Filtered samples were collected on a regular basis and analysed for various parameters (sulphate, sulphide, COD, alkalinity, pH and Eh). Additional batch studies were carried out similarly in 1 ℓ beakers by mixing biomass (obtained from one of the systems described) with fresh feedstock. Continuous studies were executed to determine the effect of hydraulic retention time on the chemical composition of the feed water and the volumetric and specific sulphate reduction rates. Batch studies were carried out to determine the effect of a number of parameters on the kinetics of sulphate reduction. The parameters are: sulphate concentration (1.1 - 3.5 g/ℓ); sulphur concentration (0 - 5 g/ℓ); sulphide concentration (0 - 1 g/ℓ); alkalinity (0 - 1 g/ℓ); $CaCO_3$ solids concentration (0 - 1 g/ℓ); COD (0.5 - 2 g/ℓ); VSS concentration (1.7 - 12.1 g/ℓ); stirring rate (20 - 265 r/min).

Analytical

Samples were collected and filtered through Whatman No. 1 filter paper. Sulphate, sulphide, MLSS and VSS determinations were carried out manually (*Standard Methods*, 1985)). Calcium and magnesium concentrations were determined using atomic absorption spectrophotometry. Alkalinity was determined by titrating the solution to pH 4.3 using HCl.

Results and discussion

Symbiotic activity of SRB and SOB

Figures 1a, 1b, and Table 1 show the performance of the single-stage sulphate removal process operating continuously during the period from start-up until steady-state conditions were attained. The complete-mixed reactor was used with sucrose (1.5 g/ℓ) as the carbon and energy source. The feed rate increased gradually from 15 to 130 ℓ/d. This corresponded with a reduction in the hydraulic retention time (HRT) from 48 to 5.5 h in the system, based on the combined volume of the reactor and clarifier. The volume of the clarifier was included as it was partially filled with biomass.

Sulphate reduction rate

The volumetric sulphate reduction rate increased during the experimental period of 78 days from 0.2 to 12.4 g SO_4/(ℓ·d), while the specific sulphate reduction rate increased from 0.09 to 1.06 g SO_4/(gVSS·d) (Fig. 1b). The increase in the volumetric sulphate reduction rate was ascribed to the increase in the biomass concentration with time, adaptation of the biomass to its environment, suitability of the complete-mixed reactor for simultaneous removal of sul-

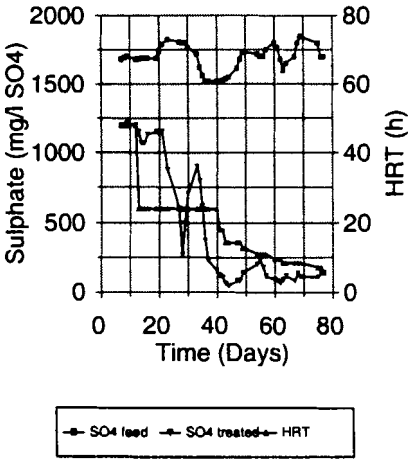


Figure 1a
The sulphate removal at different HRT

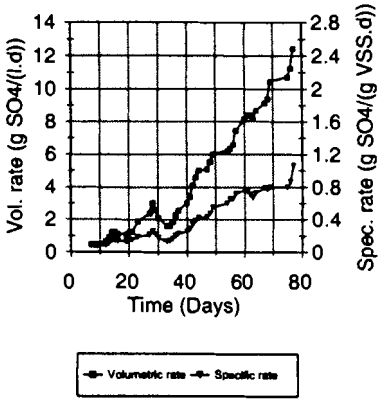


Figure 1b
The sulphate removal rates

TABLE 1
Chemical composition of feed and treated water during simultaneous biological sulphate and sulphide removal

Parameter	Quality	
	Feed	Treated
pH	4.3	7.2
Sulphate (mg/ℓ SO_4)	1672	123
Sulphide (mg/ℓ S)	0	162
COD (mg/ℓ O_2)	1781	733
Acidity (mg/ℓ $CaCO_3$)	335	
Alkalinity (mg/ℓ $CaCO_3$)		834

phate and sulphide, and the suitability of sucrose as the carbon and energy source. The increase in the specific sulphate reduction was ascribed to improved performance of the micro-organisms due to adaptation to their environment. Like sugar, ethanol can also be used as carbon and energy source for sulphate removal with the single-stage sulphate/sulphide removal process. Greben et al. (2000a) reported sulphate removal rates of 6.6 g SO_4/(ℓ·d) using ethanol as the carbon and energy source. Improved sulphate reduction rates were obtained when using ethanol as the carbon and energy source, to which a small amount of sugar (0.25 g/ℓ) was added (Greben et al., 2002a). It was reported (Greben et al., 2002b) that methanol was not effectively utilised by SRB at ambient temperatures, possibly because it was out-competed by methanogenic bacteria. Weijma (2000) however, showed the use of methanol at themophilic temperatures.

Simultaneous sulphate and sulphide removal

Sulphate removal to less than 250 mg/ℓ (as SO_4) was achieved after 37 days of continuous operation and remained at this level for the rest of the experimental period (until day 77) (Fig. 1.a). Sulphide was also partially removed. Of the 1 549 mg/ℓ sulphate (as SO_4) that was removed, only 162 mg/ℓ sulphide (as S) was measured in the effluent (Table 1). A distinct characteristic of the process is its stability. Any deterioration in the quality of the effluent was due to plant failure (e.g. loss of sludge at day 28) or change in experimental conditions (e.g. reduced HRT at day 50) (Fig. 1a). This stable performance was achieved with a complete-mixed reactor. Preliminary studies with column up-flow sludge blanket reactors showed that simultaneous sulphate/sulphide removal could also be achieved in a sludge blanket column reactor. It appeared, however, that sulphate removal is more stable in a complete-mixed reactor than in a packed-bed reactor. A possible reason why the complete-mixed reactor could be more suitable for simultaneous sulphate/sulphide removal than the column reactor, is the way in which oxygen enters the water through diffusion at the air–liquid interchange High numbers of sulphate reducers are present in the oxic zones and near the oxic-anoxic boundaries of sediments and in stratified water bodies, microbial mats and termite guts (Cypionka, 2000). Due to continuous mixing in a complete-mixed reactor, the total content of the reactor is in more direct contact with the atmosphere than in the column reactor where water comes into contact with the atmosphere only periodically. In a packed-bed reactor sulphate was not consistently removed to less than 120 mg/ℓ and a longer acclimatisation period was required for start-up.

$Sulphide_{produced}$/$Sulphate_{removed}$-ratio

A large portion (59%) of the sulphate that was converted to sulphide (Reaction 1) was converted to elemental sulphur due to the activity of sulphur oxidising bacteria (Reaction 2) and photosynthetic sulphur bacteria (Reaction 3). This shows the symbiotic existence of SRB and SOB. It is assumed that aerobic sulphur oxidising bacteria dominated the activity of the photosynthetic sulphur oxidising bacteria. Sulphide oxidation rates as high as 17 g S/(ℓ·d) have been reported for aerobic systems with reticulated polyurethane foam as support medium for bacterial growth (Buisman, 1989), compared to only 1.92 g S/(ℓ·d) for photosynthetic sulphur oxidising bacteria (Cork et al., 1986). This finding was confirmed by Greben and Maree (2002b), who showed that the sulphide oxidation is mainly a biological process under the influence of air. Elemental sulphur accumulated on the surface of the water in the clarifier. This finding shows that SRB can tolerate low levels of oxygen entering the water, if it is immediately taken up for sulphide oxidation (Cypionka et al., 1985). Greben et al. (2000) showed that the sulphide oxidation rate is a function of the sulphate reduction rate and the retention time.

$$2C + SO_4^{2-} + 2H_2O \rightarrow 2HCO_3^- + H_2S \quad (1)$$

$$H_2S + \tfrac{1}{2}O_2 \rightarrow S + H_2O \quad (2)$$

$$4H_2S + 2CO_2 \rightarrow 4S + CH_3COOH + 2H_2O \quad (3)$$

$Alkalinity_{produced}$/$Sulphate_{removed}$-ratio

The $Alk_{produced}/SO_{4removed}$-ratio was measured to be 0.99, which corresponds well with the theoretical ratio of 1.04 (Reaction 1).

Similar observations were made from batch studies. The results reported in Fig. 2 were obtained when 1.19 g/ℓ sucrose, 1.5 g/ℓ Na_2SO_4 (as SO_4) and 4.81 g/ℓ VSS were stirred in a 1 ℓ beaker. It shows the relative behaviour between the following parameters as a result of various reactions: COD and sulphate is removed in the ratio 0.81 g O_2/g SO_4 which compares with the theoretical ratio of 0.67 (Reaction 1); sulphide produced from Reaction 1 is removed due to Reaction 2. Alkalinity increased initially because of alkalinity production (Reaction 1), but thereafter decreased due to $CaCO_3$-precipitation. The $Alkalinity_{produced}/SO_{4removed}$-ratio of 0.83 compares with the theoretical value of 1.04. The pH increased slightly with increased reaction time. The E_h value remained constant at -140 mV while the sulphide concentration was greater than 90 mg/ℓ sulphide (as SO_4) and increased to 6 mV when the sulphide concentration was less than 90 mg/ℓ. The sulphide concentration decreased from 432 to 144 mg/ℓ sulphide (as SO_4). The pH increased slightly from 7.3 to 7.8.

Sulphate is reduced via intermediate products (valence of S species in brackets), such as SO_3^{2-} (+4), $S_2O_5^{2-}$ (+4), $S_2O_3^{2-}$ (+2) and S^{2-} (-2) to sulphur. During batch studies, similar to that shown in Fig. 2, the concentrations of various S-compounds were monitored. It was noted that:

- SO_4^{2-} (sulphate) (+6) was removed gradually with time over a 24 h period (from 1080 to less than 100 mg/ℓ as SO_4), while SO_3^{2-} (sulphite) (+4) and $S_4O_6^{2-}$ (tetrathionate) (+2.5) were not detected.
- •• $S_2O_3^{2-}$ (thiosulphate) (+2) was formed in small quantities with a maximum level of 38 mg/ℓ (as S) reached between 4 and 6 h.
- •• Sulphide increased to an intermediate level of 130 mg/ℓ (as S) between the time interval 2 and 10 h, whereafter it was removed completely.

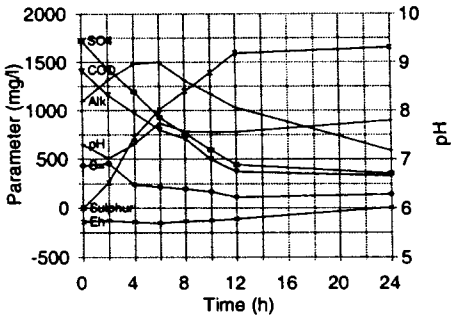


Figure 2
Relationship between various parameters during batch studies. Intermediate products

- The amount of sulphur increased gradually (calculated from other S species).

By taking the intermediate concentrations of S^{2-} (highest), $S_2O_3^{2-}$ (low), SO_3^{2-} (zero) and $S_4O_6^{2-}$ (zero) into account, it was concluded that under the specific experimental conditions, SO_4^{2-} is converted to sulphur via the various intermediate compounds at the following relative reaction rates:

$$\overset{+6}{SO_4^{2-}} \xrightarrow{\text{slow}} \overset{+4}{SO_3^{2-}} \xrightarrow{\text{fast}} \overset{+2}{S_2O_3^{2-}} \xrightarrow{\text{medium}} \overset{-2}{S^{2-}} \xrightarrow{\text{slow}} \overset{0}{S_0}$$

Effect of different parameters on the SO_4 reduction rate

The kinetics of biological reactions can be explained by the Monod and Haldane equations. The Monod equation shows the relationship between the specific growth rate constant, μ, and the substrate concentration, [S]. The Haldane equation, similarly, shows the relationship between the reaction rate, R, and the substrate concentration, S. The latter makes provision for the inhibitory effect of the substrate. The purpose of this section of the research was to determine the effects of various parameters on the rate of biological sulphate removal. For the purpose of this investigation, it was assumed that the reaction rate equation had the following functional form:

$$-d[SO_4^{2-}]/dt = k.[SO_4^{2-}]^{n1}.[S^{2-}]^{n2}.[COD]^{n3}.[VSS]^{n4} \qquad (4)$$

where:
$-d[SO_4^{2-}]/dt$ or R = rate of sulphate reduction
k = reaction rate constant
n_i = reaction order constants
$[SO_4^{2-}]$ = sulphate concentration (moles/ℓ)
$[S^{2-}]$ = sulphide concentration (moles/ℓ)
[COD] = carbon oxygen demand (mg/ℓ)
[VSS] = volatile suspended solids concentration (g/ℓ).

By varying the value of only one parameter in a series of experiments, say $[SO_4^{2-}]$, Eq. (4) can be written as:

$$-d[SO_4^{2-}]/dt = K.[SO_4^{2-}]^{n1} \text{ or}$$
$$\log(-d[SO_4^{2-}]/dt) = \log K + n_1.\log [SO_4^{2-}] \qquad (5)$$

where:
$K = k.[S^{2-}]^{n2}.[NO_3]^{n3}.[COD]^{n4}.[VSS]^{n5}.M^{n6}$

The contribution, n_1, of sulphate, to the overall reaction rate was determined from the slope of the graph when log R vs. log $[SO_4^{2-}]$ was plotted. The data in Table 2 shows that the sulphate reduction reaction in respect of SO_4 (COD not limiting), VSS, S^{2-}, COD and stirring rate (O_2), had kinetic order constants of 0.55 (~0.5), 0.6 (~0.5), -0.8 (~-1), 0.42 (~0.5) and -0.34 (~-0.5) respectively. The empirical reaction can thus be written as:

$$-d[SO_4^{2-}]/dt = k.[SO_4^{2-}]^{0.5}.[COD]^{0.5}.[VSS]^{0.5}/[S^{2-}]^{1} \qquad (6)$$

The reaction rate was zero order with respect to sulphate when the substrate was dosed in limiting concentrations, in contrast to 0.5 order, when the substrate was unrestricted. The reaction rate was also affected by stirring rate and temperature. At high stirring rates (265 r/min) the reaction rate was inhibited by too high oxygen concentrations, while at too low stirring rates (20 r/min) the sulphate reduction rate was inhibited by too high sulphide concentrations. Thus, an optimum oxygen dosage is required to control the sulphide concentration at minimum levels in solution. The finding that the rate is inversely related to the sulphide concentration is in line with the finding of Hilton et al. (1985) who demonstrated that sulphide inhibits biological processes.

General

This investigation showed that sulphate-reducing bacteria do not require strict anaerobic conditions in the bulk of the water, only in their micro-environment. They can tolerate oxygen, as long as other organisms present in the system consume it. The practical value of simultaneous sulphate and sulphide removal is that, during full-scale application, only one stage is required for removal of sulphate and partially sulphide; a conventional complete-mixed reactor can be used; sulphate can be removed in a consistent way to below 200 mg/ℓ (as SO_4) due to low sulphide concentrations in the water.

Pre-treatment combined with biological sulphate removal

Biological sulphate removal can be used for removal of sulphate from water, both under-saturated and over-saturated with respect to gypsum, as well as for treatment of acid water direct. It is, however, more cost-effective if sulphate, associated with the over-saturated fraction of gypsum, were removed through pre-treatment with $CaCO_3$ or lime in the CSIR integrated sulphate removal process (Fig. 3). This process comprises the following stages:

$CaCO_3$-neutralisation/iron(II)-oxidation

Powder $CaCO_3$ is used to raise the pH to 7. Iron(II)-oxidation is achieved through aeration in the same tank where neutralisation is applied, or biologically in a separate stage, up-steam of neutralisation, at low pH (2 to 3) (Eq. 7). Free acid in the feed water is neutralised, as well as free acid that is released when metals (Fe^{3+} and Al^{3+}) are precipitated as hydroxides. CO_2 generated during $CaCO_3$-neutralisation is utilised downstream for pH adjustment from 12 to 8 of the lime treated water, $CaCO_3$-precipitation and stripping of residual H_2S in the biological sulphate removal stage.

$$2Fe^{2+} + \tfrac{1}{2}O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \qquad (7)$$

Lime treatment/gypsum crystallisation/ $CaCO_3$-precipitation

Lime is used to raise the pH to 12 for precipitation of metals, such

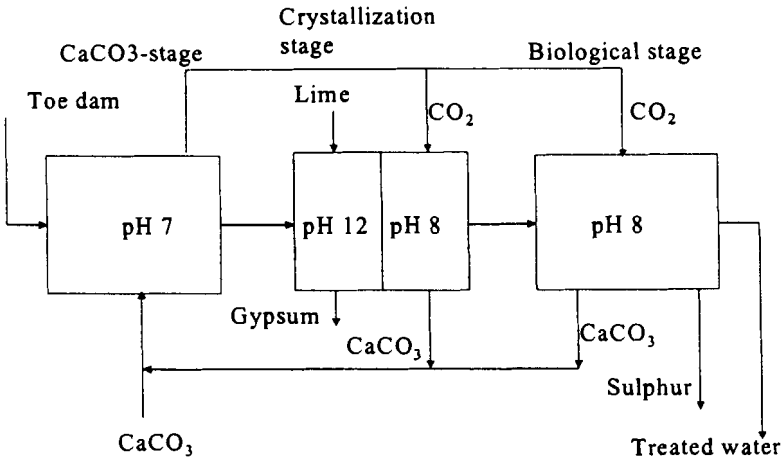


Figure 3
CSIR integrated process for step-wise sulphate removal

TABLE 2
Chemical composition when coal discard leachate is treated with the integrated sulphate removal process

Parameter	Stage				
	Untreated	$CaCO_3$	CaOH	$CaCO_3$	Biol.
pH	2.2	7.1	12.0	8.3	8.1
Sulphate (mg/ℓ SO_4)	9200	2410	1230	1220	205
Alkalinity (mg/ℓ $CaCO_3$)	0	0	1000	100	150
Calcium (mg/ℓ Ca)	377	639	903	543	140
Magnesium (mg/ℓ Mg)	202	200	3	3	3
Manganese (mg/ℓ Mn)	20	20	0	0	0
Aluminium (mg/ℓ Al)	106	3	2	0	0
Iron (II) (mg/ℓ Fe)	3040	4	0	0	0
Free acid (mg/ℓ $CaCO_3$)	1740	30	0	0	0
Total dissolved solids (mg/ℓ)	12945	3276	2738	1826	438

as magnesium and manganese, which do not precipitate in the $CaCO_3$-stage. Sulphate is also partially removed (to less than 1 200 mg/ℓ) due to gypsum crystallisation. Upon completion of gypsum crystallisation, the pH is adjusted with CO_2-gas, as described above. The produced $CaCO_3$ can be recycled to the first stage for neutralisation of the free acid, or sold as a by-product (such as a filler in various industrial applications).

Biological sulphate removal

The biological sulphate removal process forms an integral part of the integrated process. It also produces $CaCO_3$ (Eq. 8), which can be recycled to the $CaCO_3$-neutralisation stage. Residual H_2S, that is not converted to sulphur in the anaerobic reactor, is stripped off and converted to sulphur by contacting it with an iron (III)-solution. Iron (III) is produced biologically from iron (II) as described under the $CaCO_3$-neutralisation/Iron(II)-oxidation-stage.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O \qquad (8)$$

Table 3 shows the chemical composition when leachate from a coal discard dump is treated with the integrated sulphate removal process. It is noted that:

- Sulphate is removed from 9 200 mg/ℓ to 2 410 mg/ℓ, 1 230 mg/ℓ and 205 mg/ℓ (as SO_4) in the $CaCO_3$-neutralisation, gypsum crystallisation and biological sulphate removal stages, respectively.
- Free acid, iron and aluminium are completely removed in the $CaCO_3$-neutralisation stage.
- Magnesium and manganese removal and sulphate removal to less than 1250 mg/ℓ is achieved in the lime treatment/gypsum crystallisation stage.
- Sulphate can be removed to 200 mg/ℓ in the biological sulphate removal stage.

Table 3 shows the chemical cost when coal discard leachate is treated with various combinations of the stages of the integrated process. In Option A, only biological treatment is applied, while in Option B lime treatment and biological treatment is applied, and in Option C $CaCO_3$-treatment, lime treatment and biological treatment is applied. It is noted that the total chemical cost for Options A, B and C amount to R12.44/m³, R4.69/m³ and R2.94/m³ respectively. It is therefore cost-effective to remove as much as possible sulphate through gypsum crystallisation during pre-treatment with $CaCO_3$ and/or lime. Similarly, Table 4 shows the cost when magnesium-rich mine water, with a neutral pH, is treated with Options A and B. It is noted that the total chemical cost for Options A and B amount to R3.11/m³, R1.92/m³ respectively.

TABLE 3
Chemical cost when coal discard leachate is treated with various combinations of the stages of the integrated process

Stage	SO_4 conc. mg/ℓ	Dosage mg/ℓ	Price R/t	Cost R/m³	Purity %	Utilis. %	Usage g/g SO_4
Option A							
Untreated	9 000						
Biological (EtOH)	200	4 444	2 800	12.44	90	70	0.32
Total cost				**12.44**			
Option B							
Untreated	9 000						
CaOH	1 200	5 948	550	3.27	85	90	0.58
Biological (EtOH)	200	505	2 800	1.41	90	70	0.32
Total cost				**4.68**			
Option C							
Untreated	9 000						
$CaCO_3$	2 400	10 185	100	1.02	75	90	1.04
CaOH	1 200	915	550	0.50	85	90	0.58
Biological (EtOH)	200	505	2 800	1.41	90	70	0.32
Total cost				**2.93**			

TABLE 4
Chemical cost when magnesium sulphate-rich water is treated with various combinations of the stages of the integrated process

Stage	SO_4 conc. mg/ℓ	Dosage mg/ℓ	Price R/t	Cost R/m³	Purity %	Utilis. %	Usage g/g SO_4
Option A							
Untreated	2 400						
Biological (EtOH)	200	1 111	2 800	3.11	90	70	0.32
Total cost				**3.11**			
Option B							
Untreated	2 400						
CaOH	1 200	915	550	0.50	85	90	0.58
Biological (EtOH)	200	505	2 800	1.41	90	70	0.32
Total cost				**1.91**			

Conclusions

The following conclusions were drawn from this study:

- Sulphate and sulphide (partial) can be removed simultaneously due to co-existence of sulphate-reducing bacteria and sulphur oxidising bacteria.
- The volumetric sulphate reduction rate in a complete-mixed reactor with sucrose as an organic carbon and energy source amounts to 12.4 g SO_4/(ℓ.d). The corresponding specific sulphate reduction rate was 1.06 g SO_4/(gVSS.d).
- The removal rate of sulphate is influenced by the removal rate of the intermediate products. SO_4^{2-}(+6) is reduced to SO_3^{2-}(+4) at a slow rate, the latter to $S_2O_3^{2-}$ (+2) at a fast rate, the latter to S^{2-}(-2) at a medium rate and the latter to S (0) at a slow rate.
- The rate of biological sulphate removal is directly related to the square root of sulphate, COD and VSS concentrations and inversely related to the sulphide concentration.
- Sulphate, associated with the over-saturated fraction after treatment with $CaCO_3$ or lime, can be removed more cost-effectively through gypsum crystallisation, than biologically. In the integrated sulphate removal process ($CaCO_3$-neutralisation, lime treatment and biological stages), sulphate can be removed from 9 200 mg/ℓ (typical sulphate concentration of coal discard leachate) to 2 410 mg/ℓ, 1 230 mg/ℓ and 205 mg/ℓ (as SO_4) in the various stages respectively. The chemical cost with the integrated process amounts to R2.94/m³ versus R12.44/m³ when all the sulphate is removed biologically.

Similarly, the cost for treating magnesium sulphate-rich mine water amounts to R1.92/m³ for the integrated process, versus R3.11/m³ for biological treatment only.

References

BUISMAN CJN (1989). *Biotechnological Sulphide Removal with Oxygen*. Ph.D. Thesis, Agricultural University of Wageningen. 103 pp.

CORK DJ, JERGER DE and MAKA A (1986) Biocatalytic production of sulfur from process waste streams. *Biotechnology and Bioengineering Symp.* **16** 149-162.

CYPIONKA H, WIDDEL F and PFENNIG N (1985) Survival of sulfate reducing bacteria after oxygen stress and growth in sulfate free oxygen sulfide gradients. *FEMS Microbiol. Ecol.* **31** 39-45.

CYPIONKA H (2000). Oxygen respiration by *Desulfovibrio* species. *Annual Review of Microbiol.* **54** 827-848.

DU PREEZ LA, ODENDAAL JP, MAREE JP and PONSONBY M (1992) Biological removal of sulphate from industrial effluents using producer gas as energy source. *Environ. Technol.* **13** 875-882.

GREBEN HA, MAREE JP, SINGMIN Y and MNQANQENI S (2000a) Biological sulphate removal from acid mine effluent using ethanol as carbon and energy source. *Water Sci. Technol.* **42** (3-4) 339-344.

GREBEN HA, MAREE JP and MNQANQENI S (2000b) The comparison between sucrose, ethanol and methanol as carbon and energy source for biological sulphate reduction. . *Water Sci. Technol.* **41** (12) 247-253.

GREBEN HA, BOLOGO H and MAREE JP (2002a) The effect of different parameters on the biological volumetric and specific sulphate removal rates. *Water SA* (special WISA edn.) 33-37.

GREBEN HA, BOLOGO H and MAREE JP (2002b) Partial Biological Sulphide Oxidation in an Anaerobic Sulphidogenic Reactor. Proceedings Wisa Biennial Conference and Exhibition, Durban, South Africa, May 2002.

HILTON BL, OLESZKIEWICZ JA and OZIEMBLO ZJ (1985) Sulphate reduction as an alternative to methane fermentation of industrial wastes. Canadian Society for Civil Engineering Annual Conference, Saskatoon, SK. Canada.

MAREE JP and STRYDOM WF (1985) Biological sulphate removal from a packed bed reactor. *Water Res.* **19** (9) 1101-1106.

MAREE JP and HILL E (1989) Biological removal of sulphate from industrial effluents and concomitant production of sulphur. *Water Sci. Technol.* **21** 265-276.

MAREE JP, HULSE G, DODS D and SCHUTTE CE (1991) Pilot plant studies on biological sulphate removal from industrial effluent. *Water Sci. Technol.* **23** 1293-1300.

STANDARD METHODS (1985) *Standard Methods for the Examination of Water and Wastewater* (12th edn.), American Public Health Association, New York.

VAN HOUTEN RT (1996) Biological Sulphate Reduction with Synthesis Gas. Ph.D. Thesis, University of Wageningen. 39 pp.

VISSER A (1995) The Anaerobic Treatment of Sulphate Containing Waste Water. Ph.D. Thesis, University of Wageningen. 67 pp.

WEIJMA J (2000) Methanol as Electron Donor for Thermophilic Biological Sulfate and Sulfite Reduction. Ph.D. Thesis, Wageningen Agricultural University, Wageningen, The Netherlands.

CHAPTER 7. TREATMENT OF MINE WATER FOR SULPHATE AND METAL REMOVAL USING BARIUM SULPHIDE

Maree JP, Hlabela P, Nengovhela R, Geldenhuys AJ, Mbhele N, Nevhulaudzi T, and Waanders FB (2004) Treatment of Mine Water for Sulphate and Metal Removal Using Barium Sulphide, Mine Water and the Environment 23(4), 195 – 203.

Summary

The integrated barium sulphide process consists of: preliminary treatment with lime, sulphate precipitation as barium sulphate, H_2S-stripping, crystallization of $CaCO_3$, and recovery of barium sulphide. Our tests showed that during lime pre-treatment, sulphate was lowered from 2 800 mg/L to 1 250 mg/L by gypsum crystallization; metals were precipitated as hydroxides. The BaS treatment lowered sulphate to less than 200 mg/L. Sulphide was lowered from 333 to less than 10 mg/L (as S) in the stripping stage, using CO_2 gas for stripping. The stripped H_2S-gas was contacted with Fe (III)-solution and converted quantitatively to elemental sulphur. 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. Fe (II), after sulphur production, was re-oxidized to Fe (III) using an electrolytic step. The running cost of the barium sulphide process is R2.12/m^3 US$1 = SAR6.5, 2004) for the removal of 2 g/L of sulphate.

Mine Water and the Environment (2004) 23: 195–203 © IMWA Springer-Verlag 2004

Technical Article

Treatment of Mine Water for Sulphate and Metal Removal Using Barium Sulphide

J. P. Maree[1], P. Hlabela[1], R. Nengovhela[1], A. J. Geldenhuys[1], N. Mbhele[1], T. Nevhulaudzi[1], and F. B. Waanders[2]

[1]Business Unit of Water, Environment, and Forestry Technology, CSIR, PO Box 395, Pretoria, South Africa; [2]School of Chemical and Minerals Eng, North West Univ, Potchefstroom, 2531, South Africa; corresponding author's e-mail: jmaree@csir.co.za

Abstract. The integrated barium sulphide process consists of: preliminary treatment with lime, sulphate precipitation as barium sulphate, H_2S-stripping, crystallization of $CaCO_3$, and recovery of barium sulphide. Our tests showed that during lime pre-treatment, sulphate was lowered from 2 800 mg/L to 1 250 mg/L by gypsum crystallization; metals were precipitated as hydroxides. The BaS treatment then lowered sulphate to less than 200 mg/L. Sulphide was lowered from 333 to less than 10 mg/L (as S) in the stripping stage, using CO_2 gas for stripping. The stripped H_2S-gas was contacted with Fe (III)-solution and converted quantitatively to elemental sulphur. 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. Fe (II), after sulphur production, was re-oxidized to Fe (III) using an electrolytic step. The running cost of the BaS process is R2.12/m^3 (US$1 = SAR6.5) for the removal of 2 g/L of sulphate.

Key words: Barium sulphide; gypsum; sulphate removal; water treatment; sulphide stripping

Introduction

Mining is a significant contributor to water pollution, due primarily to pyrite oxidation, which generates potentially high levels of acidity, metals, and sulphate. In South Africa, the large volumes of mine water generated make the problem serious; 200 ML/d of mine water flows in Gauteng, while 50 ML/d discharges into the Olifants River Catchment in Mpumalanga. South Africa requires sulphate concentrations to be less than 500 mg/L. Several processes can be considered for sulphate removal, e.g., biological sulphate removal, SAVMIN (ettringite), ecoDose, reverse osmosis, and electrodialysis. Barium can also be used for sulphate removal and has certain advantages: sulphate can be removed to specific values due to the low solubility of barium sulphate ($BaSO_4$) and the soluble barium salt, barium sulphide (BaS), can be recovered.

