Sulphate removal from industrial effluents through barium sulphate precipitation

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ABSTRACT

The pollution of South Africa's water resources puts a strain on an already stressed natural resource. One of the main pollution sources is industrial effluents such as acid mine drainage (AMD) and other mining effluents. These effluents usually contain high levels of acidity, heavy metals and sulphate. A popular method to treat these effluents before they are released into the environment is lime neutralisation. Although this method is very effective to raise the pH of the effluent as well as to precipitate the heavy metals, it can only partially remove the sulphate. Further treatment is required to reduce the sulphate level further to render the water suitable for discharge into the environment.

A number of sulphate removal methods are available and used in industry. These methods can be divided into physical (membrane filtration, adsorption/ion exchange), chemical (chemical precipitation) and biological sulphate reduction processes. A literature study was conducted in order to compare these different methods.

The ABC (Alkali - Barium - Calcium) Desalination process uses barium carbonate to lower the final sulphate concentration to an acceptable level. Not only can the sulphate removal be controlled due to the low solubility of barium sulphate, but it can also produce potable water and allows valuable by-products such as sulphur to be recovered from the sludge. The toxic barium is recycled within the process and should therefore not cause additional problems. In this study the sulphate removal process, using barium carbonate as reactant, was investigated.

Several parameters have been investigated and studied by other authors. These parameters include different barium salts, different barium carbonate types, reaction kinetics, co-precipitation of calcium carbonate, barium-to-sulphate molar ratios, the effect of temperature and pH. The sulphate removal process was tested and verified on three different industrial effluents.

The results and conclusions from these publications were used to guide the experimental work. A number of parameters were examined under laboratory conditions in order to find the optimum conditions for the precipitation reaction to take place. This included mixing rotational speed, barium-to-sulphate molar ratio, initial sulphate concentration, the effect of temperature and the influence of different barium carbonate particle structures. It was found that the reaction temperature and the particle structure of barium carbonate influenced the process significantly. The mixing rotational speed, barium-to-sulphate dosing ratios and the initial sulphate concentration influenced the removal process, but not to such a great extent as the two previously mentioned parameters. The results of these experiments were then tested and verified on AMD from a coal mine.

The results from the literature analysis were compared to the experiments conducted in the laboratory. It was found that the results reported in the literature and the laboratory results correlated well with each other.

Though, in order to optimise this sulphate removal process, one has to understand the sulphate precipitation reaction. Therefore it is recommended that a detailed reaction kinetic study should be conducted to establish the driving force of the kinetics of the precipitation reactions. In order to upgrade this process to pilot-scale and then to a full-scale plant, continuous reactor configurations should also be investigated.

The sulphate removal stage in the ABC Desalination Process is the final treatment step. The effluent was measured against the SANS Class II potable water standard and was found that the final water met all the criteria and could be safely discharged into the environment.

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LIST OF SYMBOLS

Symbol	**Description**	**Units**
$[SO_4^{2-}]$	Sulphate concentration	mg/ℓ
E	Activation energy	J/mol
EC	Electrical conductivity	µS/cm
k	Reaction rate constant	min^{-1}
k_o	Frequency factor	min^{-1}
k_{sp}	Solubility constant	dimensionless
n	Reaction order	dimensionless
R	Ideal gas constant	J/mol K
$r_{SO_4^{2-}}$	Reaction rate	mg/ ℓ min
T	Temperature	°C and K

LIST OF ABBREVIATIONS

ABC Desalination	Alkali - Barium - Calcium Desalination
AC	Alternating current
AMD	Acid Mine Drainage
aq	Aqueous
Bact	Bacteria
CESR	Cost effective sulphate removal
CSIR	Council for Scientific and Industrial Research (South Africa)
CSTR	Continuous stirred tank reactor
DEAT	Department of Environmental Affairs and Tourism
DO	Dissolved oxygen
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
EC	Electrical conductivity
ED	Electro dialyses
EDR	Electro dialyses reversal
FWS wetland	Free water surface wetland
g	Gas
HiPRO	Hi recovery Precipitating Reverse Osmosis
l	Liquid
MBO	Magnesium Barium Oxide
ORP	Oxidation-reduction potential
RO	Reverse osmosis
s	Solid
SANAS	South African National Accreditation System
SANS	South African National Standards
SEM	Scanning electron microscopy
SF wetland	Subsurface flow wetland
SPARRO	Slurry precipitation and recycle reverse osmosis
SRO	Seeded reverse osmosis
TDS	Total Dissolved Solids
WHO	World Health Organisation
XRD	X-ray diffraction

LIST OF CHEMICALS

Formula	**Name**
$3CaO.3CaSO_4.Al_2O_3.31H_2O$	Ettringite
$Al(OH)_3$	Aluminium tri-hydroxide
$Ba(OH)_2$	Barium hydroxide
$BaCO_3$	Barium carbonate
BaS	Barium sulphide
$BaSO_4$	Barium sulphate or barite
$Ca(OH)_2$ or $2OH^-(+Ca^{2+})$	Calcium hydroxide or lime
$CaCO_3$	Calcium carbonate or limestone
$CaSO_4$ or $Ca^{2+}(+SO_4^{2-})$ or $SO_4^{2-}(Ca^{2+})$	Calcium sulphate or gypsum
CO_2	Carbon dioxide
Fe^{2+}	Iron (II) ion
FeS_2	Iron sulphide or pyrite
H^+	Hydrogen ion
H_2CO_3	Carbonic acid
H_2O	Water
H_2S	Hydrogen sulphide
H_2SO_4 or $2H^+(+SO_4^{2-})$	Sulphuric acid
$MgSO_4$	Magnesium sulphate
Na_2SO_4	Sodium sulphate
O_2	Oxygen
OH^-	Hydroxyl
R_2-Ca	Calcium - resin compound
R_2-SO_4	Sulphate - resin compound
R-H	Strong acid cation resin
R-OH	Weak base anion resin
SO_4^{2-}	Sulphate ion

GLOSSARY

ABC (Alkali - Barium - Calcium) Desalination:	A process developed and patented by the CSIR to treat AMD. This process can produce potable water and valuable by-products can be recycled/sold.
Acid Mine Drainage (AMD):	Wastewater, coupled with mining activities, that contains high levels of acidity, heavy metals and sulphates. Caused when pyrite is oxidised and produces sulphuric acid and sulphate.
Aerobic:	In the presence of oxygen.
Anaerobic:	In the absence of oxygen.
Anoxic:	Water in which the dissolved oxygen is partially depleted.
Barite formation:	Barium sulphate precipitation.
Batch reactor:	A reactor with no inflow or outflow streams for the duration of the chemical reaction. The reactor is a standalone unit.
Bioreactors:	A reactor for biological reactions.
Brine:	Wastewater, associated with membrane and filtering processes, that contains high salt concentrations.
Carbonation process:	A process where carbon dioxide gas is dissolved into water in order for the carbonate ions to react with other chemical species such as barium ions.
Class II potable water standards:	A class of potable water as defined by South Africa National Standards (SANS).
Contact time:	The time allowed for the chemicals to come into direct contact with each other.
Continuous reactor:	A reactor with an inflow stream from one unit and an outflow stream to another unit for the duration of the chemical reaction.
Continuous stirred tank reactor (CSTR):	A continuous agitated-tank reactor.
Cost Effective Sulphate Removal (CESR):	A sulphate removal process based on ettringite precipitation. In addition to sulphate removal it also effectively removes dissolved metals.

CSTRs in series:	More than one CSTR in a row operating in a series configuration.
Electrical conductivity (EC):	The measurement of a material's ability to conduct an electrical current. In the case of liquids, the ion charge within the solution.
Electro dialyses (ED):	A membrane process where an electrical potential is used to force dissolved ions through the membrane.
Electro dialyses reversal (EDR):	An ED membrane process where the flow direction through the membrane can be reversed.
Fluidised bed reactors:	A reactor where fluid (gas or liquid) is passed through a granular solid material. The fluid flowrate is high enough to suspend the solid particles and cause it to behave like a fluid.
Free water surface (FWS) wetlands:	The water flows over a vegetated subsurface from one side to the other. These engineered wetlands are generally shallow and a subsurface barrier prevents seepage.
Gas lift reactor:	A reactor where gas is injected through a tubing-casing annulus. The injected gas aerates the fluid and reduces its density. The formation pressure lifts the fluid and forces it upwards.
GYP-CIX process:	An ion-exchange technology for the removal of ions from the wastewater rich in sulphate and calcium ions.
HiPRO process:	A high recover desalination process.
Industrial effluent:	Wastewater generated by different industrial activities. This include AMD and other mining waste streams, plating industry waste, tannery waste, etc.
Lime neutralisation:	Lime or limestone is added to the acidic wastewater in order to neutralise it. This results in heavy metal precipitation and partial sulphate removal.
Magnesium Barium Oxide (MBO):	A sulphate removal process that uses barium hydroxide as barium salt source.

Over-dose:	When barium ions (in molar units) are added to a solution in excess of the sulphate ions (in molar units) present ($[Ba^{2+}]/[SO_4^{2-}] > 1$).
Packed bed reactor:	A reactor filled with solid particles.
Potable water:	Drinking water.
Reactive barium carbonate:	Barium carbonate that reacts quickly (relative to other barium carbonate types) with calcium sulphate under controlled conditions. This results in a fast sulphate removal process.
Reverse osmosis (RO):	A membrane process that uses high pressure to force the water-part of a solution through the membrane while retaining the dissolved ions.
Salinity:	High salt concentration.
SAVMIN:	A process during which sulphate removal is achieved through ettringite precipitation.
Scanning electron microscopy (SEM):	A type of electron microscope that photographs a sample by scanning it with a high-energy beam of electrons. This produces photographs of the crystal structure of the sample.
Seeded reverse osmosis (SRO):	An RO membrane process that involves a suspension of seed crystals being introduced into the effluent through recycling of the waste slurry.
Sludge blanket reactor:	A reactor where the wastewater enters the reactor from the bottom, and flows upward. A suspended sludge blanket forms that acts as a filter.
Slurry precipitation and recycle reverse osmosis (SPARRO):	An RO membrane process where seed crystals are recycled from the concentrate to the feed water.
Stoichiometric ratio dose:	The barium ions (in molar units) added to the solution is equal to the sulphate ions (in molar units) present in the solution. ($[Ba^{2+}]/[SO_4^{2-}] = 1$).
Subsurface flow (SF) wetlands:	This type of wetland holds an appropriate medium in a bed or channel. The water level remains below the bed surface covered with emergent vegetation.

Synthetic sulphate water:	Calcium sulphate is dissolved into distilled water to produce a sulphate-rich solution of which the concentration is known.
Turbidimetric method:	Standard analytical method to measure sulphates in a solution.
Under-dose:	The barium ions (in molar units) added to the solution is less than the sulphate ions (in molar units) present in the solution. ($[Ba^{2+}]/[SO_4^{2-}] < 1$).
Unreactive barium carbonate:	Barium carbonate that reacts very slowly (relative to other barium carbonate types) with calcium sulphate under controlled conditions. This results in a slow sulphate removal process.

CHAPTER 1: INTRODUCTION

Chapter 1 provides the background of this study. The problem statement and the objective of the investigation are presented.

1.1. INTRODUCTION

The water scarcity in South Africa is exacerbated by the pollution of its water resources (Morgan et al. 2008). It is a legal requirement in terms of the National Water Act (RSA 1998) that treated effluent must be returned to the water resource (Section 22(2)(e)) while also reducing or preventing pollution and degradation of water resources (Section 2(h)). According to the Department of Water Affairs (DWA), the quality of South African water resources is deteriorating mainly due to salinity coupled with effluent discharges (DWAF 2004). Effluents originating from or as a result of mining activities usually contain high levels of acidity, heavy metals and sulphates as well as low concentrations of organic material (Roman et al. 2008, Bell et al. 2006). The high sulphate concentration in mining effluent is of specific concern to water quality managers in South Africa (DWAF 2002).

The most widespread treatment method applied to acid mine drainage is lime neutralisation. Lime ($Ca(OH)_2$) is added to raise the pH, resulting in the precipitation of dissolved metals as metal hydroxides while partial sulphate removal (up to 1 200 mg/ℓ) is achieved. However, further treatment is required to lower the sulphate level to below 500 mg/ℓ, the acceptable concentration for discharge into the environment.

One such treatment technology, known as the ABC Desalination Process, developed and patented by the CSIR, uses barium carbonate to achieve this. Barium ions react with the sulphate ions to form barium sulphate. This compound is not very soluble and will precipitate out of the solution, leaving few sulphate ions in the solution (Maree et al. 2004b, Maree et al. 2004a).

1.2. BACKGROUND

Large quantities of AMD are released into the environment and have a serious negative environmental impact. Figure 1 shows an example of the impact and effects AMD has on the environment.

Figure 1: Environmental impact of AMD (Ferreira 2010, Herskovitz 2011)

The high sulphate concentration in AMD originates from a natural oxidation process. Sulphide oxidation is a common phenomenon which occurs in mine effluent. The most common source of sulphate is due to the oxidation of an iron sulphide mineral known as pyrite (FeS_2), a natural substance in the earth's crust (Oxford 2009). Pyrite containing ore is a very rich sulphuric acid source since every ton of ore with 1% pyritic sulphur can produce more than 15 kg of ochre and 30 kg of sulphuric acid (Bowell 2004).

The conversion of pyrite to sulphuric acid (H_2SO_4) and sulphate ions (SO_4^{2-}) is brought about by sulphur oxidation bacteria under aerobic conditions; the chemical reaction is shown in Reaction 1 (Sawyer et al. 2003). The products of this chemical reaction pollute the water due to the increase in acidity, heavy metals and dissolved salts (Bell et al. 2006, Sawyer et al. 2003).

$$2\mathrm{FeS_2(s)} + 7\mathrm{O_2} + 2\mathrm{H_2O} \xrightarrow{\mathrm{Bact}} 2\mathrm{Fe^{2+}} + 4\mathrm{H^+} + 4\mathrm{SO_4^{2-}}$$ **Reaction 1**

High acid and sulphate levels in the wastewater cause the water to be corrosive to equipment and piping, and can cause scaling problems in pipes and filters. It also increases the salinity of the receiving water bodies. The consumption of drinking water containing a sulphate concentration in excess of 500 mg/ℓ commonly results in laxative effects in humans (WHO 2004b). The taste threshold for the most prevalent sulphate salts ranges from 250 mg/ℓ to 500 mg/ℓ (WHO 2004b). Though the World Health Organisation (WHO) does not stipulate a health-based guideline for the sulphate level in potable water, it does recommend the health authorities are notified if the concentration exceeds 500 mg/ℓ (WHO 2004b). Accordingly, most countries in the world recommend a potable water standard for sulphate between 250 mg/ℓ and 500 mg/ℓ. This is based on the secondary drinking water recommendations of 500 mg/ℓ (INAP 2010).

The effect of high sulphate concentration in water was not always considered to be a problem because sulphate has a low impact on the environment in comparison with the acidic and heavy metal content of AMD. It therefore received little attention in many of the regulatory jurisdictions in comparison to the control of dissolved metals and acidity. The concern over an elevated sulphate level in effluents is increasing at regulatory agencies due to the impact it has on the salinity of receiving water bodies. Therefore, sulphate is being considered a significant long term water quality issue, particularly in water scarce countries such as South Africa (INAP 2003).

1.3. PROBLEM STATEMENT

The high sulphate level in acidic mine drainage (AMD) and industrial effluents released into the environment is problematic for various reasons:

- It causes scaling in pipes and filters and is corrosive to equipment.
- It has a purgative effect in humans when the sulphate concentration in potable water is higher than 500 mg/ℓ (WHO 2004b).
- Saline water can lead to the salinisation of irrigated soils, diminished crop yield and changes in biotic communities (DEAT 2006).

1.4. TREATMENT OPTIONS

A number of sulphate removal methods are available and most of them are implemented on full-scale. These methods include:

- Membrane filtration such as reverse osmosis and electro dialysis.
- Adsorption/ion-exchange.
- Biological degradation.
- Chemical precipitation such as lime/limestone addition to form gypsum, precipitation of ettringite and barite formation.

1.5. RESEARCH OBJECTIVE

Although a number of sulphate removal methods are available to industry, it was decided to investigate the barium sulphate precipitation method. The objective was to demonstrate that barium carbonate can be successfully used to achieve very nearly complete sulphate removal from AMD.

1.6. HYPOTHESIS

Barium carbonate, irrespective of its source, is capable of effective sulphate removal from acidic mine effluents as well as industrial effluents.

1.7. METHOD OF INVESTIGATION

A variety of methods exist to remove sulphate from industrial water and AMD. Therefore it was necessary to start off with a literature study. In this literature study different sulphate removal methods were compared to decide whether a specific method was suitable for solving a particular problem.

Once a sulphate removal method was chosen, a detailed literature study that focused specifically on this method was conducted. The results and conclusions found in the literature were used to guide the experimental work.

A reactor setup, where barium carbonate is used as barium source, to remove sulphate from AMD was analysed with purpose of improvement. Experiments were conducted to aid in the understanding of the conditions required for this precipitation process. A number of parameters which included the effects of temperature, mixing rotational speed, initial sulphate concentration, barium-to-sulphate molar ratio and different barium carbonate sources were considered. The results were tested and verified on industrial process water.

1.8 CONCLUSION

AMD and some industrial effluents are rich in sulphate ions and should not be released untreated into the environment. The high sulphate level in the water causes problems in industry such as equipment and piping damage due to corrosion and scaling. It also has a laxative effect in humans when the sulphate concentration in the consumed water is higher than 500 mg/ℓ.

A number of sulphate removal methods are used in industry such as membrane filtration (reverse osmosis and electro dialysis), adsorption/ion-exchange, biological degradation, chemical precipitation (lime/limestone addition to form gypsum, precipitation of ettringite and barite formation).

CHAPTER 2: LITERATURE SURVEY ON SULPHATE REMOVAL TECHNOLOGIES

2.1. INTRODUCTION

A literature study was conducted to investigate the different, generally available methods to remove sulphate from industrial wastewater. A short explanation of the operating principles of each of these methods is given. These methods can be divided into physical processes such as membrane filtration, chemical treatment such as precipitation methods and biological sulphate reduction (INAP 2003, Bowell 2000, Harries 1985, Akcil et al. 2006, Herlihy et al. 1989, Jiménez-Rodríguez et al. 2010, Aubé 2004).

2.2. PHYSICAL SULPHATE REMOVAL METHODS

2.2.1. Membrane filtration

Two important water treatment methods use membranes. These two methods are ED (electro dialysis) and RO (reverse osmosis). In ED, an electrical potential is used to force dissolved ions through the membrane (1 nm to 2 nm pore size), leaving behind pure water (Fell 1995). The RO on the other hand uses high pressure to force the water-part of the solution through the membrane (0.1 nm to 5 000 nm pore size, depending on filter type) while retaining the dissolved ions (INAP 2003, Fell 1995).

The two most important factors contributing to the operating costs are the membrane efficiency and the energy requirements. The membrane life is greatly affected by mechanical failure and fouling. The major advantage of all the membrane treatment processes is the production of high-quality water that can be used or sold as potable water. A major disadvantage is the production of brine that requires disposal and incurs additional costs (INAP 2003).

RO (Reverse osmosis)

The driving force for RO is the difference in pressure across the selective permeable membrane where an external hydraulic pressure is applied on the saline brine side of the membrane. Therefore the water is forced through the membrane against osmotic pressure (Fell 1995). A schematic diagram is shown in Figure 2. The discharge water or brine is the primary waste product (Letterman 1999).

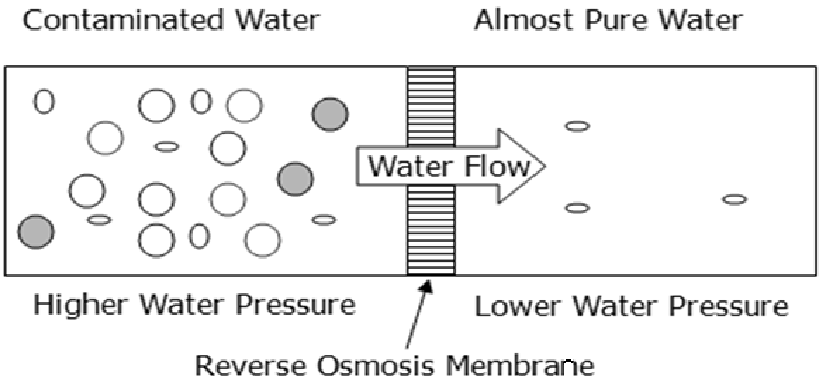


Figure 2: Schematic diagram of an RO membrane (GTAwater 2004)

An RO system consists of four basic stages, namely, pre-treatment, high-pressure pumping, membrane assembly and post-treatment. The pre-treatment prevents membrane fouling from suspended solids, mineral precipitation or microbial growth. It generally involves filtration and/or chemical treatment. A high-pressure pump is required to supply sufficient pressure to force the water through the semi-permeable membrane. This high-pressure pumping is the major contributor to the energy required for this process. Post-treatment involves conditioning of the treated water. This will include pH, alkalinity and hardness adjustments as well as hydrogen sulphide gas removal (INAP 2003). In cases where the water has a low calcium concentration (< 100 mg/ℓ) and low sulphate concentration (< 700 mg/ℓ), RO can be used as treatment method. At higher concentrations membrane scaling will occur (Bowell 2004).

HiPRO (Hi-recovery Precipitating Reverse Osmosis) process

A high recovery desalination process known as the HiPRO process has been developed by Keyplan (Pty) Ltd. Ultra high water recoveries (greater than 97%) are consistently achieved. The final products from this process are potable water (25 000 m^3/d) that is sold to the local municipality, a liquid brine stream (less than 3.0% of the total feed) and solid waste. The solid waste products are calcium sulphate of saleable grade (100 t/d) as well as a calcium and metal sulphates product. A full scale plant has been operating at full capacity since September 2007 (Blueprint 2009, Randall et al. 2011).