Kun (1972) studied the removal of sulphate with barium carbonate ($BaCO_3$) and obtained good results. However, he identified three problems: a long retention time requirement, high concentrations of soluble barium in the treated water when more $BaCO_3$ was dosed than stoichiometrically required, and the high cost of the $BaCO_3$. Volman (1984) and Maree (1989) overcame the cost problem by demonstrating that $BaSO_4$ could be reduced efficiently and economically with coal under thermic conditions to produce BaS. This compound can be used directly on site or converted to $BaCO_3$. Wilsenach (1986) demonstrated economic viability by calculating the cost of producing BaS from $BaSO_4$. Trusler et al. (1988) developed a $BaCO_3$ method using a two-stage fluidised bed reactor system to overcome the other problems identified by Kun (long retention time and high Ba levels in the treated water). However, the $BaCO_3$ became inactive when coated with metal hydroxide precipitates, which made it unsuitable for most mine water. Maree et al. (1989) also noted a problem in separating $BaSO_4$ and $CaCO_3$, which co-precipitate.

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

- Lime pre-treatment for partial sulphate removal;
- Removal of sulphate as $BaSO_4$ to below 200 mg/L by BaS treatment;
- H_2S-stripping with CO_2-gas;
- Stripping of CO_2 and $CaCO_3$ precipitation; and
- Recovery of BaS from the produced $BaSO_4$.

The specific aims were to:

- Demonstrate that sulphate can be lowered to less than 200 mg/l with BaS treatment;
- Determine optimum conditions for the following process-stages: partial SO_4 removal through lime pre-treatment, reducing $BaSO_4$ to BaS, and H_2S-stripping and processing; and
- Estimate the running cost of the process.

Materials and Methods

Feedstock

Mine water from Navigation Section of Landau Colliery was used as feed water containing 2 650

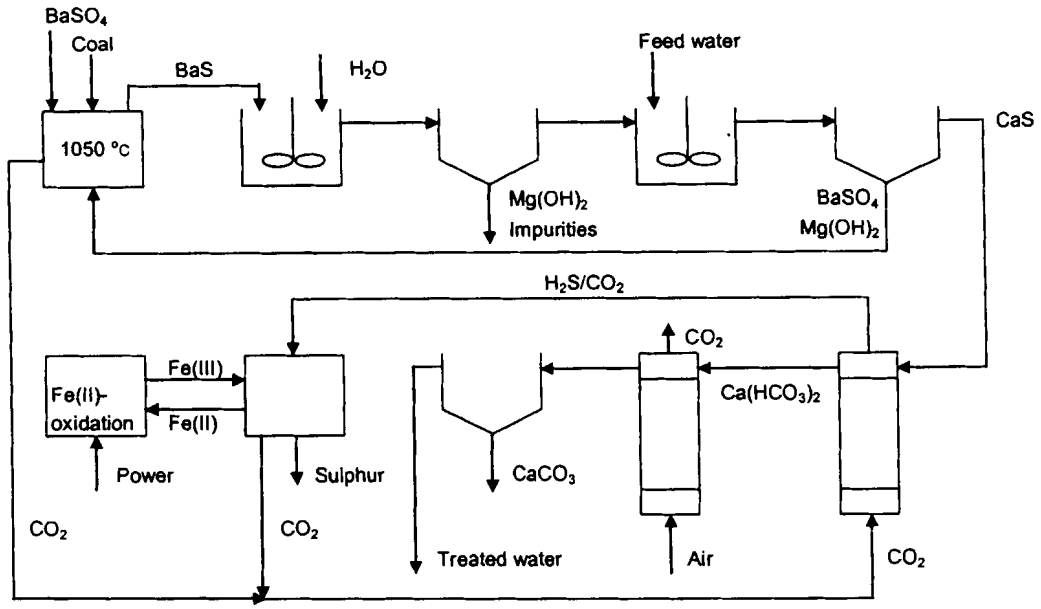


Figure 1. Process flow diagram for the barium sulphide process (pre-treatment with lime not shown)

mg/L SO_4 and 167 mg/L Mg (complete chemical analyses shown later) during continuous pilot-scale studies. Lime (Lime Distributors) and BaS (G&W Base Minerals) were used for pH adjustment and sulphate removal, respectively. For the H_2S-stripping studies, synthetic sulphide-rich feed water with sulphide concentrations between 700 and 800 mg/L was used. CO_2 gas (supplied by Afrox) was used for H_2S-stripping. A $Fe_2(SO_4)_3$ solution (11 g Fe/L) was used for absorption of the stripped H_2S-gas. During the thermic studies, chemically pure $BaSO_4$ and industrial grade $BaSO_4$ (supplied by G & W Base Minerals) were used for the BaS recovery studies.

Equipment

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

A packed bed reactor and a venturi system were used for H_2S-stripping and H_2S-absorption into an Fe (III) solution, using configurations A (Figure 2) and B (Figure 3) respectively. 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 Fe (III) solution at a pH of 2.5, to produce elemental sulphur (Reaction 1). The Fe (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 in batch mode. CO_2-rich gas was incorporated into the solution via a venturi system, hence contacting it with the sulphide-rich water for H_2S-stripping (stripping stage). The stripped H_2S-rich gas was passed through a packed bed-reactor to which the Fe (III) solution was continuously fed for sulphur production.

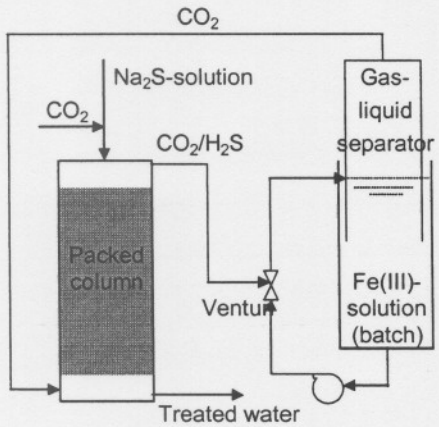
The packed column consisted of a 0.8-m randomly packed bed, with 25-mm Pall-rings used as packing material. A 240-mm diam. Perspex cylinder (adsorption) was used and Perspex plates were used to support the packing and to aid in flow distribution in the column. A Perspex plate with evenly distributed 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 Fe (III) (configuration 1) or 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 which it was pumped at a set flow rate with a peristaltic pump at NTP (normal temperature and pressure) to the H_2S-stripping stage.

General Experimental Procedures

Pre-treatment and BaS-treatment were investigated in both continuous and batch studies. In the continuous

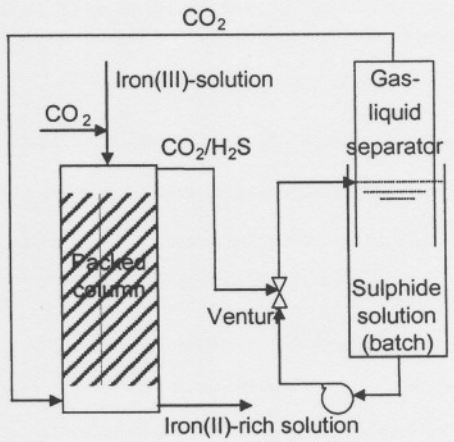
Table 1. Volume and dimensions of various reactors

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



Configuration A

Figure 2. H_2S-stripping and processing



Configuration B

Figure 3. H_2S-stripping and processing

experiments, feed water (2 650 mg/L SO_4, 83 mL/min), lime slurry (10%, 3 mL/min), BaS slurry (57.7 g/L, 3 mL/min), and a flocculant (Flocculant 3095) (3 mL/min) were fed to the system shown in Figure 2. Sludge was recycled from the underflow 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 were carried out on the BaS treated water for H_2S-stripping and softening. H_2S-stripping was achieved by bubbling CO_2 through the water; softening was achieved by dosing the water with 5 g/L $CaCO_3$ and stripping the CO_2 with air.

H_2S stripping and processing were investigated in configuration A (Na_2S fed continuously to the packed bed-reactor and contacted with Fe (III) solution 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 Fe (II) concentration was monitored in the Fe (III) solution that was handled in batch mode.

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

Thermal studies involved mixing and reacting $BaSO_4$ (industrial grade and pure $BaSO_4$) and coal at elevated temperatures in a tube or muffle furnace for various reaction periods. Solid samples were collected and analyzed for mass loss, sulphide content, and ability to remove sulphate.

Experimental Program

The BaS-treatment stage feed water and treated water were analyzed (Table 2) and the following parameters were investigated in the subsequent stages:

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 Fe(III) solution

Thermic studies stage

- C: $BaSO_4$-ratio (2, 2.5, and 3)
- Type of furnace (Tube and Muffle)
- Temperature (900°C to 1100°C)
- Reaction time (15, 30, 60, and 120 min).

Analytical

Samples were collected regularly and filtered through Whatman No 1 filter paper. Sulphate, sulphide, alkalinity, calcium, Fe (II), mixed liquor suspended solids, volatile suspended solids, acidity, and pH determinations were carried out according to standard procedures (APHA 1985). Calcium was assayed using atomic absorption spectrophotometry. Sulphide (a product from the thermic studies) was determined by mortaring the product, and analyzing it using the iodine method in a 0.5 g/100 mL BaS solution.

Results and Discussion

Water Quality

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

- During pre-treatment with lime, sulphate decreased from 2 650 mg/L to 1 250 mg/L, reflecting the solubility product of gypsum. Magnesium and other metals were completely removed.
- During BaS-treatment, sulphate was lowered to the stoichiometric BaS-limit (1 000 mg/L).
- During H_2S-stripping with CO_2 gas, sulphide was lowered from 320 to < 20 mg/L (Figure 4).
- During the softening stage, 890 mg/L of $CaCO_3$ (993 – 103 mg/L $CaCO_3$) precipitated due to CO_2 stripping with air (Figure 5). The pH increased from 5.7 to 7.2 as the CO_2 was stripped, resulting in $CaCO_3$ precipitation (since the solubility of $CaCO_3$ decreases with increasing pH).

H_2S Stripping and Processing Stage

Sulphide can be removed by CO_2 stripping to less than 20 mg/L (Figure 4). 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 by passing the sulphide solution through two stages in series at a CO_2/Na_2S feed load of 1.4 g CO_2/g S, sulphide was lowered from 834 to 434 mg/L in stage 1, and from 376 to 77 mg/L (as S) in stage 2 (Table 3). By providing a third stage, sulphide could have been decreased 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 Fe (II)

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

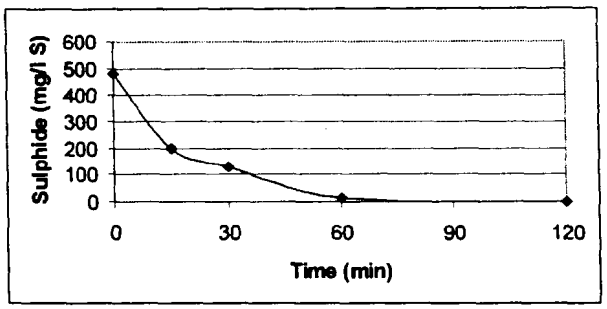


Figure 4. H_2S-stripping with CO_2

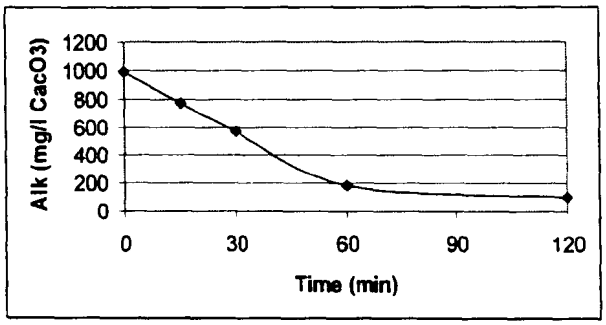


Figure 5. CO_2 stripping with air and $CaCO_3$ precipitation

produced/load of sulphide removed (3.65 g Fe/g S (average of 3.60 and 3.70) versus 3.49). More than one stripping stage was needed for complete sulphide removal as less CO_2 was dosed than theoretically required (1.75 g CO_2/g S (average of 1.70 and 1.79) versus 2.75). The theoretical ratios for load of CO_2 consumed/load of sulphide removed (2.75) and load of Fe (II) produced/load of sulphide removed (3.49) were calculated from Reactions 2 and 3.

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

$$2CO_2 + S^{2-} + 2H_2O \rightarrow 2HCO_3^- + H_2S \quad (3)$$

Table 4 shows the effect of the Na_2S feed rate on the sulphide removal. Better sulphide removal was achieved with a lower Na_2S feed rate (higher HRT). At a feed rate of 0.5 L/min (HRT = 59 min), 217 mg/L of sulphide was removed, 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), even though the actual value of dCO_2/dNa_2S of 14.53 was higher than the theoretical value of 2.75. This negative result can be ascribed to the fact that CO_2 was not completely utilized due to too little contact time with the Na_2S-solution. In the next experiments, this problem was solved by passing the Na_2S/CO_2 mixture through a 5 m pipe with a diameter of 20 mm (6.3 L volume). At a feed rate of 1 L/min, the hydraulic retention time in the 5 m pipe amounted to 6.3 min.

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.

Table 3. Sulphide removal in two stages in series at 100% CO_2, a Na_2S feed rate of 0.90 L/min, a HRT of 32.7 min, and a gas recycle rate of 22.9 L/min

Parameter	Stage1	Stage2
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
Sulphide in feed (mg/L S)	834	376
Sulphide in treated water (mg/L S)	434	77
Sulphide removed (mg/L)	400	299
pH in feed	9.05	7.0
pH in treated water	7.02	6.2
dCO_2/dNa_2S ratio (g CO_2/g S)		
Theoretical	2.75	2.75
Actual	1.70	1.79
$dFe(II)/dH_2S$		
Theoretical	3.49	3.49
Actual	3.60	3.70

Table 4. Effect of retention time (Na_2S feed rate) on sulphide removal, at 100% CO_2, and a gas recycle rate of 18.1 L/min

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
HRT (min)	14.7	29.5	58.9
Sulphide in feed (mg/L S)	742	704	688
Sulphide, treated water (mg/L S)	588	496	470
Sulphide removed (mg/L)	153.6	208	217.6
pH in feed water	12.18	12.15	12.17
pH in treated water	9.00	8.41	8.47
dCO_2/dNa_2S ratio (g CO_2/g S)			
Theoretical	2.75	2.75	2.75
Actual	14.53	7.28	5.37
$dFe(II)/dH_2S$			
Theoretical	3.49	3.49	3.49
Actual	1.80	0.98	8.90

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 2.75 (Reaction 3). This demonstrates that complete sulphide removal can be achieved by dosing excess CO_2, compared to what is stoichiometrically required. In this experiment, 30% excess CO_2 was dosed. By dosing excess CO_2, H_2S-stripping is favoured as the pH is reduced to less than 7 due to free CO_2 in solution. The rate of sulphide stripping also increase with lower pH values as the ratio of H_2S/S_T ($S_T = S^= + HS^- + H_2S$) increase with decreasing pH values. At pH 7 and less, a greater fraction of sulphide species is in the H_2S form.

Table 5. Effect of the CO_2 feed rate on sulphide removal with 29.5% CO_2, an HRT of 100 min, a Na_2S feed rate of 1 L/min, and a gas recycle rate of 18.1 L/min

Parameter			
CO_2 feed rate (L/min)	0.19	0.40	0.83
CO_2/Na_2S feed ratio (g CO_2/g S)	0.78	1.68	3.46
Sulphide in feed (mg/L S)	476	464	473
Sulphide after pipe (mg/L S)	378	265	73.6
Sulphide, treated water (mg/L S)	134	25	0
Sulphide removed (mg/L)	342	438	473
pH in feed water	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	2.75	2.75	2.75
Actual	1.02	1.77	3.46
$dFe(II)/dH_2S$			
Theoretical	3.49	3.49	3.49
Actual	0.88	1.13	1.91

Excess CO_2 gas would be available in many applications: during barium treatment, CO_2 is produced at the rotary kiln where BaS is recovered from $BaSO_4$; with the biological sulphate removal process, CO_2-gas is produced by the heating unit; during limestone neutralization of acid water, CO_2 is produced due to $CaCO_3$ dissolution. The CO_2 in these CO_2-rich gasses can be utilised for H_2S-stripping by contacting the CO_2-rich gas with the sulphide rich stream in a spray tower or a packed-bed reactor.

- Table 6 shows the effect of the CO_2 concentration on sulphide removal. By increasing the CO_2 concentration from 20 to 100%, sulphide removal was increased from 278 to 387 mg/L (as S). In the case where 100% CO_2 was dosed, the theoretical and actual values for dCO_2/dNa_2S were similar (2.75 versus 2.53).

- Table 7 shows the effect of the gas recycle rate on sulphide removal. Increasing the gas recycle rate from 9.1 to 19.6 L/min improved sulphide removal from 304 to 438 mg/L. In this experiment, sulphide was also not completely removed as the dCO_2/dNa_2S feed ratio was only slightly higher than what is stoichiometrically required for the second and third runs and even less than that for the first run.

- 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 Fe (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 also evaluate the suitability of the system 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

Table 6. Effect of CO_2 concentration on sulphide removal with an HRT of 29.5 L/min, a Na_2S feed rate of 1 L/min, and a gas recycle rate of 18.1 L/min

Parameter			
CO_2-concentration (%)	20	53	100
CO_2/Na_2S feed ratio (g CO_2/g S)	1.37	1.61	1.46
CO_2 feed rate (L/min)	0.51	0.56	0.49
Air feed rate (L/min)	2	0.5	0
Sulphide in feed (mg/L S)	739	678	665
Sulphide after pipe (mg/L S)	640	538	486
Sulphide, treated water (mg/L S)	460	393	278
Sulphide removed (mg/L)	278	284	387
pH in feed water	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	2.75	2.75	2.75
Actual	3.60	3.86	2.49
$dFe(II)/dH_2S$			
Theoretical	3.49	3.49	3.49

Table 7. Effect of gas recirculation rate on sulphide removal at a Na_2S feed rate of 1 L/min, 100% CO_2, and an HRT of 29.5 min

Parameter			
Gas recycle rate (L/min)	19.6	13.1	9.1
CO_2-concentration (%)	19.63	13.09	9.06
CO_2/Na_2S feed ratio (g CO_2/g S)	0.78	1.34	1.17
CO_2 feed rate (L/min)	0.26	0.48	0.41
Sulphide in feed (mg/L S)	665	697	681
Sulphide after pipe (mg/L S)	666	374	377
Sulphide in treated water (mg/L S)	227	371	304
Sulphide removed (mg/L)	438.4	326.4	12.34
pH in feed water	12.10	12.30	7.36
pH after pipe	7.55	7.55	7.97
pH in treated water	7.81	7.64	
dCO_2/dNa_2S ratio (g CO_2/g S)			
Theoretical	2.75	2.75	2.75
Actual	1.19	2.88	2.70
$dFe(II)/dH_2S$			
Theoretical	3.49	3.49	3.49
Actual	1.76	2.23	3.73

for sulphide stripping in batch mode, and the packed bed-reactor was used for H_2S-absoption into the Fe (III) solution under continuous conditions. Table 8 and Figure 6 show the effect of Fe (III) feed rate on sulphide removal. It was noted that:

- Better sulphide removal was achieved by increasing the Fe (III) feed rate. This is ascribed to partial absorption of H_2S at low Fe (III) feed rates in the closed circuit of configuration 2, and indicates that the packed bed reactor does not function as well as the venturi system for H_2S absorption into the Fe (III) solution.

- The experimental (actual) $dFe(II)/dH_2S$ ratio was similar to the theoretical value of 3.49 (Reaction 2). This shows that all of the Fe (III) introduced into the packed bed reactor was consumed by H_2S-absorption.

Table 8. Effect of the Fe (III) flow rate on sulphide removal, in tests where the gas recycle rate was 18.1 L/min

Parameter				
Fe^{3+}-feed rate (L/min)	1.00	1.00	3.00	4.00
Time (min)		Sulphide (mg/L S)		
	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)		pH		
0	11.35	12.13	12.84	12.9
15	10.19	11.79	10.04	8
30	8.44	10.24	8.03	11.1
45	7.65	8.93	7.04	6
60	7.41	8.05	7.23	8.34
75	7.23	7.83	7.13	7.70
90		7.74	7.08	7.30
		dCO_2/dNa_2S ratio (g CO_2/g S)		
Theoretical	2.75	2.75	2.75	2.75
Actual	8.40	8.06	8.02	7.99
		$dFe(II)/dH_2S$		
Theoretical	3.49	3.49	3.49	3.49
Actual	2.87	3.49	3.15	3.12

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. The venturi device was more efficient than the packed bed reactor, which we ascribed to the high pressure (300 kPa) and the high velocity (50 m/sec) of gas and liquid particles. Based on this observation, it was decided that a Turbulator, which consists of a motor that directly (no gear box) drives a disc via a hollow shaft, should be used during scale-up. 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 (diameter = 0.15 m; rpm = 2 000).

Thermal Studies

The cost of the BaS process is largely determined by the cost of recovering BaS from $BaSO_4$. Barium sulphide is produced by reacting $BaSO_4$ with coal at a temperature of 900°C and higher.

$$BaSO_4 + 2C \rightarrow BaS + 2CO_2 \qquad (4)$$

Table 9 shows the effect of various parameters on BaS yield during the thermic conversion. Note that:

- The conversion efficiency reduced with time when a Muffle furnace was used (Experiment 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 reacts with oxygen at the high temperature to

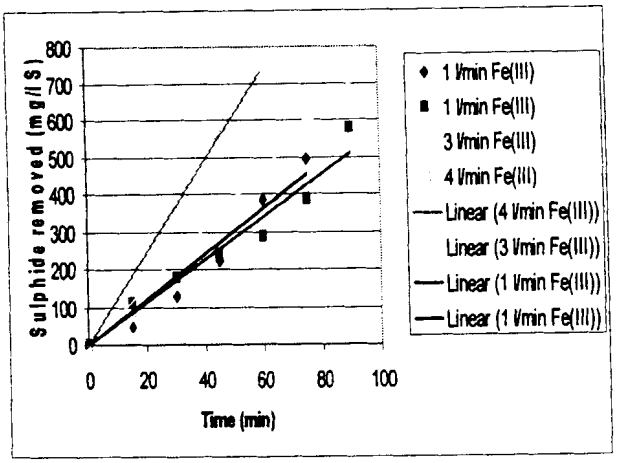


Figure 6. Effect of Fe(III) flow rate on sulphide removal

form $BaSO_4$. Therefore, all further studies (Experiments 2-8) were carried out in a tube furnace. The air was also purged with nitrogen to eliminate oxidizing conditions.

- A short reaction time (15 min) is sufficient to obtain a high yield of BaS at a temperature of 1050 °C (Experiment 2). Figure 7a shows the conversion of $BaSO_4$ to BaS as a function of time.
- The reaction starts at 900°C and its rate increases with temperature. At 1100°C, a conversion of 100% was achieved within 15 minutes (Experiment 3, Figure 7b).
- The minimum C/$BaSO_4$ mole ratio required for complete reduction is 2, which indicates that the reaction (Experiment 4, Figure 7c) proceeds according to equation 4.
- Better values are achieved with activated carbon than with coal, which may be due to impurities in the coal.
- Both analytical grade and industrial grade $BaSO_4$ (supplied by a supplier) provided good yields of BaS (Experiment 7).
- $Mg(OH)_2$ does not interfere with the reduction reaction of $BaSO_4$ to BaS (Experiment 8).

The methods used for conversion measurements (mass loss, sulphide and sulphate precipitation) compare well. The sulphide values were lower than the mass loss values, which can be ascribed to sulphide losses during dissolution, which was confirmed by a sulphide odour. The product was also tested for the ability to remove sulphate (Experiment 5). Although the sulphate method is not as accurate as the other methods, a value of the same order was achieved.

Running Cost

The running cost of the bas process amounts to R2.12/m^3 (U.S. $1 = South African Rand 6.50) for the removal of 2 g/L of sulphate (table 10). This excludes the value of the water (R2/m^3) and the by-products,

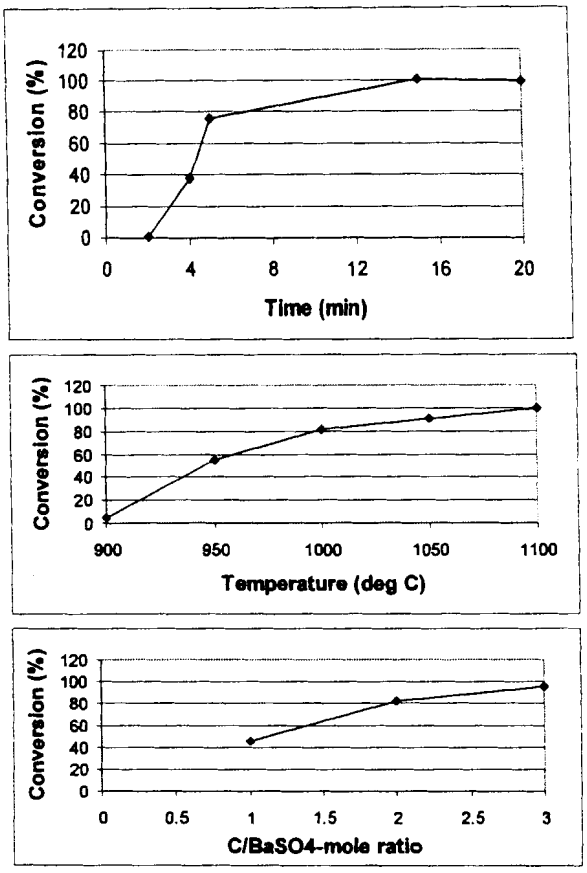


Figure 7. Effect of time, temperature, and C/$BaSO_4$ molar ratio on the conversion of $BaSO_4$ to BaS

sulphur (R0.30/m^3) and calcium carbonate (R3.33/m^3). The cost of CO_2 that is needed for H_2S-stripping is included in the running cost. CO_2 is recovered from the off gas from the kiln. Coal is used as energy source as well as the reducing agent.

Conclusions

1. During lime treatment, sulphate was lowered from 2 800 mg/L to 1 20 mg/L due to gypsum formation. Metals were precipitated as hydroxides. During BaS treatment, sulphate was lowered to less than 200 mg/L by $BaSO_4$ precipitation.

2. Sulphide was decreased from 333 to less than 10 mg/L (as S) in the stripping stage, using CO_2 gas.

3. The stripped H_2S-gas was contacted with Fe (III) solution and converted quantitatively to elemental sulphur.

4. 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.

5. Fe (II), after sulphur production, was re-oxidized to Fe (III) using an electrolytic step.

6. The running cost of the barium sulphide process for the removal of 2 g/L of sulphate totalled R2.12/m^3.

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

Expt./Parameter	Value	Conversion (%)			Experimental conditions						
		Mass loss	Sulphide analysis	SO_4 precip.	Time (min)	Temp °C	C/$BaSO_4$	Carbon	$BaSO_4$	$Mg(OH)_2$/ $BaSO_4$	Furnace
1. Time (min)	15	75.3			15	1050	3	Coal	Pure	0	Muffle
	30	63.8			30	1050	3	Coal	Pure	0	Muffle
	60	60.6			60	1050	3	Coal	Pure	0	Muffle
2. Time (min)	2	1.1	0		2	1050	3	Activated	Industrial	0	Tube
	4	37.5	35.5		4	1050	3	Activated	Industrial	0	Tube
	5	75.6	74.4		5	1050	3	Activated	Industrial	0	Tube
	15	101	96.3		15	1050	3	Activated	Industrial	0	Tube
	20	99.6	94.6		20	1050	3	Activated	Industrial	0	Tube
3. Temp. (°C)	900	5			20	900	3	Activated	Industrial	0	Tube
	950	54.7	50.7		20	950	3	Activated	Industrial	0	Tube
	1000	81.6	79.4		20	1000	3	Activated	Industrial	0	Tube
	1050	90.4	86.5		20	1050	3	Activated	Industrial	0	Tube
	1100	100	96.3		20	1100	3	Activated	Industrial	0	Tube
4. C/$BaSO_4$- molar ratio	1	45.5	40.1		20	1050	1	Activated	Industrial	0	Tube
	2	82.1	77.7		20	1050	2	Activated	Industrial	0	Tube
	3	95.3	82.8		20	1050	3	Activated	Industrial	0	Tube
5. Carbon	Activated	101.6	94.6		30	1050	3	Activated	Industrial	0	Tube
	Coal	94.6	93	90	30	1050	3	Coal	Industrial	0	Tube
6. Carbon	Activated	89.3	82.8		20	1050	3	Activated	Industrial	0	Tube
	Coal	84.4	79.4		20	1050	3	Coal	Industrial	0	Tube
7. Barium	Pure	107.1	99.7		30	1050	3	Activated	Pure	0	Tube
	Industrial	101.6	94.6		30	1050	3	Activated	Industrial	0	Tube
8.$Mg(OH)_2$/ $BaSO_4$	0	89.3	86.2		20	1050	3	Activated	Industrial	0	Tube
	0.7	93.2	78.4		20	1050	3	Activated	Industrial	0.7	Tube
	1.7	97.6	76		20	1050	3	Activated	Industrial	1.7	Tube
	4.3	96.9			20	1050	3	Activated	Industrial	4.3	Tube

Table 10. Running costs of the barium sulphide process and value of the products (water, sulphur and calcium carbonate)

Item	Cost (R/m^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
$BaSO_4$ 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 oxidation (kg/m^3)	2.33
Energy requirement:	
$BaSO_4$ reduction (MJ/kg)	2.03
Iron oxidation (kW/kg Fe)	1.07
Energy requirement:	
$BaSO_4$ reduction (kW/m^3)	2.94
Iron oxidation (kW/m^3)	2.50
Electricity cost (R/kWh)	0.16
Energy cost (R/m^3)	
Kiln	0.47
Iron oxidation	0.40
Drives, pumps, etc.	0.20
Labour	0.20
Total running cost (R/m^3)	2.12
Products	**Value**
Water value (R/m^3)	2.00
Sulphur (R/m^3)	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 (R/m^3)	5.63

Acknowledgements

We sincerely thank the following organizations for financial support: The National Research Foundation, which provided funding for CSIR projects on neutralization and sulphate removal through their Technology and Human Resources for Industry Programme; and the CSIR, who provided substantial financial support for the research programme.

References

APHA (1985) Standard Methods for the Examination of Water and Wastewater. 12th Edit, American Public Health Assoc, NY

Kun LE (1972) A report on the reduction of the sulphate content of acid mine drainage by precipitation with barium carbonate. Internal report, Anglo American Research Laboratories, Project D/3/W/1

Maree JP, Bosman DJ, Jenkins GR (1989) Chemical removal of sulphate, calcium and heavy metals from mining and power station effluents. Proc, 1st Biennial Conf of the Water Inst of Southern Africa, Cape Town

Maree, JP (1989) Treatment of water (BaS process), Republic of South Africa (Patent No. 90/1889), 28 November), Canada (Patent No. 2 012 266 8) and United States of America (Patent No. 5,035,807).

Trusler GE, Edwards RI, Brouckaert CJ, Buckley CA (1988) The chemical removal of sulphates. Proc, 5th National Mtng of the S.A. Institute of Chemical Engineers, Pretoria, W3-0 – W3-11

Volman R (1984) The use of barium sulphide to remove sulphate from industrial effluents. M.Sc. Thesis (Chem. Eng), Univ of Stellenbosch

Wilsnach IT (1986) Cost estimate for barium sulphate reduction. Internal report, Div of Water Technology, CSIR, Project 620/2616/6

Received June 17, 2004; revised manuscript submitted Sept. 30, 2004; accepted Oct. 24, 2004

CHAPTER 8. OPTIMIZING THE EFFLUENT TREATMENT AT A COAL MINE BY PROCESS MODELLING

Maree JP, Günther P, Strobos G and Waanders FB (2004) Optimizing the Effluent Treatment at a Coal Mine by Process Modelling, Mine Water and the Environment 23(2): 87 - 90.

Summary

The water network of a coal mine was audited and simulated by an interactive steady state model. The findings from this investigation were used to optimise the mine's water management strategy. Simulation of the interactions showed that $CaCO_3$ powder can be used as an alternative to lime for neutralization of acid water at a cost saving of 56%. Gypsum crystallization in the primary neutralization and coal processing plants reduced sulphate concentrations by 30% and 60%, respectively. During separate treatment of coal discard leachate and the less polluted streams, the capital cost for a neutralization/gypsum crystallization plant amounts to R3.0 million, compared to R10.3 million during combined treatment. Only slightly less (8.9 t/d versus 9.5 t/d) sulphate removal was achieved during separate treatment. The over-saturation index (OSI) value can be controlled effectively by removing sulphate from the feed water for coal processing. Sulphate had to be lowered to 350 mg/L in a flow of 222 m^3/h to obtain an OSI value less than 1. The capital cost of a 222 m^3/h biological sulphate removal plant is estimated at R21.8 million (R4.1 million/(ML/d)) and the running cost at R13.7 million/a (R4.10/m^3). Pre-washing of the coal will reduce capital and running costs.

Technical Communication

Optimizing the Effluent Treatment at a Coal Mine by Process Modelling

J. P. Maree[1], P. Günther[2] G. Strobos[1] and F. B. Waanders[3]

[1]CSIR, Water, Environment and Forestry Technology, P O Box 395, Pretoria 0001, South Africa; [2]S A Coal Estate, P O Box 2851, Witbank, 1035, South Africa; [3]Director, School of Chemical and Minerals Engineering, North West Univ (Potchefstroom campus), Potchefstroom, 2531, South Africa; corresponding author's e-mail: jmaree@csir.co.za

Abstract: The water network of a coal mine was audited and simulated by an interactive steady state model and the results were used to optimise the mine's water management strategy. Simulation of the interactions showed that calcium carbonate powder could be used as an alternative to lime for neutralization of acid water at a reagent cost saving of 56%. Gypsum crystallization would reduce sulphate concentrations in the neutralization plant by 30% and in the coal processing plant by 60%. The capital cost for a neutralization/gypsum crystallization plant for separate treatment of coal discard leachate and less polluted streams would cost 3.0 million Rand (R), compared to R10.3 million for combined treatment. Only slightly less (8.9 t/d vs. 9.5 t/d) sulphate removal would be achieved during separate treatment. The over-saturation index (OSI) value can be controlled effectively by removing sulphate from the feed water for coal processing. Sulphate has to be lowered to 350 mg/L in a flow of 222 m^3/h to obtain an OSI value less than 1. The capital cost of a 222 m^3/h biological sulphate removal plant was estimated at R21.8 million (R4.1 million/(ML/d)); the running cost was estimated at R13.7 million/a (R4.10/m^3). Pre-washing of the coal would reduce capital and running costs.

Key words: stream segregation; sulphate removal; water-network simulation

Background

Acid mine water has to be treated to make it suitable for industrial use or for discharge into public streams. Lime treatment is normally used for neutralization and metal removal. If required, desalination processes such as biological sulphate removal or membrane techniques may be used. The limestone neutralization and iron oxidation process (Maree et al. 2004a) was developed as an alternative to conventional lime treatment. This process reduces alkali cost by more than 50%. The first full-scale plant, with a capacity of 80 m^3/h, was constructed at BCL, Botswana (Maree 2004b). A second limestone neutralization plant was constructed at the Navigation Section of the Landau Colliery, Witbank, South Africa, by Anglo Coal. The latter mine was in the process of implementing a water management strategy. The objectives of the strategy included: providing water fit for coal beneficiation plant use with limited corrosion and scaling potential; mitigation of the environmental impacts associated with mine water discharges; closure of mine water circuits; and maximum re-use and utilisation of effluent streams.

Modelling is useful in selecting the most suitable water management strategy (van Tonder et al. 2000). The Toe Seep (coal discard leachate) neutralization project had been identified as the next component of the overall water management strategy to be constructed. A model was used to determine if the limestone neutralization process was appropriate for the Navigation site and to determine the:

- Degree of gypsum crystallization associated with the existing system in the primary neutralization and coal processing plants;
- The effect of gypsum crystallization on the gypsum saturation index after separate and joint treatment of Toe Seep water and less polluted streams;
- The effect of gypsum crystallization on the effluent from the coal processing plant when a side-stream of the flow from the thickener to the coal processing plant is treated;
- Additional sulphate removal required to ensure that the water in the coal processing plant is not over-saturated with respect to gypsum;
- Amount of sulphate that could be removed through pre-washing of the acid coal; and
- Capital and running costs associated with the various treatment options.

Model Description

A water flow and chemical mass balance model was developed that made provision for the following stages: the existing neutralization plant, a new gypsum crystallization plant located after the existing neutralization plant, a new Toe Seep plant, with or without gypsum crystallization, a biological sulphate removal plant, a coal processing plant, a sludge disposal pond, and a waste disposal area for fine coal and the coal discard. The various input parameters were the:

- Flow rates at the neutralization plant, discard leachate neutralization plant, sulphate removal plant, thickener underflow to discard dump, and penstock return water;
- Chemical composition of the feed waters to the neutralization plant, discard leachate, and penstock.
- Chemical composition of treated water from the sulphate removal plant;
- Percentage sulphate removal through gypsum crystallization in the stages where gypsum forms (the discard dump, the coal processing plant, and the crystallization treatment plants); and
- Alkali consumption (in the neutralization plant and in the coal processing plant).

The output parameters were: flow rate, chemical composition, gypsum saturation level of all other streams, and capital and running costs.

The model was based on the following principles:

- Electron neutrality: the molar equivalents of the cations (acidity, Fe (II), Fe (III), calcium, and magnesium) had to equal that of the anions (sulphate);
- Steady state equilibrium at each point; and
- OSI = $[SO_4]_{solution}/[SO_4]_{equilibrium}$

where: [ ] = concentration in mole equivalent/L, OSI represents the over-saturation index, and $[SO_4]_{equilibrium}$ = 1500/48 + $[Mg^{2+}]$ (determined empirically).

Results

In addition to the existing situation, we investigated: separate and combined neutralization and gypsum crystallization of Toe Seep water and less polluted streams; gypsum crystallization of water from the coal processing plant; tertiary sulphate removal; and pre-washing.

Discussion

Limestone ($CaCO_3$) powder offers the following benefits over lime for neutralization of acid water:

- Reduced alkali cost: powdered $CaCO_3$ costs 150 South African Rand (R)/t (1 U.S.$ = R6.5, June, 2004) vs. R610/t for unslaked lime. This represents an alkali saving of 56% (Table 1).
- No silo is required for storage. Only a sloped concrete slab or hard surface is needed.
- Reduced use of lime slaker.
- $CaCO_3$ is safe to handle. It reacts only under acidic conditions.
- No dust, as the product contains 20% moisture.

The water is over-saturated with respect to gypsum after neutralization with lime, resulting in scaling of pipelines, screens, and other equipment (e.g. cyclones and spirals). The model indicated that 30% of the gypsum crystallization occurs in the primary neutralization plant and that 60% occurs in the coal processing plant (Table 2).

Table 3 shows the benefit of neutralizing discard leachate with an acidity of 11.5 g/l separately from the less polluted streams (acidity = 600 mg/L). The flow rate of the discard leachate is 40 m^3/h while that of the less polluted streams totals 120 m^3/h. During separate treatment, the capacity of the capital construction is much lower than during combined treatment (R3.0 million vs. R10.3 million). Only slightly less gypsum removal is achieved during separate treatment (8.9 t/d vs. 9.5 t/d).

The OSI value in the coal processing plant needs to be 1 or less to prevent gypsum scaling. This can be achieved in the following ways:

- The make-up water of the coal processing plant needs to be sufficiently undersaturated with respect to gypsum so that the OSI value is 1 or less after acid from the coal has leached into the water and is neutralized with lime or $CaCO_3$. This option will be discussed in the next section, using the biological sulphate removal process.
- Acid that leaches out in the coal processing plant can be neutralized with $Mg(OH)_2$ instead of lime.

Table 1. Cost comparison between $CaCO_3$ and lime for the Toe Seep Neutralization plant

Parameter	Alkali	
	$CaCO_3$	Unslaked lime
Flow rate (m^3/h)	40	40
Acidity (g/l)	10	10
Acid load (t/d $CaCO_3$)	9.6	9.6
Molecular mass	100	56
Utilization efficiency	80	70
Purity (%)	75	85
Consumption (t/d)	16.00	9.04
Delivered price (R/t)	150.00	610.00
Cost (R/year)	880,000	2,010,000
Saving (R/year)	1,130	0
Cost ratio	44	100

Table 2. Gypsum crystallization in the primary neutralization plant and in the coal processing plant

Parameter	Primary neutralization plant	Coal processing plant
Feed water (ML/d)	4.08	4.08
Feed SO_4 (mg/L)	2,400	2,224
Acid leachate from coal (t/d $CaCO_3$)		6
SO_4 from coal (mg/L)		1,471
SO_4 from feed water and coal		3,695
Equilibrium SO_4 (mg/L	1,812	1,935
Effluent SO_4 (mg/L)	2,224	2,640
SO_4 removal (%)	29.9	59.9

Table 3. Effect of separate and combined neutralization and gypsum crystallization on sulphate removal

Parameter		Separate Option	Combined Option
Flow (m^3/h)	Leachate discard	40	
	Make-up	120	
	Combined		160
SO_4 feed (mg/L)	Leachate discard	11,500	
	Make-up	2,531	
	Combined		4773
SO_4 treated (mg/L)		2,289	2086
OSI after neutralization and crystallization		1.16	1.05
Gypsum (t/d)		8.9	10
Capital cost (R)		3,000,000	9,800,000
Running cost (R/m^3)		1.08	1.08

Table 4. Effect of the capacity of a gypsum crystallization plant on the OSI value of the coal processing plant

Feed rate (m^3/h)	OSI
0	1.37
100	1.30
200	1.25

requires a separate stage where Mg^{2+} is precipitated with lime at pH 12, followed by gypsum crystallization. The $Mg(OH)_2$ could be recycled.

- The water in the coal processing plant can be treated for gypsum crystallization to a level near its saturation level. Table 4, however, shows that a large volume needs to be treated to make an impact. At a high flow rate of 200 m^3/h, the OSI is still 1.25, compared to 1.37 without treatment. The total flow of 1,250 m^3/h needs to be treated to prevent gypsum scaling, which would not be an affordable option.

Biological Treatment

From the previous section, it can be concluded that the most effective way to prevent gypsum scaling in the coal processing plant is to treat the feed water to below the saturation level of gypsum. We then had to determine what volume would have to be treated and what level of sulphate would need to be removed. Table 5 shows the effect of biological treatment on the OSI value in the coal processing plant. Lowering the sulphate concentration to 350 mg/L for a flow of 210 m^3/h would produce an OSI value of 0.98 (less than 1). A 222 m^3/h biological sulphate removal plant was estimated to cost R21.8 million (R4.1 million/(ML/d)); it was estimated that the operating cost would be $R4.10/m^3$.

Pre-Wash of ROM in Coal Processing Plant

Leachate studies showed that when run-of-mine coal is submerged in water, acid is washed off from the coal within 5 min. This option would require the following modifications to the Navigation operation:

- Install a pre-wash system for the coal. Neutralized water could be used as wash water. A counter flow wash system will have the benefit that minimum acid remains on the coal that enters the coal washing plant.
- Neutralize the acid water from the washing operation in the proposed Toe Seep Neutralization plant. Although the acid load from the coal would remain the same, this change would mean that less acid would have to be neutralized in the coal processing plant and hence, scaling in the coal processing plant can be reduced. The reduction in scale will be directly related to how much acid is redirected to the Toe Seep Neutralization plant. The aim should be to transfer 80% of the acid load currently neutralized in the coal processing plant to the Toe Seep Plant. The rest of the acid could be neutralized by dosing powdered $CaCO_3$ as a slurry at one or more places in the coal processing plant (similar to the current situation where lime is dosed). The effect of such a change in the operation of the coal washing plant can be determined from the current model. Table 6 shows the effect when the alkali consumption in the coal processing plant is reduced from the current 6 t/d (as $CaCO_3$) to 3 and 1 t/d, respectively. Implementing such

Table 5. Effect of separate neutralization and biological treatment on the OSI value in the coal processing plant

Parameter	Option 1	Option 2	Option 3
OSI in CPP feed	1.21	0.86	0.12
OSI in CPP	1.41	1.28	0.98
Sulphate removal (t/d SO_4)	22.4	24.4	28.8
Toe Seep neutralization/crystallization plant capacity (m^3/h)	40	40	40
Sulphate removal plant capacity (m^3/h)	50	105	222
Capital cost for biological plant (R)	4,920,000	10,332,000	21,844,800
Capital cost for biological plant (R/(Ml/d))	4,100,000	4,100,000	4,100,000
Running cost for biological plant (R/m^3)	3.53	3.79	4.10

Table 6. Effect of pre-coal washing on the OSI value in the coal processing plant

Parameter	Option 1	Option 2	Option 3
Alkali dosage to CPP (t/d $CaCO_3$)	6	3	1
OSI for the feed to the coal processing plant	0.16	0.58	0.86
OSI in the coal processing plant	1.00	1.00	1.00
Capacity of the sulphate removal plant (m^3/h)	215	150	105
Capital cost (R)	25,295,529	18,899,529	14,471,529
Running cost (R/a)	13,429,951	10,515,088	8,505,088

an operation would reduce the required capacity of a sulphate removal plant from 222 m^3/h when 6 t/d acid is neutralized in the coal processing plant to 150 m^3/h and 105 m^3/h for 3 and 1 t/d alkali respectively.

These capacities are based on a discharge of 40 m^3/h. If the alkali dosage is reduced from 6 to 1 t/d (as $CaCO_3$), the capital cost of the sulphate removal plant would be reduced from R25.3 million to R14.5 million and the running cost from R13.4 million/a to R8.5 million/a.

Conclusions

1. Calcium carbonate powder can be used instead of lime for neutralization of acid water, saving 56%.

2. Gypsum crystallization in the primary neutralization and coal processing plants can reduce sulfate concentrations 30% and 60%, respectively.

3. During separate treatment of coal discard leachate and the less polluted streams, the capital cost for a neutralization/gypsum crystallization plant amounts to R3.0 million, compared to R10.3 million during combined treatment. Only slightly less gypsum removal would be achieved during separate treatment, namely 8.9 vs. 9.5 t/d.

4. Gypsum crystallization from the water in the coal processing plant is an inefficient method for controlling the OSI value.

5. The OSI value can be controlled effectively at 1 by treating the feed water to the coal processing for sulphate removal. A flow of 222 m^3/h would need to be treated for removal of sulphate to 350 mg/L to obtain an OSI value of 0.98 (less than 1). The capital cost of a 222 m^3/h biological sulphate removal plant is estimated at R21.8 million (R4.1 million/(Ml/d)); the running cost is estimated at R4.10/m^3.

6. Pre-washing of the coal would reduce capital and running costs.

Acknowledgements

Sincere thanks are due to Anglo Coal (Navigation Section of Landau Colliery) and the National Research Foundation (NRF) for their financial and logistical support of the research reported in this paper.

References

Maree JP, de Beer M, Strydom WF, Christie ADM (2004a) Limestone neutralisation of acidic effluent, including metal and partial sulphate removal. Mine Water and the Environment (in this issue)

Maree JP, Hagger MJ, Strobos G, Hlabela P, Cronjé H, van Niekerk A Wurster A, and Nengovhela R (2004b) Neutralization of acid leachate at a nickel mine with limestone. Submitted to Mine Water and the Environment

van Tonder GJ, Theron DJ, Maree JP (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, WISA 2000 Conf, Sun City, South Africa, 28 May-1 June

Submitted February 28, 2004; accepted April 26, 2004

CHAPTER 9. CONCLUSIONS AND ACHIEVEMENTS

The following conclusions and achievements arose from the investigations described in this thesis:

Basic research

1. A novel process, the integrated limestone and iron(II)-oxidation process, was developed, which allows the oxidation of iron(II) when limestone alone was used for neutralization. In this process powdered limestone was used for iron(II)-oxidation at pH 5.5, neutralization of free acid, metal precipitation (e.g. Fe^{3+} and Al^{3+}) and gypsum crystallization, all in the same reactor. The novelty of this development lies in the fact that conditions were identified where iron(II) can be oxidized at pH 5.5, by the addition of the limestone. Previously, lime was used to raise the pH to 7.2 where the rate of iron(II)-oxidation is rapid. A patent, as described in Appendix A.1, was registered, based on these findings. This study was discussed in Chapter 3.

2. A novel method, the handling and dosing of powdered limestone was developed. In this method, powder precipitated $CaCO_3$ was dumped onto a concrete slab, slurried to a constant density with automatic control, and used for neutralization of acid water. The method is described in Appendix A.2 and its application under full-scale conditions in Chapters 4 and 5.

3. The integrated limestone and lime process, protected by a patent as described in Appendix A.3, was developed for the treatment of acid and sulphate-rich effluents. The process consists of various stages. The bulk of the acid content is neutralized in first stage with limestone. CO_2 is produced and stripped off through aeration and transported to the third stage. In the second stage the water is treated with lime to allow precipitation of magnesium and other metals and the sulphate associated with these metals. The level to which sulphate is removed via gypsum crystallization is controlled by the solubility product of gypsum. In the third stage, the CO_2 that is produced in the first stage, is contacted with the high pH of the water from the second stage to adjust the pH to 8.3. This allows the $CaCO_3$ precipitation. Due to its high purity, this $CaCO_3$ can be sold as a valuable by-product or it can be recycled to the first stage. Otherwise it can be recycled to the first stage to supplement the limestone addition. This process offers the following benefits: (i) The treated water is under-saturated with respect to gypsum and (ii) if the feed water contains aluminium, sulphate removal is not only achieved through gypsum crystallization, but also through ettringite ($3CaO.3CaSO_4.2Al_2O_3$) formation as it precipitates in the pH range 11.3 to 11.4.

4. The integrated biological process, consisting of the heating, anaerobic treatment, H_2S-stripping and processing stages, was evaluated on laboratory and pilot scale with a capacity of 8 m^3/h. The temperature of the feed water to the anaerobic stage was increased by contacting it directly with hot coal gas to raise the temperature from 15 to 30 °C. Ethanol or sugar was used as energy source. The H_2S-stripping and processing stages were studied in a laboratory unit to evaluate the suitability of a venturi device and a packed-bed reactor for H_2S-stripping and processing: These findings were described in Chapter 5.

5. A novel biological process, the single stage sulphate removal process, was developed whereby the reduction of sulphate to sulphide and the oxidation of sulphide to elemental sulphur occur in the same reactor. The reaction rate, effect of various parameters on the reaction rate and identification of intermediate products were investigated: A patent was registered, based on the findings as described in Chapter 6 (Maree, 1997).

6. The barium sulphide process was developed for sulphate removal. Laboratory studies were carried out to demonstrate that the integrated BaS process is technically and economically viable for

sulphate removal. The BaS process consists of four stages. In the thermic stage, $BaSO_4$ is reduced to BaS at a temperature of 1050°C, using coal as the reductant. In the sulphate removal stage, sulphate is precipitated as $BaSO_4$. In the stripping stage, H_2S is stripped off with CO_2 gas. In the softening stage, $CaCO_3$ is precipitated as a result of CO_2-stripping with air. This study was discussed in Chapter 7.

7. The water network of a coal mine was audited and simulated by an interactive steady state model. The findings were used to optimize the mine's water management strategy. Simulation of the interactions in the water network was used to show: (i) that powdered limestone can be used as an alternative to lime for neutralization of acid water at a cost saving. (ii) The amount of gypsum crystallization that occurs in the primary neutralization and coal processing plants could be established. (iii) The benefits associated with separate treatment of the most polluted stream versus combined treatment of all streams and (iv) The gypsum OSI (gypsum over-saturation index) value can be controlled effectively at 1.0 by treating the feed water to the coal processing for sulphate removal. The capacity of the sulphate removal plant that is needed could be determined as well as the associated capital and running costs. This was discussed in Chapter 8.

Integrated process

8. As a result of the above mentioned investigations, an integrated process, as shown in Figure 10.1, was proposed for the treatment of acid water rich in sulphate and metals. The process consists of the following stages:

- $CaCO_3$ handling and dosing system (Stages A and B). The system consists of a sloped concrete slab (A) onto which the $CaCO_3$ powder is dumped and stored, slurry tank (B), recycle pump, density meter, feed pump, clear water feed line with ball valve or level control. The $CaCO_3$ powder is slurried with a water jet and collected in a slurry tank through gravity flow. A float valve in the slurry tank maintains the water level at a specific height. The slurried $CaCO_3$ or clear water is pumped onto the $CaCO_3$ dump so as to maintain a constant $CaCO_3$ concentration. A side-stream from the delivery side of the recycle pump is passed through a density meter, which controls the $CaCO_3$ concentration of a fixed slurry volume, based on the mass, which is continually measured with a load cell. Based on the measurement, a water jet is automatically directed on to the $CaCO_3$ dump when the slurry density is below a set value or onto a clean section of the slab when the density is equal to or above the set slurry density.
- Limestone neutralization reactor 1 and H_2S-processing (Stage C). Discard leachate, which typically has a pH of 2.8 and contains 4 000 mg/l Fe(II), 1 500 mg/l Fe(III), 15 000 mg/l acid (as $CaCO_3$) and 18 000 mg/l sulphate (as SO_4), is fed to stage C. Limestone slurry from Stage B and H_2S gas that is stripped from Stage F (H_2S-stripping stage) is contacted with the discard leachate to neutralize the free acid and to precipitate iron(II) as FeS. The limestone dosage is such that the free acid as well is the acid generated from iron(II) and FeS-oxidation in Stage D is neutralized.
- Limestone neutralization reactor 2 (Stage D). This stage allows for iron oxidation, FeS oxidation, precipitation of metals (e.g. $Fe(OH)_3$ and $Al(OH)_3$), neutralization and gypsum crystallization. The novelty of this development lies in the fact that conditions were identified where Fe (II) can be oxidised at pH 5.5 by the addition of $CaCO_3$. Previously, lime was used to raise the pH to 7.2 where the rate of iron oxidation is rapid.
- Sludge separation (Stage E). Sludge rich in gypsum, $Fe(OH)_3$ and $Al(OH)_3$ is separated from the water and discarded on a waste dump. Water is passed on to the next stages for sulphate removal.

- Heating unit (not shown in Figure 10.1). Feed water to the biological stage is passed through a heating unit to control the temperature at 25 to 30 °C, the optimum temperature for sulphate reducing bacteria. The Heating unit consists out of the following items: coal bunker, speed control spiral feeder, heating unit and fan and water spray reactor where feed water is sprayed through spiral jet nozzles while hot air is flowing upwards.
- Biological sulphate removal (Stages F, G and H). This stage exists out of the following sub stages:
  - Biological sulphate reduction (Stage F). The anaerobic reactor consists of a completely mixed reactor with a cone in the top of the reactor to allow for sludge separation. The reactor contents were stirred with a side entry stirrer positioned at the bottom of the reactor and additional mixing was provided by a recycle pump. An alternative to the biological process is the barium sulphide process.
  - H_2S-stripping (Stage G). H_2S is stripped from the water with CO_2-gas that is generated in Stage 3.
  - Aerobic stage (Stage H). The feed water to this stage is rich in $Ca(HCO_3)_2$ and acetate (in case of biological sulphate removal). Aeration is applied to biodegrade the acetate to CO_2. CO_2, from the acetate that is biodegraded, and from the $Ca(HCO_3)_2$ is stripped off with air to allow $CaCO_3$-precipitation.
  - Sludge separation (Stage I). Sludge rich in $CaCO_3$ and biomass is separated from the water and recycled to Stage C to supplement the limestone.

Benefits

This approach offers the following benefits:

- The cheapest alkali, a by-product from the paper industry, is used for neutralization of the acid and for the removal of the bulk of the sulphate concentration through gypsum crystallization. The more advanced biological process is then used only for removal of the remaining sulphate, to low concentrations.
- A robust biological process (or the barium sulphide process) is used for sulphate removal to produce water suitable for use as process water that is non-scaling and suitable for discharge into public streams.
- CO_2 produced during $CaCO_3$-neutralization is used for H_2S-stripping in the biological stage. The stripped H_2S-gas is led to the $CaCO_3$-neutralization stage for precipitation of iron as iron sulphide, followed by iron oxidation and precipitation of inert $Fe(OH)_3$ and gypsum in the $CaCO_3$-neutralization stage. This has the advantage of being a fully integrated process.
- By incorporating all the described systems a full integrated process can be operated ensuring that any effluent from the mine be safe for discharge into public streams, be reused as industrial water.

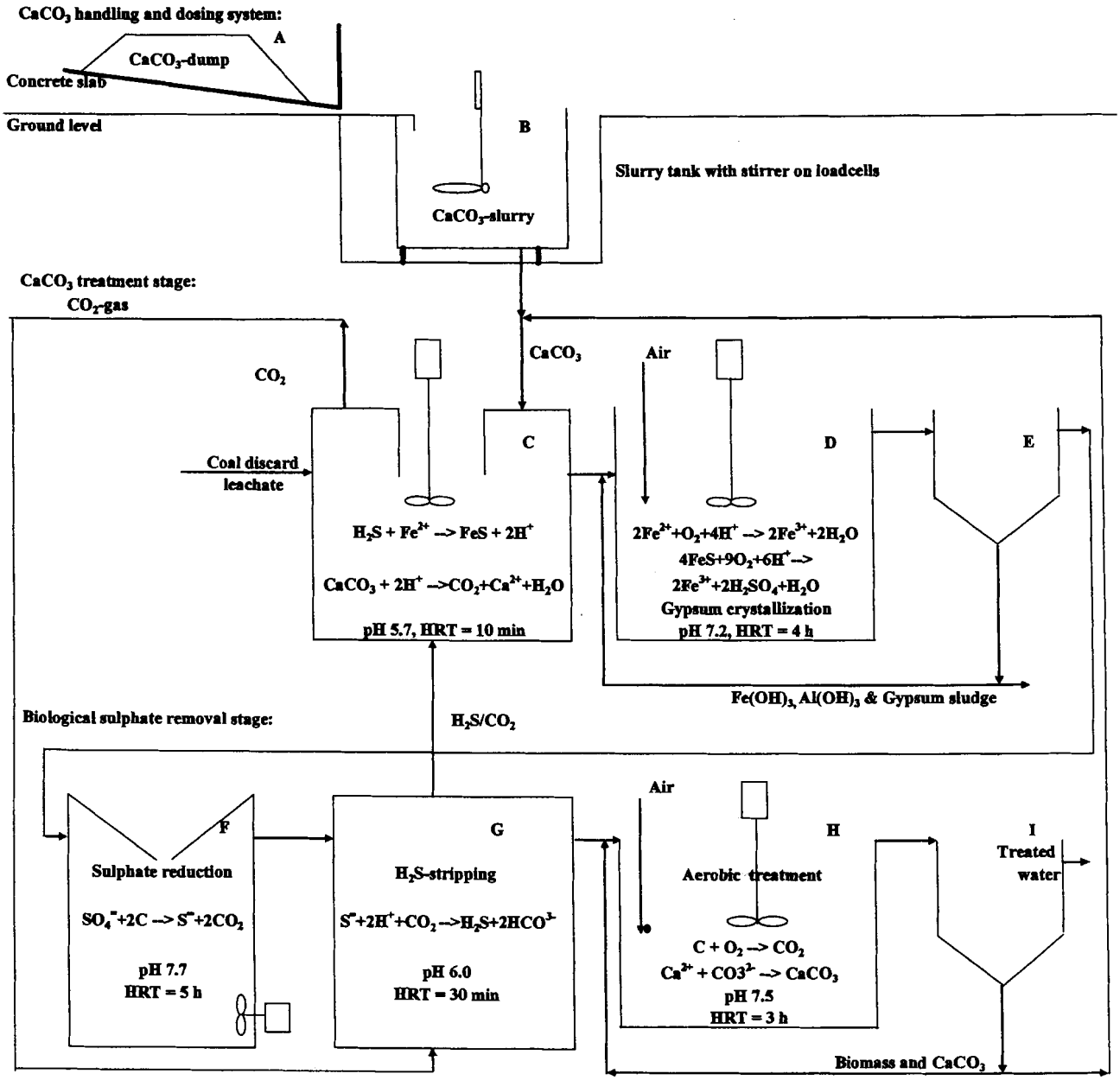


Figure 10.1 Process flow diagram for the treatment of acid and sulphate-rich effluents.

Full-scale applications

These studies have made a contribution to the field of treatment of industrial effluents, rich in acid and sulphate. This includes the following specific developments which were implemented on full-scale:

- The limestone handling and dosing system (Figure 10.2). A robust system has been developed using waste $CaCO_3$ from the paper industry, which is slurried to a constant density.

- The development of a density meter (Figure 10.3), used to monitor and control the limestone slurry concentration.