SPO (Seeded Reverse Osmosis)

A modified RO process known as seeded reverse osmosis (SRO), is used to treat mine water in South Africa (Harries 1985). The SRO process actively promotes precipitation of calcium sulphate prior to membrane treatment, reducing membrane deterioration and fouling by salt precipitation. This pre-treatment method involves a suspension of seed crystals being introduced into the effluent through recycling of the waste slurry. A number of disadvantages exist with this modified process, despite its advantages that include high salt and water recovery at reduced cost. The disadvantages include the high energy consumption and poor calcium sulphate seed control (Harries 1985). Redevelopment of the SRO process contributed to the patent on the slurry precipitation and recycle reverse osmosis (SPARRO) process (Bowell 2004).

SPARRO (Slurry Precipitation and Recycle Reverse Osmosis)

Water with high levels of calcium and sulphate severely limits water recovery in conventional RO treatment systems. Then again, SRO is particularly attractive for this type of water. Gypsum seed crystals are added to the feed water to serve as nucleation sites for the crystallisation and precipitation of gypsum and other minerals. This prevents mineral precipitation, that causes clogging and fouling, on the membranes. When the seed crystals are recycled from the concentrate to the feed water, the process is called the SPARRO process. The design incorporates three major improvements in comparison to the conventional RO process. These include lower energy consumption, independent control of gypsum seed and concentrate blow-down as well as the utilisation of a novel pumping system (INAP 2003). A flow diagram of the SPARRO process is shown in Figure 3.

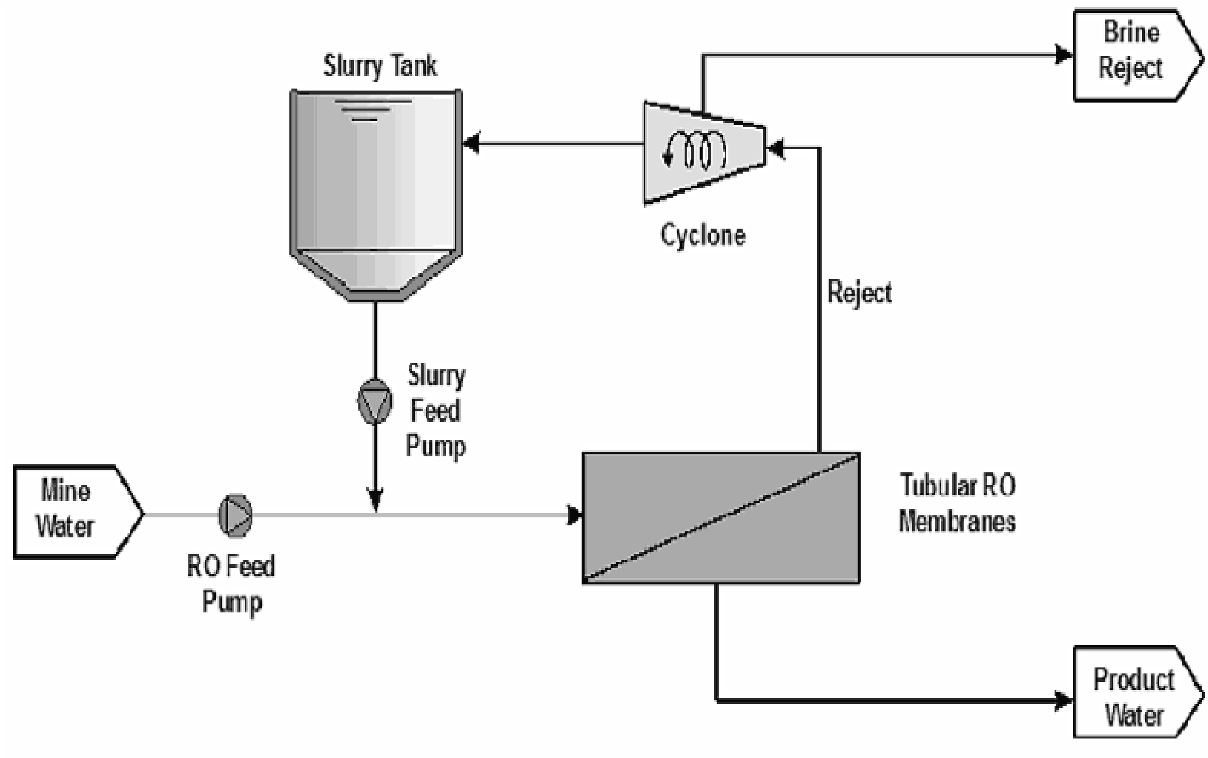


Figure 3: SPARRO process flow diagram (INAP 2010)

ED (Electro Dialysis) and EDR (Electro Dialysis Reversal)

The ED process uses direct electrical current across a stack of alternating cation and anion selective membranes. Anions in the effluent are attracted to the anode but cannot pass through the anion impermeable membranes and are thus concentrated. Cations move in the opposite direction and are obstructed by cation impermeable barriers. In this process the initial feed solution is rid of salts and clean water can be extracted.

The anode and cathode can be changed periodically, a process known as EDR. This could occur several times an hour. This reversing of the anode and cathode reduces the potential for membrane fouling and facilitates regeneration of the membrane by self-cleaning. A major advantage of EDR is that the system is not sensitive to effluent temperature or pH. Capital and working costs are reduced due to lower working pressures. However, calcium sulphate scaling can occur due to inadequate pre-treatment (Strathmann 1995). The internal construction of an ED or EDR cell is shown in Figure 4.

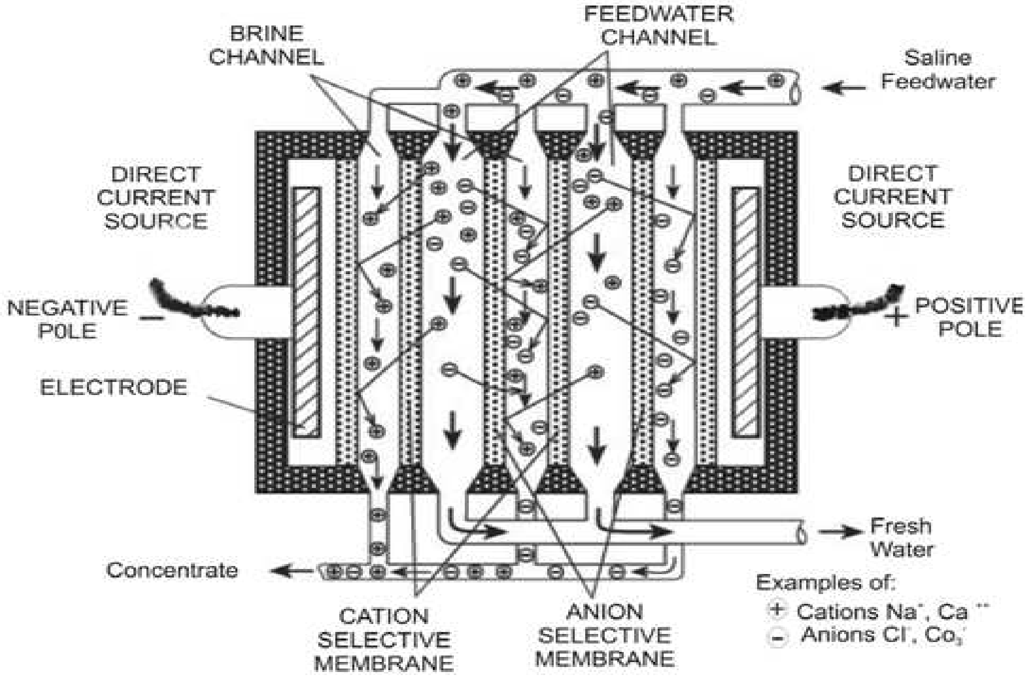


Figure 4: ED or EDR cell (UNEP 1998)

The basic ED and EDR units consist of several hundred cell pairs connected to electrodes, known as membrane stacks (INAP 2003). An EDR unit consists of five basic components: pre-treatment, the membrane stack, low-pressure pumps, power supply for direct current and post-treatment. The pre-treatment is necessary to prevent material that could cause damage to the membranes or clog the channels inside the cells to enter the membrane stacks. The low-pressure pump is necessary to ensure that water circulates through the membrane stack, which is in turn powered by the direct current. Post-treatment involves water conditioning such as the adjustment of pH, alkalinity and hardness (INAP 2003).

2.2.2. Adsorption/ion-exchange

The ion-exchange process operates on the basis of absorption of ions in the solution onto an ion-exchange resin. Ion-exchange resins contain large polar exchange groups. Therefore, this process involves the exchange of ions or molecules between the solid phase and the liquid phase with no substantial change to the solid ion-exchange resin structure. One of the targeted ions is removed from the liquid phase and attached to the solid structure in exchange for another ion. This ion is typically a hydrogen ion (H^+) or a hydroxyl ion (OH^-), thus rendering the target ion immobile (Metcalf 2003).

In the case of calcium sulphate, the anionic sulphate ion would be exchanged for a hydroxyl ion on a positively charged resin. While the cationic calcium ion would be exchanged for a hydrogen ion and so be attached to a negatively charged resin. In this process calcium sulphate scaling is a common problem. To overcome the scaling problem, a modified ion-exchange process has been developed specifically for calcium sulphate water. This process is known as the GYP-CIX process (Bowell 2004).

GYP-CIX Process

The GYP-CIX process is a low-cost ion-exchange technology for the removal of ions from wastewater such as those rich in sulphate and calcium (Wood 2003). This is based on the use of ion-exchange resins that uses cheap regeneration reagents such as lime and sulphuric acid (Akcil et al. 2006). These resins have been designed to target calcium and sulphate so as to reduce gypsum levels in effluent. By achieving this, the TDS (Total Dissolved Solids) levels in effluent are reduced and the corrosion potential limited.

Additionally, a pure gypsum product is produced from both cationic and anionic exchange (Wood 2003). Therefore, the GYP-CIX process is suitable for the treatment of scaling mine water that is high in sulphate and calcium (INAP 2003).

The process flow diagram of the GYP-CIX process is shown in Figure 5. The sulphate removal process is illustrated to the left of the figure while the cationic and anionic regeneration steps are shown on the right.

The principle of operation of the GYP-CIX process is as follows. The untreated wastewater is pumped into the cation loading section where it passes through fluidised contact stages. Calcium ions and other cations are removed from the feed water through cation-exchange with strong acid cation resin (R-H). This is demonstrated in Reaction 2 (INAP 2003).

$$2R - H + \ Ca^{2+}(+SO_4^{2-}) \rightarrow R_2 - Ca + 2H^{+}(+SO_4^{2-}) \qquad \textbf{Reaction 2}$$

After the wastewater has flown through the cation resin contactor, the water is pumped to a degassing tower to remove carbonate alkalinity. Next the water is pumped into the anion loading section where it passes through fluidised contact stages. Anions such as sulphate ions are then removed from the wastewater through anion-exchange with a weak base anion resin such as lime (R-OH). This is shown in Reaction 3 (INAP 2003).

$$2R - OH + SO_4^{2-}\ (+Ca^{2+}) \rightarrow R_2 - SO_4 + 2OH^{-}(+\ Ca^{2+}) \qquad \textbf{Reaction 3}$$

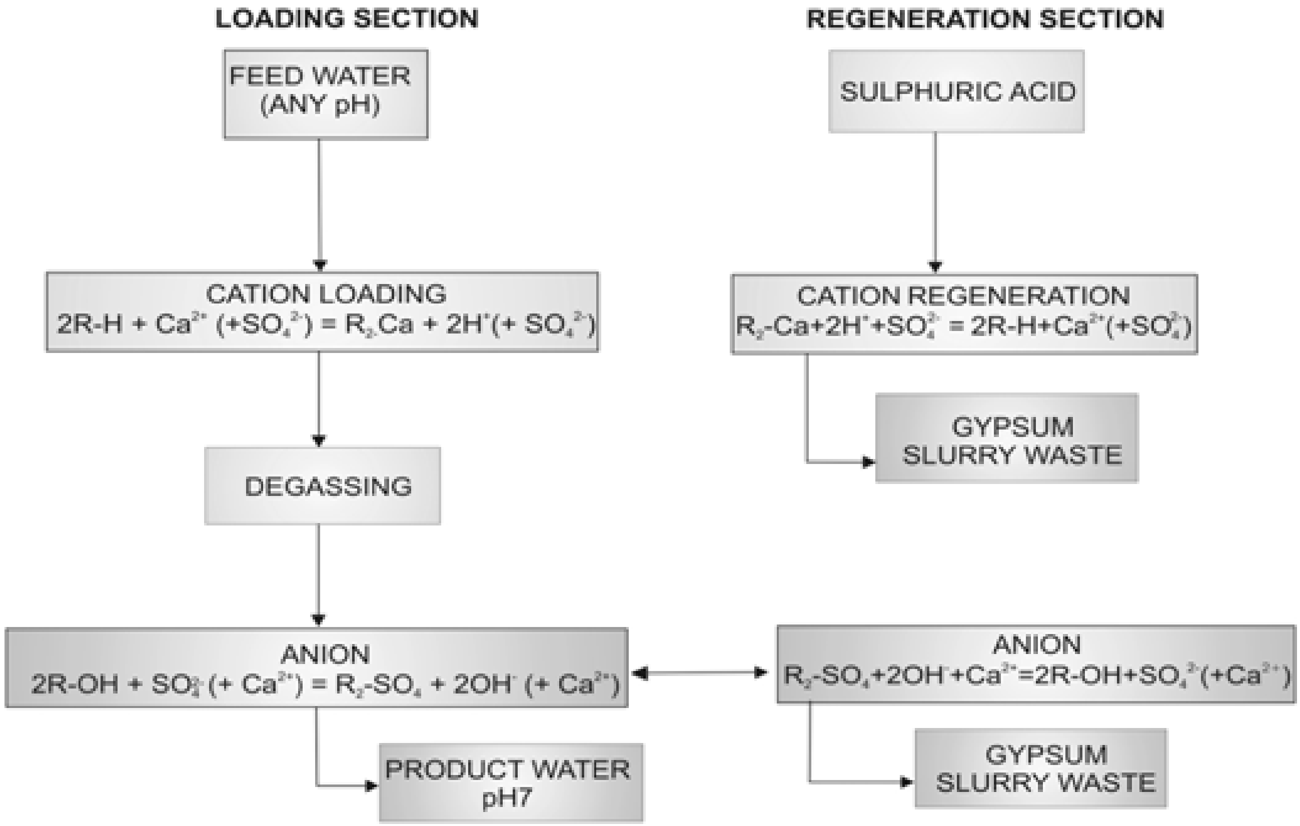


Figure 5: GYP-CIX process (McNee 2003)

The treated water has a neutral pH, and is also low in dissolved calcium, sulphate and other dissolved substances including metals (INAP 2003).

2.3. BIOLOGICAL SULPHATE REMOVAL METHODS

There are a number of biological processes to remove sulphate from wastewater. These include bioreactors and constructed wetlands (INAP 2003, Herlihy et al. 1989, Jiménez-Rodríguez et al. 2010).

2.3.1. Bioreactors

The use of bioreactors is one method to biologically reduce the sulphate concentration of wastewater. In the development and use of these reactors several problems occurred that needed special attention, in order to develop a successful sulphate removal process. These issues included the type of substrate used in the reactor, the toxicity of the wastewater and the type/design of the bioreactor (INAP 2003).

What happens inside the bioreactors is complex. In short, the reactors usually operate under anoxic conditions. The sulphate is then removed as stable sulphide precipitate. In the case where a reactor operates under anaerobic conditions, the sulphate is converted to hydrogen sulphide gas. This transformation is brought about by specialised, strictly anaerobic bacteria (Herlihy et al. 1989, Jiménez-Rodríguez et al. 2010).

A large selection of bioreactors is currently available including CSTRs (continuous stirred tank reactors), packed bed reactors, fluidised bed reactors, sludge blanket and gas lift reactors. The most significant progress in bioreactor design was made in 1988 where a continuous flow, fluidised bed reactor was used for the first time (INAP 2003). The hydrogen sulphide gas generated in the reactor was stripped with an inert gas. This stripped hydrogen sulphide gas was then used in a separate reactor to precipitate the metals out of the AMD. Thus the sulphate removal and the metal removal occurred in two different reactors.

The advantage of the reactor setup is that the bacteria are no longer exposed to potential toxins coupled with the wastewater to be treated. Also, the waste stream loading occurs in a separate reactor and is no longer dependent on the biomass retention. This implies that smaller reactors can be used as well as a greater variety of substrates. The metal sulphide precipitation can be controlled in such a manner that it is possible to control the successive precipitation of the different metal sulphides in separate reactors. This allows recovery of individual metals from the AMD (INAP 2003).

The use of bioreactors appears to be one of the most efficient biological treatment processes for sulphate removal. Operating costs of the bioreactor are high owing to the expensive carbon and energy sources required as nutrients for the microorganisms (INAP 2003). A typical bioreactor setup for sulphate removal is shown in Figure 6.

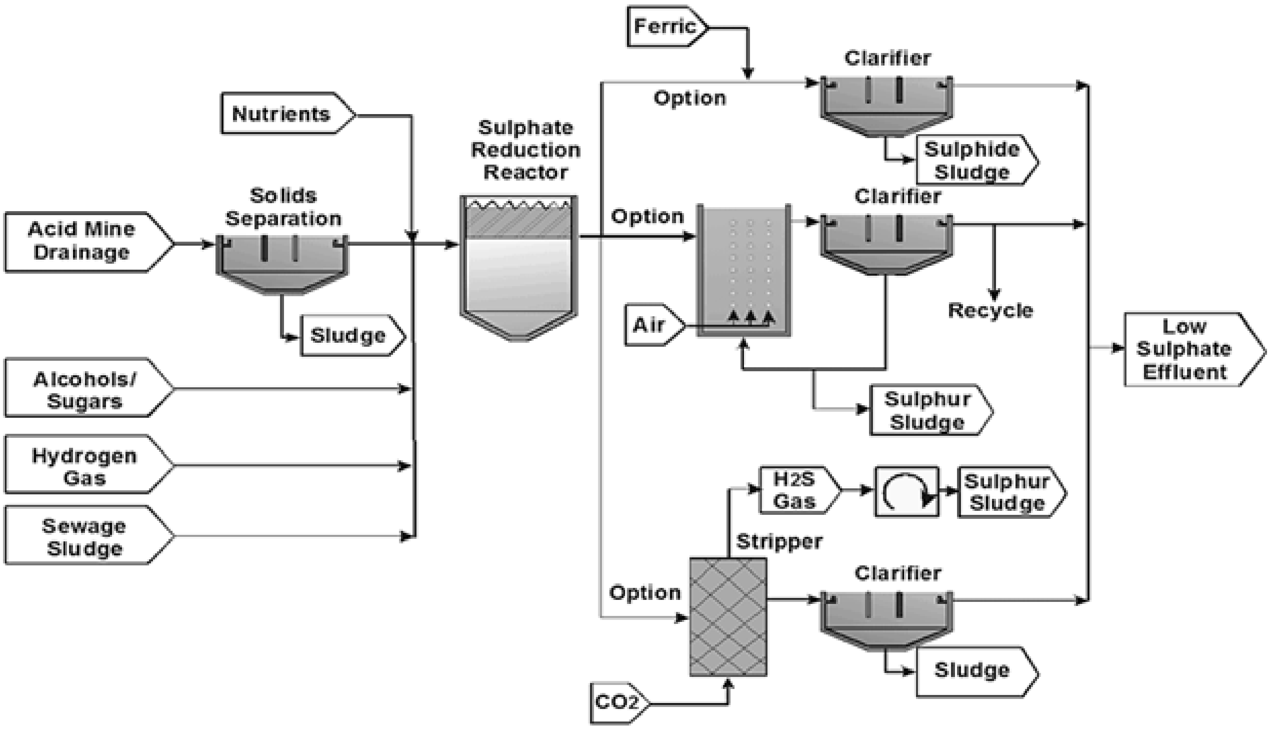


Figure 6: Typical bioreactor setup for sulphate removal (INAP 2010)

2.3.2. Constructed wetlands

Two main categories exist for constructed wetlands, namely, free water surface (FWS) wetlands and subsurface flow (SF) wetlands. The majority of natural wetlands are classified as FWS wetlands. In this type of wetland, the water flows over a vegetated subsurface from one side to the other. These wetlands are generally shallow and a subsurface barrier prevents seepage. An example is shown in Figure 7.

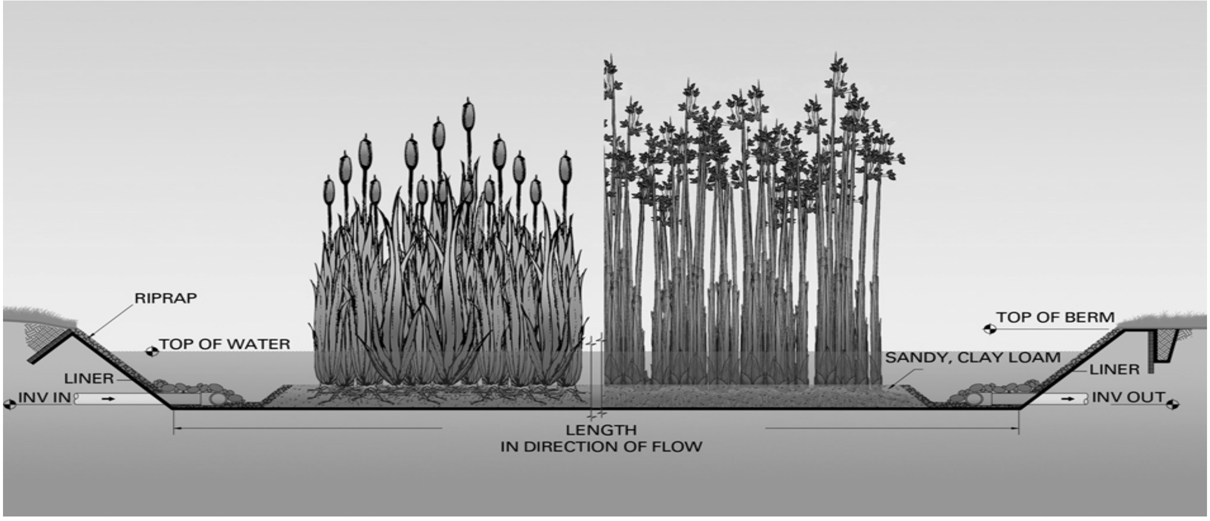


Figure 7: Schematic diagram of a FWS wetland (NSI 2011)

An SF wetland, on the other hand is designed for water treatment. This type holds an appropriate medium in a bed or channel. The water level remains below the bed surface covered with emergent vegetation. An example of such a wetland is shown in Figure 8. The volume of medium used in SF wetlands is generally larger than that in FWS wetlands. For biological sulphate removal FWS wetlands are more suitable than SF wetlands (INAP 2003).

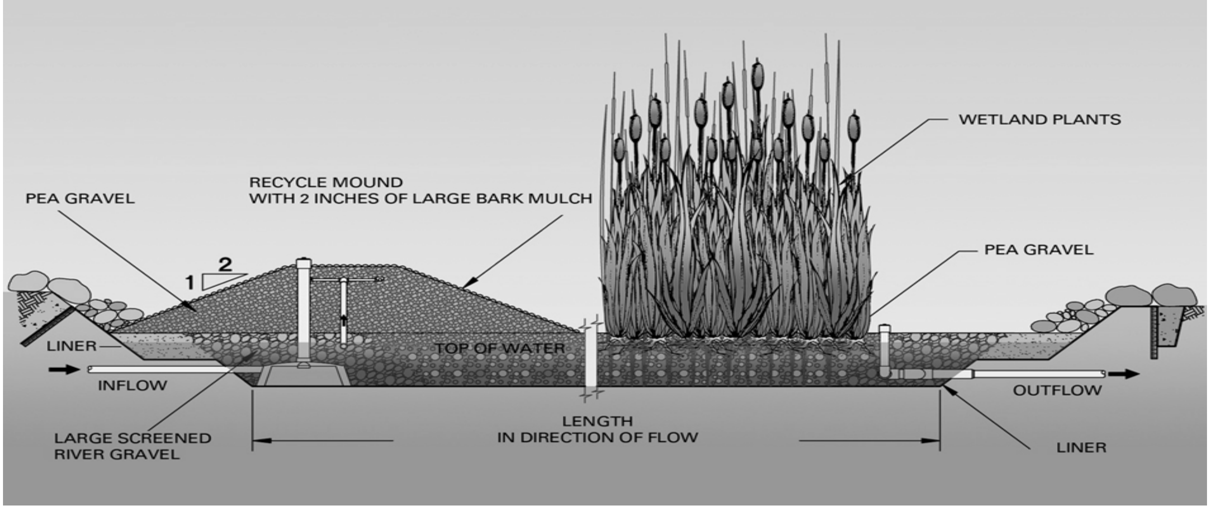


Figure 8: Schematic diagram of a SF wetland (NSI 2011)

The FWS wetlands are either aerobic or anaerobic. Aerobic wetlands are used because they provide sufficient residence time and aeration to enhance the metal precipitation through biotic and abiotic oxidation. Anaerobic wetlands are often used for the treatment of acidic water. The alkalinity used in the neutralisation of the wastewater is obtained from the dissolution of limestone and results in the reduction of sulphate in the subsurface (INAP 2003).

2.4. CHEMICAL PRECIPITATION SULPHATE REMOVAL METHODS

Chemical treatment processes that are used in conjunction with mineral precipitation processes include the addition of lime or limestone to form gypsum, addition of barium salts for barium sulphate precipitation and the SAVMIN process that is based on ettringite precipitation (Bowell 2004, INAP 2003, Aubé 2004).

2.4.1. Gypsum precipitation

Sulphate removal via lime/limestone addition is achieved by means of calcium sulphate saturation. In essence this means that the pH of the raw water is raised to a point where the metals that are of concern are no longer soluble. In turn these metals precipitate out as hydroxides resulting in a clear effluent which is in accordance with regional criteria (Aubé 2004).

The addition of lime/limestone seems to be one of the most suitable sulphate removal methods in the treatment of AMD. The limitation of this process is that it can only lower the sulphate concentration to 1 200 mg/ℓ. But, since it is a simple and inexpensive process, it can be used successfully as pre-treatment for other more expensive processes that lower the sulphate concentration to 500 mg/ℓ or less (INAP 2003).

This process is traditionally used in neutralising AMD where lime ($Ca(OH)_2$) and/or limestone ($CaCO_3$) is added to the effluent. These chemicals can also be used for partial removal of sulphate through gypsum ($CaSO_4$) precipitation. These reactions are shown in Reaction 4 and Reaction 5 (INAP 2003).

$$\mathrm{Ca(OH)_2\ (s) + H_2SO_4 \rightarrow CaSO_4\ 2H_2O\ (s)} \qquad \textbf{Reaction 4}$$

$$CaCO_3\ (s) + H_2SO_4 + H_2O \rightarrow CaSO_4\ 2H_2O + CO_2\ (g) \qquad \textbf{Reaction 5}$$

The solubility of gypsum depends on the composition and ionic strength of the solution. This solubility ranges between 1 500 mg/ℓ and 2 000 mg/ℓ and it controls the level and extent to which sulphate concentration can be reduced. This process consists of the following three steps.

First, the pH is raised which results in the production of carbon dioxide gas and gypsum precipitation. Second, the pH is raised to 12 by adding more lime to the wastewater to induce gypsum crystallisation and, if the waste contains magnesium, to precipitate it as magnesium hydroxide. Third, the pH is adjusted to 7 by adding carbon dioxide gas that is recovered from step one, and causes calcium carbonate to precipitate (INAP 2003).

The waste products from this process are gypsum and limestone sludge. This is relatively pure limestone sludge and can therefore be recycled back to the first step (INAP 2003). A flow diagram of the lime/limestone addition process is shown in Figure 9.

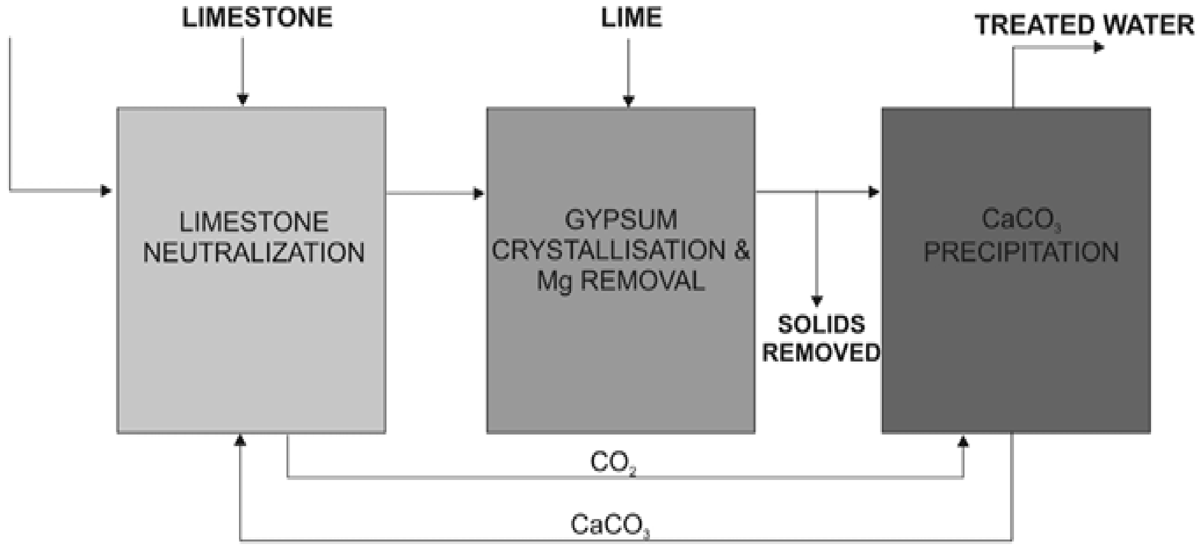


Figure 9: Gypsum precipitation process via lime/limestone addition (Geldenhuys 2004)

2.4.2. Ettringite precipitation

SAVMIN

This is a process during which sulphate removal is achieved through ettringite precipitation. This is a four-stage process as depicted in Figure 10. First, lime addition as pre-treatment removes metals as metal hydroxides. The second stage is the removal of gypsum through seed crystallisation. Stage three, is the addition of aluminium hydroxide in order to form insoluble ettringite ($3CaO.3CaSO_4.Al_2O_3.31H_2O$). The last step, before discharging the water, is to reduce the pH by the addition of carbon dioxide gas and simultaneously precipitate pure calcium carbonate. The ettringite that forms may be handled in one of two ways. One is to dispose of it as a waste product.

The other, is more profitable and requires the ettringite to be dissolved in sulphuric acid in order to recycle the aluminium tri-hydroxide. The process of recycling the aluminium tri-hydroxide complicates the process. Aluminium tri-hydroxide is also not very expensive and makes this option less attractive financially (Usinowicz et al. 2006). There are reports where plants have successfully treated 500 m^3 of wastewater that had a sulphate concentration of 800 mg/ℓ and reduced the concentration to less than 200 mg/ℓ (Bowell 2004).

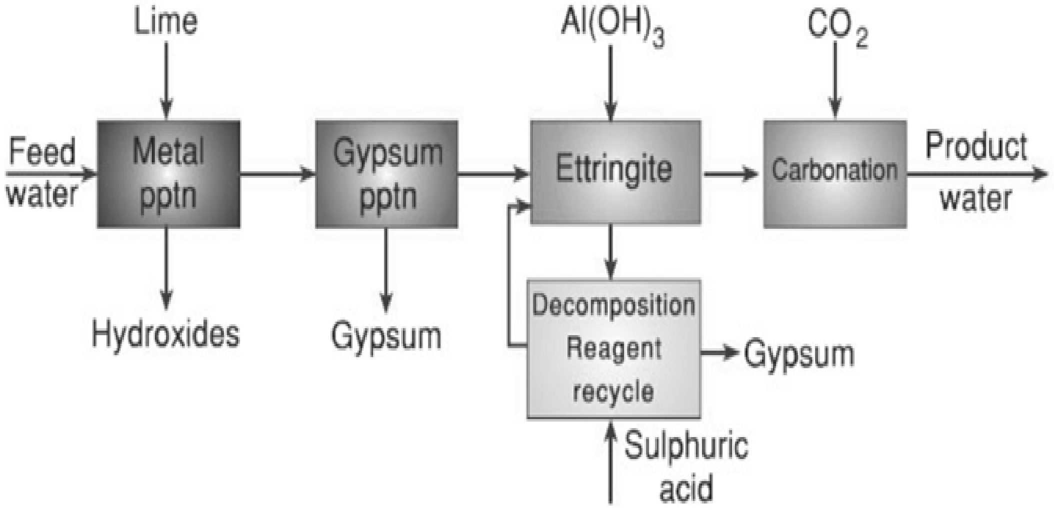


Figure 10: Flow diagram of the SAVMIN Process (McNee 2003)

“pptn” = precipitation

CESR (Cost Effective Sulphate Removal)

The CESR (Cost Effective Sulphate Removal) process is similar to the SAVMIN process since it is also based on ettringite precipitation. In addition to sulphate removal it also removes dissolved metals effectively (INAP 2003).

The process consists of three steps. First, hydrated lime is added to the feed water to induce gypsum precipitation. The pH of the wastewater is maintained at a level where metal precipitation is restricted and therefore the metal rich sludge volume is kept to a minimum. The non-hazardous gypsum sludge is separated from the water by dewatering and filtration. Second, additional lime is added to the water to raise the pH to 10.5 where metal hydroxide precipitation and additional gypsum formation will occur. In the final step the dissolved sulphate is removed. After adding more lime to raise the pH to 11.5, a proprietary reagent is added to precipitate ettringite (INAP 2003).

The more expensive SAVMIN process can reduce sulphate concentrations to very low levels; it can also remove trace metals from the AMD. The CESR processes are probably the most expensive and produce the largest amount of sludge. The primary difference between the SAVMIN process and CESR process is that the SAVMIN process uses aluminium hydroxide in the third step instead of the proprietary reagent used in the CESR process. Unlike the SAVMIN process, CESR does not recycle the ettringite (INAP 2003).

2.*4.3. Barite (barium sulphate) formation*

The removal of sulphate ions in the form of barium sulphate was first demonstrated to be effective more than 30 years ago (Kun 1972). Barite ($BaSO_4$) is highly insoluble with a k_{sp} value of 1.08×10^{-10} at 25°C (2.45 mg/ℓ), making it an excellent candidate to remove sulphate ions from wastewater (Kotz & Treichel, 2003). In this process barium salt is added to the sulphate-rich water. The barium salts commonly used include barium carbonate, barium sulphide and barium hydroxide. The reactions that take place are shown in Reaction 6, Reaction 7 and Reaction 8 (INAP 2003).

$$BaCO_3\,(s) + H_2SO_4 \rightarrow BaSO_4\,(s) + H_2CO_3$$ **Reaction 6**

$$Ba(OH)_2\,(s) + H_2SO_4 \rightarrow BaSO_4\,(s) + 2H_2O$$ **Reaction 7**

$$BaS\,(s) + H_2SO_4 \rightarrow BaSO_4\,(s) + H_2S(g)$$ **Reaction 8**

A greater quantity of sulphate is recovered when barium sulphide is used, but not as much gypsum is produced. However, hydrogen sulphide gas that has an unpleasant odour is produced (INAP 2003). The use of barium hydroxide is proposed for solutions where most metals have already precipitated as metal hydroxides (Bowell 2004).

Barium salts are expensive, thus, the barium sulphate sludge is often recycled and treated to reduce the costs. Additional income could be generated by selling the sulphur that can be recovered (INAP 2003).

2.5. CONCLUSION

A number of sulphate removal methods are available to industry. These include:

- Physical processes such as membrane filtration (RO, HiPRO, SPO, SPARRO, ED and EDR) and adsorption/ion-exchange processes (GYP-CIX Process),
- Biological processes (bioreactors and constructed wetlands), and
- Chemical precipitation (Barite formation, Gypsum and Ettringite precipitation).

For the present study, the barite precipitation method was chosen because the final sulphate concentration in the treated water can be controlled due to the low solubility of barium sulphate. As a consequence the final sulphate level can be reduced to less than 0.02 mg/ℓ.

CHAPTER 3: LITERATURE SURVEY ON BARIUM SULPHATE PRECIPITATION

3.1. INTRODUCTION

Barium sulphate precipitation as a sulphate removal method was effectively demonstrated more than 30 years ago (Kun 1972). Three main problems were identified with this method on an industrial scale: the requirement for more soluble barium in solution than is required stoichiometrically, long retention time and the high cost of barium salts. All three problems were solved.

The barite formation method forms part of the process developed and patented by the CSIR (Council for Scientific and Industrial Research) called the ABC (Alkali - Barium - Calcium) Desalination Process.

This process consists of two stages, namely the water-stage and the sludge handling-stage. In the sludge handling-stage the barium sulphate that is produced in the water-stage is converted to barium carbonate, which is then recycled back to the water-stage. The water-stage consists of three main processes. First the raw AMD undergoes a neutralisation and metal removal process. Second, gypsum crystallisation is induced by adding lime to the AMD. Partial sulphate removal occurs here and if the AMD contains magnesium, it will precipitate. In the final step the barium carbonate, recycled from the sludge handling-stage, is used to remove the residual sulphate still present in the treated AMD via barium sulphate precipitation or barite formation. The final product of the ABC Desalination Process is potable water. Most of the by-products generated can be recycled to a different part in the process, used in another process or sold. A flow diagram of this process is shown in Figure 11.

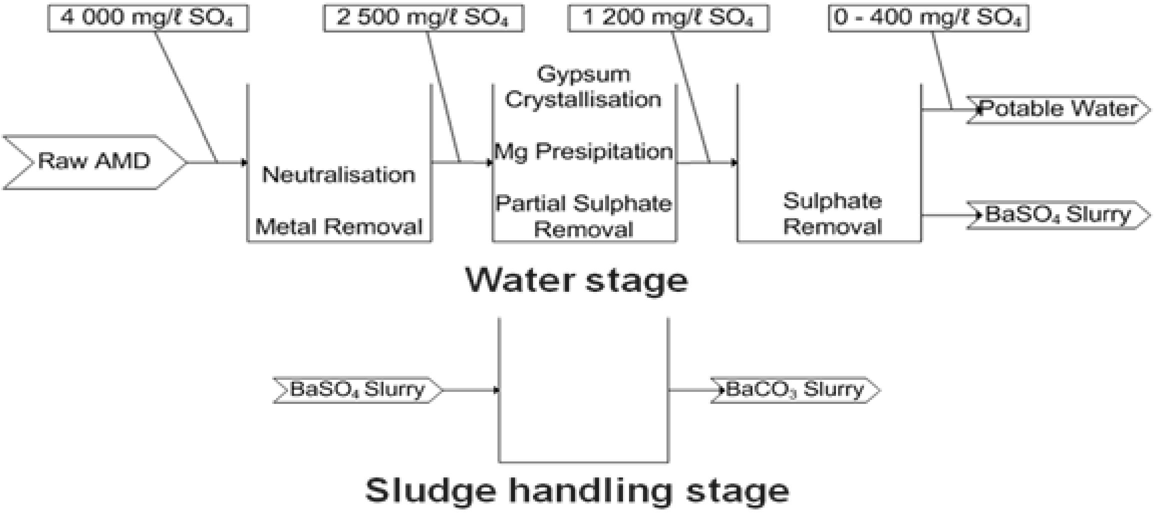


Figure 11: ABC Desalination Process flow diagram (Swanepoel 2011)

3.2. BATCH STUDIES

A number of parameters have been investigated and studied by other authors and are summarised in the following section.

3.2.1. Different barium salts

Barium sulphide, barium hydroxide and barium carbonate can be used to remove sulphate from wastewater that contains sulphate and calcium ions. Barium carbonate is favoured above barium sulphide because it does not require stripping of hydrogen sulphide gas from the solution (Hlabela et al. 2007). When barium hydroxide is used, a significant amount of calcium sulphate is (source) produced that increases the volume of sludge (Bowell 2004, Bologo et al. 2009, Bologo et al. n.d.).

The problem when using barium carbonate is that it becomes inactive when the particles are coated with metal hydroxides. Thus, the removal of metals form wastewater is required before sulphate precipitation occurs. It also required the separation of the barium sulphate from the calcium carbonate that co-precipitates in this process (Maree et al. 2004b).

Another compound that can be used to remove sulphate from wastewater is barium sulphide. In this process two by-products are produced, namely, sulphur and calcium carbonate (Bosman et al. 1990). A sulphate reduction of 95% is obtained and a variety of metals such as iron, nickel, cobalt and manganese are removed during experiments done at ambient temperature. The industrial water used to test this process was from the uranium process raffinate and AMD from a coal mine. Initially, this water was neutralised with lime/limestone and clarified before the sulphate was removed. The final sulphate content was reduced to less than 200 mg/ℓ (Bosman et al. 1990).

The barium sulphide process consists of the preliminary treatment with lime, sulphate precipitation as barium sulphate, hydrogen sulphide gas stripping, gypsum crystallisation and finally, the recovery of barium sulphide. During the lime neutralisation step, the sulphate concentration was reduced from 2 800 mg/ℓ to 1 250 mg/ℓ by means of gypsum crystallisation. The metals in the effluent were precipitated as metal hydroxides. The barium sulphide treatment stage then lowered the sulphate ions concentration to less than 200 mg/ℓ (Maree et al. 2004b).

The advantage of the barium carbonate process is that the sulphate levels can be reduced to specific values due to barium sulphate's low solubility. The soluble barium salts such as barium sulphide can be recovered as well. Three problems were identified with this process. First, a long retention time is required; second, the high concentration of soluble barium remaining in the treated water after the barium carbonate was over-dosed relative to the stoichiometric requirements of the reaction and, thirdly the high cost of the barium salt. To overcome the high cost problem, it was demonstrated that the barium sulphate can be reduced efficiently and economically with coal under high temperatures (± 1 050°C) to barium sulphide. This barium sulphide can then be either used directly on site or be converted to barium carbonate (Maree et al. 2004b).

Another study was done where barium sulphide was used. In this study lime treatment was incorporated as pre-treatment where the sulphate concentration decreased from 2 650 mg/ℓ to 1 250 mg/ℓ during work done at ambient temperature. During the barium sulphide treatment the sulphate concentration was lowered to 1 000 mg/ℓ (Maree et al. 2004b, Maree et al. 2004a).

Barium hydroxide can also be used. The Magnesium Barium Oxide (MBO) process consists of three steps: the metal removal stage, that uses magnesium hydroxide followed by the magnesium and sulphate removal stage, using barium hydroxide, and lastly, the calcium removal stage using carbon dioxide gas. The raw materials used in this process, magnesium hydroxide and barium hydroxide, can be recovered from the waste sludge that is produced, namely barium sulphate and magnesium hydroxide sludge. In this process the sulphate can be reduced to low concentrations (Bologo et al. 2009, Bologo et al. n.d.).