- A limestone neutralization process (Figure 10.4) in which a fluidized-bed reactor was used for the neutralization of acid water, rich in metals (e.g. iron(III) and aluminium(III)) using crushed limestone.

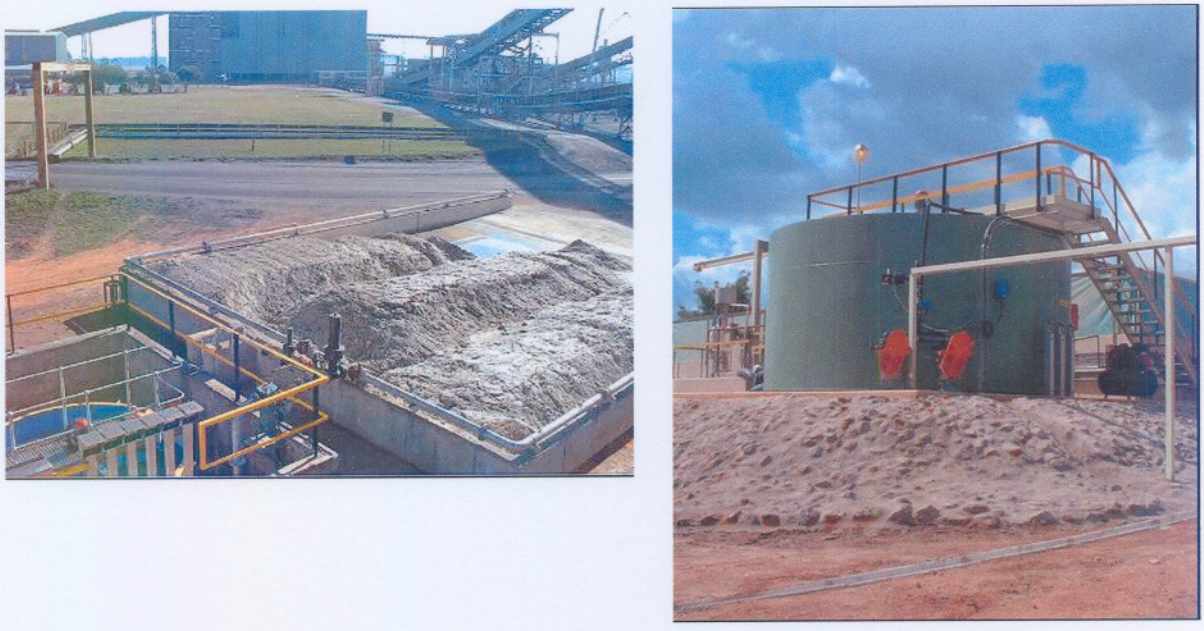
- The integrated iron(II)-oxidation/limestone neutralization process (Figure 10.5). In this process powdered limestone was used as catalyst for the iron(II)-oxidation for the neutralization and gypsum crystallization processes, occurring in the same reactor. The novelty of this development lay in the finding that iron(II) can be oxidized at pH 6, which was achieved using limestone. Previously lime was used to raise the pH to 7.2 at which pH the iron(II)-oxidation rate is rapid.

- Partial sulphate removal applying the gypsum crystallization technology (Figure 10.6). In this process limestone and lime were used for removal of sulphate to below the saturation level of gypsum. In the first stage, acid water is neutralized with limestone while CO_2-gas is released. This is followed by lime treatment to pH 12 in the next stage, achieving maximum gypsum crystallization. After sludge separation, the water is treated in a third stage where the high pH water from the second stage is contacted with the CO_2-gas produced in the first stage. This results in pH adjustment to 8.6 and precipitation of $CaCO_3$, a valuable by-product, which can be recycled to the first stage. Such plants are under construction at Namakwa Sands (Western Cape) and Illuka Resources (Australia).

- The biological sulphate removal process (Article 4). In this anaerobic biological process sulphate is removed by using organic material (e.g. ethanol, sugar, hydrogen or carbon monoxide) as the carbon and/or energy source. The results from this project gave Anglo Coal sufficient confidence in the biological sulphate removal technology to construct a 3 Ml/d full-scale plant commissioned in October 2003.

The construction cost of the neutralization plants that have been constructed or are under construction over the period 2000 to 2005 amounts to R90 million.

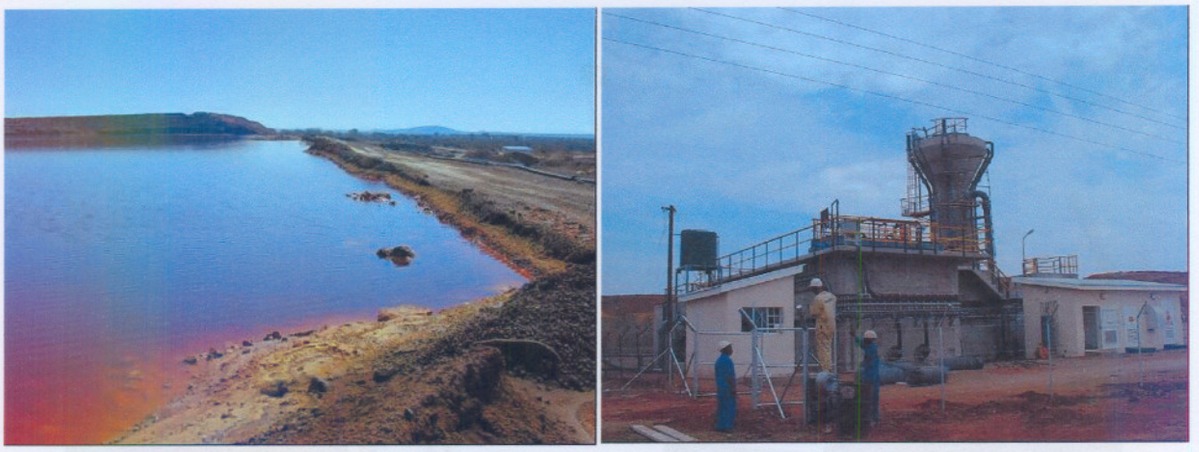
All the above developments were published in international journals, presented at international conferences, while patents were registered in South Africa, USA and certain other countries.



a. b.

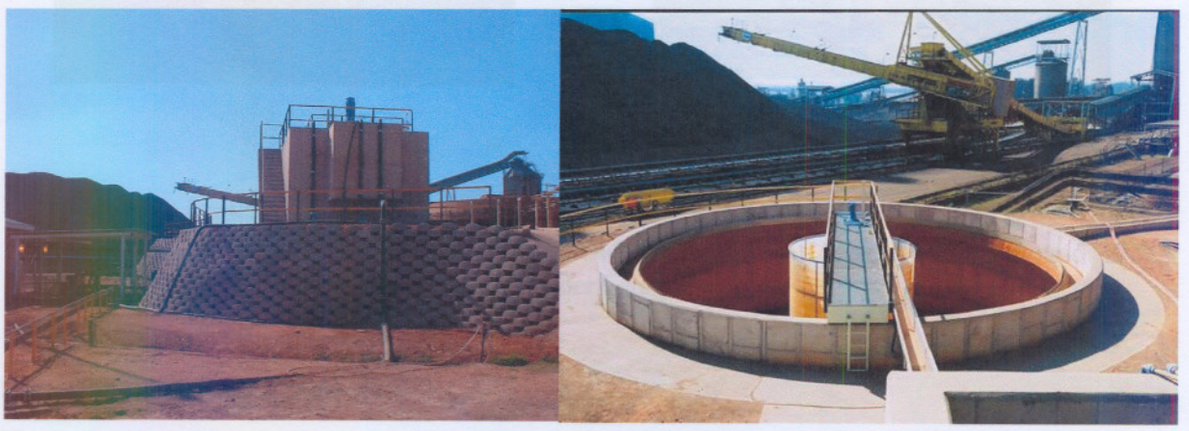
Figure 10.2 Limestone handling and dosing system. (a) Navigation section of Landau Colliery, Anglo Coal (Commissioned: 15 July 2001). (b) Kromdraai section of Landau Colliery, Anglo Coal (Commissioned: January 2003) b. Kromdraai section of Landau Colliery, Anglo Coal (Commissioned: January 2003)

Figure 10.3 Density meter



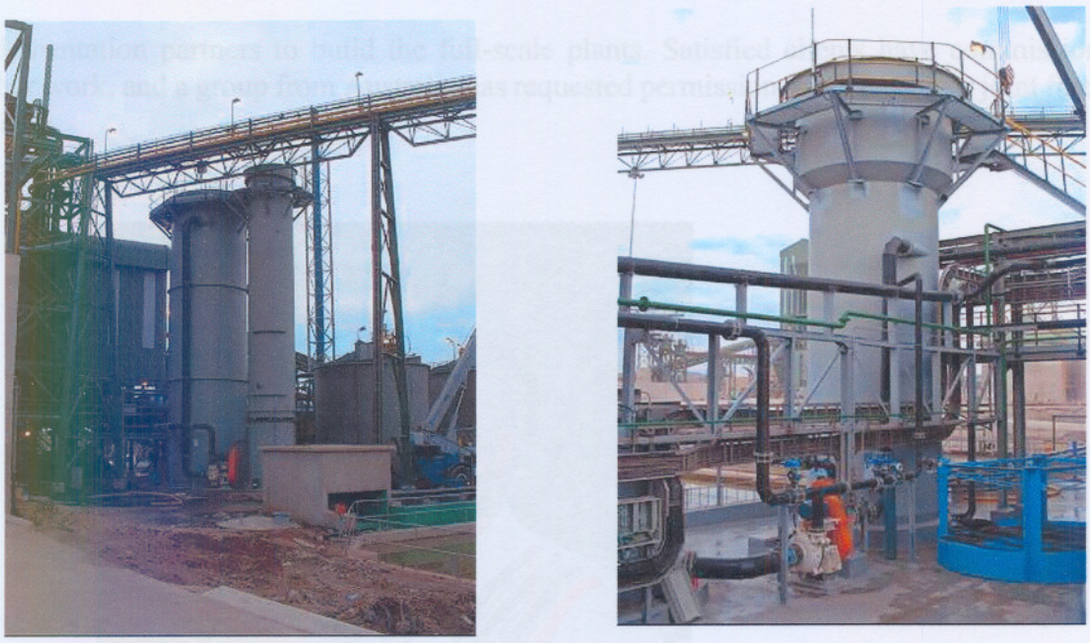
a. b.

Figure 10.4 Limestone neutralization at BCL, Botswana. (a) Red water lake (b) Fluidized-bed reactor for limestone neutralization (Commissioned: June 2002)



a. b.

Figure 10.5 Integrated limestone neutralization and iron(II)-oxidation plant at Navigation for treatment of Coal Discard Leachate (Commissioned: July 2004) (a) Completely-mixed reactor (b) Clarifier



a. b.

Figure 10.6 Limestone/Lime treatment plant for partial sulphate removal at IHM Heavy Minerals, Empangeni (Commissioned: July 2001) (a) Limestone and lime treatment stages (b) CO_2-treatment stage.

Relevance to South Africa

The technologies described in this thesis have a direct impact on the improvement and protection of the environment. Through the implementation of cost-effective treatment technologies, good quality water can be discharged into public streams. Full-scale implementation of these technologies have contributed to job creation, e.g. in companies involved with plant construction, in chemical processing plants and through training of students and graduates to enter the work-place as managers, researchers and operators.

The development work will be continued aimed at treatment of SO_2-rich gases, which are responsible for acid rain.

Awards to the author

CSIR Commercialization Award (2003)

The following citation accompanied the award:

Based on his innovative line of mine water treatment technologies, Jannie Maree's bold commercialization strategies have been highly successful in ensuring that five families of patents protect this Intellectual Property. By tapping into THRIP funding, Jannie was able to construct reference plants in industry, and has licensed leading engineering companies in the water field as

implementation partners to build the full-scale plants. Satisfied clients have commissioned further work, and a group from Australia has requested permission for licensing or joint further research.

Jannie Maree with Dr Sibisi at the award ceremony.

Reference

Maree JP and Gerber A (1997) Single Stage Sulphate Removal, South Africa (Patent No. 98/6902) and United States of America (Patent No. 6,306,302)

APPENDIX A PATENTS

PATENT 1. INTEGRATED IRON OXIDATION AND LIMESTONE NEUTRALIZATION

Maree, J.P. 1997. **Integrated iron oxidation and limestone neutralization**, Republic of South Africa (98/5777), Australia (Patent No 732237), United States of America (6,419,834), Canada (2 294 058), Germany (698110927-08), Great Britain (1012120).

US006419834B1

(12) **United States Patent**
Maree

(10) **Patent No.: US 6,419,834 B1**
(45) **Date of Patent: Jul. 16, 2002**

(54) **TREATMENT OF ACIDIC WATER CONTAINING DISSOLVED FERROUS CATIONS**

(75) Inventor: **Johannes Philippus Maree**, Pretoria (ZA)

(73) Assignee: **CSIR**, Pretoria (ZA)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/446,100**

(22) PCT Filed: **Jun. 30, 1998**

(86) PCT No.: **PCT/GB98/01912**

§ 371 (c)(1),
(2), (4) Date: **Mar. 13, 2000**

(87) PCT Pub. No.: **WO99/01383**

PCT Pub. Date: **Jan. 14, 1999**

(30) **Foreign Application Priority Data**

Jul. 2, 1997 (ZA) 97/5899

(51) **Int. Cl.**[7] **C02F 1/52**

(52) **U.S. Cl.** **210/722**; 210/713; 210/724; 210/738; 210/758

(58) **Field of Search** 210/602, 620, 210/713, 722, 724, 738, 758

(56) **References Cited**

U.S. PATENT DOCUMENTS

2,829,964	A		4/1958	Zimmerley et al.
3,738,932	A		6/1973	Kostenbader
4,139,456	A	*	2/1979	Yabuuchi et al.
4,465,597	A		8/1984	Herman et al.
5,427,691	A		6/1995	Kuyucak et al.

FOREIGN PATENT DOCUMENTS

CH	590 791	8/1977
JP	60-084196	5/1985
WO	WO 97/36829	10/1997

OTHER PUBLICATIONS

"Advanced Inorganic Chemistry" 4th Ed., (Cotton & Wilkinson), p. 754, John Wiley & Sons, 1980. ISBN 0-471-02775-8.

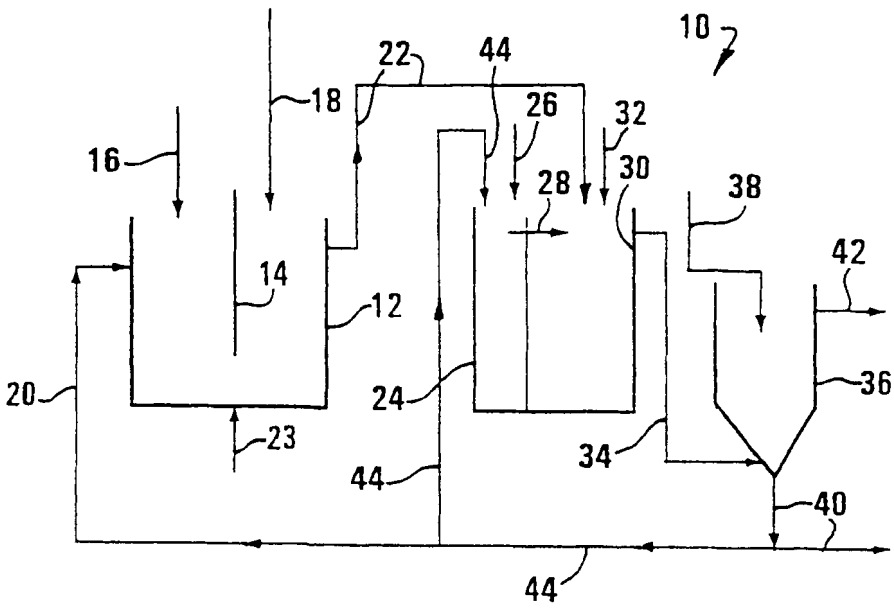
* cited by examiner

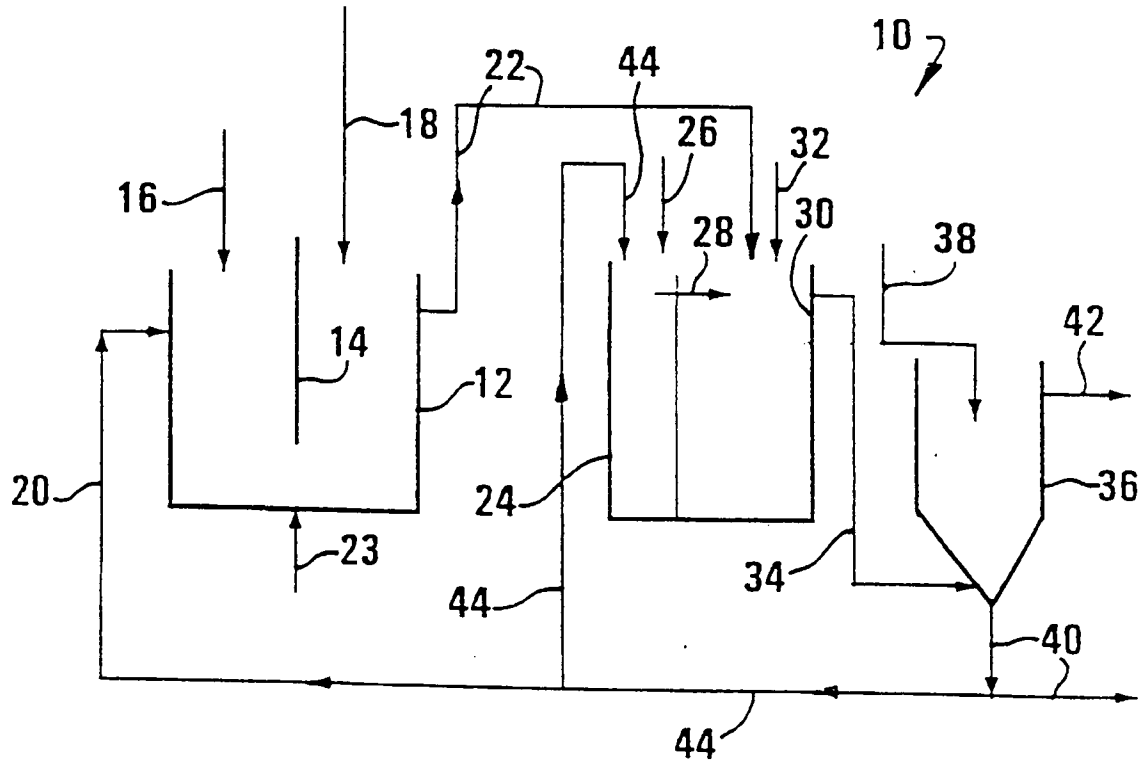
Primary Examiner—Betsey Morrison Hoey
(74) *Attorney, Agent, or Firm*—Klarquist Sparkman, LLP

(57) **ABSTRACT**

A water treatment process for raw water containing dissolved Fe^{2+} and H^+ cations to reduce the Fe^{2}+ cation concentration therein involves oxidation of the Fe^{2}cations to Fe^{3+} cations with the formation in the water of solid $Fe(OH)_3$ from the Fe^{3+} cations. The process comprises the steps of oxygenating the water and raising the pH of the water. The oxidation of the Fe^{2+} cations and the fromation of the $Fe(OH)_3$ are carried out in the presence of suspended particulate material in the water, the particulate material being present in the water at a concentration of at least 5 g/l.

15 Claims, 1 Drawing Sheet




10
22
44
18
26
32
16
28
30
38
42
14
12
20
24
36
23
34
44
40
44

1

TREATMENT OF ACIDIC WATER CONTAINING DISSOLVED FERROUS CATIONS

THIS INVENTION relates to the treatment of water. More particularly, the invention relates to a process for the treatment of water which is acidic and contains dissolved ferrous (Fe^{2+}) cations, optionally in association with dissolved sulphate (SO_4^{2-}) anions.

The Applicant is aware of relevant prior art constituted by U.S. Pat. Nos. 5,427,691, 3,738,932, CH-A-590 791 and Patent Abstracts of Japan, Volume 009, No. 222 (1985) & Database WPI, AN 85-1501615 & JP-A-60 084196.

In U.S. Pat. No. 5,427,691 processes are disclosed for the treatment of acidic waters containing dissolved Fe^{2+} cations by means of aeration to oxygenate the water and by raising the pH of the water in the presence of suspended particulate material, to oxidize the Fe^{2+} cations to Fe^{3+} cations and precipitate them as $Fe(OH)_3$. Lime is employed to raise the pH of the water to above 7 and the aeration takes place with the water at a pH above 7. A prior art process is also discussed in U.S. Pat. No. 5,427,691, in which limestone is used to remove Fe^{3+} cations. To remove Fe^{2+} cations using limestone, however, the Fe^{2+} cations must first be oxidized to Fe^{3+} cations, and doing so at acidic pH levels with air (dissolved oxygen) is described as 'almost impossible' because of the slow reaction rates.

In U.S. Pat. No. 3,738,932, similarly, a process is disclosed for the treatment of acidic waters containing dissolved Fe^{2+} cations by means of aeration to oxygenate the water and by raising the pH in the presence of suspended particulate material, to oxidize the Fe^{2+} cations and precipitate them as $Fe(OH)_3$. In this case, likewise, lime is used to raise the pH of the water to above 7 and the aeration takes place with the water at a pH above 7. No se of limestone or dolomite is described.

In CH-A-590 791 and Patent Abstracts of Japan supra, it is disclosed that it is known to use the oxidizing action of specific bacteria to oxidize Fe^{2+} cations to Fe^{3+} cations; and in said Patent Abstracts of Japan a two-stage process is disclosed whereby acidic sulphuric acid-containing waste water containing high concentrations of Fe^{2}+ cations is subjected, in a first stage, to a bacterial oxidation wherein the Fe^{2+} cations are bacterially converted to Fe^{3+} cations. Then, in a second stage, calcium carbonate is added to the water which has been subjected to the bacterial oxidizing treatment, to precipitate $Fe(OH)_3$.

According to the invention there is provided a process for the treatment of raw water containing dissolved Fe^{2+} cations and dissolved H^+ cations so as to reduce the concentration of Fe^{2}+ cations therein, the process comprising the oxidation of dissolved Fe^{2+} cations and the formation in the water of solid $Fe(OH)_3$ from said Fe^{3+} cations, the process comprising the steps of:

oxygenating the water to achieve a dissolved oxygen concentration in the water of at least 0.1 mg/l, effective to oxidize the Fe^{2+} cations to Fe^{3+} cations; and

raising the pH of the water, the oxidation of the Fe^{2+} cations and the formation of the $Fe(OH)_3$ being carried out in the presence of suspended particulate material in the water, the particulate material being present in the water at an effective concentration of at least 5 g/l,

the process being characterized in that, in combination,

the raising of the pH acts partially to neutralize the water;

the raising of the pH is by dissolving limestone or dolomite in the water; and

2

the dissolving of the limestone or dolomite in the water and the oxidation by dissolved oxygen of the Fe^{2+} cations to Fe^{3+} cations in the water take place together in the same body of partially neutralized water in the presence of the particulate material.

The process may comprise an agitation step whereby the water is agitated as it undergoes the oxygenating and the raising of its pH. Agitating the water may be by fluidizing it in a fluidized bed, fluidized eg by upward flow of air or oxygen through a body of the water containing the particulate matter, the particulate matter comprising particulate matter, such as calcium carbonate, added to neutralize the water, particulate matter precipitated from the water such as ferric hydroxide or gypsum, and/or slimes added to the water as a microorganism support. Instead, agitating the water may be by upward flow of the water through a fixed bed of particulate matter, or a packed bed of a support medium of the type described hereunder, conveniently at turbulent flow rates. Instead, the water may be mechanically agitated, so as to provide a fully-mixed or completely-mixed body of water, which again may be turbulent. Instead, the process can be carried out in a pipe or tube, along which turbulent flow takes place; and the water may be circulated through said beds or along said pipe or tube by means of a pump.

The water to be treated, i.e. the raw water, will typically have a Fe^{2+} cation concentration of at least 100 mg/l, usually 150–5000 mg/l and more usually 200–4000 mg/l; and will typically have a pH of at most 7, usually 1–6 and more usually 2–5. Often, the water to be treated will also contain SO_4^{2-} ions at a concentration of at least 200 mg/l, usually 200–25 000 mg/l, and more usually 1000–10 000 mg/l. This water will typically have an Acidity, i.e. an HCO^-_3 acidity, expressed as mg/l of $CaCO_3$, of 200–30 000, usually 400–25 000 and more usually 1000–10 000.

Oxygenating the water may be such as to achieve a dissolved oxygen concentration in the water of at least 0.5–8 mg/l, the suspended solid material having a particle size distribution whereby at least 50% by mass thereof has a particle size of less than 500 μm, the particulate material being present in the water at a concentration of at least 10 g/l, the raw water having a dissolved Fe^{2+} cation concentration of more than 100 mg/l, and the process acting to to decrease the dissolved Fe^{2+} cation concentration to less than 100 mg/l.

More particularly, the raw water may contain dissolved SO_4^{2-} anions, the process including the biological oxidation of dissolved Fe^{2+} cations to Fe^{3+} cations and the process being carried out at a temperature of 0–90° C., preferably 5–40° C. In this case the raw water may have a dissolved SO_4^{2-} anion concentration of at least 200 mg/l, the biological oxidation being carried out by microorganisms selected from

Ferrobacillus ferrooxidans;

Ferrobacillus thiooxidans;

Thiobacillus thiooxidans; and

mixtures of any two or more thereof.

The microorganisms may be supported on a support medium, to increase the concentration of microorganisms in the agitated water. While the support medium may be of metal or synthetic plastics material, such as rings, plates (which may be corrugated) and superimposed corrugated plates such as those available in South Africa under the Trade Mark TERBO PLASTIC, to provide a surface area for microorganism growth of at least 10 m^2 of support medium area/m^3 of agitated water, preferably 100–1000 m^2/m^3 and more preferably 200–500 m^2/m^3, the support medium instead is conveniently a packed or suspended particulate

material, in particular a finely divided particulate material, such as a slimes or sludge material or sediment added to the agitated water either continuously, or at the start of the process to be progressively supplanted by solids produced by the process as the process proceeds. The particulate material present in the agitated water may have a particle size of at most 500 μm, preferably 5–200 μm, and more preferably 10–100 μm. This particulate material may be present at a concentration of 10–500 g/l, preferably 50–200 g/l; and the particulate material may provide a particle surface area in the agitated water of at least 100 m^2/m^3 of agitated water, preferably 100–10 000 000 m^2/m^3. Examples of suitable particulate materials for initial employment are waste coal fines and gypsum (when sulphate is precipitated by calcium salts addition as described hereunder), and will be progressively supplanted by precipitated $Fe(OH)_3$ optionally admixed with gypsum ($CaSO_4.2H_2O$) if calcium salts (as described hereunder) are used for the neutralization, and if the water to be treated contains SO_4^{2-} anions. If desired, both a support medium in the form of rings or plates, as described above, can be used, and a particulate support medium, such media both acting to provide an increased surface area for growth of microorganisms.

The raw water may have a pH of at most 7, the raw water having an Acidity, expressed as mg/l of $CaCO_3$ dissolved therein, of at least 200, and the suspended particulate material providing a particle surface area in the water of at least 100 m^2/m^3 water. When the raw water contains dissolved SO_4^{2-} anions, raising the pH of the water may comprise adding $CaCO_3$ thereto to cause the formation of solid $CaSO_4.2H_2O$ in the water, the $CaSO_4.2H_2O$ being allowed to precipitate from the water. In this case, the oxidation of dissolved Fe^{2+} cations to Fe^{3+} cations, the addition of $CaCO_3$ to the water and the precipitation of $CaSO_4.2H_2O$ from the water will take place together in the same body of water.

The process may be carried out at ambient temperatures such as the temperature of 0–90° C. as mentioned above, preferably 5–40° C. and more preferably 15–30° C. While the process can in principle be carried out on a batch basis, it is conveniently carried out on a continuous basis; and it may be carried out in a single stage or in a plurality of stages arranged in parallel and/or series. When the process is in operation, any biological oxidation of Fe^{2+} to Fe^{3+} tends to cause a drop in pH, so that neutralization must be effected continuously or intermittently, so as to keep the pH up to a desired level of at least 3, eg above 4, preferably above 5 and more preferably above 6. Typically the water will be treated for an average period or reaction time of at least 1 minute, usually 20–1440 minutes and more preferably 30–480 minutes, which will be its average residence time in a single stage when a single stage is used or its total residence time in a plurality of stages, when a plurality of stages is used.

At least partially neutralizing the water may be by adding a suitable base or alkali, optionally in particulate form, thereto, examples of suitable alkalis being $CaCO_3$, $Ca(OH)_2$, CaO and NaOH, in particular limestone or calcium carbonate ($CaCO_3$), but not excluding dolomite or waste alkalis obtainable in mixed form as steel industry waste products. The alkali added preferably has a particle size of at most 500 μm, more preferably at most 100 μm and conveniently as small as practicable, bearing economic considerations in mind.

Oxygenating the water may be by feeding oxygen to the water, and this may be by bubbling oxygen or conveniently air through the water. The feed rate may be such as to achieve a preferred dissolved oxygen content in the water of 1–5 mg/l.

In accordance with the invention water may be treated continuously by the process and may pass on to a settling or sedimentation stage where metal hydroxides or oxides, in particular $Fe(OH)_3$, optionally containing $CaSO_4.2H_2O$, will be precipitated therefrom, and slimes or sediment from this sedimentation stage may be recirculated to the process to give the particulate material which provides the surface area which promotes the oxidation of Fe^{2+} to Fe^{3+}. This particulate material can also support the microorganisms which carry out the biological oxidation of the Fe^{2+} to Fe^{3+}.

In terms of a variation of the process, treated water flowing from the oxidation of Fe^{2+} to Fe^{3+} to the sedimentation stage may be used to dispose of acidic waste water with a pH of 2–6. Such acidic waste water may have a pH of 3–4, and an Fe^{2+} cation concentration of at least 100 mg/l, usually 100–2000 mg/l, and more usually 100–800 mg/l; it may have an Acidity, expressed as mg/l of $CaCO_3$ of at least 200, usually 200–4000 and more usually 200–1600; and it may have a SO_4^{2-} anion concentration of at least 200 mg/l, usually 200–4000 mg/l and more usually 200–2600 mg/l. This can be effected by mixing the water issuing from the Fe^{2+} oxidation stage with the acidic waste water and dosing it with a strong alkali such as lime (CaOH) to raise its pH to a value of 6–9, eg about 7, eg in an aeration tank. This may be done by first adding the strong alkali in a conditioning tank to water or sludge recirculated from the sedimentation stage, to raise its pH to 11–12, this water, at a pH of 11–12, being used in the aeration stage to raise the pH, after which, in the sedimentation stage, a suitable flocculant may be used to promote settling of the $Fe(OH_3)$ and optionally of the $CaSO_4.2H_2O$.