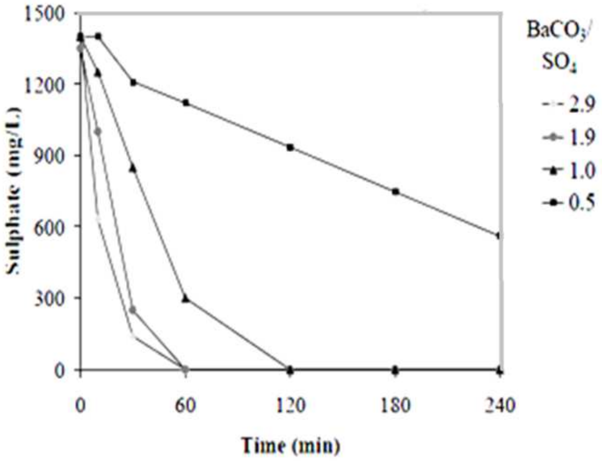
In the case where the MBO Process was used to treat a coal mine effluent, the sulphate levels were lowered from 2 493 mg/ℓ to 181 mg/ℓ by means of barium sulphate precipitation at ambient temperature. In the case where sulphates were removed from gold mine effluents the concentration remained unchanged during magnesium hydroxide treatment because of the high solubility of magnesium sulphate. During the next step in the MBO Process, barium hydroxide treatment takes place at a pH of 12. Most of the magnesium in the wastewater precipitated and only 1 mg/ℓ magnesium remained. Simultaneously, the sulphate concentration was lowered from 4 398 mg/ℓ to 24 mg/ℓ at ambient temperature by means of barium sulphate precipitation (Bologo et al. n.d.).

3.2.2. Different barium carbonate types

Two different types of barium carbonate were used to remove sulphate ions from sulphate-rich water. One was commercial barium carbonate imported from China and the other a barium carbonate produced in the laboratory. The commercial barium carbonate exhibited much slower reaction rates compared to the barium carbonate produced in the laboratory. The reasons for the differences in removal efficiency were not investigated (Motaung et al. 2009).

3.2.3. Kinetics

Reaction kinetic studies were reported in two different publications (Hlabela et al. 2007, Motaung et al. 2008). The sulphate concentrations of the samples taken over time that were used to determine this kinetics are shown in Figure 12. The reaction order of the sulphate removal process was determined by plotting the sulphate removal reaction rates against the barium carbonate concentrations on a log-log graph as shown in Figure 13. A reaction order of unity was found because the graph resulted in a straight line (Hlabela et al. 2007, Motaung et al. 2008).



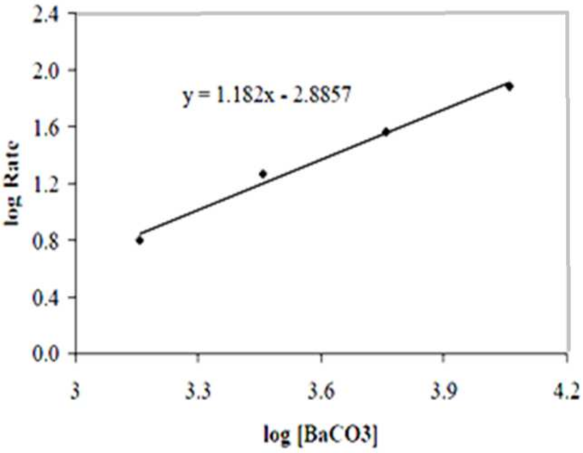


Figure 12: Sulphate removal profiles (for reaction kinetics) (adapted from Hlabela et al. 2007)

Figure 13: Log of SO_4^{2-} vs. log $BaCO_3$ concentrations (adapted from Hlabela et al. 2007)

3.2.4. Co-precipitation of calcium carbonate

A study was conducted with the aim of comparing sulphate removal efficiency when different sulphate salts are present in the effluent. Two different sulphate salts were used namely calcium sulphate and sodium sulphate. The sulphate concentration profiles as the sulphate is removed from the feed water are shown in Figure 14.

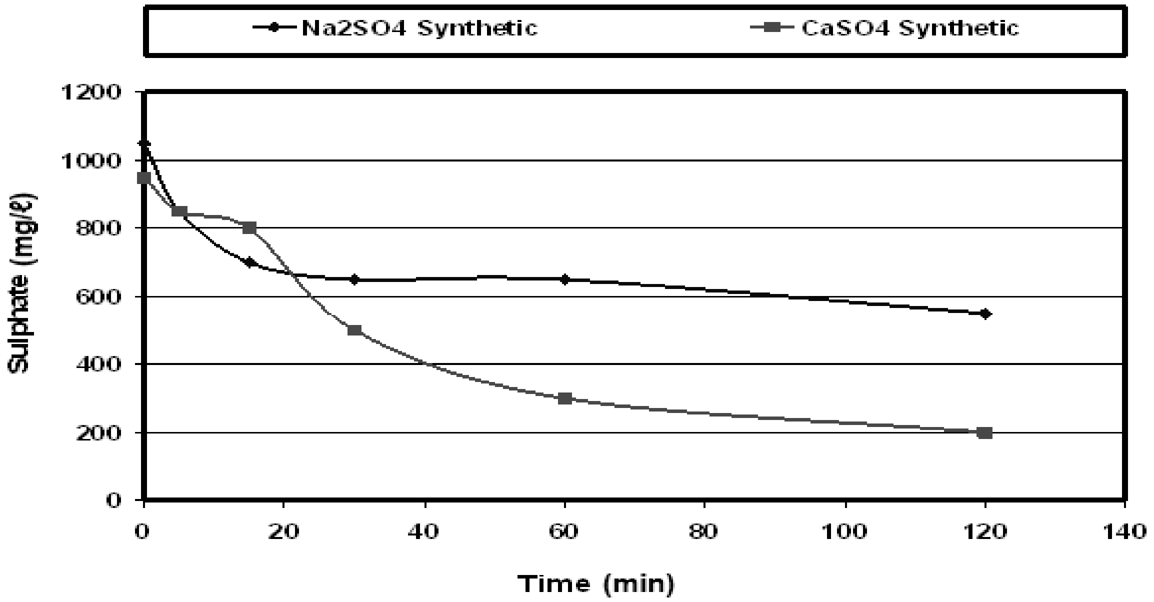


Figure 14: Different sulphate salts as sulphate sources (Motaung et al. 2009)

In the scenario where calcium sulphate was used in the solution the reaction proceeded quicker than in the case where sodium sulphate was used. The conclusion was reached that the cation coupled with the sulphate ion influenced the rate and amount of the sulphate being removed when barium carbonate is used (Motaung et al. 2009).

Another study indicated that sulphate can only precipitate as barium sulphate when barium carbonate is used after the magnesium ions are removed from the solution (Trusler et al. 1988). An investigation was launched to determine the effect on sulphate removal when the sulphate ions in solution were coupled with magnesium ions and when they were not. In the experiments where the magnesium was coupled with the sulphate ions, only the sulphate ions that were not coupled with magnesium, those coupled with calcium were removed.

The results are shown in Figure 15. In the experiments where the sulphate ions were not coupled with magnesium, almost complete sulphate removal was achieved irrespective of the magnesium concentration, as indicated in Figure 16. The conclusion was that the magnesium concentration only influenced the sulphate removal if it was coupled with sulphate ions; if not, then it will not interfere with the sulphate removal process (Hlabela et al. 2007, Hlabela et al. 2005). In short, the formation of magnesium sulphate ion pairs retards the rate of sulphate removal due to the greater solubility of magnesium carbonate (Trusler et al. 1991).

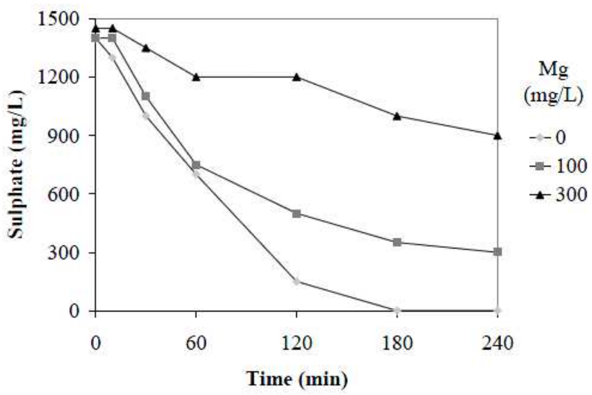


Figure 15: Magnesium-sulphate association (Hlabela et al. 2007)

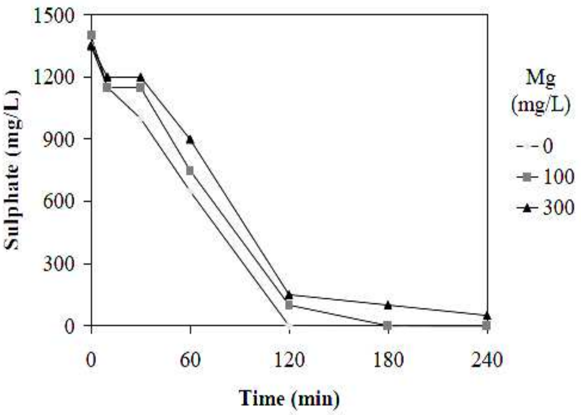


Figure 16: No magnesium-sulphate association (Hlabela et al. 2007)

The above was explained by Hlabela et al. (2007) as follows. The ionic compound, barium carbonate, dissolves partially, releasing barium ions to bind with the sulphate ions in the solution to precipitate as barium sulphate. Due to barium carbonate's low solubility, both the barium ions and the carbonate ions in the solution have to be removed, before the dissolution of the remainder solid barium carbonate particles can occur. The barium ions in the solution are removed through barium sulphate precipitation while the carbonate ions are removed through calcium carbonate precipitation (Hlabela et al. 2007, Hlabela et al. 2005).

3.2.5. Barium-to-sulphate molar ratios

The kinetics of the sulphate removal process is influenced by the amount of barium carbonate that is dosed into the feed water. The sulphate removal occurs faster when excess barium carbonate is used (Hlabela et al. 2007, Hlabela et al. 2005). In experimental work the sulphate level in the wastewater can be removed to a concentration lower than 200 mg/ℓ (at ambient temperature) in less than one hour (Motaung et al. 2009). Although the fast sulphate removal is favourable, it causes additional problems due to the fact that barium is toxic. Over-dosing of barium carbonate will result in excess barium in the final water product.

However, it takes about two hours to reduce the sulphate concentration to less than 200 mg/ℓ (at ambient temperature) when the barium carbonate was under-dosed. In both these cases the initial sulphate concentration in the feed water was 1 000 mg/ℓ. Taking the toxicity of barium into consideration, it is preferred to use a barium-to-sulphate ratio that is less than stoichiometric (Motaung et al. 2009).

3.2.6. Effect of temperature

Only one author mentioned the importance of temperature on the sulphate precipitation process. In general the higher the reactor temperature, the faster the sulphate removal rate became. Thus, the increase in the reaction rate at higher temperatures was significant in this process (De Beer et al. 2010).

3.2.7. pH effect

Sulphate removal is only slightly influenced by the pH of the process water (Herskovitz 2011, Hlabela et al. 2005). The removal rate decreases slightly with increased pH. This is due to the solubility of barium carbonate that decreases with increased pH (Hlabela et al. 2007, Hlabela et al. 2005).

Barium carbonate, with a solubility product (k_{sp}) of 2.58×10^{-9}, is scarcely soluble in water. For sulphate precipitation to occur when barium carbonate is added to the feed water, the barium carbonate should be dissociated. The dissociation of barium carbonate is dependent on the solution pH as shown in Figure 17. The lower the pH of the solution, the more barium carbonate dissociates and becomes available for the sulphate removal process (Motaung et al. 2009). Thus, it is expected that the sulphate removal rate will be slower at a higher pH because of the lower barium ion concentration (Motaung et al. 2008). This is supported by the results illustrated in Figure 18.

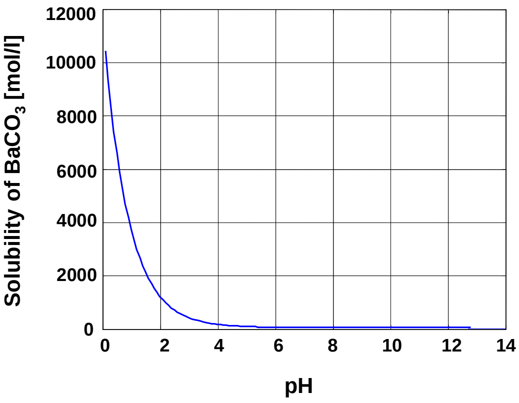


Figure 17: pH dependency of $BaCO_3$ solubility (Motaung et al. 2009)

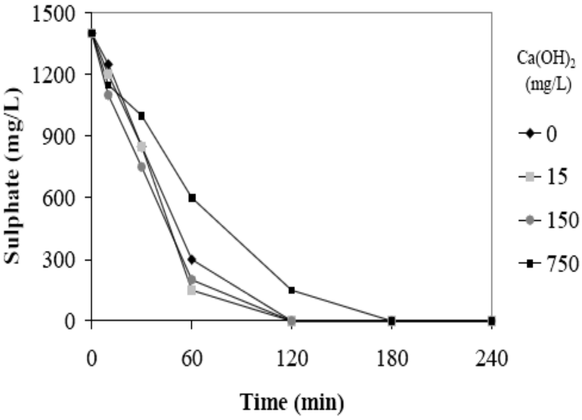


Figure 18: Effect of pH on sulphate removal (Hlabela et al. 2005)

3.3. CASE STUDIES

Three case studies are discussed in this section. The sulphate removal process was tested and verified on AMD, zinc plant effluent and power station cooling-water effluent.

The sulphate removal from AMD using commercial barium carbonate was carried out before the magnesium was removed. Sulphate ions were removed from the AMD that contained 120 mg/ℓ magnesium. The sulphate concentration in the feed water was reduced from about

2 000 mg/ℓ to 500 mg/ℓ with a stoichiometric barium-to-sulphate molar ratio and a four hours run time. But, when synthetic barium carbonate was used on the feed water from which the magnesium had been removed, a significant amount of sulphate was removed. The sulphate was reduced from 2 000 mg/ℓ to less than 500 mg/ℓ even when the barium carbonate was under-dosed (Motaung et al. 2009).

In the second case study, it was seen that by treating zinc plant effluent with barium carbonate the effluent was effectively neutralised. Also, all the zinc and most of the calcium and manganese were removed. The sulphate concentration could not be sufficiently reduced from this feed water within the three-hour experimental run time. But when this effluent was treated with lime prior to the barium carbonate dosing stage, the sulphate, zinc and cadmium in the feed water were almost completely removed (Trusler et al. 1991).

In the last case study, the sulphate removal from power station cooling-water was investigated. In contrast to AMD, the sulphate removal with barium carbonate was less effective if lime was added. Reducing the pH of the feed water with sulphuric acid appeared to aid the sulphate and calcium removal process. It appeared as though some additives to the power station cooling-water, such as anti-scalants and/or anti-bacterial agents, had a significant impact on the sulphate removal process (Trusler et al. 1991).

3.4. CONCLUSION

The sulphate removal literature based on barite formation was investigated. This sulphate removal method is part of the process developed and patented by the CSIR known as the ABC Desalination Process. In this process the sulphate in the AMD is removed by barium sulphate precipitation when a barium carbonate is added to the effluent. The sulphate removal can be controlled due to the very low solubility of barium sulphate. It can even be removed completely if required.

A number of experiments have previously been carried out and these results and conclusions were documented. These investigations covered parameters such as:

- Different barium compounds such as barium sulphide, barium hydroxide and barium carbonate,
- Different barium carbonate types such as commercial imported barium carbonate form China and laboratory-produced, synthetic barium carbonate,
- The kinetics of the sulphate removal process,
- Co-precipitation of calcium carbonate,
- Barium-to-sulphate molar ratios,
- The effect of temperature on the sulphate removal process, and
- The effect of pH on the sulphate removal process.

Three case studies were discussed where the sulphate removal process was tested and verified on AMD, zinc plant effluent and on power station cooling-water.

CHAPTER 4: SULPHATE REMOVAL EXPERIMENTS

4.1. INTRODUCTION

Barium salts are successfully used to remove sulphate from AMD. When barium carbonate is added to the AMD, a white precipitate will form. The precipitate is barium sulphate and calcium carbonate, both insoluble compounds. The operating parameters were investigated.

These parameters were all tested using a batch reactor setup. The results of these experiments were then tested and verified on AMD. The sulphate removal reaction that takes place is given by Reaction 9.

$$CaSO_4(aq) + BaCO_3(s) \rightarrow CaCO_3(s) + BaSO_4(s)$$ **Reaction 9**

4.2. EXPERIMENTAL METHOD

4.2.1. Chemicals and equipment

The chemicals and equipment used during the experimental work are listed in Table 1. Calcium sulphate (Merck) was used to prepare synthetic sulphate feed water. Three different types of barium carbonate were used to remove the sulphate from the sulphate-rich water as listed in Table 1. AMD from a coal mine was used to verify the results from the synthetic feed water experiments. The experimental setup is described in more detail in Paragraph 4.2.4.

Table 1: Chemicals and Equipment for experimental work

Chemicals	Equipment
• $BaCO_3$ (Imported from China (CIF Durbsan)) • $BaCO_3$ (Produced in the laboratory) • $BaCO_3$ (Recycled from the ABC Desalination Process) • $CaSO_4$ (Merck) • Distilled Water • Process water (AMD from a coal mine)	• 100 ml Glass beaker • 100 ml Measuring cylinder • 1ℓ Measuring cylinder • 2ℓ Measuring cylinder • Computer (download data from Multimeter datalogger) • Funnels • Magnetic stirrer with magnetic bar • Multimeter Datalogger with measuring probe • Overhead agitator with impeller • Perspex reactor with baffles (3 ℓ) • Pipette for sampling • Sample bottles • Stop watch • Whatman nr 1 filter paper

4.2.2. Synthetic sulphate water

Several laboratory experiments were conducted where barium carbonate was used to remove sulphate ions from sulphate-enriched water. Synthetic sulphate water was prepared by dissolving calcium sulphate in distilled water to determine the effect that different parameters have on this process. All of these experiments were done in a batch reactor configuration on laboratory scale. After the optimum operation conditions were determined, this sulphate removal method was tested on AMD. The parameters that were investigated included:

- The effect of mixing on sulphate removal,
- The effect of initial sulphate concentration in the feed water,
- The barium (Ba^{2+}) (dosed as barium carbonate) to sulphate (SO_4^{2-}) (present in the feed water) molar ratio,
- The effect of temperature on the entire sulphate removal process, and
- Barium carbonate morphology.

4.2.3. Barium carbonate

Barium carbonate from two different sources was used to determine whether the barium carbonate characteristics, such as its crystal surface structure or morphology, had an effect on the sulphate removal process. One source of barium carbonate is commercially available and was imported from China. The other barium carbonate source was prepared in the laboratory.

In an effort to confirm the importance of the barium carbonate crystal structure used to remove sulphate from water, a separate set of experiments was conducted. In these experiments barium carbonate was produced through a carbonation process where barium sulphide is carbonated with carbon dioxide gas. Different batches of barium carbonate were produced each under a unique set of conditions; this ensured that each batch of barium carbonate had a different crystal structure and surface area. The investigation was aimed at confirming whether or not all barium carbonate is equally effective in removing sulphate ions from sulphate enriched water and whether certain crystal characteristics are more favourable than others.

4.2.4. AMD (Acid Mine Drainage)

The AMD was collected from a coal mine. The selected sulphate removal method was used to determine how the optimised parameters, from the synthetic sulphate-enriched water experiments, would work on authentic industrial effluents. An industrial effluent, at different pH levels, was used to confirm whether this method was applicable to industrial water.

4.2.5. Batch reactor

For the batch experiments, a 3 ℓ reactor equipped with baffles was used together with an overhead agitator. First the required amount of calcium sulphate was dissolved in distilled water to prepare a sulphate-rich solution. During the experiments, sulphate ions were removed in order to determine to what extent the sulphate could be precipitated under the specific operating conditions. Barium carbonate slurry (approximately 100 ml) was simultaneously prepared in a small beaker adjacent to the reactor. Barium carbonate has a low solubility, and approximately 10 min. mixing time was required to ensure that the maximum amount of barium carbonate had dissolved into the distilled water before it was added to the sulphate-rich solution, as experimentally determined beforehand. The concentration of the barium carbonate slurry, after adding it to the sulphate-rich water, depended on the sulphate concentration of the sulphate-rich water.

After sufficient mixing of the barium carbonate slurry, it was added to the sulphate-rich solution to initiate the sulphate removal process. During this process the pH, temperature and electrical conductivity (EC) were continuously measured using a multiple parameter probe that recorded and stored the data. At EC-dependent time intervals, samples were collected for sulphate and barium analysis (Turbidimetric method) (APHA 1992). Figure 19 is a photograph of the reactor setup in the laboratory before the addition of barium carbonate.

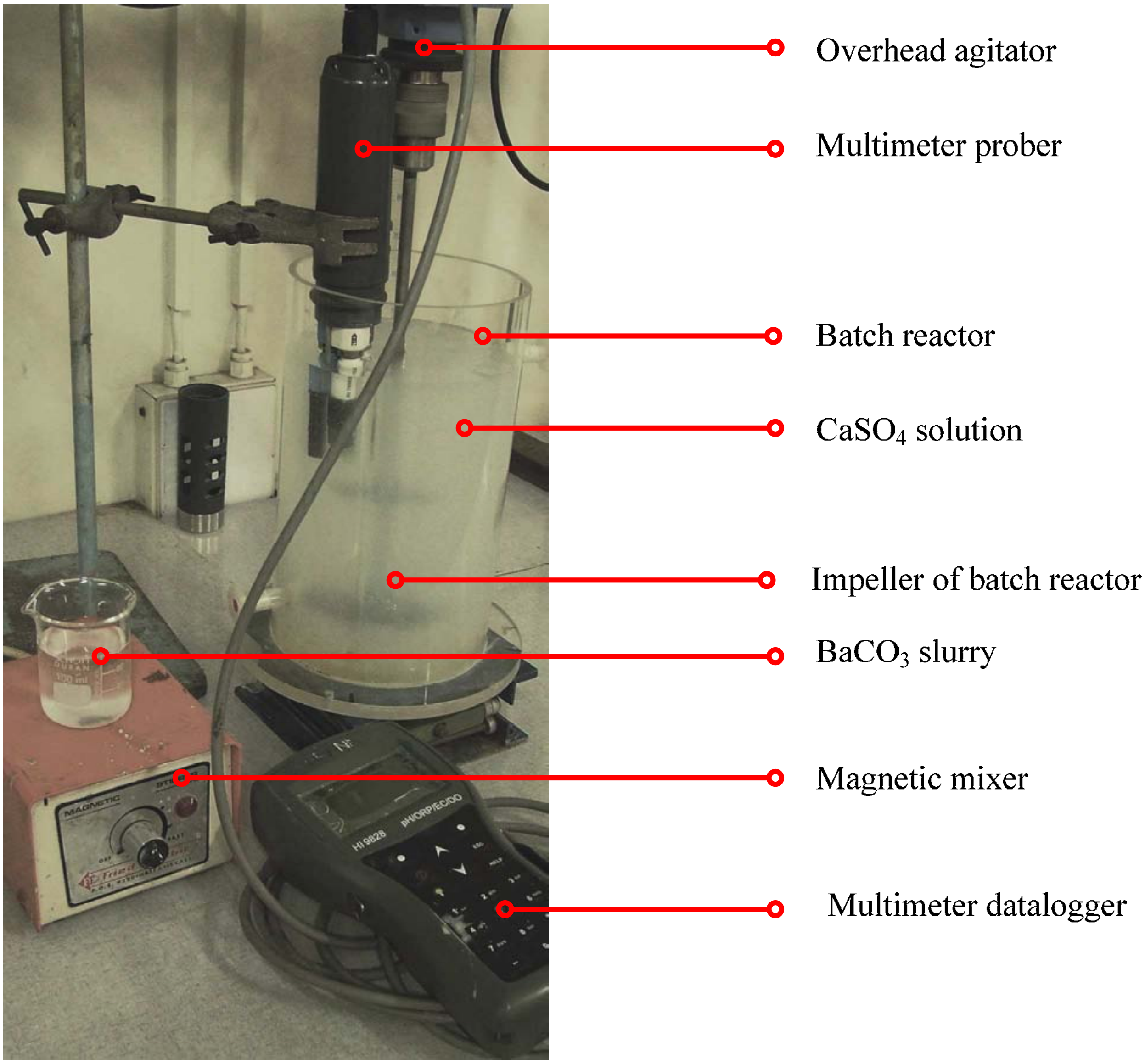


Figure 19: Laboratory setup before barium carbonate addition

A detailed description and the limitations of all the measuring equipment used during the experiments are available in Appendix A.

Numerous experiments were conducted to determine the effect of different parameters on the sulphate removal process. These included:

- Different barium-to-sulphate molar ratios (Ba^{2+}/SO_4^{2-} equal to 0.50, 0.75, 1.00, 1.25 and 1.50, respectively);
- Initial sulphate concentrations (400 mg/ℓ, 800 mg/ℓ, 1 200 mg/ℓ, 1 600 mg/ℓ and 2 000 mg/ℓ, respectively);
- The mixing rotation speed of the impeller (60 min^{-1}, 160 min^{-1}, 260 min^{-1}, 350 $min^{-1}$and 450 min^{-1}, respectively);
- The reactor temperature (commercial barium carbonate: 13°C and 34°C,respectively; laboratory produced barium carbonate: 14°C, 21°C and 34°C, respectively); and
- Using barium carbonate from different sources. These included industrial grade barium carbonate imported from China, recycled barium carbonate from the ABC Desalination Process (De Beer et al. 2010) and barium carbonate produced under different conditions in the laboratory during the carbonation of barium sulphide with carbon dioxide gas.

4.2.6. Electrical conductivity (EC) correlation

The reaction progress of the sulphate ion removal process was followed by electrical conductivity (EC) measurement. Only four chemical compounds were present in the solution during the testing of sulphate removal from synthetic-sulphate water, namely calcium sulphate, barium carbonate, calcium carbonate and barium sulphate. All four of these chemicals are a white powdery substance. The calcium sulphide was the source of sulphate ions. The barium carbonate was added to the sulphate solution in order to precipitate sulphate from the solution. Calcium carbonate and barium sulphate formed as products during the chemical reaction.

Due to the low solubility of barium carbonate, barium sulphate and calcium carbonate it was assumed that these three compounds were present in their solid, crystal form. The assumption was supported by analysing the feed solution for barium ions (< 0.02 mg/ℓ) and sulphate ions (1 600 mg/ℓ). Therefore, the majority of the dissolved ions in the solution originated from the dissolution of calcium sulphate. Since the calcium ions and the sulphate ions were both removed from the solution during the sulphate removal process, it was assumed to be realistic to track the sulphate reduction with EC measurements (Swanepoel et al. 2011).

The above correlation makes sense because the conductivity of a solution is the result of the ion charge within the solution (Perry et al. 1997). Thus, when the EC values stabilise it implies that the reaction could be considered complete, i.e., the sulphate removal process had progressed to a point where no more sulphates could be removed from solution.

An experiment was conducted to establish the correlation between the sulphate concentration in the solution and its EC value. The sulphate removal profile correlated very well with the EC profile, by inspection, as shown in Figure 20.

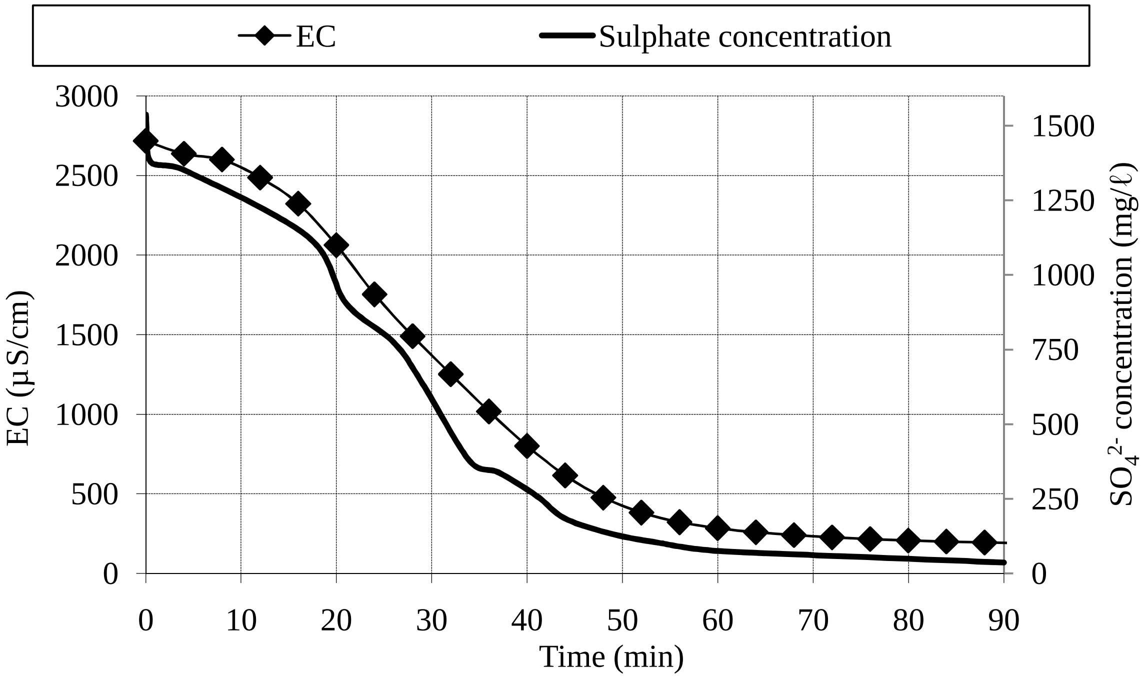


Figure 20: The sulphate concentration and EC profile correlation

The experimental parameters were as follows. The initial sulphate concentration in the sulphate-rich water was 1 600mg/ℓ and the mixing rotational speed was 350 min^{-1}. The reactor temperature was constant at ambient temperature (21°C ± 1.5°C). Laboratory produced barium carbonate was used and the dosing ratio was stoichiometrically equal to the sulphate present in the solution. After 90 min. the sulphate concentration was reduced by 97.7% (36 mg/ℓ) according to sulphate analyses.

Different models were used to find the mathematical relationship between the EC values and the sulphate concentrations. The numerical relation between these two profiles was determined by plotting the EC values against the sulphate concentrations, as shown in Figure 21. The EC measurements (and also the temperature and the pH of the solution) were recorded and stored by a Hanna Data Logger (Hanna Instruments HI 9828). Sulphate analyses were conducted by an SANAS accredited laboratory (Waterlab (Pty) Ltd, Persequor Park, Pretoria). These different models are listed in Appendix B.

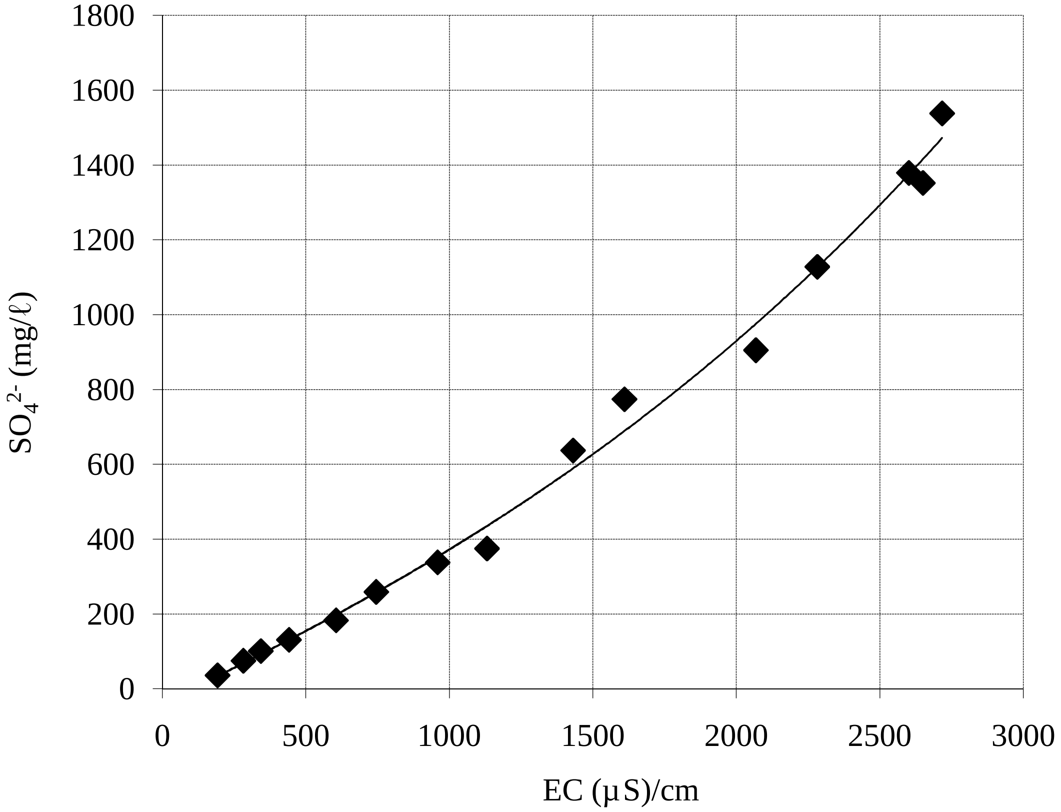


Figure 21: Sulphate concentration – EC correlation

From Figure 21 it was concluded that the relationship between the sulphate concentration changes and the EC changes in the solution are represented by a third order polynomial equation (Equation 1). This empirical formula enabled the sulphate concentration of the solution to be calculated in mg/ℓ from the EC (µS/cm) values.

$$[SO_4^{2-}] = (2 \times 10^{-8})\,EC^3 + (3 \times 10^{-5})\,EC^2 + 0.3678\,EC - 37.877 \qquad \textbf{Equation 1}$$

The difference between the measured and calculated values was 0.1%. According to the above mathematical expression the sulphate concentration was reduced by 97.9%. The measured and calculated results are given in Table 2.

Table 2: Model comparison

	SO_4^{2-} measured by analysis (mg/ℓ)	SO_4^{2-} calculated (mg/ℓ)
Initial value	1538	1584
Final value	36	34
% removal	97.8	97.9

Owing to limited funding granted for this project, the sulphate concentration levels were established by logging the EC values of the solution. Equation 1 was used to calculate the sulphate concentration of the solution instead of sending the samples to a SANAS accredited laboratory.

4.2.7. Repeatability

The repeatability of the sulphate removal process was determined by repeating the same experiment twice under identical conditions within the boundaries of experimental error. The experimental parameters for these experiments were as follows. The initial sulphate concentration in the sulphate-rich water was approximately 1 000mg/ℓ and the mixing rotational speed was 350 min^{-1}. The reactor temperature was constant at ambient temperature (21°C ± 1.5°C). Laboratory produced barium carbonate was used and the dosing ratio was stoichiometrically equal to the sulphate present in the solution.

The repeatability was excellent as can be seen in Figure 22 and Figure 23. The EC profiles for the three separate experiments are shown in Figure 22. From this figure it was evident that the three graphs were superimposed. In Figure 23 the pH profiles of the three experiments are shown and again, by inspection, the three graphs were identical. Statistical analyses were, therefore, performed to confirm this.

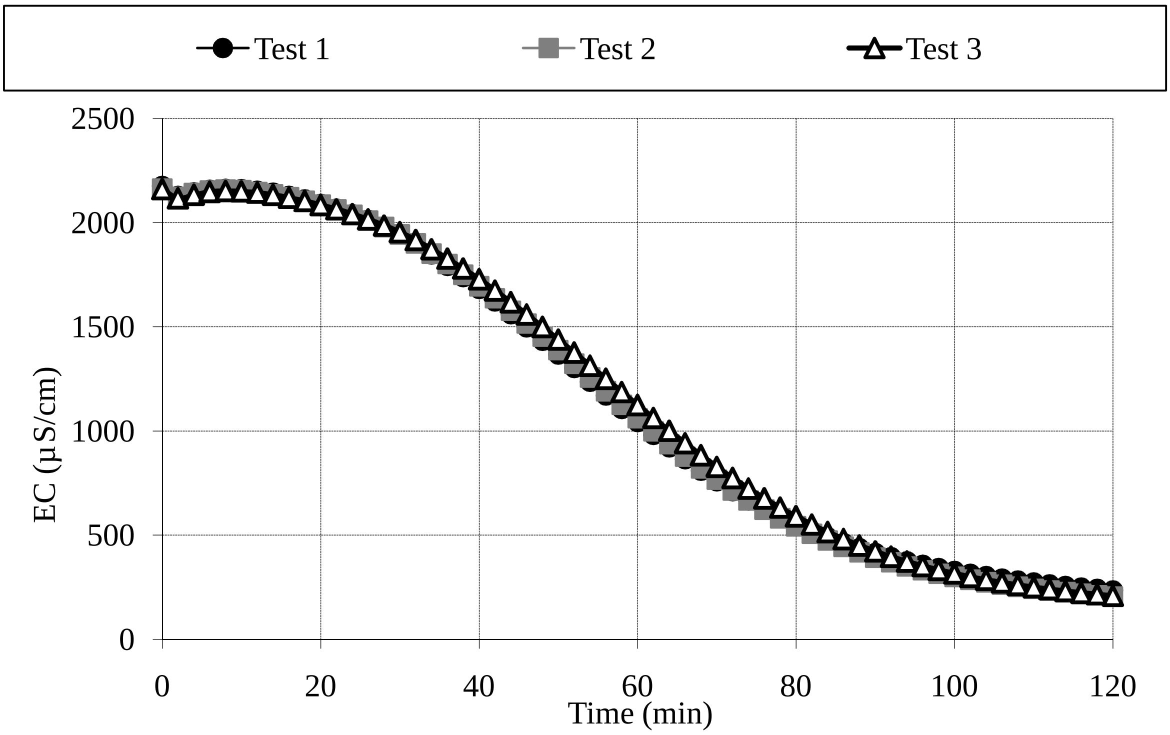


Figure 22: EC profiles tested for repeatability with three replications

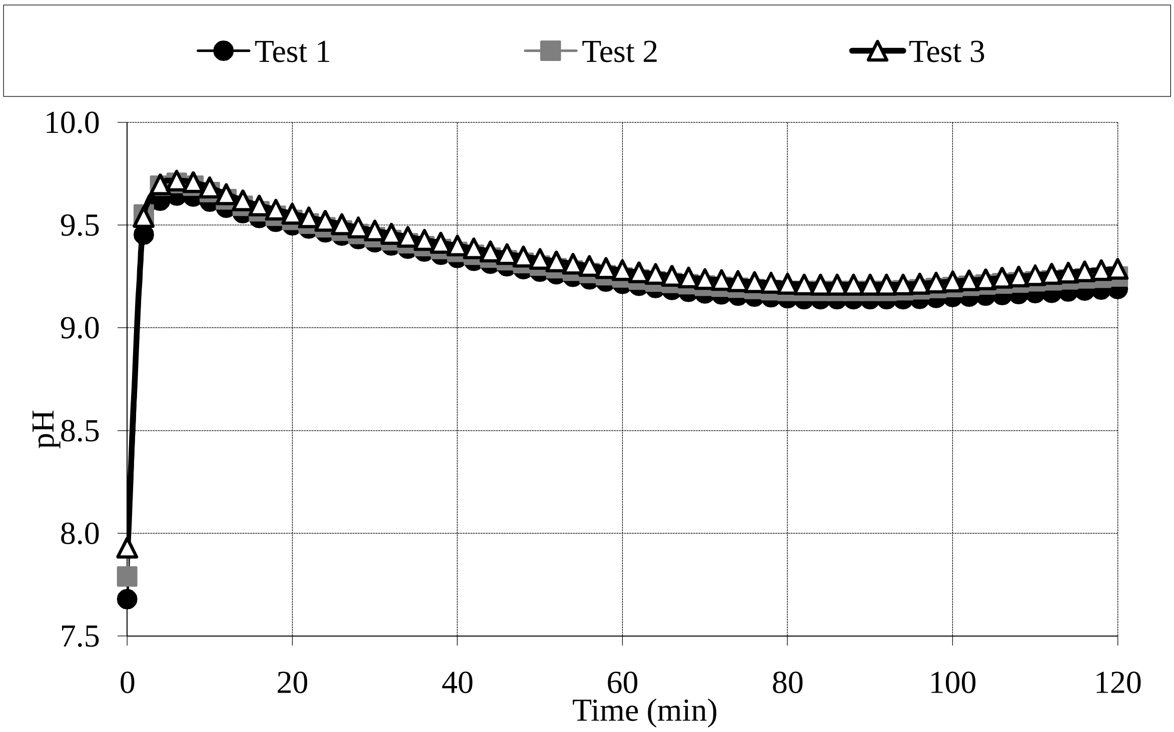


Figure 23: pH profile repeatability after three replications

The calculated initial and final sulphate concentrations for each of these experiments are given in Table 3. The percentage sulphate removal for each experiment was calculated in order to determine the average sulphate concentration as well as the variance.

Table 3: Repeatability of sulphate removal experiment

	Test 1	**Test 2**	**Test 3**	**Standard deviation**	**Variance**
Initial SO_4^{2-} (mg/ℓ)	1037.10	1028.95	1026.91	5.392	29.070
Final SO_4^{2-} (mg/ℓ)	26.15	36.21	35.77	5.685	32.324
% SO_4^{2-} removal	97.4	96.4	96.4	0.577	0.333

The average sulphate removal was 96.7%. The standard deviation was 0.577 and the variance 0.333. The variance gives an indication of the dispersion of the data. Thus, the greater the variance of the data is, the larger the deviation from the mean. The low variance of 0.333 amongst the three tests therefore indicated a small deviation from the average of 96.7%. The standard deviation records the actual distribution of the mean. Even though the test was replicated only three times, the low standard deviation gives proof of consistent test results around the mean. Thus, this process was considered to be repeatable.

4.3. RESULTS AND DISCUSSION

4.3.1. Barium-to-sulphate molar ratios

The ratio of dissociated barium ions from the barium dosed as barium carbonate relative to the sulphate ions present in the feed water will influence the sulphate removal process. This was investigated under laboratory conditions and the results are presented in Figure 24. The initial sulphate concentration was kept constant in these experiments while the barium carbonate slurry concentration added to the feed water was varied (Swanepoel et al. 2011).

The experimental parameters for this experiment were as follow. The initial sulphate concentration in the sulphate-rich water was 1 600mg/ℓ and the mixing rotational speed was 350 min^{-1}. The reactor temperature was kept constant at ambient temperature (20°C ± 1.5°C). Laboratory produced barium carbonate was used. The dosing ratios were varied from an under-dosed 0.5 dosing ratio to over-dosed 1.5 dosing ratio.