Accordingly, after the formation of the $Fe(OH)_3$, the water may be subjected to a sedimentation step to settle suspended solids therefrom. In particular, the water may be treated on a continuous basis, the sedimentation step being carried out separately from the oxygenating of the water and separately from the raising of the pH thereof, solids settled by the sedimentation step being recirculated and the oxidation of the Fe^{2+} cations taking place in the presence of the recirculated solids. In this case, the oxygenation of the water may include an aeration step, separate from the step of raising the pH of the water, solids settled by the sedimentation step being recirculated to the pH-raising step and to the aeration step.

The oxidation reactions which take place according to the process can be expressed by:

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

and

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

and, when SO_4^{2-} is present in the water to be treated by the biological oxidation and a calcium salt is used for neutralization of that water, gypsum is produced according to the chemical reaction:

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

When weakly acid waste water of a pH of above 4 is treated according to the process of the invention, the treated water may have, in combination, a pH of 5.0 or more, an Fe^{2+} cation content of 100 mg/ l or less, an acidity as mg/l of $CaCO_3$ of 500 or less, and a SO_4^{2-} anion content of 4000 mg/ or less. When the process is used also to dispose of highly acid waste water with a pH of less than 4, the treated water may have a pH of 4.0 or more, an Fe^{2+} cation content of 100 mg/l or less, an Acidity as mg/l of $CaCO_3$ of 1000 or

less, and a SO_4^{2-} anion content of 4000 mg/l or less, typically less than 3000 mg/l.

The invention will now be described, by way of example, with reference to the accompanying diagrammatic drawing, in which the single Figure is a schematic flow diagram of an installation suitable for carrying out the process of the present invention.

In the drawing, reference numeral **10** generally designates an installation for carrying out the process of the present invention. The installation comprises a fully-mixed tank **12** provided with a mechanical agitator **14**, a feed line **16** for water to be treated, a limestone powder feed line **18**, a slimes or sludge recirculation feed line **20**, and a treated water discharge flow line **22** and an air feed line **23**.

Flow line **22** feeds into an aerator tank **30**, and a conditioning tank **24** provided with a lime feed line **26** and provided with a discharge flow line **28** feeds into the aeration tank **30**, which is provided with an acid waste water feed line **32** and an outlet flow line **34**.

Flow line **34** leads to a sedimentation tank **36** provided with a flocculant feed line **38**, a sludge or sediment outlet flow line **40** and a product water outlet flow line **42**. A branch line **44** leaves line **40** and feeds respectively into line **20** and into tank **24**.

In accordance with the process of the invention water to be treated is fed at a temperature of 18° C. and at a pH of 2.5, with a Fe^{2+} content of 3000 mg/l, an acidity of 10 000 mg/l as $CaCO_3$ and a SO_4^{2-} content of 12 000 mg/l at a rate of 80 000 l/h along line **16** into tank **12**. Powdered limestone of a particle size of less than 100 μm is fed at a rate of 800 kg/h along flow line **18** into tank **12** which is kept fully mixed by agitator **14**. Air is fed to tank **12** along line **23**. Sludge is fed along line **20** to tank **12**. The limestone feed along line **18** is at a slight stoichiometric excess (20%) above that required to react with the sulphate ions and to achieve the desired pH rise.

The tank **12** contains *Ferrobacillus ferrooxidans* microorganisms and acts as a biological oxidation stage for the biological metabolization and oxidation of Fe^{2+} to Fe^{3+} according to the reaction:

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

The respective feed rates along lines **16**, **18**, **20** and **22** are selected to provide water in the tank **12** with a pH of 5.0 at a temperature of 18° C., with a sludge content of at least 50 g/l and a dissolved oxygen content of 3 mg/l, and to provide the water in the tank **12** with an average or mean residence time in the tank **12** of 2 hours. The water leaves the tank **12** with a Fe^{2+} cation content of at most 50 mg/l, an acidity of at most 100 mg/l $CaCO_3$ and a SO_4^{2-} content of at most 2000 mg/l.

Water leaves the tank **12** along line **22** to tank **30** which acts as a aeration stage where weakly acid water is added along line **32**. Lime added along line **26** to tank **24** is used to raise the pH of water in tank **24** to a value of 12. This water is water recirculated with sludge as a slurry along line **44** from the sedimentation stage **36**. This slurry at pH 12 then leaves the tank **24** along line **28** to tank **30** which acts as an aeration tank, having an air supply (not shown) and to which said weakly acid waste water at a pH of 2.4 is added along line **32** at a rate such that a pH of at least 6 is obtained in the water in the tank **30**. Mean residence times in the tanks **24** and **30** are respectively 10 minutes and 20 minutes, and the aeration in the tank **30** is such as to achieve a dissolved oxygen content in the water therein of at least 0.5 mg/l. Temperatures in the tanks **24** and **30** are respectively 18° C. and 18° C.

Water leaves tank **30** along line **34** to tank **36** which acts as a sedimentation stage. A flocculant eg comprising MAGNAFLOC 333 is fed along line **38** to tank **36** at a rate of 2–3 mg of. flocculant/l of water fed along line **34** to tank **36**. Sedimentation of flocculated $Fe(OH)_3$ and $CaSO_4$ precipitates takes place at 18° C. in tank **36**, the precipitates having been respectively formed according to the chemical reactions:

$$Fe^{3+}+3H_2O \rightarrow Fe(OH)_3\downarrow+3H^+;$$

and

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

Product water at a pH of about 7, having a Fe^{2+}/Fe^{3+} content of at most 100 mg/l, an acidity of at most 200 mg/l $CaCO_3$, and having a sulphate content of at most 3000 mg/l leaves tank **36** along line **42** and sludge leaves it along line **40** to waste. Sludge is recirculated from line **40** via lines **44** and **20** to tank **12** to provide a microorganism support medium for the microorganisms in the tank **12**; and sludge is recirculated via line **44** to the tank **24** as described above.

Usually, a sedimentation stage (not shown) will be provided in flow line **22**, this sedimentation stage having a sludge outlet into tank **12** and a water outlet along line **22** to the tank **30**.

It is to be noted that variations, in accordance with the present invention, of the process illustrated by the specific flow diagram shown in the drawing are possible. Thus, in particular, the tanks **24** and **30** can be omitted and line **22** can feed downwardly directly into tank **36**. In this case line **44** will not feed into tank **24** but will only feed into line **20** and thence into tank **12**, lines **26** and **32** also being omitted. Furthermore, tank **12** may, instead of being a fully-mixed tank, provided with an agitator, be a packed tower or a fluidized bed.

It is an advantage of the invention, as described with reference to the drawing, that it provides an efficient and effective process for disposing of acid waters containing dissolved Fe^{2+} cations and SO_4^{2-} anions, while simultaneously disposing of highly acid waste water with a pH as low as 2.5. It should also be noted that, if desired, the biological Fe^{2+} oxidation in tank **12** can be operated on a batch basis, two suitable equalization—or surge tanks (not shown) being provided respectively before tank **12**, and after tank **12** and before tank **30**, from which water received in batches from tank **12** can be fed continuously to tank **30**.

More particularly, it is an advantage of the invention that a high density sludge having a density of 500–600 g/l or more, is obtainable in the tank **36**, particularly if the level of dissolved $CaSO_4$ in the water exceeds the saturation limit of $CaSO_4$ in the water at the temperature in question. Furthermore, with increases in pH of the water, metal ions other than those of Fe^{2+} can, if they are present in the water, be removed from the water so as to reduce their concentration therein if not eliminate them from the water.

Thus, if $CaCO_3$ is used to raise the pH of the water, reduction in the concentration of any Mn ions in the raw water can take place in response to oxidation of Mn^{2+} ions to Mn^{4+} ions by aeration in the presence of MnO_2 in the recirculated sludge. MnO_2 is thus formed which can then form part of the eventual precipitate. Similarly, at least partial reduction of the concentrations of any As, Cd, Co, Cu and Zn ions in the raw water can take place, in response to the addition of $CaCO_3$ to the water, being precipitated respectively as As_2O_3, $Cd(OH)_2$, $Co(OH)_2$, $Cu(OH)_2$, $Pb(OH)_2$ and $Zn(OH)_2$. When lime ($Ca(OH)_2$) is used to

raise the pH of the water, substantially greater reductions in the concentrations of the metals in question can in principle be achieved. The Applicant understands that, typically, precipitation will take place when the pH is increased to a value of about 7, exceptions being the precipitation of $Zn(OH)_2$ which can take place at a pH of about 8, and the precipitation of MnO_2 which can take place at a pH of about 9.8. It is further to be noted, in particular, that whether $CaCO_3$ or $Ca(OH)_2$ is used to raise the pH, an at least partial reduction of the concentration of any Se ions in the raw water can take place by co-precipitation during gypsum crystallization, when the raw water contains SO_{4-} anions.

What is claimed is:

1. A process for the treatment of raw water containing dissolved Fe^{2+} cations and dissolved H^+ cations so as to reduce the concentration of Fe^{2+} cations therein, the process comprising the oxidation of dissolved Fe^{2+} cations in the water to Fe^{3+} cations and the formation in the water of solid $Fe(OH)_3$ from said Fe^{3+} cations, the process comprising the steps of:

oxygenating the water; and

raising the pH of the water to a value below 7,

the oxidation of Fe^{2+} cations and the formation of the $Fe(OH)_3$ being carried out in the presence of suspended particulate material in the water, the particulate material being present in the water at a concentration of at least 5 g/l, wherein raising the pH of the water comprises adding $CaCO_3$ thereto.

2. A process as claimed in claim **1**, which comprises an agitation step whereby the water is agitated as it undergoes the oxygenation and the raising of its pH.

3. A process as claimed in claim **1**, in which oxygenating the water is such as to achieve a dissolved oxygen concentration in the water of at least 0.1 mg/l, the suspended solid material having a particle size distribution whereby at least 50% by mass thereof has a particle size of less than 500 μm, the particulate material being present in the water at a concentration of at least 10 g/l, the raw water having a dissolved Fe^{2+} cation concentration of more than 100 mg/l, and the process acting to decrease the dissolved Fe^{2+} cation concentration to less than 100 mg/l.

4. A process as claimed in claim **1**, in which the raw water contains dissolved So_4^{2-} anions, the process including the biological oxidation of dissolved Fe^{2+} cations to Fe^{3+} cations and the process being carried out at a temperature of 5–40° C.

5. A process as claimed in claim **4**, in which the raw water has a dissolved SO_4^{2-} anion concentration of at least 200 mg/l, the biological oxidation being carried out by microorganisms selected from

Ferrobacillus ferrooxidans;

Ferrobacillus thiooxidans;

Thiobacillus thiooxidans; and

mixtures of any two or more thereof.

6. A process as claimed in claim **1**, in which the raw water has a pH of at most 7, the raw water having an Acidity, expressed as mg/l of $CaCO_3$ dissolved therein, of at least 200, and the suspended particulate material providing a surface area in the water of at least 100 m^2/m^3 water.

7. A process as claimed in claim **1**, in which the raw water contains dissolved SO_4^{2-} anions, adding the $CaCO_3$ thereto being by adding an alkali selected from the group consisting of limestone, dolomite and mixtures thereof thereto to cause the formation of solid $CaSO_4.2H_2O$ in the water, the $CaSO_4.2H_2O$ being allowed to precipitate from the water.

8. A process as claimed in claim **7**, in which the oxidation of dissolved Fe^{2+} cations to Fe^{3+} cations, the addition of the $CaCO_3$ to the water, and the precipitation of the $CaSO_4$ from the water take place together in the same body of water.

9. A process as claimed in claim **1**, in which, after the formation of the $Fe(OH)_3$, the water is subjected to a sedimentation step to settle suspended solids therefrom.

10. A process as claimed in claim **9**, in which the water is treated on a continuous basis, the sedimentation step being carried out separately from the oxygenating of the water and separately from the raising of the pH thereof, solids settled by the sedimentation step being recirculated and the oxidation of the Fe^{2+} cations taking place in the presence of the recirculated solids.

11. A process as claimed in claim **9**, in which the oxygenation of the water includes an aeration step, separate from the step of raising the pH of the water, solids settled by the sedimentation step being recirculated to the pH-raising step and to the aeration step.

12. A process for the treatment of raw water containing dissolved Fe^{2+} cations and dissolved H^+ cations so as to reduce the concentration of Fe^{2+} cations therein, the process comprising the oxidation of dissolved Fe^{2+} cations in the water to Fe^{3+} cations and the formation in the water of solid $Fe(OH)_3$ from said Fe^{3+} cations, the process comprising the steps of:

oxygenating the water; and

raising the pH of the water,

the oxidation of Fe^{2+} cations and the formation of the $Fe(OH)_3$ being carried out in the presence of suspended particulate material in the water, the particulate material being present in the water at a concentration of at least 5 g/l, oxygenating the water being such as to achieve a dissolved oxygen concentration in the water of at least 0.1 mg/l, the suspended solid material having a particle size distribution whereby at least 50% by mass thereof has a particle size of less than 500 μm, the particulate material being present in the water at a concentration of at least 10 g/l the water having a dissolved Fe^{2+} cation concentration of more than 100 g/l, and the process acting to decrease the dissolved Fe^{2+} cation concentration to less than 100 mg/l.

13. A process for the treatment of raw water containing dissolved Fe^{2+} cations and dissolved H^+ cations so as to reduce the concentration of Fe^{2+} cations therein, the process comprising the oxidation of dissolved Fe^{2+} cations in the water to Fe^{3+} cations and the formation in the water of solid $Fe(OH)_3$ from said Fe^{3+} cations, the process comprising the steps of:

oxygenating the water; and

raising the pH of the water,

the oxidation of Fe^{2+} cations and the formation of the $Fe(OH)_3$ being carried out in the presence of suspended particulate material in the water, the particulate material being present in the water at a concentration of at least 5 g/l, the raw water containing dissolved SO_4^{2-} anions, the process including the biological oxidation of dissolved Fe^{2+} cations to Fe^{3+} cations and the process being carried out at a temperature of 5–40° C.

14. A process for the treatment of raw water containing dissolved Fe^{2+} cations and dissolved H^+ cations so as to reduce the concentration of Fe^{2+} cations therein, the process comprising the oxidation of dissolved Fe^{2+} cations in the water to Fe^{3+} cations and the formation in the water of solid $Fe(OH)_3$ from said Fe^{3+} cations, the process comprising the steps of:

oxygenating the water; and

raising the pH of the water,

the oxidation of Fe^{2+} cations and the formation of the $Fe(OH)_3$ being carried out in the presence of suspended

particulate material in the water, the particulate material being present in the water at a concentration of at least 5 g/l, the raw water having a pH of at most 7, the raw water having an Acidity, expressed as mg/l of $CaCO_3$ dissolved therein, of at least 200, and the suspended particulate material providing a surface area in the water of at least 100 m^2/m^3 water.

15. A process for the treatment of raw water containing dissolved Fe^{2+} cations and dissolved H^+ cations so as to reduce the concentration of Fe^{2+} cations therein, the process comprising the oxidation of dissolved Fe^{2+} cations in the water to Fe^{3+} cations and the formation in the water of solid $Fe(OH)_3$ from said Fe^{3+} cations, the process comprising the steps of:

oxygenating the water to achieve a dissolved oxygen concentration in the water of at least 0.1 mg/l; and

raising the pH of the water,

the oxidation of Fe^{2+} cations and the formation of the $Fe(OH)_3$ being carried out in the presence of suspended particulate material in the water, the particulate material being present in the water at a concentration of at least 5 g/l, in which process, in combination,

the raising of the pH acts partially to neutralize the water;

the raising of the pH is by dissolving limestone or dolomite in the water; and

the dissolving of the limestone or dolomite in the water and the oxidation by dissolved oxygen of the Fe^{2+} cations to Fe^{3+} cations in the water take place together in the same body of partially neutralized water in the presence of the particulate material.

* * * * *

PATENT 2 LIMESTONE HANDLING AND DOSING SYSTEM

Maree, J.P. 2000. **Limestone Handling and Dosing System**, South Africa (2001/7086), Botswana (BW/A/2001/00014 - Pending), Zambia (24/2001 - Pending), United States of America (US 6,592,246).

US006592246B2

(12) **United States Patent**
Maree

(10) **Patent No.: US 6,592,246 B2**
(45) **Date of Patent: Jul. 15, 2003**

(54) **METHOD AND INSTALLATION FOR FORMING AND MAINTAINING A SLURRY**

(75) Inventor: **Johannes Phillippus Maree**, Gauteng (ZA)

(73) Assignee: **CSIR**, Pretoria (ZA)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/941,886**

(22) Filed: **Aug. 28, 2001**

(65) **Prior Publication Data**

US 2002/0104805 A1 Aug. 8, 2002

(30) **Foreign Application Priority Data**

Aug. 28, 2000 (ZA) 2000/4450

(51) **Int. Cl.**[7] **B01F 15/02**

(52) **U.S. Cl.** **366/132**; 366/136; 366/153.1; 366/160.2; 366/183.1

(58) **Field of Search** 366/132, 134, 366/136, 137, 151.1, 152.1, 152.4, 153.1, 160.1, 160.2, 162.1, 179.1, 181.1, 183.1

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,830,473 A * 8/1974 Lieferman et al.
4,820,053 A * 4/1989 Rivers
5,114,239 A * 5/1992 Allen
5,769,536 A * 6/1998 Kotylak
5,951,161 A * 9/1999 Blagg

FOREIGN PATENT DOCUMENTS

JP 55-41351 * 3/1980

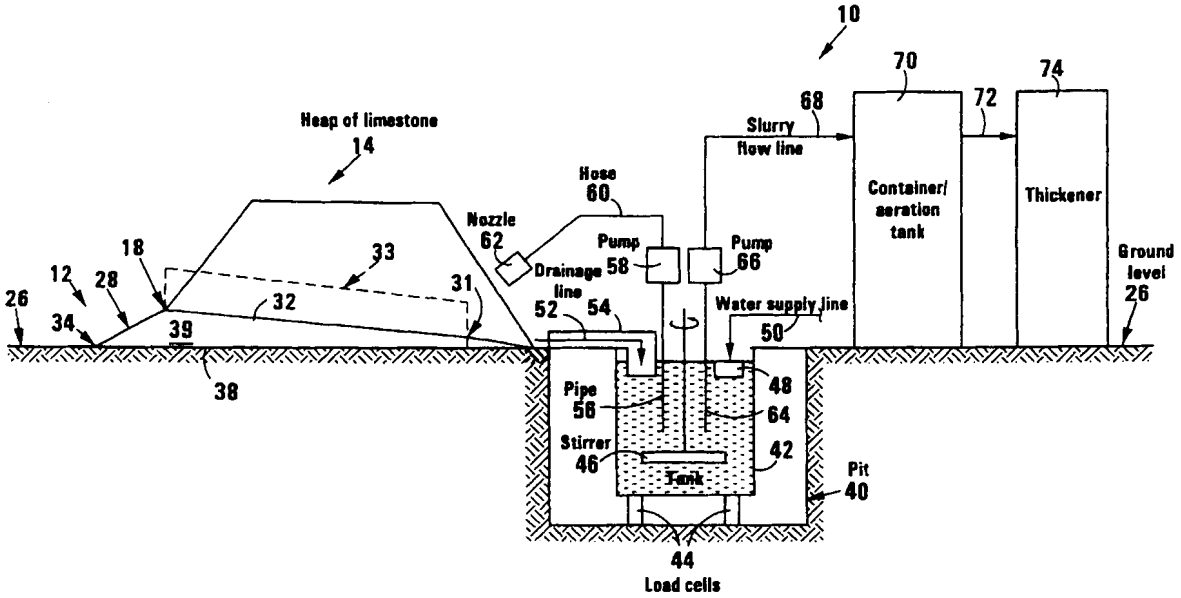
* cited by examiner

Primary Examiner—Charles E. Cooley
(74) *Attorney, Agent, or Firm*—Klarquist Sparkman, LLP

(57) **ABSTRACT**

A method and installation for forming and maintaining a slurry are disclosed. The method withdraws a slurry from a reservoir and directs it at a heap of solid material from which the slurry is drained into the reservoir, the slurry containing additional solid material from the heap to increase its specific gravity. The volume of slurry in the reservoir and its specific gravity are controlled. The installation comprises a support having a support surface which slopes to permit slurry to drain therefrom A reservoir receives slurry draining from the support and has a liquid feed. A pump withdraws the slurry from the reservoir and pumps it to a spray nozzle for spraying slurry at a heap of material on the support.

21 Claims, 2 Drawing Sheets



U.S. Patent Jul. 15, 2003 Sheet 1 of 2 US 6,592,246 B2

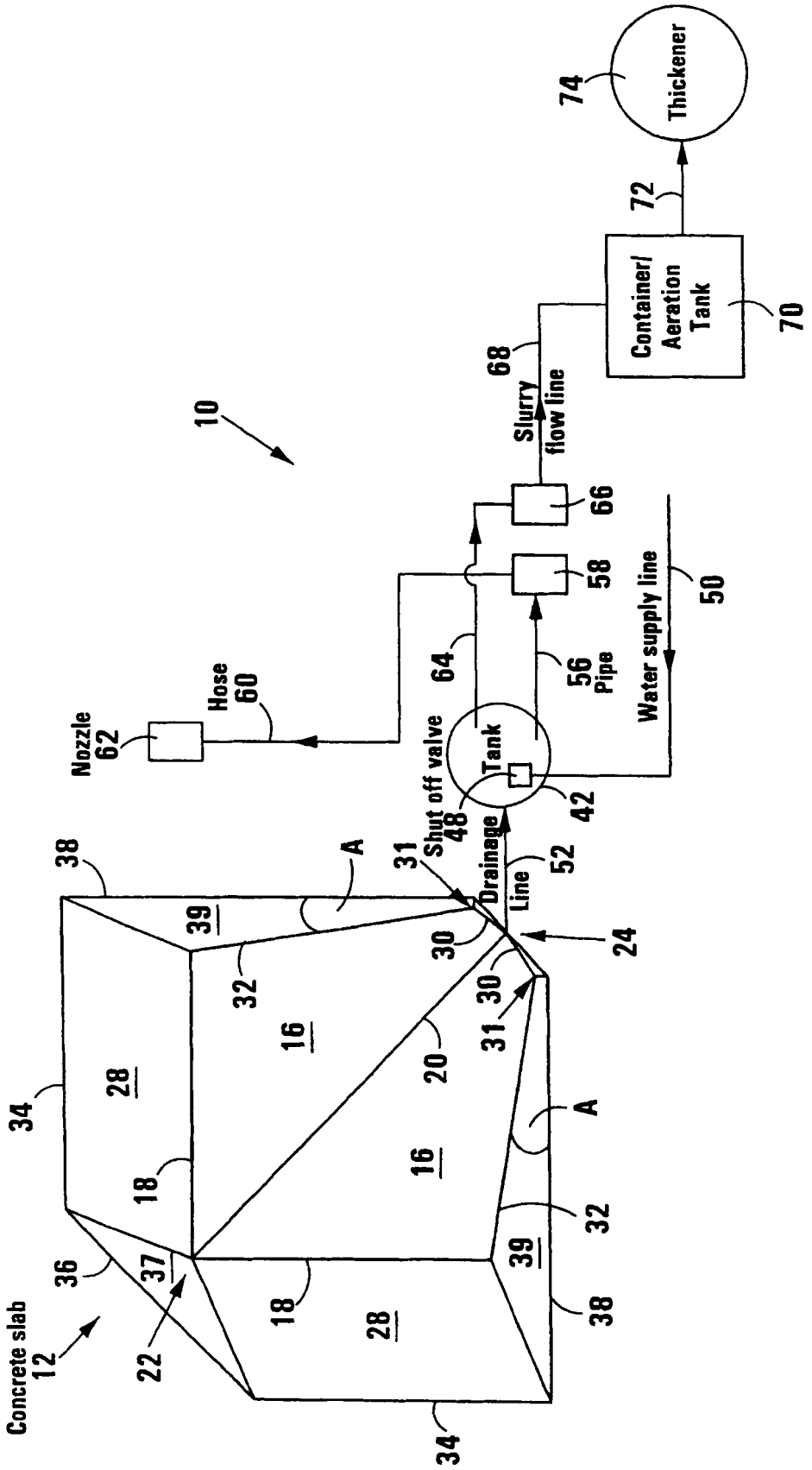


FIG 1

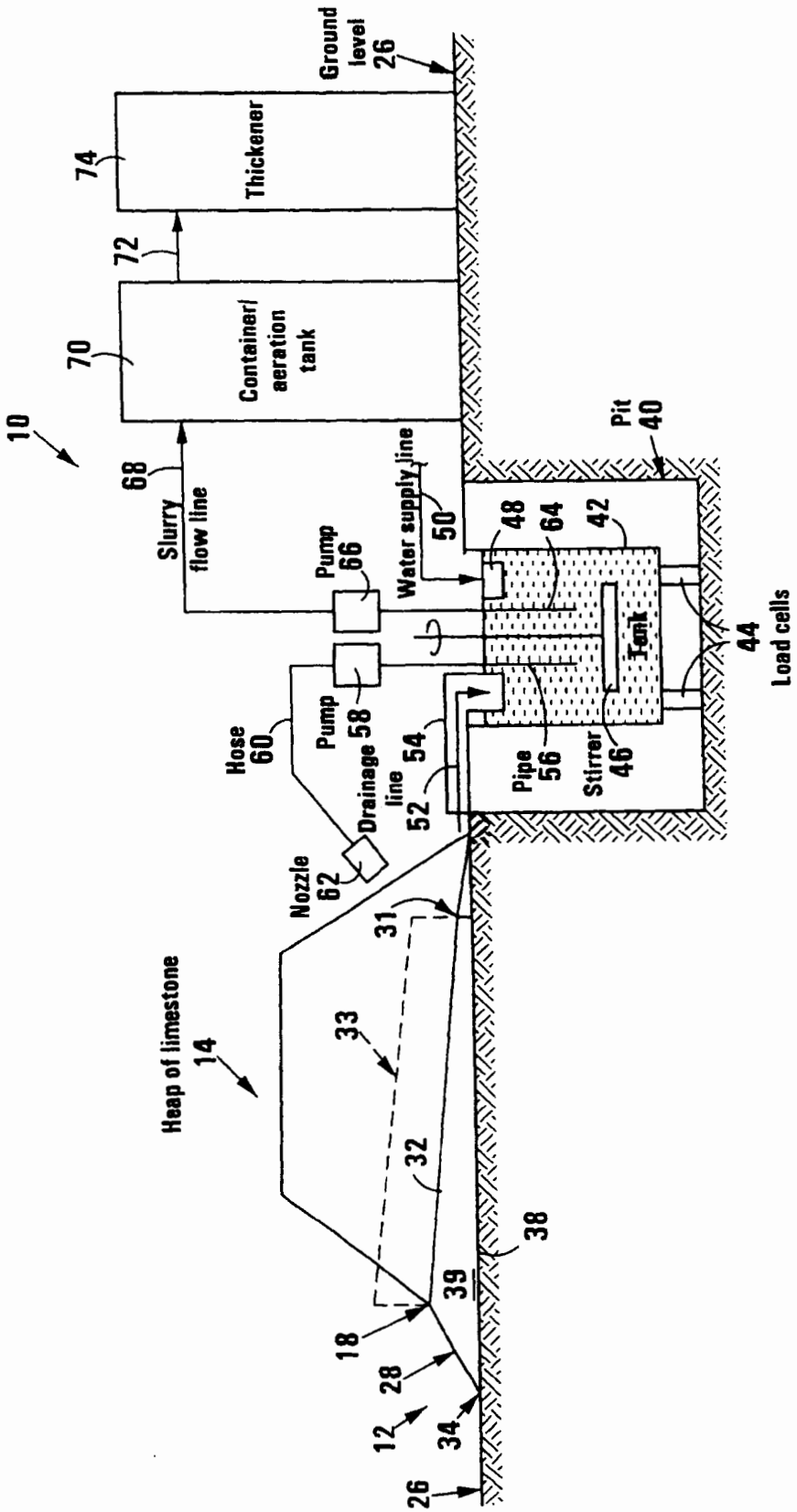

Ground level
26
Thickener
74
72
Container/ aeration tank
70
10
68
Slurry flow line
Pump
66
Water supply line
50
Pit
40
48
64
42
Tank
44
Load cells
Hose
60
Pump
58
54
Drainage line
52
Pipe
56
Stirrer
46
Nozzle
62
31
Heap of limestone
14
33
32
38
39
18
28
12
34
26

FIG 2

METHOD AND INSTALLATION FOR FORMING AND MAINTAINING A SLURRY

FIELD OF THE INVENTION

THIS INVENTION relates to slurries. More particularly, the invention relates to a method and to an installation for forming and maintaining, for consumption, a stock of slurry.

SUMMARY OF THE INVENTION

According to one aspect of the invention there is provided a method of forming and maintaining for consumption a stock of slurry derived from a liquid and from a particulate solid material, the method including the steps of:

withdrawing a slurry of the liquid and the solid material from a stock of the slurry in a reservoir;

directing a stream of the liquid or of the withdrawn slurry at a bulk supply of the solid material in the form of a heap of the solid material, and on to the solid material of the heap;

allowing the stream directed at the heap to drain under gravity from the heap into the reservoir, the stream, while draining from the heap, entraining therein solid material from the heap to increase the specific gravity of the stream and to carry solid material from the heap into the stock of slurry in the reservoir to increase the specific gravity thereof; and

feeding liquid to the reservoir to maintain the volume of the slurry in the reservoir, the method including controlling both the volume of slurry in the reservoir and the specific gravity of the slurry in the reservoir, the feeding of the liquid into the reservoir being initiated, or having its feed rate increased, in response to decreases in the volume of the slurry in the reservoir associated with withdrawal of slurry from the reservoir for consumption thereof, and the directing of the stream at the heap of solid material being initiated, or having its flow rate increased, in response to decreases in the specific gravity of the slurry in the reservoir associated with feeding the liquid to the reservoir, thereby both to maintain the volume of slurry in the reservoir at a desired value, and to maintain the specific gravity of the slurry in the reservoir at a desired value, the feeding of liquid to the reservoir being reduced in rate or discontinued when the desired slurry volume is regained, and the directing of the stream at the heap being reduced in rate or discontinued when the desired specific gravity value is regained.