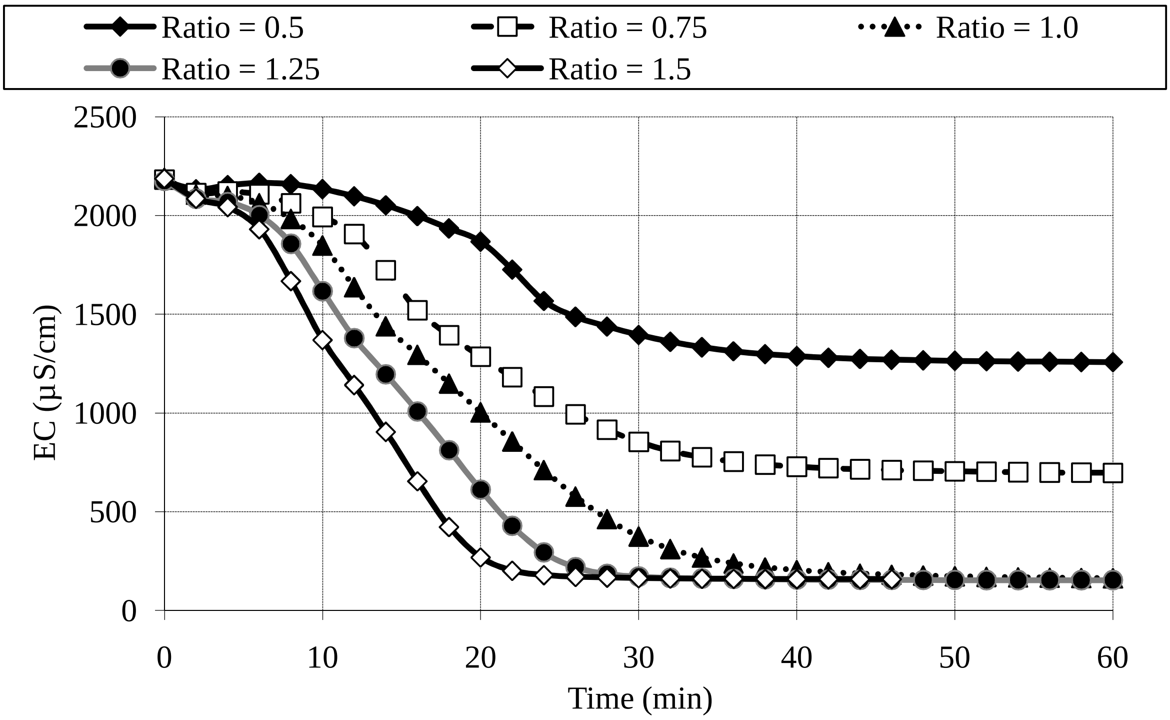


Figure 24: The effect of barium-to-sulphate molar ratio

In the first two experiments the barium ions were under-dosed (i.e., the barium-to-sulphate ratio was less than stoichiometric ($[Ba^{2+}]/[SO_4^{2-}] < 1$)). It was found that only partial sulphate removal could be achieved, because there were not enough barium ions available to react with all the sulphate ions present in the feed water. During the first experiment, of Figure 24, the barium to sulphate dosing ratio was 0.5, which lowered the sulphate concentration by 68.0%. In a second experiment the ratio was set to 0.75. This led to a reduction of the sulphate concentration by 85.8%.

In the last two experiments of Figure 24, the barium ions were over-dosed in comparison with the sulphate ions present in the feed water (i.e., where the barium-to-sulphate ratio was greater than stoichiometric ($[Ba^{2+}]/[SO_4^{2-}] > 1$)). In these cases almost complete sulphate removal was achieved. For the 1.25 dosing ratio and 1.5 dosing ratio the sulphate removals were 98.2% and 98.1%, respectively. The maximum of sulphate that can be removed from the sulphate-rich water is approximately 98% (See Appendix A).

The slopes of the graphs are an indication of how rapidly the reaction took place. Therefore, the steeper the slope of the graph, the shorter the time required to achieve maximum sulphate removal. According to Figure 24, by over-dosing the barium, the sulphate removal process accelerates. This is beneficial since a shorter reaction time requires a smaller reactor (at a constant flowrate), which leads to lower construction costs. However, a major disadvantage of over-dosing is the resulting excess of barium compounds in the end product. This is a major concern and highly undesirable since barium is very toxic to humans and animals (Sciencelab 2010). Barium carbonate is slightly soluble with a k_{sp} value of 2.58×10^{-9} (Kotz et al. 2003), but even at low concentrations the barium in the waste stream may have serious environmental impacts.

When the barium carbonate is dosed in stoichiometric ratio (i.e. $[Ba^{2+}]/[SO_4^{2-}] = 1$), it was found that the sulphate concentration was reduced to about the same final concentration (98.0% sulphate removal) as in the case where barium was over-dosed. The most important advantage is that there is a negligible concentration of barium in the final product stream, 0.04 mg/ℓ according to analysis done by an accredited laboratory (CSIR, CAS) (Swanepoel et al. 2011).

4.3.2. Effect of initial sulphate concentration

The initial sulphate concentration of the AMD could influence the sulphate removal process. Therefore, experiments were conducted to determine its effect on the process. The results of these experiments, where the initial sulphate concentration of the feed water were varied whilst a stoichiometric amount of barium as barium carbonate was dosed, are shown in Figure 25.

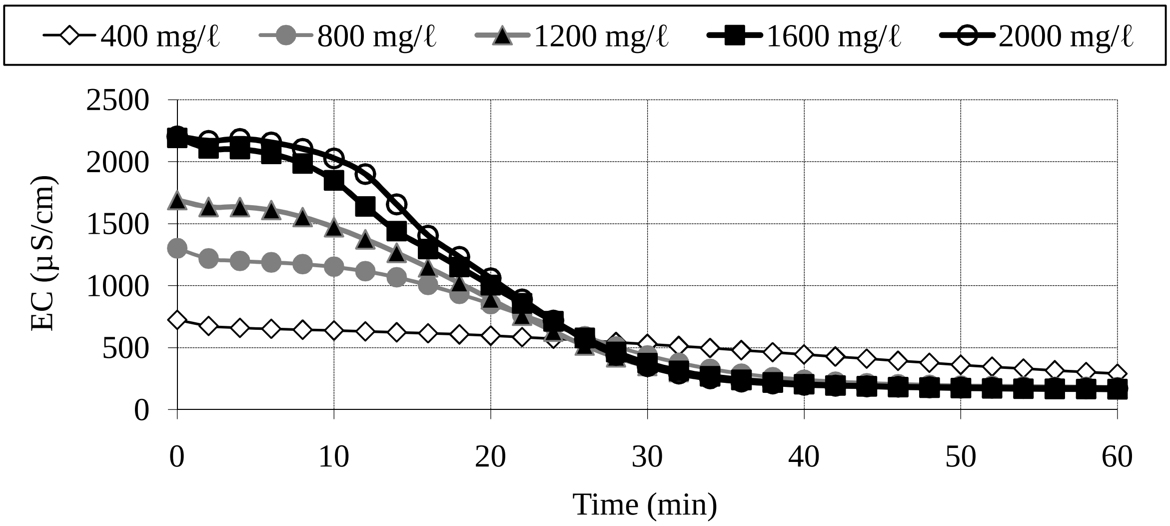


Figure 25: The effect of initial sulphate concentration

The experimental parameters were as follows. The initial sulphate concentration was varied for each experiment. The mixing rotational speed was 350 min^{-1}, while the reactor temperature was constant at ambient temperature (21°C ± 1.5°C). Laboratory-produced barium carbonate was used and the dosing ratio was equal to the stoichiometric relationship.

Only a limited amount of calcium sulphate, also known as gypsum, can be dissolved in distilled water since its solubility constant (k_{sp}) is 4.93×10^{-5} at 25°C. It also depends on the composition and ionic strength of the solution. Thus, gypsum's solubility ranges between 1 500 mg/ℓ and 2 000 mg/ℓ at 25°C (Kotz et al. 2003). This is supported by the fact that the initial EC was the same for experiments with initial sulphate concentrations of 1 600 mg/ℓ and 2 000 mg/ℓ, according to Figure 25 (Swanepoel et al. 2011).

When more gypsum was added to the feed water than the amount that could be immediately dissolved, solid gypsum particles were present in the reactor. The dissolved calcium sulphate reacted with the barium carbonate. As the dissolved gypsum reacted (thus decreasing in concentration), the solid gypsum particles dissolved. Thus, causing the dissolved gypsum concentration to increase until all the solid gypsum particles have dissolved. Up to that point the actual dissolved gypsum concentration in the solution was constant. Only after all the solid gypsum particles had dissolved, could a change in sulphate concentration (and EC values) be observed. This explains the delay in sulphate concentration lowering in the experiments having an initial sulphate concentration of 1 600 mg/ℓ and 2 000 mg/ℓ in Figure 25.

The final sulphate removal percentages for these experiments were 92.8% (400 mg/ℓ SO_4^{2-}), 96.3% (800 mg/ℓ SO_4^{2-}), 97.8% (1 200 mg/ℓ SO_4^{2-}), 98.6% (1 600 mg/ℓ SO_4^{2-}) and 98.7% (2 000 mg/ℓ SO_4^{2-}). From this it was found that the amount of sulphate removed from the effluent was very nearly the same after 45 min, i.e. almost maximum sulphate removal. The only differences seemed to be in the slope of the graphs, and hence the rate at which the sulphate was removed from the water. For higher initial sulphate concentration the sulphate removal rate was faster. Therefore the amount of sulphate removed from the sulphate-rich water was independent of the initial sulphate concentration; only the rate of the sulphate removal process was affected.

4.3.3. Effect of the mixing rotational speed

The effect of reactor stirring rate on sulphate removal is shown in Figure 26. Sulphate removal was affected only at very low mixing rotational speeds (60 min^{-1}). At higher mixing rotational speeds, almost no differences in the sulphate removal profiles were visible. It seemed that a slow mixing rotational speed (60 min^{-1}) was insufficient. The lower sulphate removal using this low stirring rate was probably due to the amount of solids that accumulated beneath the impeller of the overhead agitator, that were not participating in the reaction due to insufficient contact time with the sulphate solution. At the higher mixing rotational speeds all the solid particles had sufficient contact time with the sulphate feed solution, and better sulphate removal occurred.

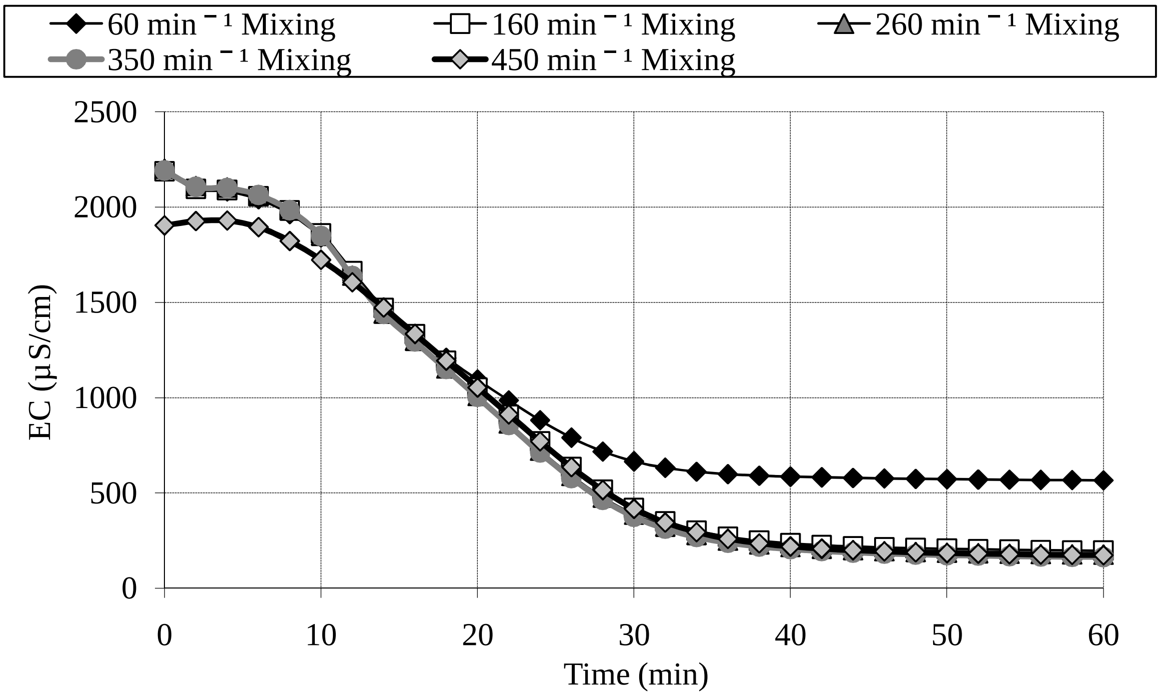


Figure 26: The effect of reactor mixing rotational speed

For these experiments the initial sulphate concentration was 1 600 mg/ℓ. The mixing rotational speed of each experiment was different while the reactor temperature was constant at ambient temperature (20°C ± 1.5°C). Laboratory produced barium carbonate was used and the dosing ratio was equal to the stoichiometric relationship.

Only 88.7% sulphate removal was obtained at a mixing rotational speed of 60 min^{-1} while sulphate removal percentages of 97.8%, 98.3%, 98.6% and 98.3% were obtained for the mixing rotational speeds of 160 min^{-1}, 260 min^{-1}, 350 min^{-1} and 450 min^{-1}, respectively. Thus, the sulphate removal percentage decreased by more than 10% at a mixing rotational speed of 60 min^{-1} in comparison to the higher mixing rotational speeds of 160 min^{-1}.

4.3.4. Effect of temperature

In general it was found that the higher the reactor temperature is, the faster the reaction rates are (Levenspiel 1999). But some reactions are more sensitive to temperature changes than others. This precipitation reaction was found to be very sensitive to temperature changes. Because temperature is a difficult parameter to control on laboratory scale, this investigation was carried out using barium carbonate from two different sources in order to confirm the results. The first barium carbonate was a commercially available material imported from China. The second barium carbonate had been produced in the laboratory where a barium sulphide solution was carbonated as described in Paragraph 4.2. (Swanepoel et al. 2011).

Barium carbonate from China

The effect of temperature on sulphate removal using barium carbonate from China was investigated. The results are shown in Figure 27 and Figure 28. The first experiment was conducted at a temperature of 13°C and the second at 34°C. These two temperatures were the limits of the thermostat bath that was used. The minimum temperature that could be reached and sustained on this particular day with this particular thermostat bath was 13°C and the maximum temperature was 34°C.

The initial sulphate concentration for these two experiments was 1 600 mg/ℓ. The mixing rotational speed was 350 min^{-1}. The dosing ratio of the barium-to-sulphate was equal to stoichiometry.

In Figure 27 the EC profiles of the two experiments are shown while Figure 28 shows the pH profiles. At 34°C the EC curve initially showed a negative slope, which flattened out at approximately 500 µS/cm, after about 150 min. The EC profile of the experiment conducted at 13°C stayed almost constant over the entire duration of the experiment of about 180 min.

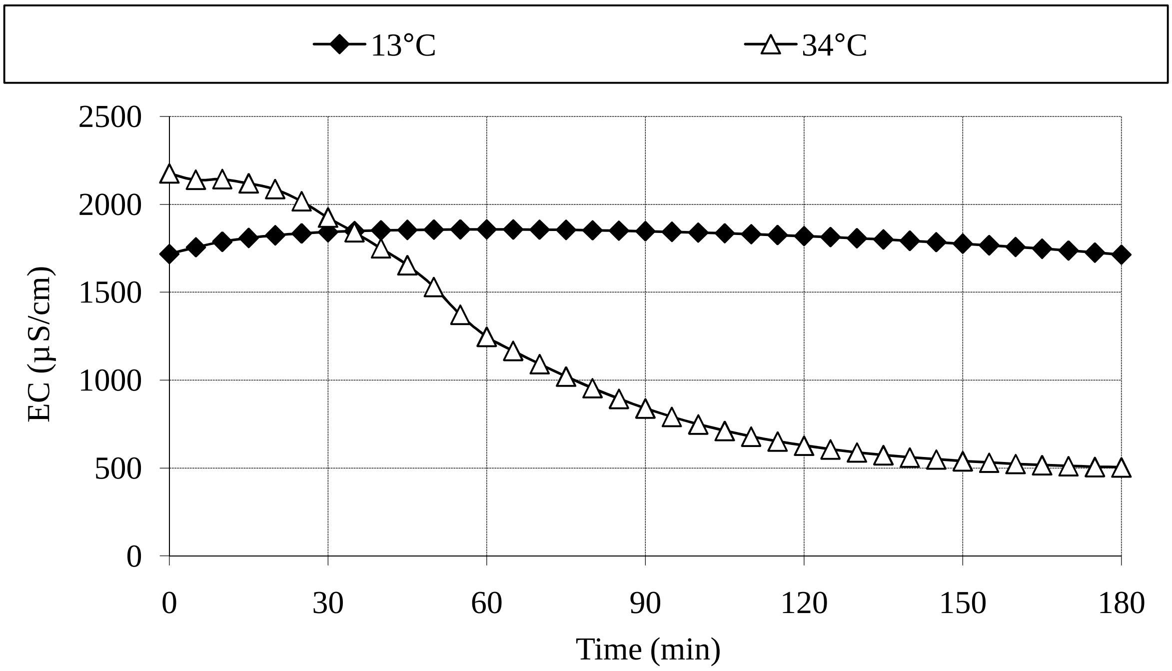


Figure 27: EC profile regarding to different temperatures (commercial barium carbonate)

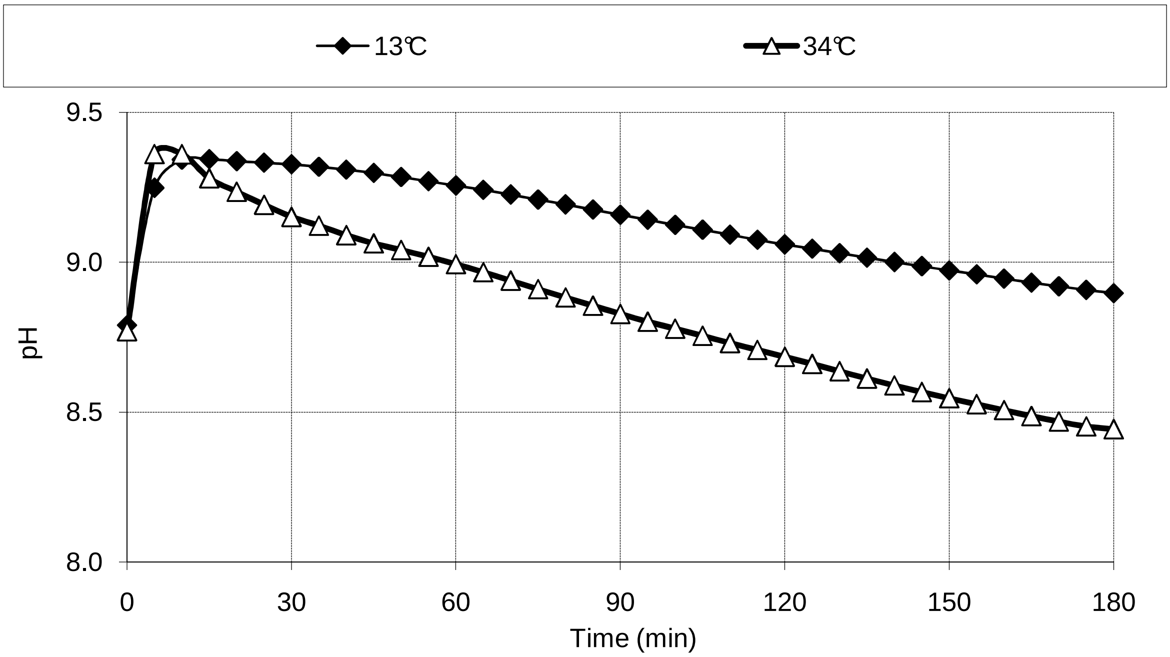


Figure 28: pH profiles corresponding to Figure 27

The final sulphate removal conducted at 13°C was 85.5% while that done at 34°C was 90.2%. Therefore, the higher the temperature of the reactor, the faster the sulphate removal process takes place and the better the sulphate removal from solution is.

Laboratory Produced Barium Carbonate

The effect of reactor temperature was also investigated on barium carbonate prepared in the laboratory as described earlier. The results obtained at three different temperatures (14°C, 21°C and 33°C) are shown in Figure 29 and Figure 30. Again, the minimum and maximum temperatures were chosen to be 14°C and 33°C due to the limits of the thermostat bath. The ambient temperature of the laboratory on this specific day was 21°C and was chosen as the middle temperature. From Figure 29 it is clear what the effect of temperature was. At the highest temperature (33°C) the EC value dropped rapidly to (and then stabilised) a point, in this case, approximately 400 µS/cm.

The experiment carried out at the lowest temperature (14°C) took 180 min. for the EC values to reach 400 µS/cm and eventually stabilised at this value. The sulphate removal experiment at 33°C, in contrast, was completed in about 30 min. The 21°C experiment EC profile fitted between the other two profiles. It took about 100 min. for the 21°C reaction to proceed to completion. In Figure 30 the pH profiles of these experiments are shown. The same trend can be seen as with the EC profiles.

The initial sulphate concentration for these two experiments was 1 600 mg/ℓ. The mixing rotational speed was 350 min^{-1}. The dosing ratio of the barium-to-sulphate was equal to stoichiometry.

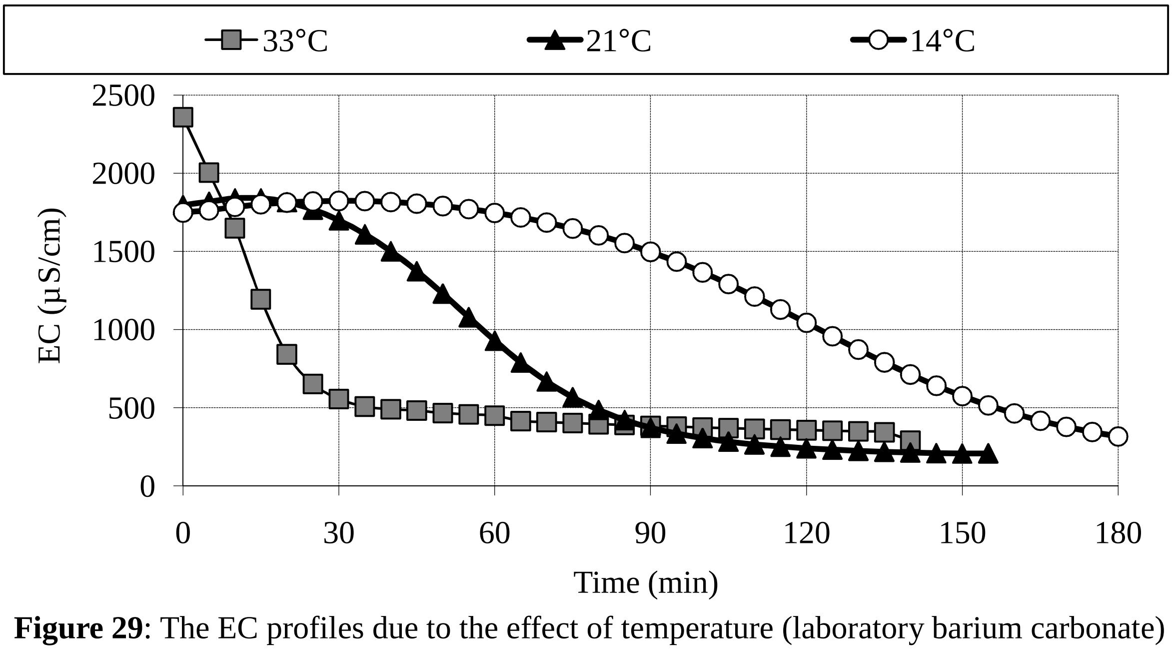


Figure 29: The EC profiles due to the effect of temperature (laboratory barium carbonate)

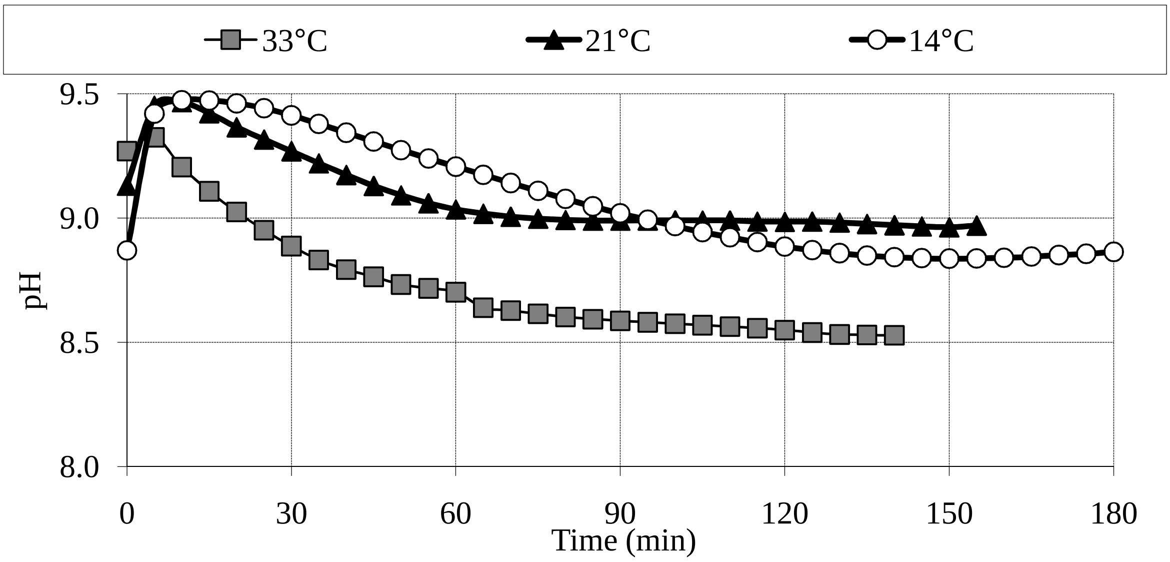


Figure 30: The pH profiles corresponding to Figure 29

The sulphate removal for the 14°C experiment was 98.2% while the sulphate removal for the 21°C experiment was 97.5% and for the 33°C experiment, 94.5%. In all three experiments the sulphate concentration was reduced significantly (on average 96.7%). Though, from Figure 29 it is seen that at 33°C, 90.05% of the initial sulphate was removed after 35 min while at 14°C, 89.95% of the initial sulphate was removed after 155 min. Thus, the reaction time increased with 120 min in order to obtain approximately 90% sulphate removal when the reaction temperature decreased from 33°C to 14°C. Thus, this experiment confirmed that the higher the reactor temperature is, the faster the sulphate removal rate is.

In Appendix C the reaction rates were determined and are given in Equation 12, Equation 13 and Equation 14. These reaction rates were determined at 50% sulphate removal at a concentration of 800 mg/ℓ. See Appendix C for more detailed calculations regarding the reaction kinetics.

$$-r_{SO_4^{2-}}|_{33} = 0.0915\ [SO_4^{2-}]^1 = 0.0915\ [800]^1 = 73.2\ mg/\ell\ min$$ **Equation 2**

$$-r_{SO_4^{2-}}|_{21} = 0.0375[SO_4^{2-}]^1 = 0.0375[800]^1 = 30.0\ mg/\ell\ min$$ **Equation 3**

$$-r_{SO_4^{2-}}|_{14} = 0.0215[SO_4^{2-}]^1 = 0.0215[800]^1 = 17.2\ mg/\ell\ min$$ **Equation 4**

From these two studies it was concluded that a higher reactor temperature led to a faster sulphate removal rate. Even if the initial reactor temperature is just slightly elevated it can result in a significant increase in the reaction rate. The opposite is also true, if the reactor temperature is just slightly cooler than planned, the reaction rate will be much slower and result in a much longer reaction time to remove the sulphate in the process fluid to the desired concentration.

It was observed that there was a marked difference between the curves when the results using imported barium carbonate were compared with the corresponding results using the laboratory-produced barium carbonate. This phenomenon was investigated in more detail.

4.3.5. Different barium carbonate types

The sulphate removal process was investigated using commercially available barium carbonate, imported from China (CIF Durbsan) and the process was repeated, using barium carbonate recycled from the ABC Desalination plant. Both these barium carbonate sources were very pure; approximately 99.95% pure according to XRD analyses.

The experimental parameters for these two experiments were as follows. The initial sulphate concentration in the sulphate-rich water was 1 300mg/ℓ and the mixing rotational speed was 350 min^{-1}. The reactor temperature was constant at ambient temperature (22°C ± 1.5°C). The dosing ratio of the barium-to-sulphate was equal to the stoichiometric relationship.

The results are shown in Figure 31. From this figure it became clear that the origin, and probably the morphology, of the barium carbonate particles is important.

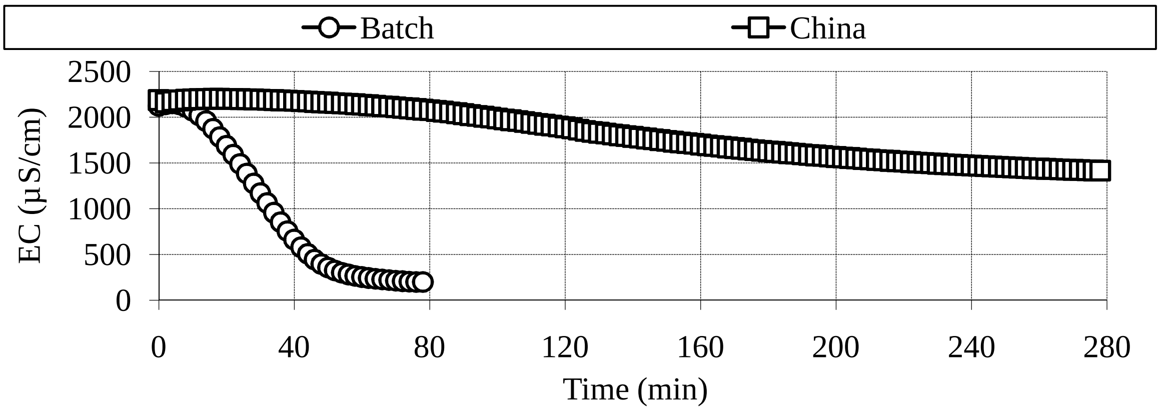


Figure 31: Effect of barium carbonate crystal surface characteristics

From Figure 31 it was seen that the commercial barium carbonate took a long time to remove even small amounts of sulphate from solution. Only 53.8% sulphate removal was obtained after 300 min. In contrast, the recycled barium carbonate removed 97.2% of the sulphate in the solution within 60 min. This phenomenon was confirmed by plotting the sulphate concentration profiles shown in Figure 32.

Since it takes the commercial barium carbonate much longer to remove about 50% of the sulphates in the process water, it is deemed as being *less-reactive* in comparison to the recycled (Batch) barium carbonate. While the Batch barium carbonate takes a short time to remove more than 97% of the sulphates from the process water, it is seen as *reactive* barium carbonate in comparison with the China barium carbonate.

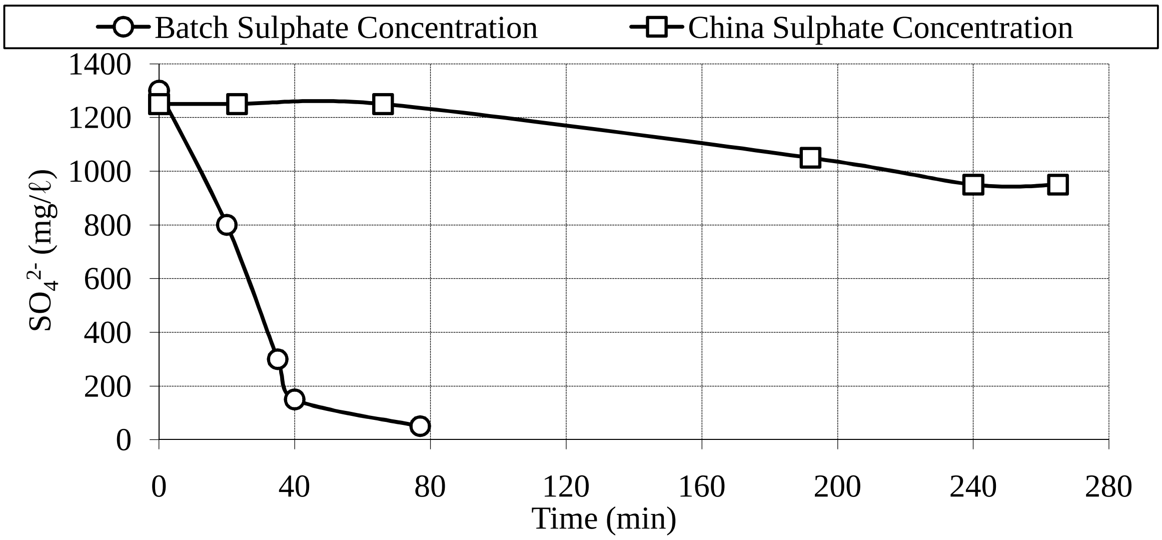


Figure 32: Effect of barium carbonate types

For increased clarity and to easily differentiate between these two barium carbonate types, the Chinese barium carbonate will be called *unreactive barium carbonate*. This description was convenient although not entirely true since this barium carbonate is capable of removing sulphates from the feed solution; it just removes very little sulphate over a long period (53% in 300 min.). The Batch barium carbonate will be denoted *reactive barium carbonate* since it is able to remove almost all the sulphate (97.2%) from the same feed solution within an hour.

The differences in the results using these two different barium carbonate types, needed to be understood. An investigation was initiated to determine the effect that the different barium carbonate types, and therefore the particle shape and size, have on the sulphate removal process.

Three different barium carbonate batches (Batch 1 to Batch 3) were prepared in the laboratory. Each of these batches was prepared differently by the carbonation of barium sulphide solution by carbon dioxide gas. In each case different preparation parameters were used. The differences in the parameters included the carbon dioxide flowrates and its purity as well as the initial barium sulphide concentration in the solution. The details of this work were considered to be beyond the scope of this study. What is important is that each barium carbonate batch was prepared in a unique experiment which resulted in different crystal characteristics as will become evident later (De Beer et al. 2010).

The commercial barium carbonate from China, the original recycled barium carbonate from the ABC Desalination Process, and the three barium carbonate batches were compared. The results are shown in Figure 33.

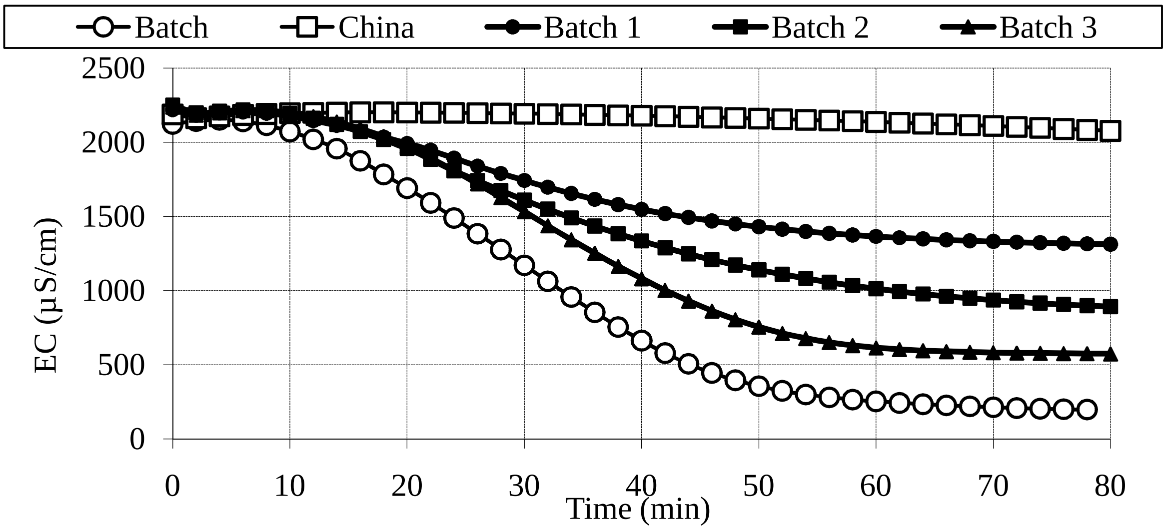
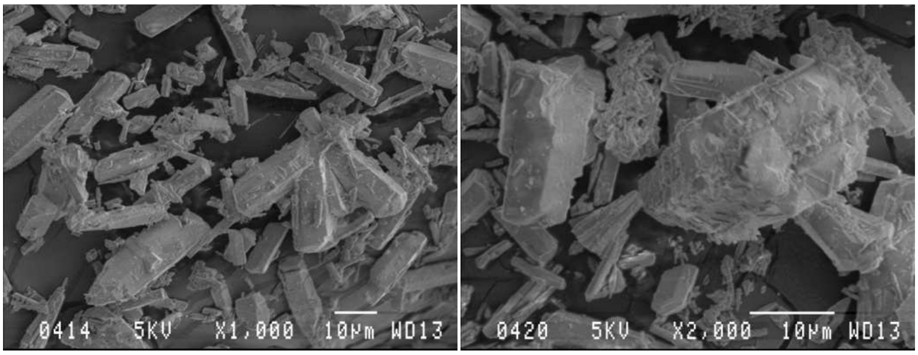


Figure 33: Effect of barium carbonate crystal surface characteristics

From Figure 33 one can see that the different barium carbonate types reacted differently from each other and therefore produced different results. The top graph represents the results from the *unreactive barium carbonate*, while the bottom graph represents the results from the *reactive barium carbonate*. The results from the three additional barium carbonate types are arranged reasonably equally spread between the two “extreme” types where Batch 1 removed 96.8% of the sulphates, Batch 2 removed 77.2% and Batch 3 obtained 59.5% removal.

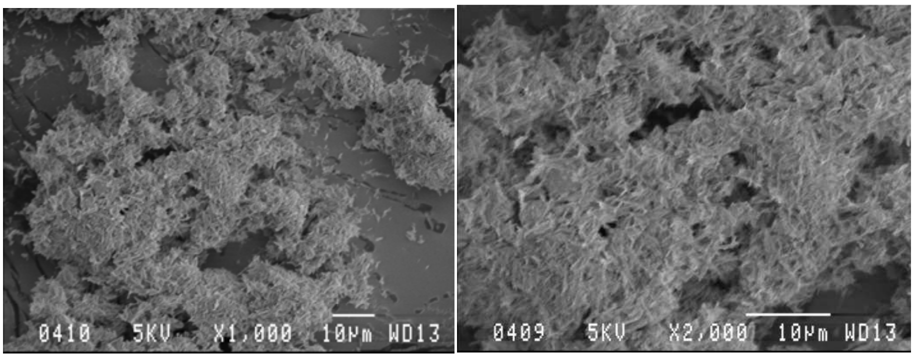
A sample of each of these barium carbonate types was analysed with SEM (scanning electron microscopy) to determine the particle surface structure. These photographs are shown in Figure 34 to Figure 38. The photographs on the left represent the particle shape and size of each of the barium carbonate samples when it is magnified 1 000 times (× 1 000) , while the photographs on the right represents the same barium carbonate sample as on the left, but at 2 000 times (× 2 000) magnification.

The first two photographs (Figure 34) represent the imported barium carbonate, known as the *unreactive barium carbonate*. The second set of photographs (Figure 35) represents the *reactive barium carbonate* recycled from the ABC Desalination process. The remainder of the photographs show the barium carbonate that was additionally prepared for this study in the order of Batch 1 (Figure 36), Batch 2 (Figure 37), and Batch 3 (Figure 38).



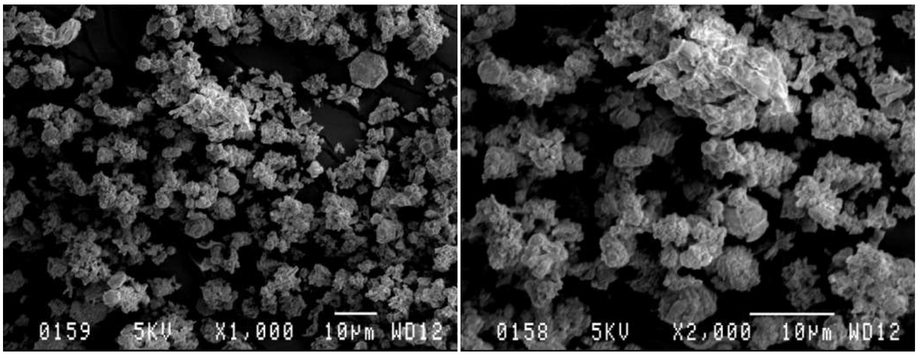
(a) **(b)**

Figure 34: SEM image of *Unreactive barium carbonate* (Chinese barium carbonate) (a) × 1 000 magnification (b) × 2 000 magnification



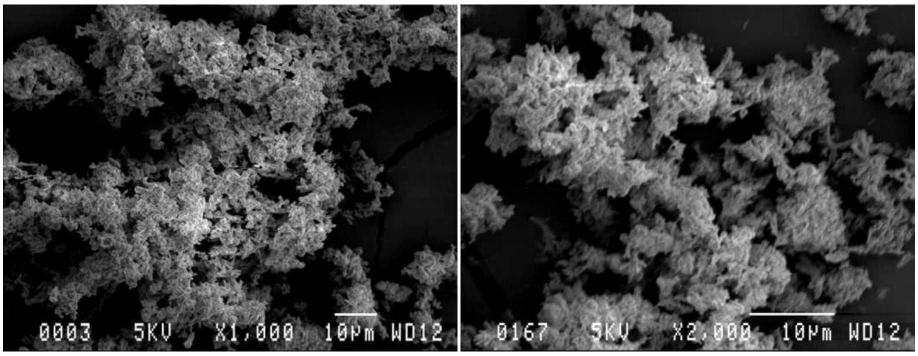
(a) **(b)**

Figure 35: SEM image of *reactive barium carbonate* (recycled barium carbonate) (a) × 1 000 magnification (b) × 2 000 magnification



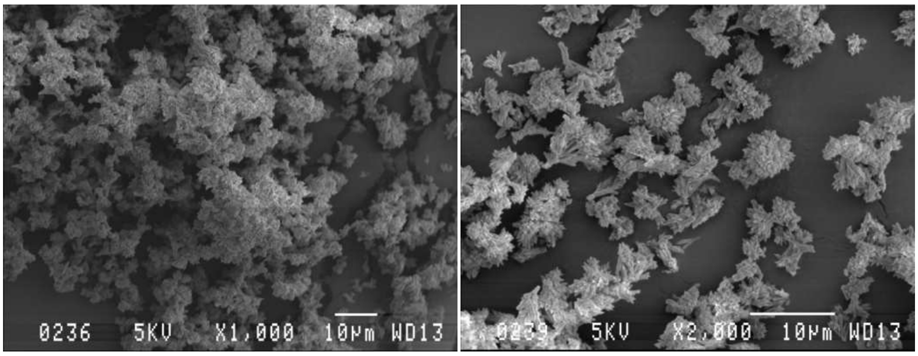
(a) **(b)**

Figure 36: SEM image of laboratory produced barium carbonate Batch 1
(a) × 1 000 magnification (b) × 2 000 magnification



(a) **(b)**

Figure 37: SEM image of laboratory produced barium carbonate Batch 2
(a) × 1 000 magnification (b) × 2 000 magnification



(a) **(b)**

Figure 38: SEM image of laboratory produced barium carbonate Batch 3
(a) × 1 000 magnification (b) × 2 000 magnification

From these photographs it was seen that the *unreactive barium carbonate* has a large, well-defined crystal structure while the *reactive barium carbonate* almost seems fuzzy with small, fine crystals. Therefore, the conclusion was made that barium carbonate with a small, fine crystal structure is more reactive than barium carbonate that consists of large, well-defined crystals.

From the additional barium carbonate types it seems that this conclusion was valid since the barium carbonate from Batch 1 had larger, better defined crystals than the other two types, while Batch 3 had smaller and finer crystals. The crystals from Batch 2 were intermediate between those of Batch 1 and Batch 3. Figure 33 revealed that, among the three barium carbonate types, Batch 1 was less reactive than the other two; Batch 3 was more reactive, and Batch 2 fell between them with respect to reactivity.

4.3.6. Process water

All of the above experiments were done on synthetic sulphate-rich water. In this section the experiments were conducted on two different types of industrial process water from a coal mine. Both came from the same process but were collected at two different treatment points. The first point was after lime neutralisation and gypsum crystallisation (if the raw AMD contained magnesium, it precipitated here) with a pH of 12. The second collection point was after the water had again been neutralised and had a pH of 7 (Swanepoel et al. 2011).

The experimental parameters for these experiments were as follows. The initial sulphate concentration in the feed water was approximately 2 400mg/ℓ and the mixing rotational speed was 350 min^{-1}. The reactor temperature was constant at ambient temperature (22°C ± 1.5°C). The dosing ratio of the barium-to-sulphate was equal to the stoichiometric relationship.