It will be appreciated that increases and decreases to the specific gravity of the slurry are associated respectively with increases and decreases to the solids content thereof.

While it is in principle possible to carry out the method by directing a stream of the liquid at and on to the solid material of the heap, to form a slurry having a solids content and specific gravity greater than the solids content and specific gravity respectively of the slurry in the reservoir, to permit drainage of a slurry from the heap into the reservoir which increases the solids content and specific gravity of the slurry in the reservoir, it is preferable to employ slurry withdrawn from the reservoir for this purpose. The stream directed at the heap may thus be a stream of the slurry withdrawn from the reservoir.

The method of the invention contemplates that withdrawal of slurry from the reservoir for consumption thereof may be continuous or intermittent, and that the liquid feed to the reservoir, which may be continuous or intermittent,

will be at a rate such that the volume of slurry in the reservoir is maintained at the desired value when slurry is withdrawn for consumption at any rate up to the maximum intended rate. Similarly, the withdrawal of the stream of slurry from the reservoir to direct at the heap, which withdrawal may also be continuous or intermittent, will in turn be at a rate such that the specific gravity of the slurry in the reservoir is maintained at the desired value when the slurry is withdrawn for consumption at any rate up to the maximum intended withdrawal rate for consumption. Thus, the desired volume of the slurry, at least on average and with no more than acceptable departures from the desired value, can be maintained in the reservoir while the specific gravity, ie the density or solids content, of the slurry is likewise maintained, at least on average and with no more than acceptable departures from the desired value. In a particular embodiment of the invention, when the stream directed at the heap is a stream of slurry withdrawn from the reservoir, the liquid feed to the reservoir may be intermittent, being at a fixed rate no less than the maximum rate at which the slurry is withdrawn from the reservoir for consumption, the stream directed at the heap being withdrawn from the reservoir intermittently and at a fixed rate.

In a further particular embodiment of the invention the liquid may be water, the solid material being particulate or powdered limestone, or possibly dolomite. In other words, the liquid may be water, the solid material being selected from the group consisting of limestone, dolomite and mixtures thereof.

The controlling of the volume of slurry in the reservoir may be automatic, being by controlling the depth of slurry in the reservoir by means of a valve, the valve being selected from the group consisting of ultra-violet (UV)-controlled valves and, preferably, float-controlled valves and the valve controlling the liquid feed to the reservoir. Similarly, controlling the specific gravity of the slurry in the reservoir may be automatic, for example by using one or more load cells on which the reservoir is supported, to measure the mass of the reservoir, or by using one or more pressure cells in the interior of the reservoir to measure the static pressure in the reservoir, said cell or cells controlling the withdrawal of the stream of liquid from the reservoir which is directed at the heap. In other words, the controlling of the specific gravity of the slurry in the reservoir may be automatic, being by using a cell selected from load cells which measure the mass of the reservoir and pressure cells which measure static pressure in the reservoir, to control the directing of the stream at the heap. The liquid feed to the reservoir or the slurry stream withdrawal from the reservoir may be provided with on/off flow control, and/or they may incorporate variation of their flow rates in response to the magnitude of any departure of the slurry volume or specific gravity from the respective desired values thereof.

Indeed, instead of using load cells or pressure cells, the reservoir can in principle float in a body of water, the depth at which the reservoir floats in the body of water being related to the mass of the reservoir and hence to the specific gravity of the slurry therein, changes in this depth being used to control the directing of the stream at the heap, although it is expected that use of load cells or pressure cells will be preferred.

The method may involve agitation of the slurry in the reservoir to promote maintenance of the solid material in suspension in the liquid and to resist its settling out from the liquid, and the method may include replenishing the bulk supply of particulate material in the heap, as and when required, e.g. intermittently by means of vehicles loaded

therewith Withdrawal of slurry from the reservoir, either as a stream to be directed at the heap, or for consumption thereof, may be by pumping it, and directing the stream of slurry at the heap may be by spraying it, e.g. from one or more spray nozzles at the ends of respective hoses, which may be hand-held. In particular, the method may include the step of agitating the slurry to promote maintenance of the solid in suspension in the liquid, withdrawal of slurry from the reservoir being by pumping, directing the stream at the heap being by spraying it from one or more hand-held nozzles, and feeding the liquid to the reservoir being by directing it at the heap.

If desired, the method may make provision for the removal of stones and/or grit from the slurry, between the reservoir and the hose or hoses, e.g. by passing the slurry upwardly through an inverted-conical tank, the slurry from the reservoir being fed into the tank at a low level where its diameter is small, and the slurry issuing from the tank at a high level where its diameter is large, the tank shape and size and the slurry flow rate being selected to promote retention of stones and grit in the tank, while an overflow from the tank takes the place of slurry containing particles of acceptably small size, and stones and grit are removed, e.g. intermittently from the lower parts of the tank; and slurry can, if desired, be recirculated from the top of the tank to its bottom, to achieve upward flow rates in the tank which keep small slurry particles in suspension.

The feeding of the liquid to the reservoir to maintain the volume of slurry in the reservoir may be directly from a liquid supply into the reservoir, or it may be indirect, the liquid being fed from the liquid supply into the stream of slurry which is directed at the bulk supply, so that the liquid enters the reservoir as part of the slurry draining into the reservoir

According to another aspect of the invention there is provided an installation for forming and maintaining, for consumption, a stock of slurry derived from a liquid and from a bulk supply of particulate solid material, the installation including;

- a support having an upwardly facing support surface for supporting a heap of particulate solid material, the support surface sloping so that it is inclined to the horizontal to permit a slurry of liquid and particulate solid material to drain under gravity therefrom;
- a reservoir arranged to receive slurry draining under gravity from the support surface of the support and to hold a stock of slurry;
- a liquid feed for feeding liquid to the reservoir;
- a slurry withdrawal device for withdrawing slurry from a stock of slurry in the reservoir;
- a spray device for spraying a liquid or slurry at a heap of particulate material supported on the support and on to the particulate material of the heap;
- a volume control device for controlling the volume of the stock of slurry in the reservoir and operative, in response to a decrease in said volume below a desired value, to initiate, or increase the rate of, the feeding of liquid by the liquid feed to the reservoir; and
- a specific gravity control device for controlling the specific gravity of the stock of slurry in the reservoir and operative, in response to a decrease in said specific gravity below a desired value, to initiate, or increase the rate of, the spraying of the liquid or slurry at the heap,
- the volume control device being operative to discontinue, or to reduce the rate of feeding of, liquid to the reservoir, when the desired volume is regained and the specific gravity control device being operative to discontinue, or to reduce the rate of spraying of, the liquid or slurry at the heap, when the desired specific gravity is regained.

The support may be a cementitious, e.g. concrete, slab resting on the ground and having a shaped support surface for supporting the heap, the support surface having, for example, two flat portions which slope and converge downwardly to meet at a line of intersection therebetween, which line in turn slopes downwardly towards a drainage point where the support surface drains into the reservoir. The slab may have a pair of ramps, respectively sloping upwardly from ground level to peripheral edges of the flat portions of the support surface, to facilitate the tipping of particulate material from load vehicles on to the support surface. In a particular embodiment of the installation, the support may thus be a slab of cementitious material having a shaped support surface for supporting the heap, the support surface sloping downwardly to a drainage point and the slab being provided with a vehicle ramp leading upwardly from ground level to a peripheral edge of the slab, which edge is raised above ground level, the reservoir being a completely mixed tank located below the level of the drainage point and provided with a stirrer in its interior.

The reservoir may in turn be in the form of an open-topped completely mixed tank, located in a pit below ground level, at a position where the support surface can drain under gravity into the open top of the tank, and having a stirrer in its interior.

The slurry withdrawal device may be a pump. The pump for withdrawal of slurry for consumption may simply feed into a pipe or similar flow line; and there may be a further similar pump for withdrawal of a stream of slurry to be directed at the heap, which further pump may feed Into one or more hoses, each optionally provided with a spray nozzle at its free end. Thus, the spray device may comprise one or more hoses, each of which has a free end provided with a spray nozzle.

The volume control device may be in the form of a liquid level control means and may thus be an ultra-violet (UV)-controlled valve or preferably a float-controlled valve controlling feeding of liquid from the liquid feed, which may be a pipe, into the reservoir, the valve conveniently being a shut-off or on-off valve arranged to open fully and permit feeding of liquid at a fixed rate into the reservoir if the level of slurry in the reservoir decreases below a desired value, equivalent to the desired slurry volume in the tank, and to shut off liquid flow from the pipe when said desired level is regained. Accordingly, the volume control device may be a shut-off valve selected from the group consisting of ultra-violet (UV)-controlled valves and float-controlled valves, the shut-off valve being arranged to open if the level of slurry in the reservoir decreases below a desired value and to close when said desired value is regained.

The specific gravity control device may be one or more load cells on which the tank is supported in the pit, arranged to control withdrawal of the stream of slurry from the tank by automatically starting the associated pump, or increasing its pumping rate, when the mass of the tank and the desired volume of slurry in the tank contents decreases below a predetermined value corresponding to the desired specific gravity, and arranged automatically to discontinue the pumping, or reduce its rate, when the predetermined value is regained Thus, generally, the specific gravity control device may comprise at least one cell selected from the group consisting of load cells on which the reservoir is supported for sensing the mass of the reservoir, and pressure cells in

the interior of the reservoir for sensing static pressure in the reservoir, the cell being operatively connected to a shut-off valve for supplying liquid or slurry to the spray device.

In this regard it will be appreciated that spraying slurry on to the heap and allowing it to drain under gravity into the tank while entraining particulate solid material from the heap, will increase the concentration of solid material in the slurry in the tank and hence will increase the mass of the slurry and hence will increase the total mass of the tank and its contents when filled with the desired volume of slurry. Correspondingly, feeding liquid into the tank will dilute the slurry and reduce the mass of the slurry and hence reduce the total mass of the tank and its contents when filled with slurry to the desired volume or level. Withdrawal of slurry from the tank for consumption leads to feeding liquid into the tank and to a decrease in specific gravity of the slurry, which in turn leads to spraying of slurry on to the heap and washing solid material from the heap into the tank, thereby causing a compensatory increase in specific gravity. Thus, both the volume or level of slurry in the tank, and its specific gravity, can automatically be maintained.

Instead of comprising one or more load cells, the specific gravity control device may comprise one or more pressure cells in the tank, e.g. at or near its bottom, arranged to control the withdrawal of the stream of slurry from the tank by automatically starting the associated pump, or increasing its pumping rate, when the pressure sensed by the pressure cells decreases below a predetermined value corresponding to the desired specific gravity, the pressure cells being arranged automatically to discontinue the pumping, or to reduce its rate, when the sensed pressure regains its predetermined value. In this regard it will be appreciated that the pressure exerted by the slurry, at a particular depth, is directly related to the specific gravity of the slurry which in turn is, directly related to the solids concentration in the slurry. The pressure cell or cells are thus functionally equivalent to the load cell or cells, the cell or cells in question in each case being, for example, electrically connected to a switch or pump flow control means for switching the associated pump on or off or for controlling its pumping rate, which pump is thus conveniently electrically driven. In particular, the specific gravity control device may comprise at least one cell selected from the group consisting of load cells on which the reservoir is supported for sensing the mass of the reservoir, and pressure cells in the interior of the reservoir for sensing static pressure in the reservoir, the cell being operatively connected to a shut-off valve for supplying liquid or slurry to the spray device.

The pump for withdrawing the slurry stream from the tank, and the pump for withdrawing slurry for consumption from the tank, may each be submersible pumps suspended in slurry in the tank, or, conveniently, may each be outside the tank having inlet pipes projecting downwardly into the slurry in the tank, in each case extending downwardly via the open top of the tank into the slurry, so that the mass of or pressure in the tank is essentially unaffected thereby, there being no direct physical connection between said pumps (or the their inlet pipes), and the tank walls of floor, particularly when load cells are employed. If desired, the inlet pipes to the pumps which project downwardly from the pipes into the slurry, may be replaced by flexible pipes or hoses connected to the tank, in which case it may be preferable to replace the load cells with pressure cells which function as described above.

If desired, the installation may be in the form of a portable apparatus. Thus, the reservoir and the associated slurry withdrawal means, volume control means and separate gravity control means may be of a size which permits them to be taken from site to site, where they are installed, on a vehicle such as a truck or lorry, and the support may, instead of being a concrete slab, be a container, such as a portable shipping container, having an open top to permit loading thereof, for example, with particulate material by means of a front end loader, and having a closeable slot at an end thereof from which drainage of slurry can take place if the container is mounted at an angle with the slot lowermost.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described by way of example, with reference to the accompanying diagrammatic drawings, in which:

FIG. **1** is a schematic plan view of an installation according to the invention; and

FIG. **2** is a schematic side elevation of the installation of FIG. **1**.

In FIGS. **1** and **2** of the drawings the same reference numerals are used to designate the same parts, unless otherwise specified, and, in the drawings an installation for forming and maintaining a stock of slurry, in the form of a limestone or calcium carbonate slurry is generally designated by reference numeral **10**.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The installation **10** comprises a concrete slab, generally designated **12**, shown in FIG. **2** to be supporting a heap **14** of limestone powder. The slab **12** has a flat lower surface (not shown) resting on the ground surface and an upwardly facing support surface supporting the heap **14**, the support surface being made up of two flat portions **16** (see in particular FIG. **1**). The portions **16** shape and converge downwardly from uppermost ridges **18** to meet at a line of intersection **20** therebetween. The ridges **18** meet at a position **22** which is at the uppermost end of the line of intersection **20**, the line of intersection sloping downwardly from an upper end thereof at the position **22**, to a lower end thereof at **24**, at the level of the ground **26**. The line of intersection **20** defines the bottom of a drainage channel formed in the support surface of the slab **12** by and between the portions **16** which drains, downwardly from position **22** to position **24**, position **24** forming a drainage point where the slab **12** finally drains.

The slab has a pair of ramps **28** sloping upwardly from the level of the ground **26** respectively to the ridges **18**. The ridges **18** are horizontal and the ramps **28** are flat and slope at an angle of 13° to the horizontal, upwardly from ground level to their respective ridges **18**, which are 1.14 m above ground level and are each 12.02 m long. The line of intersection **20** is 13.05 m long.

The portions **16** of the support surface of the slab **12** each have a short edge **30** sloping downwardly from an upper end thereof, at a position **31** which is 0.35 m above the ground, towards the line of intersection **20**, which they meet at the position **24** Each portion **16** further has an edge **32** sloping upwardly from the associated position **31** to the adjacent end of the associated ridge **18**. Each edge **32** has a 0.3 m high wall (broken lines at **33** in FIG. **2**) extending along its length. The ground level periphery of the slab **12** is made up of the lower edges **34** of the ramps **28**, the lower edge **36** of a triangular face **37** on the slab **12** whose corners are at the adjacent ends of the edges **34** and the position **22**, and edges **38** of quadrangular faces **39** of the slab **12**. The edges **32** of

the faces **39** are at an included acute angle A of 7.1° to the edges **38** of said faces **39**. Each face **39** has its corners respectively at opposite ends of its edge **38**, at the associated position **31** and at the end of its edge **32** remote from the position **31**. While the face **37** in fact slopes upwardly and inwardly from its edge **36** to the position **22**, the faces **39** are vertical, the end of each ridge **18** remote from the position **22** being directly above the associated edge **38**. The ramps **28** are elongate rectangular in outline having end edges joining the edges **18**, **34** thereof, the end edges being 5.06 m in length, the edge **36** in turn being 6.97 m long and each edge **32** being 12.09 m long, while each edge **38** is 16.93 m long.

Adjacent the edges **30** of the portions **16** of the upwardly facing support surface of the slab **12** is a pit **40** in the ground **26** (the pit **40** not being shown in FIG. **1**). In the illustrated pit an open topped tank **42** is mounted on a pair of load cells **44**. The tank **42** contains a stirrer **46** (not shown in FIG. **1**) and a valve, such as the illustrated float controlled inlet valve **48**, is suspended in the top of the tank **42** at the end of a water supply line **50**. A drainage line **52** is shown feeding from the lower end **24** of the line **20** of intersection **20** of the slab **12** into the tank **42**, the line **52** being defined by a pipe **54** (not shown in FIG. **1**).

A flow line defined by a pipe **56** extending downwardly into the tank **42** via its open top leads to a pump **58** which feeds into a hose **60** having a spray nozzle at its end remote from the pump **58**. Similarly a flow line defined by a pipe **64** extending downwardly into the tank **42** via its open top leads to a pump **66** which feeds Into a pipe **68** leading to a container/aeration tank **70** of an acid water neutralization plant, the tank **70** being shown feeding via a line **72** into a thickener **74**.

In a variation of the slab **12** (which is not drawn to scale in FIGS. **1** and **2**), the dimensions are somewhat different. Thus, in the variation the ridges **18** are 12.03 m long, the line of intersection **20** being 13.09 m long, while the ramps **28** remain inclined at 13° to the horizontal. The ridges **18** are 1.5–1.6 m above the flat bottom of the slab and the position **31** is 0.4–0.5 m above the bottom of the slab. Edge **32** of face **39** is 6.41 m in length and edge **38** is 7.63 m in length, angle A being 8.5° Face **37** has its edge **36** 1.83 m long and the short edges of the ramps **28** interconnecting the ends of the edges **34** and the ends of the ridges **18**, are 1.33 m in length. In use it is intended that this variation of the slab be partially embedded in the ground, with its flat lower surface horizontal and 1.07 m below ground level, and its ridges **18** horizontal and 0.3 m above ground level. Edges **32** of faces **39** will in this case be provided with walls having horizontal upper edges which project 0.5 m above ground level; and the top of the tank **42** will be sufficiently sunken below ground level to permit drainage from position **24** on the slab into the open top of the tank **42**. In a yet further variation, if it is desired, for example, to have the tank **42** on and above the ground to avoid the need for a pit **40** (see FIG. **2**) either of the slabs **12** described above can be raised above ground level on a platform or plinth, in which case loading of the slab **12** can, instead of being by means of a tipper truck as described hereunder for FIGS. **1** and **2**, be by means of a front end loader. Finally, with regard to the slab **12**, it need not be entirely solid, and its lower surface need not be flat, the slab, for example having downwardly facing cavities or indentations to effect a saving of concrete.

In accordance with the method of the present invention, and with reference to FIGS. **1** and **2** of the drawings, at start-up, one or more loads of calcium carbonate may be loaded on to the upwardly facing support surface constituted by the portions **16** of the upper surface of the slab **12**. This is conveniently carried out by tipper trucks, which can reverse up either of the ramps **28** prior to tipping, so as to tip on to the portions **16**, to form the heap **14** (FIG. **2**) of calcium carbonate there The tank **42** can, at the same time, be at least partially filled with water, from the water supply line or pipe

Then, the pump **58** is used to pump water from the tank **42** along the pipe **56** and hose **80** to the nozzle **62**, and the nozzle **52** is directed by hand at and on to the calcium carbonate of the heap **14**, above or adjacent the position **24** at the lower end of the channel defined by the line of intersection **20** between the portions **16**. A slurry of calcium carbonate is formed, which is washed towards said position **24**, the slurry then draining in the direction of flow line **52** along the pipe **54** (FIG. **2**) into the open top of the tank **42** In this way a starting charge or load of slurry can be charged into the tank **42**, up to a desired level or depth, which can be determined by the float-controlled valve **48** which admits water into the tank **42** from the pipe **50**.

Thereafter, after start-up, slurry for consumption is pumped by pump **66** along fines **64** and **68** and line **72** in series to the conditioner/aeration tank **70** and thickener **74**, as required. As soon as such pumping for consumption takes place, the float-controlled valve **48** will open, to admit further water into the tank **42** from flow line **50**. The load cells **44** on which the tank **42** is mounted measure the mass of the tank **42** and it slurry contents. In this regard it is to be noted that the pipe **54**, the stirrer **46** which is employed to keep the contents of the tank **42** agitated and to resist settling of solids from the slurry, and the pipes **50**, **56** and **64** and the float-controlled valve **48**, are not connected to the tank **42**, but are merely suspended to project downwardly into its interior, into the slurry in the tank **42**. The thus do not contribute to the mass of the tank **42** and its contents, as measured by the load cells **44**.

As slurry for consumption is withdrawn by pump **66** and water is admitted from pipe **50** via float-controlled valve **48**, the specific gravity of the slurry in the tank **42** progressively decreases, until it falls below a desired level (unless it was already below the desired specific gravity value at start-up). If the specific gravity is, or as soon as its falls below this desired level, the load cells **44** automatically cause operation of the pump **58** to spray slurry from the nozzle **62** on to the heap **14**. This washes additional calcium carbonate from the heap into the tank **42** along line **52**, thereby raising the specific gravity of the slurry in the tank **42**, until it exceeds said desired level, at which stage the load cells **44** switch off the pump **58**.

From time to time the calcium carbonate on the heap **14** is replenished from tipper trucks, and in this fashion a full charge of slurry of the appropriate specific gravity is maintained in the tank **42**, for consumption as and when desired, in the conditioning/aeration tank **70** and thickener **74**.

The method as described above will involve intervention by an operator from time to time to tip calcium carbonate on to the slab **12**, and to direct the hand-held hose **60** and nozzle **62** at appropriate parts of the heap **14**. Naturally, however, if increased automation is desired, several hoses **60** may be provided with nozzles **60** which are either directed in fixed attitudes and in fixed positions at different parts of the heap **14**, or which are moved automatically and mechanically when the pump **58** is operative, to lay down a desired spray pattern on the calcium carbonate of the heap **14**. Thus the calcium carbonate can be progressively entrained in the circulating slurry, and is washed into the tank **42** in a fashion such that, if the calcium carbonate of the heap **14** is not replenished, it will eventually all be washed into the tank **42**.

It should be noted that the capacity of pump **58**, and the capacity of the water supply along pipe **50**, should be selected so that the slurry level in the tank **42** can be maintained at the desired level even if the pump **66** is operated continuously, and so that the solids concentration and specific gravity of the slurry can also be maintained at the desired level, in the event of such continuous pump operation.

It is an advantage of the invention that it provides a method and installation for forming and maintaining a stock of slurry in the tank **42**, for example a water/calcium carbonate slurry, in a easily applied automated or semi-automated fashion.

What is claimed is:

1. A method of forming and maintaining for consumption a stock of a slurry derived from a liquid and from a particulate solid material, the method including the steps of:

withdrawing the slurry of the liquid and the solid material from the stock of the slurry in a reservoir;

directing a stream of additional said liquid or of the withdrawn slurry at a bulk supply of additional said solid material in the form of a heap of the solid material, and on to the solid material of the heap;

allowing the stream directed at the heap to drain under gravity from the heap into the reservoir, the stream, while draining from the heap, entraining therein the additional solid material from the heap to increase the specific gravity of the stream and to carry said additional solid material from the heap into the stock of the slurry in the reservoir to increase the specific gravity of the stock of the slurry in the reservoir; and

feeding additional said liquid to the reservoir to maintain the volume of the slurry in the reservoir,

the method including controlling both the volume of the slurry in the reservoir and the specific gravity of the slurry in the reservoir, the feeding of the additional liquid into the reservoir being initiated, or the feed rate of the additional liquid being increased, in response to decreases in the volume of the slurry in the reservoir associated with the withdrawal of the slurry from the reservoir for consumption of the slurry, and the directing of the stream at the heap of the solid material being initiated, or the flow rate of the stream being increased, in response to decreases in the specific gravity of the slurry in the reservoir associated with the feeding of the additional liquid to the reservoir, thereby both to maintain the volume of the slurry in the reservoir at a desired value, and to maintain the specific gravity of the slurry in the reservoir at a desired value, the feeding of the additional liquid to the reservoir being reduced in rate or discontinued when the desired slurry volume is regained, and the directing of the stream at the heap being reduced in rate or discontinued when the desired specific gravity value is regained.

2. A method as claimed in claim **1**, in which the stream directed at the heap is a stream of the slurry withdrawn from the reservoir.

3. A method as claimed in claim **2**, in which the additional liquid feed to the reservoir is intermittent and is at a fixed rate no less than the maximum rate at which the slurry is withdrawn from the reservoir for consumption, the stream directed at the heap being withdrawn from the reservoir intermittently and at a fixed rate.

4. A method as claimed in claim **1**, in which the liquid is water, the solid material being selected from the group consisting of limestone, dolomite and mixtures thereof.

5. A method as claimed in claim **1**, in which the controlling of the volume of slurry in the reservoir is automatic, being by controlling the depth of the slurry in the reservoir by means of a valve, the valve controlling the additional liquid feed to the reservoir.

6. The method of claim **5**, wherein the valve is selected from the group consisting of ultra-violet (UV)-controlled valves and float-controlled valves.

7. The method of claim **6**, wherein the valve is a float-controlled valve.

8. A method as claimed in claim **1**, in which the controlling of the specific gravity of the slurry in the reservoir is automatic, being by using a cell to control the directing of the stream at the heap.

9. The method of claim **8**, wherein the cell is selected from the group consisting of load cells which measure the mass of the reservoir and pressure cells which measure static pressure in the reservoir.

10. The method of claim **9**, wherein the cell is a load cell.

11. A method as claimed in claim **1**, which includes the step of agitating the slurry in the reservoir to promote maintenance of the solid material in suspension in the liquid, the withdrawal of the slurry from the reservoir being by pumping, the directing of the stream at the heap being by spraying the stream from at least one hand- held nozzle, and the feeding of the liquid to the reservoir being by directing the liquid at the heap.

12. An installation for forming and maintaining, for consumption, a stock of a slurry derived from a liquid and from a bulk supply of a particulate solid material, the installation including:

a support having an upwardly facing support surface for supporting a heap of the particulate solid material, the support surface sloping so that the support surface is inclined to the horizontal to permit a said slurry of the liquid and of the particulate solid material to drain under gravity from the support surface;

a reservoir arranged to receive the slurry draining under gravity from the support surface of the support and to hold a said stock of slurry;

a liquid feed for feeding additional said liquid to the reservoir;

a slurry withdrawal device for withdrawing the slurry from the stock of slurry in the reservoir;

a spray device for spraying additional said liquid or said slurry at a said heap of particulate material supported on the support and on to the particulate material of the heap;

a volume control device for controlling the volume of the stock of slurry in the reservoir and operative, in response to a decrease in said volume below a desired value, to initiate, or to increase the rate of, the feeding of the additional liquid by the liquid feed to the reservoir; and

a specific gravity control device for controlling the specific gravity of the stock of the slurry in the reservoir and operative, in response to a decrease in said specific gravity below a desired value, to initiate, or to increase the rate of, the spraying of the additional liquid or of the slurry at the heap,

the volume control device being operative to discontinue, or to reduce the rate of the feeding of the additional liquid to the reservoir, when the desired volume is regained and the specific gravity control device being operative to discontinue, or to reduce the rate of, the spraying of the additional liquid or the slurry at the heap, when the desired specific gravity is regained.

13. An installation as claimed in claim 12, in which the support is a slab of cementitious material having a shaped said support surface for supporting the heap, the support surface sloping downwardly to a drainage point and the slab being provided with a vehicle ramp leading upwardly from ground level to a peripheral edge of the slab, which edge is raised above ground level, the reservoir being a tank located below the level of the drainage point and provided with a stirrer in its interior.

14. An installation as claimed in claim 12, in which the slurry withdrawal device is a pump.

15. An installation as claimed in claim 12, in which the spray device comprises at least one hose having a free end provided with a spray nozzle.

16. An installation as claimed in claim 12, in which the volume control device is a shut-off valve, the shut-off valve being arranged to open if the level of slurry in the reservoir decreases below a desired value and to close when said desired value is regained.

17. An installation as claimed in claim 16, wherein the valve is selected from the group consisting of ultra-violet (UV)-controlled valves and float-controlled valves.

18. An installation as claimed in claim 17, wherein the valve is a float-controlled valve.

19. An installation as claimed in claim 12, in which the specific gravity control device comprises at least one cell, the cell being operatively connected to a shut-off valve for supplying the additional liquid or the slurry to the spray device.

20. An installation as claimed in claim 19, wherein the valve is selected from the group consisting of load cells which the reservoir is supported for sensing the mass of the reservoir, and pressure cells in the interior of the reservoir for sensing static pressure in the reservoir.

21. An installation as claimed in claim 20, wherein the cell is a load cell.

* * * * *

PATENT 3 INTEGRAL CHEMICAL/BIOLOGICAL PROCESS

Maree, J.P. 2003. **Integral Chemical/Biological Process**, South Africa (2003/1362), Australia (2001279996 – Examination Requested), Canada (2,418,472 - Examination Requested) EPO (1,313,668), USA (US 6,863,819), China (01816205.3), Great Britain (1,313,668), France (1,313,668), Germany (1,313,668)

US006863819B2

(12) **United States Patent**
Maree

(10) **Patent No.: US 6,863,819 B2**
(45) **Date of Patent: Mar. 8, 2005**

(54) **WATER TREATMENT METHOD**

(75) Inventor: **Johannes Phillippus Maree**, Pretoria (ZA)

(73) Assignee: **CSIR**, Pretoria (ZA)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **10/362,277**

(22) PCT Filed: **Aug. 21, 2001**

(86) PCT No.: **PCT/IB01/01513**

§ 371 (c)(1),
(2), (4) Date: **Feb. 20, 2003**

(87) PCT Pub. No.: **WO02/16272**

PCT Pub. Date: **Feb. 28, 2002**

(65) **Prior Publication Data**

US 2003/0160003 A1 Aug. 28, 2003

(51) **Int. Cl.**[7] **C02F 1/64**

(52) **U.S. Cl.** **210/631**; 44/621; 44/624; 210/713; 210/716; 210/718; 210/721; 210/724; 210/726; 210/912; 423/636

(58) **Field of Search** 44/621, 624; 210/713, 210/716, 718, 721, 722, 723, 724, 726, 727, 912, 913, 631; 423/34, 55, 101, 140, 636

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,630,504	A *	12/1971	Reynolds	423/175
3,736,254	A	5/1973	Croom	
3,960,513	A *	6/1976	Agarwal et al.	44/625
4,059,513	A *	11/1977	Zadera	210/696
4,076,620	A	2/1978	Opferkuch, Jr. et al.	
5,035,807	A *	7/1991	Maree	210/711
5,156,746	A	10/1992	Maree et al.	
5,954,969	A *	9/1999	Hedin	210/709
6,280,630	B1 *	8/2001	Ramsay	210/711
6,419,834	B1 *	7/2002	Maree	210/722

FOREIGN PATENT DOCUMENTS

EP	0072885	3/1983
JP	01075093	3/1989
WO	WO 99/01383	6/1998
ZA	984724	6/1998

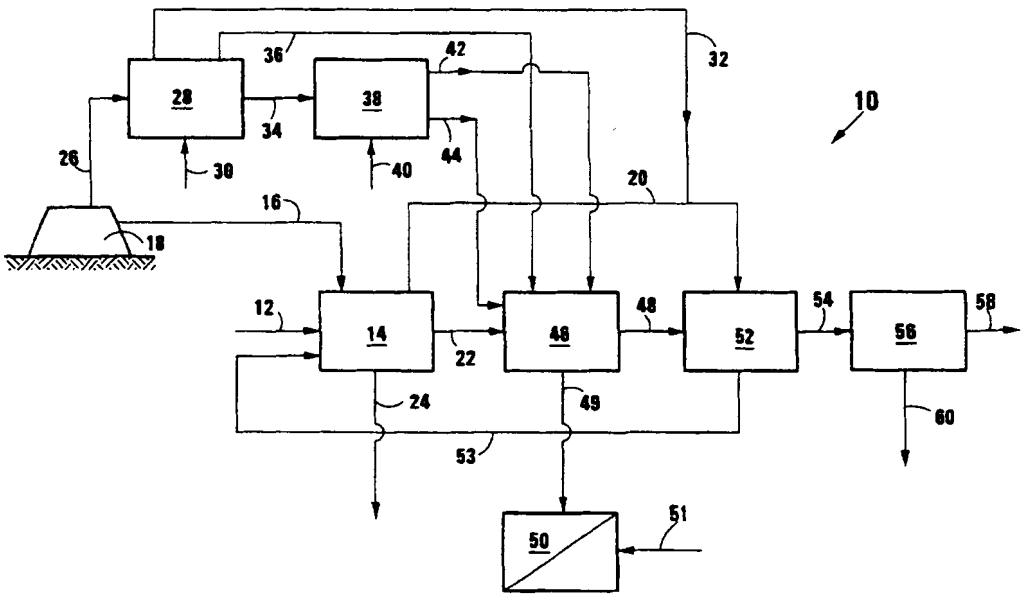
* cited by examiner

Primary Examiner—Peter A. Hruskoci
(74) *Attorney, Agent, or Firm*—Klarquist Sparkman LLP

(57) **ABSTRACT**

The invention provides a method treating acid raw water including the step of neutralising the water by adding calcium carbonate to it in a neutralising stage. The neutralised water is then rendered alkaline or more alkaline by adding an alkali thereto selected from calcium hydroxide, calcium oxide and mixtures thereof in a lime treatment stage. The alkaline water is then treated with carbon dioxide in a carbon dioxide treatment stage, with the carbon dioxide reacting in the carbon dioxide treatment stage with calcium hydroxide dissolved in the water.

16 Claims, 2 Drawing Sheets



U.S. Patent Mar. 8, 2005 Sheet 1 of 2 US 6,863,819 B2

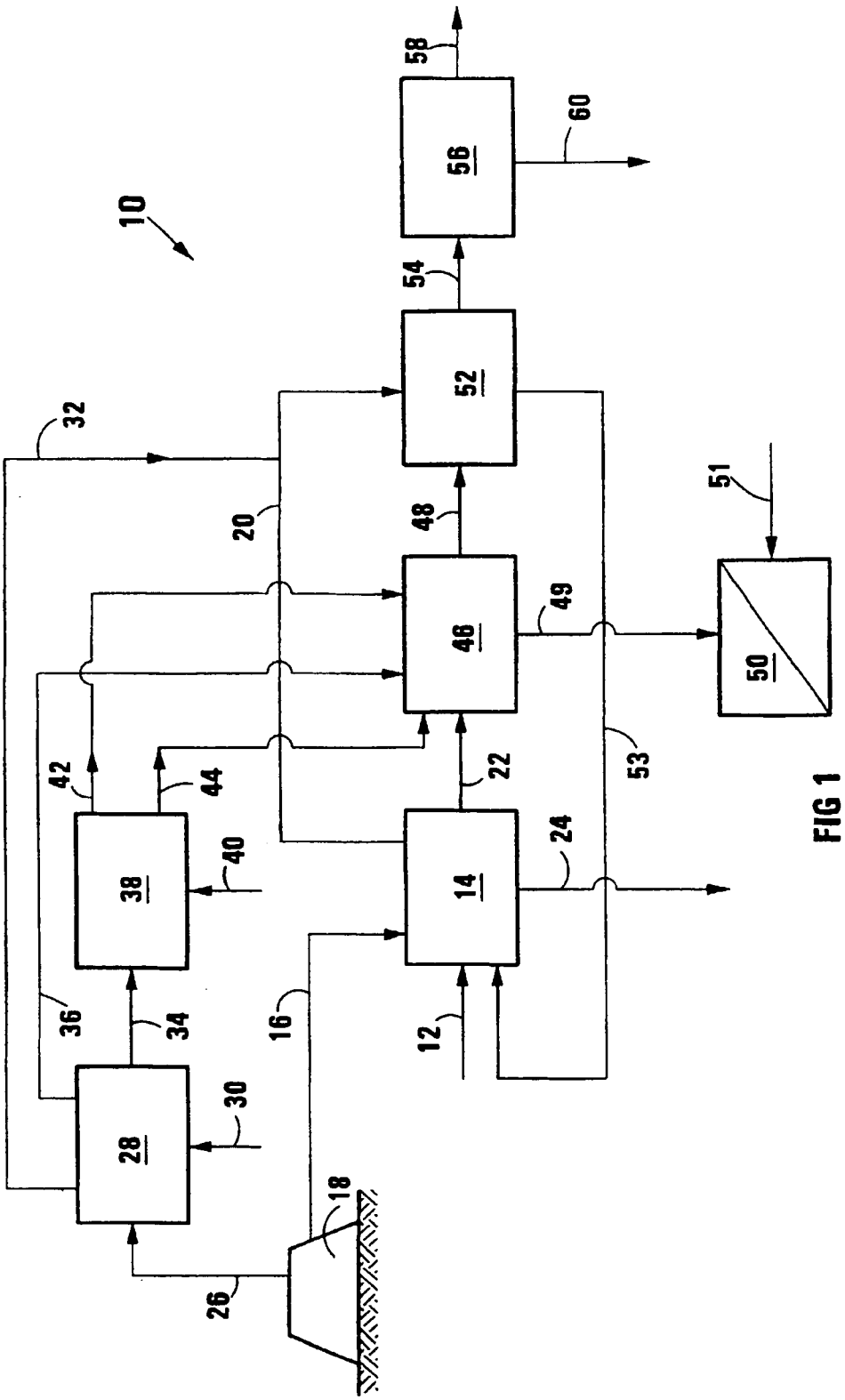


FIG 1

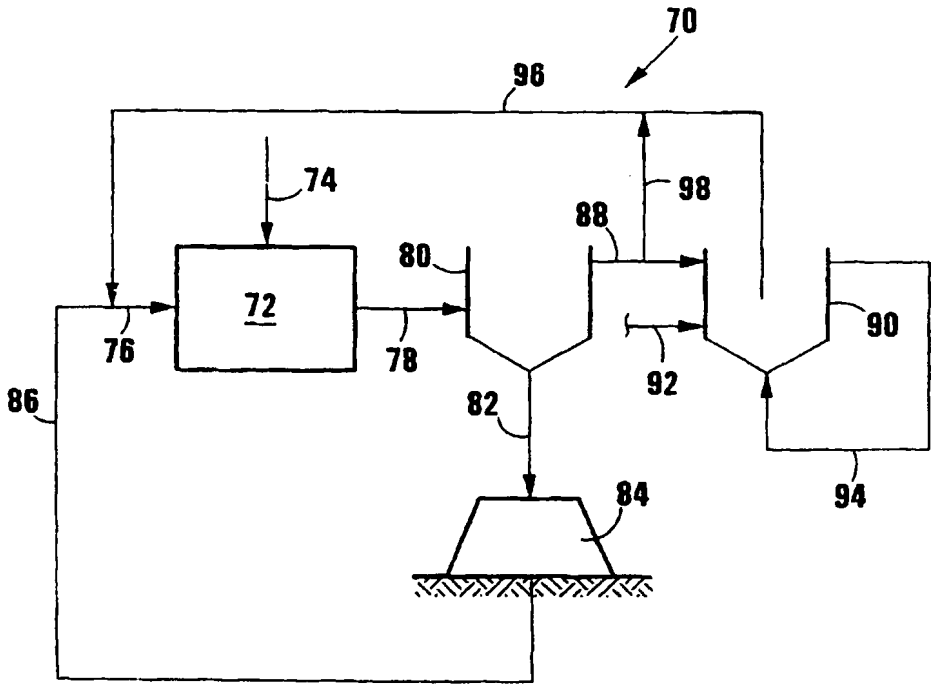


FIG 2

WATER TREATMENT METHOD

CROSS REFERENCE TO RELATED APPLICATIONS

This is the U.S. National Stage of International Application No. PCT/IB01/01513, filed Aug. 21, 2001 (published in English under PCT Article 21(2)), which in turn claims a right of priority from South African Application No. 2000/4290, filed Aug. 21, 2000. Both applications are incorporated herein in their entirety.

This invention relates to the treatment of water. More particularly, the invention relates to a method of treating raw water, suitable for the treatment of acid raw water, in particular acid water containing sulphate anions.

According to the invention, there is provided a method of treating acid raw water containing sulphate anions, the method including the steps of neutralising the raw water by adding calcium carbonate to the raw water in a neutralising stage, rendering the neutralised water alkaline or more alkaline by adding thereto an alkali selected from the group consisting of calcium hydroxide, calcium oxide and mixtures thereof in a lime treatment stage, and then treating alkaline water from the lime treatment stage with carbon dioxide in carbon dioxide treatment stage, the carbon dioxide reacting, in the carbon dioxide treatment stage, with calcium hydroxide dissolved in the water, the treating of the alkaline water with carbon dioxide including feeding carbon dioxide produced in the neutralising step according to the reaction:

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

into the alkaline water from the lime treatment stage, to react with calcium hydroxide in the water at a pH of not less than 8.6 according to the reaction:

$$Ca(OH)_2+CO_2 \rightarrow CaCO_3\downarrow H_2O.$$

While treating the alkaline water from the lime treatment stage with carbon dioxide in the carbon dioxide treatment stage can act to reduce the pH of the water in the carbon dioxide treatment stage to a value below 8.6 to produce dissolved calcium bicarbonate in the water, it is expected that the carbon dioxide addition will usually act to reduce the pH to a minimum value which is no less than 8.6, so that calcium carbonate precipitation will take place in the carbon dioxide treatment stage. Accordingly, the carbon dioxide treatment stage may form a calcium carbonate precipitation stage, the carbon dioxide treatment lowering the pH in the carbon dioxide treatment stage to a minimum value of no less than 8.6, and causing precipitation of calcium carbonate from the water in the carbon dioxide treatment stage.

Typically, in the neutralization stage, a raw water with a pH of below 5, is treated by the addition of particulate calcium carbonate thereto, to increase its pH to 5–8.5, eg about 7. In the lime treatment stage, in turn, particulate calcium hydroxide and/or calcium oxide is added to the neutralized water from the neutralization stage, to raise its pH to about 9–12.6, eg about 12. In particular, the neutralizing of the raw water may be by adding particulate calcium carbonate thereto, the neutralizing acting to increase the pH of the raw water from a value of below 5, to a value, in the neutralized water, of 5–8.5, the rendering of the neutralized water alkaline or more alkaline acting to raise the pH of the water to a value to 9–12.6, before the treating of the alkaline water with carbon dioxide takes place.

In the neutralization stage, the calcium salt of the acid is produced, together with carbon dioxide. Frequently, the raw water contains sulphate anions, the acid being sulphuric acid, so that the neutralization reaction is:

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

In this case, at pH's of 7 or less, the $CaSO_4$ remains partially in solution and gaseous CO_2 is produced, which can be employed later, as described hereunder. Some of the $CaSO_4$ will crystallize as $CaSO_4.2H_2O$ (gypsum). The gaseous CO_2 produced in the neutralization stage may be withdrawn from the neutralization stage under vacuum or by stripping it from the water in the neutralization stage with air.

In addition to sulphate anions, the raw water often contains dissolved cations, such as Fe^{3+}, Fe^{2+}, Al^{3+}, Ti^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+} and also Ca^{2+} cations. Accordingly, in the neutralization step, the hydroxides of these cations which are insoluble at pH's of 7 or less, will precipitate, eg $Fe(OH)_3$ and $Al(OH)_3$. In accordance with the method of the invention such hydroxide precipitates may be separated from the water in a separation step such as a filtration step or preferably a settling step, optionally employing a coagulant and/or a flocculant, following the neutralization step, and sludge may be recirculated from this separation step to the neutralization step, to maintain a solids concentration of 10–300 g/l in the neutralization step, the remaining sludge from this separation step being discarded to waste or being conveyed, with the water being treated, from the neutralization step to the lime treatment step. In a particular embodiment of the invention, in which the raw water contains sulphate anions, calcium cations and one or more metal cations selected from the group consisting of Fe^{3+}, Fe^{2+}, Al^{3+}, Ti^{2+}, Zn^{2+}, Mn^{2+} and Mg^{2+} cations, the method may include separating from the water as a sludge the hydroxides of any metal cations of said group which are present in the raw water and which give rise to solid hydroxides in the neutralizing step, and recirculating sufficient of the separated sludge to the neutralising step to maintain a solids concentration of 5–300 g/l in the neutralizing stage.

If desired, $Fe(OH)_3$ precipitation in the neutralization step can be improved and promoted by aeration to oxidize Fe^{2+} cations to Fe^{3+} cations, and this oxidation may be promoted by agitation of the water in the neutralization step. Accordingly, when the raw water contains Fe^{2+} cations, the method may include agitating and aerating the water in the neutralizing stage to promote oxidation of the Fe^{2+} cations to Fe^{3+} cations in the neutralizing stage, which Fe^{3+} cations become insoluble at a lower pH than the pH at which the Fe^{2+} cations become insoluble. In the lime treatment step $Fe(OH)_2$, $Mn(OH)_2$, $Fe(OH)_2$ and $CaSO_4$ are typically precipitated, and ettringite ($3CaSO_4.Al_2O_3.3CaO.31H_2O$) is optionally precipitated, and the lime treatment step may also incorporate a separation step such as a filtration step or a settling step, where a calcium sulphate sludge, optionally containing the above hydroxides and/or ettringite when they are produced in the neutralization step and/or in the lime treatment step, is settled from the water being treated. When solid calcium sulphate forms in the water in the lime treatment stage, the method may include the step of separating a calcium sulphate-containing sludge from the water in the lime treatment stage before the treating of the alkaline water with calcium dioxide takes place.

When the raw water contains Zn^{2+} cations, any Fe^{3+}, Fe^{2+} and/or Al^{3+} cations dissolved in the water can be removed in the neutralization stage by precipitating the hydroxides thereof, leaving the Zn^{2+} cations for removal in the lime treatment stage. Although zinc can be removed in the neutralization stage, this is not preferred, because of long reaction times and the need for carbon dioxide stripping.

In accordance with the method of the invention, the lime treatment step is as described above, followed typically by a calcium carbonate precipitation step, and the calcium carbonate precipitation step in turn may be followed by a final treatment step, the calcium carbonate precipitation step, when employed, taking place between the lime treatment step and the final treatment step, in the direction of flow of the water being treated.

The calcium carbonate precipitation step, can employ carbon dioxide gas from the neutralizing step, carbon dioxide from the neutralizing step being fed into water obtained from the lime treatment step, after settling of solids therefrom, to react with lime in the water and reduce the pH of the water to below 9 and as low as about 8.6, according to the reaction:

$$Ca(OH)_2+CO_2 \rightarrow CaCO_3\downarrow+H_2O.$$

In other words, the treating of the alkaline water with carbon dioxide may include feeding carbon dioxide produced in the neutralizing step according to the reaction:

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

into the alkaline water from the lime treatment stage, to react with calcium hydroxide in the water at a pH of at least 8.6 according to the reaction:

$$Ca(OH)_2+CO_2 \rightarrow CaCO_3\downarrow+H_2O.$$

This precipitated calcium carbonate can be employed to supplement a feed of calcium carbonate from a calcium carbonate bulk supply to the neutralization step, or, as it will be of high purity, it can be sold as a by-product. The water produced is, furthermore, undersaturated as regards calcium sulphate or gypsum.

It is contemplated that, in practice, for the treatment of acid water, such as acid mine water or acid coal washing water, containing sulphate anions and at least some of said metal cations, the calcium carbonate will be obtained from a bulk supply, such as a supply of limestone, or as a by-product from another industry, such as the paper production industry, and in powder form. This supply of limestone can be used to provide CaO, by burning the $CaCO_3$ at 800–900° C. according to the reaction:

$$CaCO_3 \rightarrow CaO+CO_2\uparrow$$

the CaO being used in the lime treatment step and the CO_2 optionally being used to supplement or supplant the CO_2 from the neutralization step, and which is used in the calcium carbonate precipitation step. Heat derived from this burning can be used to raise the water temperature, to promote gypsum crystallization from the water.

When the calcium carbonate which is burnt is limestone powder, the burnt product will contain both pure CaO particles and impure CaO particles. These particles can be separated, conveniently gravimetrically, eg in a fluidized bed as $Ca(OH)_2$, into a pure fraction and an impure fraction, the pure fraction being used in the lime treatment step, in particular in the later part thereof, when the lime treatment step is carried out in several reaction zones, and the impure fraction being used to treat the water in the earlier part of the lime treatment step, when several such reaction zones are employed. Optionally the neutralization step can incorporate a settling step for settling solids in the water before the water enters the lime treatment step, and solids settled in this settling step can be recirculated to the neutralization step to provide the neutralization step with said solids content, eg 5–300 g/l, suitable for facilitating oxidation of Fe^{2+} cations to Fe^{3+} cations by aeration and agitation, and for facilitating gypsum crystallization. Similarly, sludge settled from the water in the lime treatment step can be recirculated to the lime treatment step to maintain a solids content in the lime treatment step of 5–300 g/l, to facilitate gypsum crystallization. As indicated above, when adding the alkali to the neutralized water is by adding lime thereto, the method may include, as a preliminary step, obtaining the lime by heating limestone to cause it to decompose according to the reaction:

$$CaCO_3(\text{limestone}) \rightarrow CaO(\text{lime})+CO_2\uparrow.$$

In this case, when the limestone contains, as impurities, substances other than calcium carbonate, the method may include heating the limestone in powder form to produce pure lime particles and impure lime particles, the adding of the lime to water taking place in a said lime treatment stage which is made up of a plurality of lime treatment reaction zones arranged in series, the method including separating the lime particles into a pure fraction and an impure fraction, which fractions are fed to the lime treatment reaction zones, lime from the pure fraction being fed to one or more lime treatment reaction zones which are later in the series than any lime treatment reaction zones to which lime from the impure fraction is fed, lime from the impure fraction being fed to one or more lime treatment reaction zones which are earlier in the series than any lime treatment reaction zones to which lime from the pure fraction is fed.

Sludge obtained from the neutralization step and any lime pretreatment step, and sludge from the lime treatment step, can be discarded on a waste dump, or can be used to recover metals contained therein, such as Fe, Al, Mg, Mn, Zn, Ca or the like, as it will contain compounds such as $Fe(OH)_2$, $Mn(OH)_2$, $Mg(OH)_2$, $Zn(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$, $3CaSO_4.Al_2O_3.3CaO.31H_2O$ (ettringite), $CaSO_4.2H_2O$ (gypsum), $CaSO_4.\frac{1}{2}H_2O$, $CaSO_4$ and the like. If desired, aluminium cations, for example as aluminium hydroxide, may be added to the water, before or in the lime treatment step, or the later lime treatment stages when there are several, to promote the precipitation of ettringite in such lime treatment stages. In other words, the method may include the step of admixing aluminium cations into the water being treated, no later than the lime treatment stage, to promote the precipitation of ettringite in the lime treatment stage. If desired, a coagulant and/or a flocculant may be added to either or both of the lime treatment stage and the calcium carbonate precipitation stage.

In particular, if the sludge is $Mg(OH)_2$-rich, it can be used for neutralization of acid water, such as is obtained from coal washing in a coal processing plant. The $Mg(OH)_2$ in such sludge can raise the pH of such spent coal washing water to about 10, and other compounds such as gypsum and other metal hydroxides in the sludge need cause no problem as they can, together with any excess solid $Mg(OH)_2$, be separated, with waste coal fines, in a thickener forming part of the coal processing plant, from which they can be pumped with the coal fines to a coal discard dump. Clear water from the coal discard dump which is returned for re-use in the coal processing plant can undergo a build-up in the $MgSO_4$ content thereof, but this $MgSO_4$ forms no scale layer on the equipment of the coal processing plant. Gypsum scale layers on such equipment can, in contrast, be a problem when coal processing plant water is neutralized with lime. High $MgSO_4$ levels in the coal processing plant water can be reduced or controlled by treating a side stream thereof with $Ca(OH)_2$ according to the reaction:

$$MgSO_4+Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow+CaSO_4(\text{s and aq})$$

the $Mg(OH)_2$ precipitating, and some of the $CaSO_4$ precipitating as gypsum ($CaSO_4.2H_2O$), the side stream being recycled to reduce the overall $MgSO_4$ concentration in the coal processing plant water. Any Mg^{2+} requirements can be met by replacing a proportion of the limestone bulk supply with dolomite, and any excess Mg^{2+} can simply be discarded to waste as $Mg(OH)_2$. It follows that, when the raw water contains Mg^{2+} cations which lead to the production of a magnesium hydroxide-containing sludge in the neutralization stage, the method may include adding the sludge to coal washing water containing sulphuric acid, the coal washing water circulating through a coal washing plant and the magnesium hydroxide in the sludge reaction with the sulphuric acid in the coal washing water according to the reaction:

$$H_2SO_4+Mg(OH)_2 \rightarrow MgSO_4+H_2O.$$

With regard to the neutralization step and the lime treatment step, these steps can each be carried out in a reactor such as a completely mixed reactor, a column reactor, a fluidized bed reactor, a spiral reactor or in a stage formed by a plurality of such reactors in series, with regard to the direction of water flow.

In the case of the neutralization step, the neutralization may be carried out, for example, as described in U.S. Pat. No. 5,156,746 or as described in International Patent Application PCT/GB98/01912 published as WO 99/01383.

In each case, for either the neutralization step or the lime treatment step, a series of completely mixed reactors (incorporating respective settling stages), a series of column reactors or a series of fluidized bed reactors can be used. When a spiral reactor is used, the calcium carbonate being added in the neutralization step, or the $Ca(OH)_2$ and/or CaO being added in the lime treatment step, can be added at a plurality of spaced positions along the spiral of the reactor, along which spiral the water flows, so that the addition has the same effect as addition thereof in each of a series of reactors making up the stage in question. Thus, when metals are present as cations in the raw water and are precipitated, for example as the hydroxides, at different pH's, each of a plurality of reactors making up the neutralization stage or making up the lime treatment stage may be operated at a particular pH (or various parts of a spiral reactor may each be operated at a particular pH), the pH being selected to precipitate predominantly a particular metal hydroxide, which hydroxide, if separated from the water in or after that reactor or reactor part, can be used as a source for the recovery of the metal in question. Thus, as the pH of the lime treatment stage increases during the lime treatment step, $Zn(OH)_2$ precipitation occurs at a pH of 8, $Mn(OH)_2$ precipitation occurs at a pH of 9.5, $Mg(OH)_2$ precipitation occurs at a pH of 11, while gypsum crystallization and precipitation is promoted by high pH's such as 12.4 or more. Gypsum crystallization occurs gradually with calcium carbonate/lime addition in the various stages of the method, up to a maximum pH of 12.5 where lime solubility becomes the limiting factor regarding gypsum crystallization. The lime neutralization step may thus be carried out in a series of reactors where the pH is increased stepwise to 8, 9.5, 11 and eventually to 12.4. While $Mn(OH)_2$ will precipitate at a pH of 9.5, its precipitation as MnO_2 can be promoted by aeration at pH 11 to oxidize the Mn^{2+} to Mn^{4+}. If metal recovery is not important, a single stage can naturally be employed.

As regards metal recovery from the various precipitated sludges, this can be effected by selective dissolution thereof during a stepwise pH reduction by means of CO_2. Thus, for example, magnesium dissolves as Mg^{2+} at a pH of 9.5–11, manganese dissolves as Mn^{2+} at a pH of 8–9.5, and zinc dissolves as Zn^{2+} at a pH of 6–8.5. With decreasing pH calcium in precipitated gypsum will also dissolve as Ca_{2+} and will then precipitate as $CaCO_3$ by reacting with HCO_3^- anions arising from dissolved CO_2. At pH's below 8, this $CaCO_3$ will also dissolve. In this way, solutions containing predominantly dissolved Mg^{2+} anions, Mn^{2+} anions, Zn_{2+} anions or Ca_{2+} anions can be obtained, from which solutions these metals can be recovered. Any residual sludge can be added to sludge from the neutralization step or from the lime treatment step for disposal to waste.

It follows that, when the raw water contains a plurality of species of metal cations, the neutralization stage of the lime treatment stage may each be divided into a plurality of reaction zones, each reaction zone having a different pH, the pH's of the reaction zones being selected to promote the production of respective sludges therein which differ from one another with regard to the proportions of different metals contained therein. In particular, when the plurality of species of metal cations contained in the raw water is made up of species selected from the group consisting of Fe^{3+}, Fe^{2+}, Al^{3+}, Ti^{2+}, $Zn^{2+}Mn^{2+}$, Mg^{2+} and Ca^{2+} cations, the reaction zones of the neutralizing stage and of the lime treatment stage may have respective pH's of <6, 6–8, 8–8.5, 8.5–9.5, 9.5–11, 11–12.4 and >12.4.

In a particular embodiment of the invention, the lime treatment step can be carried out in a lime treatment stage formed from two reactors incorporating settling stages or clarifiers, in the earlier one of which the pH is raised to 11, to cause precipitation of all the above metals from solution, other than calcium, and in the later of which reactors aluminium hydroxide is added while the pH is raised to 12.4 with lime to cause precipitation of ettringite as $3CaSO_4.Al_2O_3.3CaO.31H_2O$, for example as described in South African Patent 98/4724. The ettringite-containing sludge can then have its pH reduced to below 7, for example using carbon dioxide from the neutralizing step, to cause decomposition of the ettringite to insoluble $Al(OH)_3$ and calcium sulphate in solution. The calcium sulphate in solution can be recycled to the neutralization step or to an early part of the lime treatment step where the pH is about 11, for gypsum crystallization and precipitation therefrom, and the $Al(OH)_3$ can be returned to the high-pH reactor of the lime treatment stage for ettringite formation, or it can be discarded to waste or used for aluminium recovery. In this case, when the $Ca(OH)_2$ is separated, as described above, into an impure fraction and a pure fraction by gravimetric separation in a fluidized bed, impure $Ca(OH)_2$ from the bottom of the bed can be dosed into the reactor whose pH is raised to 11 whose sludge is discarded to waste or is used for selective metal recovery, pure $Ca(OH)_2$ from the top of the bed being used in the reactor whose pH is raised to 12.4, to form the ettringite, to reduce any build-up of impurities in the ettringite-containing sludge.

Water from the calcium carbonate precipitation step, typically at a pH of 8.3, can have the residual sulphate content thereof reduced, eg to less than 200 mg/l, and at a pH of 8–9, by biological treatment thereof, for example as described in said PCT/GB98/01912 (WO 99/01383), or by the addition thereto of BaS and/or BaO, in the final treatment step. In the case of BaS or BaO addition, the sulphate is precipitated as $BaSO_4$, after which the pH of the water can be reduced to acceptably neutral levels using carbon dioxide obtained from the neutralization step. When BaS is employed, S^{2-} sulphide anions can be stripped as H_2S by means of carbon dioxide from the water and converted to

sulphur, while calcium carbonate will precipitate from the water if excess carbon dioxide is stripped by air from the water. When BaO is employed, Ca^{2+} is precipitated as $CaCO_3$ by contacting it with carbon dioxide. When biological treatment is employed, H_2S is produced, which is stripped from the water by means of carbon dioxide, excess carbon dioxide in turn being stripped from the water, as described above for BaS addition, to cause or permit calcium carbonate precipitation. Calcium carbonate or H_2S or sulphur can be returned to the neutralization step where the calcium carbonate will act to neutralize the water, while the H_2S and sulphur will be oxidized to H_2SO_4 ($S+1.5O_2+H_2O \rightarrow H_2SO_4$ or $H_2S+O_2 \rightarrow H_2SO_4$) and this H_2SO_4 will then automatically be treated according to the method of the invention.

In particular, the method may thus include, after the lime treatment stage, reducing the dissolved sulphate ion content of the water; and reducing the dissolved sulphate ion content of the water may be by biologically treating the water to reduce the sulphate ion content thereof to a value of <200 mg/l.

It is contemplated that raw waters which will typically be treated according to the method of the invention will have the following composition:

pH	2–4
Sulphate Content	1500–40000 mg/l (as SO^{2-}_4)
Alkalinity	0 mg/l (as $CaCO_3$)
Calcium Content	0–16000 mg/l (as Ca^{2+})
Magnesium Content	0–2000 mg/l (as Mg^{2+})
Manganese Content	0–400 mg/l (as Mn^{2+})
Aluminium Content	0–600 mg/l (as Al^{3+})
Iron (II) Content	0–1000 mg/l (as Fe^{2+})
Free Acid Content	900–50000 mg/l (as $CaCO_3$)
Total Dissolved Solids Content	6500–60000 mg/l.

After the neutralization step the water can have the following composition:

pH	6–8
Sulphate Content	1200–4800 mg/l
Alkalinity	0 mg/l
Calcium Content	300–1200 mg/l
Magnesium Content	0–400 mg/l
Manganese Content	0–400 mg/l
Aluminium Content	0–5 mg/l
Iron (II) Content	0–5 mg/l
Free Acid Content	0–60 mg/l
Total Dissolved Solids Content	1600–6500 mg/l.

After the lime treatment step the water can have the following composition:

pH	11–13
Sulphate Content	600–3000 mg/l
Alkalinity Content	50–2000 mg/l
Calcium Content	400–2000 mg/l
Magnesium Content	0–5 mg/l
Manganese Content	<1 mg/l
Aluminium Content	0–5 mg/l
Iron (II) Content	<1 mg/l
Free Acid Content	<1 mg/l
Total Dissolved Solids Content	1400–5600 mg/l.

After the calcium carbonate precipitation step the water can have the following composition:

pH	8–9
Sulphate Content	600–2400 mg/l
Alkalinity	50–200 mg/l
Calcium Content	50–1000 mg/l
Magnesium Content	0–5 mg/l
Manganese Content	<1 mg/l
Aluminium Content	<1 mg/l
Iron (II) Content	<1 mg/l
Free Acid Content	<1 mg/l
Total Dissolved Solids Content	900–3600 mg/l.

Finally, after the final sulphate reduction step, eg by biological treatment thereof, the product water can have the following composition:

pH	7–9
Sulphate Content	100–400 mg/l
Alkalinity	70–300 mg/l
Calcium Content	70–300 mg/l
Magnesium Content	0–5 mg/l
Manganese Content	<1 mg/l
Aluminium Content	<1 mg/l
Iron (II) Content	<1 mg/l
Free Acid Content	<1 mg/l
Total Dissolved Solids Content	200–900 mg/l.

In a typical case, a coal discharge leachate, when treated in accordance with the method of the present invention can have various compositions set out in the following Table, when raw and when treated by the various steps of the method:

TABLE

	Water Composition				
Parameter	Raw	After Neutralization	After Lime Treatment	After $CaCO_3$ Precipitation	After Biological Treatment
pH	2.2	7.1	12.0	8.3	8.1
Sulphate Content (mg/l)	9200	2410	1230	1220	205
Alkalinity Content (mg/l)	0	0	1000	100	150
Calcium Content (mg/l)	377	639	903	543	140
Magnesium Content (mg/l)	202	200	3	3	3
Manganese Content (mg/l)	20	20	0	0	0
Aluminium Content (mg/l)	106	3	2	0	0
Iron (II) Content (mg/l)	3040	4	0	0	0
Free Acid Content (mg/l)	1740	30	0	0	0
Total Dissolved Solids Content (mg/l)	12945	3276	2738	1826	438

The method of the present invention will typically be carried out at ambient temperatures and under atmospheric pressure, temperatures of the various steps thus being in the range of 0–100° C., usually 10–50° C., for example 10–40° C. A feature of the lime treatment stage when CaO is used is that it can assist in raising water temperatures to the range 10–40° C., suitable for any biological treatment stage.

The invention will now be described, by way of example, with reference to the accompanying drawings, in which:

FIG. **1** shows a schematic flow diagram of a method in accordance with the present invention; and

FIG. **2** shows a schematic flow diagram of an optional variation of the method of FIG. **1**

In FIG. **1** of the drawings, reference numeral **10** generally designates a schematic flow diagram of a method in accordance with the invention. In the flow diagram a raw water feed line is designated **12**, and is shown feeding into a neutralization stage **14** incorporating a settling stage. A calcium carbonate powder feed line **16**, leading from a calcium carbonate powder bulk supply **18**, is also shown feeding into stage **14**. A carbon dioxide discharge line **20** and a water discharge line **22** are shown issuing from stage **14**, as is a sludge discharge line **24**.

From the bulk supply **18**, a calcium carbonate powder feed line **26** feeds to a calcium carbonate burning stage **28** provided with a fuel (coal) supply line **30**, and with a carbon dioxide discharge line **32** issuing therefrom. A pair of calcium oxide discharge lines **34**, **36** issue from burning stage **28**, the line **34** leading to a fluidized bed gravimetric separation stage **38** provided with a fluidizing water supply line **40** and a pair of calcium hydroxide discharge lines **42**, **44**.

The water discharge line **22** from the neutralization stage **14** and the calcium oxide discharge line **36** from the lime burning stage **28** lead to the lime treatment stage **46**. The calcium hydroxide discharge line **42** from the gravimetric separation stage **38** leads to the later part of the lime treatment stage **46**, and the lime **44** from the separation stage **38** leads to the earlier part of the lime treatment stage **46**. The line **44** from the separation stage **38** leads to the earlier part of the lime treatment stage **46**. The lime treatment stage **46** incorporates a settling stage and has a water discharge line **48** and a sludge discharge line **49**. The sludge discharge line **49** leads to a metal recovery stage **50** fed by a carbon dioxide supply line **51**, which may branch (not shown) from either line **20** or line **32**.

Water discharge line **48** discharges from lime treatment stage **46** into a calcium carbonate precipitation stage **52**, which is fed by carbon dioxide flow line **20**, flow line **20** in turn being fed by carbon dioxide discharge line **30** from lime burning stage **28**. Calcium carbonate precipitation stage **50** has a calcium carbonate sludge discharge line **53** feeding into neutralization stage **14**, and a water discharge line **54** leading into a biological treatment stage **56**. The biological treatment stage **56** is a final treatment stage for the water and incorporates a sludge settling stage. Thus, the final (biological) treatment stage has a product water outlet line **58** and a sludge discharge line **60**.

In FIG. **2**, a variation of the method illustrated by the flow diagram of FIG. **1** is generally designated **70**, illustrating the treatment of water in a coal processing plant, designated **72**. The plant **72** is shown fed by a coal feed line **74** and by a water supply line **76** for coal washing water. The plant **72** has a spent water discharge line **78** leading to a thickener stage **80** which has a solids (sludge) discharge line **82** leading to a waste dump **84**. The dump **84** in turn has a clear water discharge line **86** leading into the water supply line **76**.

A side stream flow line **88** is shown feeding from the thickener stage **80** to a contact reaction stage **90** such as a fluidized bed reactor or a completely mixed reactor/clarifier combination which is also fed by a calcium hydroxide supply line **92**. The reactor has a recirculation line **94** for fluidizing suspended material (gypsum) if the reaction stage is a fluidized bed reactor; or, when the reaction stage is a completely mixed reactor associated with a clarifier or settling stage, the recirculation line **94** returns sludge from the clarifier to the reactor; and the reactor has a slurry discharge line **96** which feeds into the water supply line **76**. A branch line **98** feeds from the side stream flow line **88** into the slurry discharge line **96**.

In accordance with the method of the present invention and with reference to FIG. **1** of the drawings, a raw water, typically having a composition as set forth in the Table hereinabove, is fed along feed line **12** into the neutralization stage **14**, together with calcium carbonate powder fed from the bulk supply **18** along feed line **16** into the stage **14**. In the neutralization stage the pH of the water is reduced by the reactions:

$$H_2SO_4+CaCO_3 \rightarrow CaSO_4+H_2O+CO_2\uparrow;$$

and

$$H_2SO_4+Ca(OH)_2 \rightarrow CaSO_4+2H_2O.$$

In this example the stage **14** is provided by a completely mixed reactor/settler combination which incorporates a reaction stage and a settling stage from which sludge is recycled to the reaction stage to maintain a solids content in the neutralization stage **14** of 10–300 g/l. This sludge includes $Fe(OH)_3$ and $Al(OH)_3$ which are precipitated from the raw water, and calcium sulphate crystallized and precipitated from the water as gypsum. The pH of the water is increased from about 2 in the raw water, to about 7 after neutralization, the solids content of 10–300 g/l promoting oxidation of Fe^{2+} in the water to Fe^{3+} by aeration arising from the mixing, for effective $Fe(OH)_3$ precipitation, and the solids also promoting good $CaSO_4.2H_2O$ crystallization. Excess sludge is discharged from stage **14** to waste along line **24**, and carbon dioxide produced issues from stage **14** along line **20**.

Neutralized water passes from stage **14** along discharge line **22** to lime treatment stage **46**. Stage **46** is fed with calcium oxide from burning stage **28** along line **36**, and/or stage **46** is fed in the later part thereof with pure calcium hydroxide from gravimetric separation stage **38** along line **42**, while the earlier part of stage **46** is fed with impure calcium hydroxide from separation stage **38** along line **44**. In this regard it is to be noted that powdered lime stone is fed from bulk supply **18** along line **26** to burning stage **28** where it is burnt at about 860° C. to form calcium oxide and carbon dioxide according to the reaction:

$$CaCO_3 \rightarrow CaO+CO_2\uparrow$$

Calcium oxide is fed from stage **28**, as described above, along line **36** to stage **46**, where it contributes to heating the water, and is also fed along line **34** to gravimetric separation stage **38** which is fed with water along supply line **40**. In stage **38** the calcium oxide reacts with water to form calcium hydroxide according to the reaction:

$$CaO+H_2O \rightarrow Ca(OH)_2.$$

The calcium hydroxide formed in stage **38** is gravimetrically separated in the fluidized bed in the stage **38**, fluidized by the

water fed along line **40**, into a top pure fraction which passes along line **42** to the later part of stage **46**, and a bottom impure fraction which passes along line **44** to the earlier part of stage **46**, as described above. The carbon hydroxide produced in burning stage **28** passes along line **32** to line **20**.

In lime treatment stage **46** the calcium hydroxide from line **42** and the calcium oxide from line **36** react with sulphuric acid, increasing the Ph of the water to **12**, according to the reactions:

$$H_2SO_4+Ca(OH)_2 \rightarrow CaSO_4+2H_2O$$

$$H_2SO_4+CaO \rightarrow CaSO_4+H_2O$$

Calcium sulphate crystallizes as gypsum ($CaSO_4.2H_2O$) at below 30° C. (or as $CaSO_4.\frac{1}{2}H_2O$ at 30–80° C. or as $CaSO_4$ at 70–110° C.) and issues from stage **46** along discharge line **49** as a sludge which contains $Zn(OH)_2$, $Mg(OH)_2$ and $Mn(OH)_2/MnO_4$, all of which precipitate as the pH of the water increases from about 7 to about 12. The lime treatment stage **46** incorporates a reaction stage and a settling stage from which solids are recirculated to the reaction stage, to keep the solids content at 10–300 g/l.

Water discharged from lime treatment stage **46** along discharge line **48** to calcium carbonate precipitation stage **52** is treated with carbon dioxide from line **20** to reduce its pH to 8.3 to cause calcium carbonate precipitation therefrom. This calcium carbonate passes as a sludge along line **53** to neutralization stage **14** where it supplements the calcium carbonate from line **16**. Water issues from stage **52** along discharge line **54** to biological treatment stage **56**. In biological treatment stage **56** the water is subjected to a biological treatment according to PCT/GB98/01912 (WO 99/01383) whereby its sulphate content and its total dissolved solids content are reduced, product water issuing from stage **56** along product water outlet line **58** and sludge issuing therefrom along sludge discharge line **60** to waste. Optionally, the sludge from line **60** can, if desired, be fed into line **53** for recirculation to neutralization stage **14**.

Sludge passing along line **49** contains potentially valuable metals such as zinc, magnesium and manganese, and is treated in metal recovery stage **50** for the recovery of these metals. This is done by progressively acidifying the water, using carbon dioxide from line **51**, to dissolve the metals in question. Thus, magnesium sulphate goes into solution at a pH of 9.5–11 while manganese sulphate goes into solution at a pH of 8–9.5 and zinc sulphate goes into solution at a pH of 6–8.5, from which solutions these metals can be recovered.

In a variation of the method of the invention aluminium hydroxide can be fed to the lime treatment stage, to promote the precipitation of ettringite ($3CaSO_4.Al_2O_3.3CaO.31H_2O$) as described in South African Patent 98/4724. This ettringite can be decomposed, by reduction of the pH of the sludge containing it, to less than 7, to form aluminium hydroxide $Al(OH)_3$ and calcium sulphate.

With reference to FIG. **2** a further variation of the invention is shown, whereby the metal recovery stage **50** of FIG. **1** is replaced by a coal processing plant wherein magnesium hydroxide-rich slurry from line **49** is used to treat coal washing water. In accordance with this variation of the method, slurry from discharge line **49** (FIG. **1**) is fed into coal washing water at one or more points (not shown) in the coal processing plant **72** (FIG. **2**), to which coal is fed along coal feed line **74** and waste water is fed along supply line **76**.

In the wash water in the plant **72**, magnesium hydroxide reacts with sulphuric acid from the coal washing according to the reaction:

$$H_2SO_4+Mg(OH)_2 \rightarrow MgSO_4+2H_2O$$

while any small quantities calcium hydroxide in the slurry react in analogous fashion. A progressive build-up of dissolved magnesium sulphate in the coal wash water takes place, as it circulates along line **78** to the thickener stage **80** where coal fines are settled, and from which a slurry is discharged along line **82** into the waste dump **84**. Clear water draining from the dump **84** is circulated along line **86** to the water supply line **76**.

To counteract this build-up of dissolved magnesium sulphate in the coal wash water, a side stream of water is removed from the thickener stage **80** along line **88** to the contact reaction stage **90**. Calcium hydroxide is dosed into the contact reaction stage **90** along supply line **92** (which can receive calcium oxide from line **34** or line **36**—FIG. **1**) and recirculation of the contents of the reaction stage **90** takes place along recirculation line **94**. In the reaction stage **90** the magnesium sulphate reacts with the calcium hydroxide according to the reaction:

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

and a slurry of water containing precipitated $Mg(OH)_2$ and gypsum ($CaSO_4.2H_2O$) leaves the reaction stage **90** along slurry discharge line **96** which feeds into water supply line **76**. The bulk of the water from thickener stage **80** bypasses reaction stage **90**, and passes directly into line **96** via the branch line **98**. The part of line **96** which is upstream of the connection of line **96** to branch line **98** has its flow controlled by the acid load of water from line **74** and by the solid magnesium hydroxide concentration in said part of line **96**. The amount of calcium hydroxide dosed along line **92** into reaction stage **90** depends on the amount of sulphuric acid leached out of the coal in plant **72**, by the magnesium hydroxide, which acts as an intermediate alkali, and which is precipitated in reaction stage **90**.

The invention extends also to a method of treating neutral water containing sulphate anions which omits the neutralization step described above, but combines the lime treatment step with one or more of the additional method steps described above, for example with the magnesium hydroxide treatment step described above with particular reference to FIG. **2**, or with the calcium carbonate precipitation step described above and with reference to FIG. **1**.

It is an advantage of the invention that it provides a versatile and effective method for treating acid waters containing sulphate anions and metal cations.

What is claimed is:

1. A method of treating acid raw water containing sulphate anions, the method including the steps of

neutralising the raw water by adding calcium carbonate to the raw water in a neutralising stage,

rendering the neutralised water alkaline or more alkaline by adding thereto an alkali selected from the group consisting of calcium hydroxide, calcium oxide and mixtures thereof in a lime treatment stage, and then

treating alkaline water from the lime treatment stage with carbon dioxide in a carbon dioxide treatment stage, the carbon dioxide reacting, in the carbon dioxide treatment stage, with calcium hydroxide dissolved in the water to precipitate calcium carbonate, the treating of the alkaline water with carbon dioxide including feeding carbon dioxide produced in the neutralising stage according to the reaction:

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

into the alkaline water from the lime treatment stage, to react with calcium hydroxide in the water at a pH of not less than 8.3 according to the reaction:

$$Ca(OH)_2+CO_2 \rightarrow CaCO_3\downarrow+H_2O$$

calcium carbonate produced as a precipitate in the carbon dioxide treatment stage forming at least part of the calcium carbonate added to the raw water in the neutralising stage, the alkali addition in the lime treatment stage acting to precipitate one or more calcium sulphate-containing compounds, the process including separation of calcium sulphate-containing precipitate from the water issuing from the lime treatment stage before it is treated with carbon dioxide in the carbon dioxide treatment stage, and the carbon dioxide fed into the carbon dioxide treatment stage acting to render the water issuing from the carbon dioxide treatment stage undersaturated with regard to calcium sulphate.

2. A method as claimed in claim **1**, in which the carbon dioxide treatment lowers the pH of the carbon dioxide treatment stage to a minimum value of not less than 8.6.

3. A method as claimed in claim **1**, in which the neutralising of the raw water is by adding particulate calcium carbonate thereto and acts to increase the pH of the raw water from a value of below 5, to a value, in the neutralised water, of 5–8.5, the rendering of the neutralised water alkaline or more alkaline acting to raise the pH of the water to a value of 9–12.6, before the treating of the alkaline water with carbon dioxide takes place.

4. A method as claimed in claim **1**, in which the raw water contains sulphate anions, calcium cations and one or more metal cations selected from the group consisting of Fe^{3+}, Fe^{2+}, Al^{3+}, Ti^{2+}, Zn^{2+}, Mn^{2+} and Mg^{2+} cations, the method including separating from the water as a sludge the hydroxides of any metal cations of said group which are present in the raw water and which give rise to solid hydroxides in the neutralising step, and recirculating sufficient of the separated sludge to the neutralising step to maintain a solids concentration of 5–300 g/l in the neutralising stage.

5. A method as claimed in claim **4**, in which the raw water contains Fe^{2+} cations, the method including agitating and aerating water in the neutralising stage to promote oxidation of the Fe^{2+} cations to Fe^{3+} cations in the neutralising stage.

6. A method as claimed in claim **1**, in which solid calcium sulphate forms in the water in the lime treatment stage, the method including the step of separating a calcium sulphate-containing sludge from the water in the lime treatment stage before the treating of the alkaline water with carbon dioxide takes place.

7. A method as claimed in claim **1**, in which adding the alkali to the neutralised water is by adding lime thereto, the method including, as a preliminary step, obtaining the lime by heating limestone to cause it to decompose according to the reaction:

$$CaCO_3(\text{limestone}) \rightarrow CaO(\text{lime})+CO_2\uparrow.$$

8. A method as claimed in claim **7**, in which the limestone contains, as impurities, substances other than calcium carbonate, the method including heating the limestone in powder form to produce pure lime particles and impure lime particles, and the adding of the lime to the water taking place in a said lime treatment stage which is made up of a plurality of lime treatment reaction zones arranged in series, the method including separating the lime particles into a pure fraction and an impure fraction, which fractions are fed to the lime treatment reaction zones, lime from the pure fraction being fed to one or more lime treatment reaction zones which are later in the series than any lime treatment reaction zones to which lime from the impure fraction is fed, lime from the impure fraction being fed to one or more lime treatment reaction zones which are earlier in the series than any lime treatment reaction zones to which lime from the pure fraction is fed.

9. A method as claimed in claim **1**, which includes the step of admixing aluminium cations into the water being treated, no later than the lime treatment stage, to promote the precipitation of ettringite in the lime treatment stage.

10. A method as claimed in claim **1**, in which the raw water contains Mg^{2+} cations which lead to the production of a magnesium hydroxide-containing sludge in the neutralisation stage, the method including adding the sludge to coal washing water containing sulphuric acid, the coal washing water circulating through a coal washing plant and the magnesium hydroxide in the sludge reacting with the sulphuric acid in the coal washing water according to the reaction:

$$H_2SO_4+Mg(OH)_2 \rightarrow MgSO_4+H_2O.$$

11. A method as claimed in claim **1**, in which the raw water contains a plurality of species of metal cations, the neutralisation stage and the lime treatment stage each being divided into a plurality of reaction zones, each reaction zone having a different pH, the pH's of the reaction zones being selected to promote the production of respective sludges therein which differ from one another with regard to the proportions of different metals contained therein.

12. A method as claimed in claim **11**, in which the plurality of species of metal cations contained in the raw water is made up of species selected from the group consisting of Fe^{3+}, Fe^{2+}, Al^{3+}, Ti^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+} and Ca^{2+} cations, the reaction zones of the neutralising stage and of the lime treatment stage having respective pH's of <6, 6–8, 8–8.5, 8.5–9.5, 9.5–11, 11–12.4 and >12.4.

13. A method as claimed in claim **1**, which includes, after the lime treatment stage, reducing the dissolved sulphate ion content of the water.

14. A method as claimed in claim **13**, in which reducing the dissolved sulphate ion content of the water is by biologically treating the water to reduce the sulphate ion content thereof to a value of <200 mg/l.

15. A method of treating acid raw water containing sulphate anions, the method including the steps of

neutralising the raw water by adding calcium carbonate to the raw water in a neutralising stage,

rendering the neutralized water alkaline or more alkaline by adding thereto an alkali selected from the group consisting of calcium hydroxide, calcium oxide and mixtures thereof in a lime treatment stage, and then

treating alkaline water from the lime treatment stage with carbon dioxide in a carbon dioxide treatment stage, the carbon dioxide reacting, in the carbon dioxide treatment stage, with calcium hydroxide dissolved in the water, the treating of the alkaline water with carbon dioxide including feeding carbon dioxide produced in the neutralising stage according to the reaction:

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

into the alkaline water from the lime treatment stage, to react with calcium hydroxide in the water at a pH of not less than 8.3 according to the reaction:

$$Ca(OH)_2+CO_2 \rightarrow CaCO_3\downarrow+H_2O,$$

adding the alkali to the neutralised water being by adding lime thereto, the method including, as a preliminary step, obtaining the lime by heating limestone to cause it to decompose according to the reaction:

$CaCO_3(limestone) \rightarrow CaO(lime) + CO_2\uparrow$,

the limestone containing, as impurities, substances other than calcium carbonate, the method including heating the limestone in powder form to produce pure lime particles and impure lime particles, and the adding of the lime to the water taking place in a said lime treatment stage which is made up of a plurality of lime treatment reaction zones arranged in series, the method including separating the lime particles into a pure fraction and an impure fraction, which fractions are fed to the lime treatment reaction zones, lime from the pure fraction being fed to one or more lime treatment reaction zones which are later in the series than any lime treatment reaction zones to which lime from the impure fraction is fed, lime from the impure fraction being fed to one or more lime treatment reaction zones which are earlier in the series than any lime treatment reaction zones to which lime from the pure fraction is fed.

16. A method of treating acid raw water containing sulphate anions, the method including the steps of

neutralising the raw water by adding calcium carbonate to the raw water in a neutralising stage,

rendering the neutralised water alkaline or more alkaline by adding thereto an alkali selected from the group consisting of calcium hydroxide, calcium oxide and mixtures thereof in a lime treatment stage, and then treating alkaline water from the lime treatment stage with carbon dioxide in a carbon dioxide treatment stage, the carbon dioxide reacting, in the carbon dioxide treatment stage, with calcium hydroxide dissolved in the water, the treating of the alkaline water with carbon dioxide including feeding carbon dioxide produced in the neutralising stage according to the reaction:

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

into the alkaline water from the lime treatment stage, to react with calcium hydroxide in the water at a pH of not less than 8.3 according to the reaction:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O,$$

the raw water containing Mg^{2+} cations which lead to the production of a magnesium hydroxide-containing sludge in the neutralisation stage, and the method including adding the sludge to coal washing water containing sulphuric acid, the coal washing water circulating through a coal washing plant and the magnesium hydroxide in the sludge reacting with the sulphuric acid in the coal washing water according to the reaction:

$$H_2SO_4 + Mg(OH)_2 \rightarrow MgSO_4 + H_2O.$$

* * * * *

APPENDIX B – LIST OF CONFIRMATIONS

Unit of Natural Resources and the Environment
PO Box 395
Pretoria, 0001
Republic of South Africa
Tel: +27 (0)12 841-2285
Fax: +27 (0)12 841-2506
Cell: +27 (0)82 465 3547
Email: jmaree@csir.co.za

Date: 1 November 2005

Dear Jannie and Prof Waanders

We hereby give our authorisation that Jannie Maree may use the following publications for the purpose of his Ph.D.-thesis at the North West University:

1. Maree JP, de Beer M, Strydom WF, Christie ADM and Waanders FB (2004) Neutralizing Coal Mine Effluent with Limestone to Decrease Metals and Sulphate Concentrations, Mine Water and the Environment, 23(2), 81 – 86.

2. Maree JP, Hagger MJ, Strobos G, Hlabela P, Cronjé H, Van Niekerk A, Wurster A, Nengovhela R and Waanders FB (2004) Design Criteria for Limestone Neutralization at a Nickel Mine, Mine Water and the Environment 23(3), 152 – 156.

3. Maree J P, Strobos G, Greben H, Netshidaulu E, Steyn E, Christie A, Günther P and Waanders FB (2004) Treatment of Acid Leachate from Coal Discard using Calcium Carbonate and Biological Sulphate Removal, Mine Water and the Environment 23(3), 144 - 151.

4. Maree J P, Greben H and De Beer M (2004) Treatment of acid and sulphate-rich effluents in an integrated biological/chemical process, Water SA 30(2): 183-189.

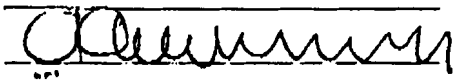
5. Maree JP, Hlabela P, Nengovhela R, Geldenhuys AJ, Mbhele N, Nevhulaudzi T, and Waanders FB (2004) Treatment of Mine Water for Sulphate and Metal Removal Using Barium Sulphide, Mine Water and the Environment 23(4), 195 – 203.

6. Maree JP, Günther P, Strobos G and Waanders FB (2004) Optimizing the Effluent Treatment at a Coal Mine by Process Modelling, Mine Water and the Environment 23(2): 87 - 90.

Kind regards

1. Christie ADM
2. Cronjé H
3. de Beer M
4. Geldenhuys AJ
5. Greben H
6. Günther P
7. Hagger MJ
8. Hlabela P
9. Mbhele N
10. Nengovhela R
11. Netshidaulu E
12. Nevhulaudzi T
13. Steyn E
14. Strobos G
15. Strydom WF
16. Van Niekerk A
17. Waanders FB
18. Wurster A

1. Christie ADM ______________________
2. Cronjé H ______________________
3. de Beer M ______________________
4. Geldenhuys AJ ______________________
5. Greben H ______________________
6. Günther P ______________________
7. Hagger MJ ______________________
8. Hlabela P ______________________
9. Mbhele N ______________________
10. Nengovhela R ______________________
11. Netshidaulu E ______________________
12. Nevhulaudzi T ______________________
13. Steyn E ______________________
14. Strobos G ______________________
15. Strydom WF ______________________
16. Van Niekerk A ______________________
17. Waanders FB ______________________
18. Wurster A ______________________

1. Christie ADM _____
2. Cronjé H _____
3. de Beer M _____
4. Geldenhuys AJ 
5. Greben II _____
6. Günther P _____
7. Hagger MJ _____
8. Hlabela P _____
9. Mbhele N _____
10. Nengovhela R _____
11. Netshidaulu E _____
12. Nevhulaudzi T _____
13. Steyn R _____
14. Strobos G _____
15. Strydom WF _____
16. Van Nickerk A _____
17. Waanders FB _____
18. Wurster A _____

1. Christie ADM _____
2. Cronjé H _____
3. de Beer M _____
4. Geldenhuys AJ _____
5. Greben H _____
6. Günther P _____
7. Hagger MJ _____
8. Hlabela P _____
9. Mbhele N _____
10. Nengovhela R _____
11. Netshidaulu E 
12. Nevhulaudzi T _____
13. Steyn E _____
14. Strobos G _____
15. Strydom WF _____
16. Van Niekerk A _____
17. Waanders FB _____
18. Wurster A _____

1. Christie ADM _____
2. Cronjé H _____
3. de Beer M _____
4. Geldenhuys AJ _____
5. Greben H _____
6. Günther P _____
7. Hagger MJ _____
8. Hlabela P _____
9. Mbhele N _____
10. Nengovhela R _____
11. Netshidaulu E _____
12. Nevhulaudzi T T.P. Nevhulaudzi
13. Steyn E _____
14. Strobos G _____
15. Strydom WF _____
16. Van Niekerk A _____
17. Waanders FB _____
18. Wurster A _____

1. Christie ADM _____
2. Cronjé H _____
3. de Beer M _____
4. Geldenhuys AJ _____
5. Greben H _____
6. Günther P _____
7. Hagger MJ _____
8. Hlabela P _____
9. Mbhele N _____
10. Nengovhela R _____
11. Netshidaulu E _____
12. Nevhulaudzi T _____
13. Steyn E _____
14. Strobos G _____
15. Strydom WF _____
16. Van Niekerk A _____
17. Waanders FB _____
18. Wurster A _____

1. Christie ADM _____
2. Cronjé H _____
3. de Beer M _____
4. Geldenhuys AJ _____
5. Greben H _____
6. Günther P _____
7. Hagger MJ _____
8. Hlabela P _____
9. Mbhele N _____
10. Nengovhela R _____
11. Netshidaulu E _____
12. Nevhulaudzi T _____
13. Steyn E _____
14. Strobos G _____
15. Strydom WF _____
16. Van Niekerk A _____

17. Waanders FB _____
18. Wurster A _____

1. Christie ADM _____
2. Cronjé H _____
3. de Beer M _____
4. Geldenhuys AJ _____
5. Greben H _____
6. Günther P _____
7. Hagger MJ _____
8. Hlabela P _____
9. Mbhele N _____
10. Nengovhela R _____
11. Netshidaulu E _____
12. Nevhulaudzi T _____
13. Steyn E _____
14. Strobos G _____
15. Strydom WF _____
16. Van Niekerk A _____
17. Waanders FB _____
18. Wurster A A. Wurster

From: "Gunther, Peter" <PGunther@anglocoal.co.za>
To: "Jannie Maree" <jmaree@csir.co.za>
Date: 02/11/2005 13:43:37
Subject: RE: Thesis - J P Maree

No problem by me.

Peter

-----Original Message-----
From: Jannie Maree [mailto:jmaree@csir.co.za]
Sent: 31 October 2005 11:30
To: Andre.Geldenhuys@afrox.boc.com; Hagger, Mike; Christie, Angus; Gunther, Peter; Ellenore Steyn; Njabulo Mbhele; Gerhard Strobos; Harma Greben; Marinda de Beer; Patrick Hlabela; Ryneth Nengovhela; Wilma Strydom; AMvanniekerk@golder.co.za; awurster@golder.co.za; hennie@hemcro.co.za; CHIFBW@puknet.puk.ac.za
Cc: Jannie Maree
Subject: Thesis - J P Maree

Dear Colleague/Collaborator

I have submitted 6 publications in the field of limestone neutralization, biological sulphate removal and the barium process for a Ph.D.-thesis at the North West University.

As you have acted as a co-author in one or more of the articles, it is my pleasure to request your permission that I may use the mentioned publications for the purpose of the thesis.

I would appreciate it if you could sign the attached document and return it to me by hand, fax, or email.

Fax: 012 841 2506

Email: jmaree@csir.co.za

Thank you for your support during the years.

Best regards

Jannie Maree

Jannie Maree
Environmentek, CSIR, P O Box 395, Pretoria
jmaree@csir.co.za
Tel: 012 841 2285
Fax: 012 841 2506
Cell: 082 465 3547