The gypsum crystallisation step is important if the raw AMD contains magnesium. Barium carbonate can only remove sulphate ions that are coupled with calcium ions, since calcium ions are required to remove the carbonate ions coupled with the barium cations. The sulphates that are coupled with magnesium and sodium will not be removed in this process (Hlabela et al. 2007, Hlabela et al. 2005). Thus, to successfully achieve sulphate removal, the magnesium and sodium ions have to be removed from the solution before sulphate precipitation.

From laboratory tests, as shown in Figure 39, it was clear that this sulphate removal process works well with AMD. In this case, the *reactive barium carbonate* that was recycled from the ABC Desalination Process was used to remove sulphate from the AMD.

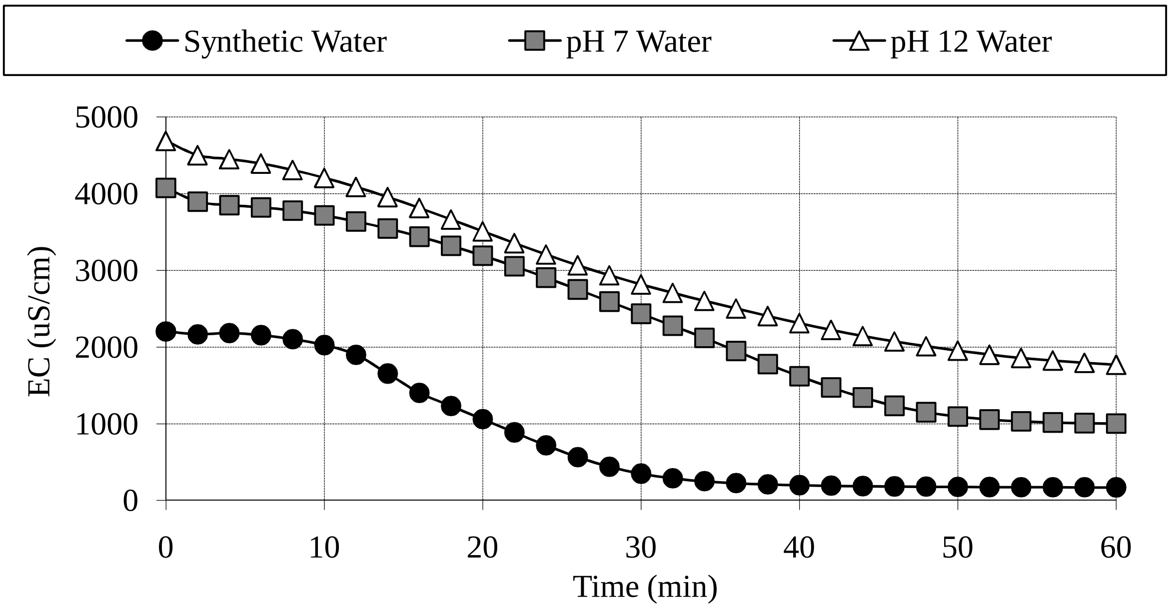


Figure 39: Sulphate removal from different process fluids

The EC of the AMD did not decrease as much as the synthetic sulphate-enriched water, due to other ions being present, such as sodium, magnesium, iron and manganese. The empirical EC-sulphate ion concentration correlation derived earlier could also not, due to the presence of these ions. Thus, samples were sent to a SANAS accredited laboratory for sulphate analysis.

The sulphate concentration for the pH 7 experiment decreased from 2 350 mg/ℓ to less than 50 mg/ℓ (98% sulphate removal), and for the pH 12 experiment it decreased from 2 400 mg/ℓ to 250 mg/ℓ (90% sulphate removal). The sulphate removal percentages for the synthetic water and the pH 7 water correlated well with each other.

The difference in EC values between the pH 7 water and pH 12 water can be explained by the solubility variation of barium carbonate for different pH levels, as explained in Paragraph 3.2.7. In short, barium carbonate is more soluble at lower than at higher pH levels. Thus, at a pH of 7, more barium ions were available to precipitate with sulphate ions, than at pH 12. Therefore it will result in a higher percentage sulphate removal as can be seen from the results (Hlabela et al. 2007, Hlabela et al. 2005).

4.4. WATER QUALITY

To legally discharge water into the environment, the water has to be of a certain quality. In Table 4 the list of parameters and their requirements are presented. These compositions of raw AMD and AMD treated by the ABC Desalination Process were compared. The results are shown in Table 4.

Table 4: Potable water standards (WHO 2004a, DWAF 1995, SANS 2011)

Parameter		Units	Class II Potable Water Standard	Raw AMD	Treated AMD
pH			4 – 10	3.35	7.9
Total Alkalinity	TAlk	mg/ℓ as $CaCO_3$	No Spec.	0	140
Aluminium	Al	mg/ℓ	0.5	2.97	0.01
Sodium	Na	mg/ℓ	400	46.5	53.2
Potassium	K	mg/ℓ	100	4.40	4.8
Calcium	Ca	mg/ℓ	300	205	75
Magnesium	Mg	mg/ℓ	100	124.6	0.98
Total Iron	Fe	mg/ℓ	2	182	0.3
Manganese	Mn	mg/ℓ	1	63.7	0.09
Sulphate	SO_4	mg/ℓ	500	1910	90
Chloride	Cl	mg/ℓ	600	44.5	49.5
Fluoride	F	mg/ℓ	5	5.4	0.07
Silicon	Si	mg/ℓ	No Spec.	11	0.45
Barium	Ba	mg/ℓ	0.7	< 0.02	< 0.02

From Table 4 it is clear that there was a major improvement in the quality of the AMD following treatment. When the treated AMD was compared to SANS Class II potable water standards, the final water quality easily complied with the required standards for all the variables (WHO 2004a, DWAF 1995). Since the potable water standards were met, this wastewater can be safely discharged into the environment (Swanepoel, 2011).

4.5. CONCLUSION

From the experimental work that was conducted, and by studying the results, the conclusions that were made are summarised as follows:

- *Barium-to-sulphate molar ratios:* When the barium (as barium carbonate) was under-dosed relative to the sulphate present in the feed water, only partial sulphate removal could be achieved. When the barium was over-dosed close to complete sulphate removal was achieved (98%). This caused barium to be present in the final product water which should be avoided at all costs due to its toxicity to humans and animals. Therefore the barium-to-sulphate molar ratio equal to the stoichiometric requirement is optimum.

- *Effect of initial sulphate concentration:* A limited amount of calcium sulphate dissolves in distilled water at one instance. This explains the delay in sulphate concentration reduction when the initial sulphate concentration was higher than 1 600 mg/ℓ. The initial sulphate concentration did not influence the final sulphate concentration in the solution (96.8% removal)

- *Effect of mixing rotational speed:* The mixing rotational speed inside the reactor should be high enough (160 min^{-1}, or higher) to ensure that all the solid particles have sufficient contact time with the sulphate feed solution.

- *Effect of temperature:* The sulphate removal process is very sensitive to the reactor temperature. Even if the initial reactor temperature is just 7°C higher than the optimised temperature, it could result in quite an increase in the reaction rate (from 17.2 mg/ℓ min at 14°C to 30.0 mg/ℓ min at 21°C). Therefore, proper temperature control is required for this process.

- *Different barium carbonate types:* It is found that the morphology of the barium carbonate plays an important role in the sulphate removal process. Barium carbonate with a small, fine crystal structure (Figure 35) is more reactive than barium carbonate that consists of large, well-defined crystals, as shown in Figure 34.

- *Process water:* This sulphate removal process works well with AMD. A 98% (pH 7 water) and 90% (pH 12 water) sulphate removal, respectively, was obtained on two different AMD types.

- *Water quality:* A major improvement occurred in the quality of the AMD after it was treated with the ABC Desalination Process. When measured against the SANS Class II potable water standards, it was found that the final water conformed to all the criteria and could be safely discharged into the environment.

The spread-sheets with the raw data of the experiments are available on the DVD included in Appendix D.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1. INTRODUCTION

This chapter consolidates the work done in this research project. All conclusions from the literature surveys and experiments conducted in the laboratory are compared. The outcomes of the project are linked with the original study objectives. Recommendations for potential future studies are given.

5.2. BACKGROUND

Sulphide oxidation in AMD is a common phenomenon, whereby pyrite is oxidised by sulphur oxidation bacteria under aerobic conditions. This result in a deterioration of water quality due to acidity, leached heavy metals and dissolved salt levels (Bell et al. 2006, Sawyer et al. 2003).

Sulphate removal by barite formation can achieve low sulphate concentrations due to the low solubility of barium sulphate. The final sulphate levels can be lower than 0.02 mg/ℓ. This method forms part of the ABC Desalination Process, developed and patented by the CSIR. In this process a barium carbonate is added to the sulphate-rich effluent in order to precipitate barium sulphate.

Barium sulphide, barium carbonate, and barium hydroxide can all be used to remove sulphate from wastewater. Barium carbonate is favoured because it does not require stripping of the foul smelling hydrogen sulphide gas from the main water stream as in the case of barium sulphide (Hlabela et al. 2007, Hlabela et al. 2005). When barium hydroxide is used a significant amount of calcium sulphate is produced, which increases the volume of waste sludge. (Bowell 2004, Bologo et al. 2009, Bologo et al. n.d.). The problem when using barium carbonate is that it becomes inactive when the particles are coated with metal hydroxides. It could also be problematic to separate the barium sulphate precipitate from the calcium carbonate that co-precipitates in this process (Maree et al. 2004b, Maree et al. 2004a).

The original three major problems that were identified with this process are as follows:

- A long retention time is required,
- The high concentrations of soluble barium in the treated water after the barium carbonate is over-dosed relative to the stoichiometric relationship of the reaction, and
- The high cost of the barium salt.

The first problem is solved by producing highly reactive barium carbonate. This study showed that the morphology of barium carbonate is important and that a specific particle structure (small, fine structure) is favoured. The second is solved by dosing the barium in stoichiometric quantities relative to the sulphate concentration in the water. This will result in the absence of barium ions in the final effluent. To overcome the high cost of barium carbonate, it has been demonstrated that the barium sulphate sludge, after dewatering, can be reduced efficiently and economically with coal at high temperatures (1 050°C) to produce barium sulphide. This can then be either used directly on site or be converted to barium carbonate (Maree et al. 2004b).

5.3. BARIUM SULPHATE PRECIPITATION: BATCH PROCESSES

5.3.1. Electrical conductivity (EC) correlation

A correlation was drawn between the reduction of the sulphate concentration and the EC values of the synthetic water being treated. The sulphate removal profile and the EC profile correlated very well with each other and an empirical relationship (Equation 1) was determined to enable the sulphate concentration to be calculated in mg/ℓ from the EC (µS/cm) values. This was discussed in detail in Paragraph 4.2.5.

5.3.2. Repeatability

The same experiment was replicated three times under identical conditions. The average sulphate removed for these three runs was 96.7%. The standard deviation was 0.577 and the variance 0.333. The low variance of 0.333 indicated a small deviation from the average of 96.7%, and the low standard deviation gave proof of consistent test results around the mean. Thus, this process was repeatable. A detailed discussion was given in Paragraph 4.2.6.

5.3.3. Kinetics

Two different reaction kinetics studies have been reported (Hlabela et al. 2007, Motaung et al. 2008). Both reported that the sulphate removal reaction is first-order. A detail discussion was given in Paragraph 3.2.3.

5.3.4. Co-precipitation of calcium carbonate

Two different studies were found in the literature, which investigated the effect of calcium carbonate co-precipitation. The first study used calcium sulphate and sodium sulphate as sulphate salts (Motaung et al. 2009). The second study used calcium sulphide and magnesium sulphate (Hlabela et al. 2007).

In both cases it was found that the sulphate removal process was more successful when calcium sulphate was used as sulphate source instead of sodium sulphate or magnesium sulphate (Trusler et al. 1988). A detailed discussion was given in Paragraph 3.2.4.

5.3.5. Barium-to-sulphate molar ratios

According to the literature the sulphate removal process is influenced by the amount of barium carbonate dosed into the effluent (Hlabela et al. 2007, Hlabela et al. 2005). It was found that it is preferred to under-dose the barium carbonate due to the toxicity of barium (Motaung et al. 2009). A detailed discussion was given in Paragraph 3.2.5.

Experiments were done where the barium carbonate was over-dosed, under-dosed and dosed according to stoichiometric ratio, relative to the sulphate present in the effluent. In the case of under-dosing, only partial sulphate removal could be achieved. Two experiments were conducted; in the first experiment (0.5 dosing ration) 68.0% sulphate removal was achieved and in the second experiment (dosing ratio of 0.75) a sulphate removal of 85.8% was obtained. When barium ions were over-dosed, almost complete sulphate removal was achieved (98.2%). Excess barium was present in the final product stream which should be avoided due to its toxicity.

In the scenario where barium carbonate was dosed in stoichiometric ratio it was found that the sulphate concentration was also lowered by 98.0%, similar to the scenario where barium was over-dosed. The most important advantage was that there was no excess barium in the final product stream. A detailed discussion was given in Paragraph 4.3.1.

5.3.6. Effect of initial sulphate concentration

It was found in the laboratory that the initial sulphate concentration influences the sulphate removal rate to certain extent, but not the final sulphate concentration of the effluent. A detailed discussion was given in Paragraph 4.3.2.

5.3.7. Effect of the mixing rotational speed

During the experimental work it was noted that the sulphate removal was affected only at a very low mixing rotational speed (60 min^{-1}). Only 88.7% sulphate was removed at this mixing rotational speed in comparison with the higher mixing rotational speeds of 160 min^{-1}, (97.8%). Some of the solids accumulated beneath the impeller of the overhead agitator at the lower mixing rotational speed. A detailed discussion was given in Paragraph 4.3.3.

5.3.8. pH effect

The dissociation of barium carbonate is dependent on the pH of the solution; the lower the pH of the solution the more barium carbonate would dissociate (Motaung et al. 2009). Therefore, sulphate removal is slightly influenced by the pH of the process water (Hlabela et al. 2007, Hlabela et al. 2005). A detailed discussion was given in Paragraph 3.2.7.

5.3.9. Effect of temperature

It was confirmed in the literature that the reactor temperature is a key factor in barium sulphate precipitation (De Beer et al. 2010). A detailed discussion was given in Paragraph 3.2.6.

Two different barium carbonate sources were used to investigate this in the laboratory. The sulphate concentration was reduced by 90.2% (34°C) after about 130 min and 85.8% (13°C) after 180 min, when using commercial barium carbonate. When laboratory-produced barium carbonate was used, the final sulphate concentration was reduced by 94.5% (33°C) in about 30 min. at a reaction rate of73.2 mg/ℓ min., 97.5% (21°C) in approximately 100 min at a reaction rate of 30.3 mg/ℓ min., and 98.2% (14°C) after 180 min at a reaction rate of 17.2 mg/ℓ min.

The study confirmed that the sulphate removal process is very sensitive to the reactor temperature. Therefore, proper temperature control is needed for this process. A detailed discussion was given in Paragraph 4.3.4.

5.3.10. Different barium carbonate types

Different types of barium carbonate were used to remove sulphate from sulphate-rich water. It was found that the different barium carbonate types gave different results.

In the literature barium carbonate from two different sources were used, namely, commercial barium carbonate imported from China and barium carbonate that was produced in the researcher’s laboratory. It was found that the commercial barium carbonate displayed a much slower reaction rate in comparison with the laboratory produced material. The reason for this was not investigated at that stage (Motaung et al. 2009). A detailed discussion was given in Paragraph 3.2.2.

Experiments were conducted to investigate this phenomenon. The commercial barium carbonate and a recycled barium carbonate from the ABC Desalination plant were used. It was found that the commercial material lowered the initial sulphate concentration (1 300 mg/ℓ) by only 53.8% in 300 min, while the recycled barium carbonate (Batch) removed 97.2% within 30 min.

By conducting SEM analyses, photographs of the particles were obtained of the different barium carbonate types (Figure 34 and Figure 35). It was found that the less reactive, commercial barium carbonate has a large, well-defined crystal structure. The more reactive barium carbonate’s structure almost seems fuzzy with small, fine crystals.

Thus, the barium carbonate crystal surface structure does have an influence on the sulphate removal reaction. Barium carbonate with a small, fine crystal structure is more reactive than barium carbonate that consists of large, well-defined crystals. A detailed discussion was given in Paragraph 4.3.5.

5.5. BARIUM SULPHATE PRECIPITATION: CASE STUDIES

Three case studies from the literature are discussed in Paragraph 3.3 where the sulphate removal process is tested and verified on AMD, zinc plant effluent and on power station cooling water effluent. In the first two case studies, the AMD and zinc plant effluent, the ABC Desalination process successfully removed the sulphate from the effluent (Motaung et al. 2009; Trusler et al. 1991). In the third case study it was found that, the sulphate removal from the power station cooling water was not as effective. It appeared as though some additive to the power station cooling water had severe impact on the sulphate removal process (Trusler et al. 1991). A detailed discussion was given in Paragraph 3.3.

Experiments were conducted in the laboratory where the sulphate removal method was tested on two different AMD streams from a coal mine. In both cases the sulphate was successfully removed. The sulphate concentration of the one AMD stream at a pH of 7 was reduced to 50 mg/ℓ (98% sulphate removal), and the sulphates on the second AMD stream at a pH of 12 was decreased to 250 mg/ℓ (90% sulphate removal). Both concentrations were well below the recommended level of 500 mg/ℓ. A detailed discussion was given in Paragraph 4.3.6.

5.6. WATER QUALITY

By comparing the compositions of raw AMD and AMD treated by the ABC Desalination Process, it was found that the quality of the treated AMD had improved. The treated AMD compared well to the SANS Class II potable water standards (SANS 2011), and therefore it had been rendered suitable to be safely discharged into the environment (WHO 2004a, DWAF 1995). A detailed discussion was given in Paragraph 4.4.

5.7. CONCLUSION

Barium carbonate from different sources was used to test its effectiveness in the removal of sulphate from sulphate-rich water. Different results were obtained.

A commercial barium carbonate imported from China (CIF Durbsan), could only reduce the effluent’s initial sulphate concentration with 53.8% while the recycled barium carbonate removed 97.2% of the initial sulphate. Not only did the recycled barium carbonate remove double the sulphates from the effluent, the reaction was also completed 10-times faster (30 min.) than the reaction where commercial barium carbonate was used (300 min.).

From SEM photos (Figure 34 and Figure 35) it was clear that the barium carbonate that was deemed *unreactive* relative to the other barium carbonate types had a large, well-defined crystal structure. The barium carbonate types that were more *reactive* relative to the commercial barium carbonate possessed small crystals with a fine structure.

Nonetheless, all the barium carbonate sources that were used in this study were able to remove the sulphate from the sulphate rich water, although some were more efficient than others. Therefore the hypothesis stated in Chapter 1 was supported, i.e. “barium carbonate, irrespective of its source, is capable of effective sulphate removal from acidic mine drainage and from industrial effluents”.

5.8. RECOMMENDATION

In order to optimise the sulphate removal process, the chemical reaction that takes place inside the reactor has to be completely understood. Therefore it is recommended that a detailed reaction kinetic study should be conducted, in order to find the actual driving force of the reaction kinetics. In other words: What is the limiting step during the sulphate removal reaction? Is it the dissolution of barium carbonate into solution, the precipitation of barium sulphate or calcium carbonate?

Motaung (2011) found that the reaction does not occur in the absence of calcium ions. It is recommended that this phenomenon be investigated as well to understand the dynamics of the chemical reactions that take place. The effect of the initial calcium concentration in the effluent could also be considered.

A study involving a continuous reactor configuration for sulphate removal is recommended in order to upgrade this process first to a pilot-scale, and then to a full-scale plant.

CHAPTER 6: REFERENCES AND BIBLIOGRAPHY

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APPENDIX A:
MEASURING INSTRUMENTS

A.1. INTRODUCTION

The measuring equipment used in the experimental work (described in Chapter 4) is listed. This included pH, temperature and EC sensors, temperature control bath, the Scanning Electron Microscopy (SEM) imaging and the analytical methods used for determining sulphate and barium concentrations.

A.2. INSTRUMENTATION

A.2.1. Sulphate measuring method

Waterlab (Pty) Ltd, a SANAS accredited analytical laboratory, used the Turbidimetric method (Method Number 4500-SO_4^{2-} E) to determine the concentration of sulphate ions in the samples. This method can accurately detect sulphate ions in solution between 1 mg/ℓ and 40 mg/ℓ (APHA 1992).

This is one of the methods recommended by the United States Environmental Protection Agency (USEPA) for sulphate monitoring purposes (APHA 1992).

A.2.2. Barium measuring method

CAS (CSIR), a SANAS accredited analytical laboratory, used an Inductively Coupled Plasma Optical Emission Spectrometer (Varian Vista Pro ICP-OES) to analyse the barium content in the samples. This method is able to determine trace elements in solutions at concentrations below one part per trillion (1 ppt = 1×10^{-12} mg/ℓ). It has the advantages of being fast, precise and sensitive (APHA 1992). The uncertainty of the instrument was 3.7% within a detection limit of 0 mg/ℓ to 5 mg/ℓ at a wavelength of 385.368 nm.

A.2.3. Temperature, EC and pH measuring instrument

A portable data logger known as a Multiparameter instrument (HI 9828 from Hanna Instruments) was used to measure the temperature, pH and EC of the reactor fluid. This instrument can measure up to 12 different parameters, including dissolved oxygen (DO), pH, ORP, conductivity, temperature, atmospheric pressure and seawater specific gravity. Up to 60 000 data points in a 100 different files can be captured on the instrument itself and be downloaded onto a computer. This instrument is shown in Figure A1.

Figure A1: Multiparameter measuring instrument (Hanna Instruments)

The time interval between two sampling points can be controlled. For this study, a pH, temperature and EC measurements were collected every second. This instrument was equipped with a conductivity sensor, a pH sensor and a temperature couple.

The conductivity sensor (HI 769828-3) was a four ring system. This allowed for stable and linear readings. The measuring range for this sensor is between 0.000 mS/cm to 200.000 mS/cm with an accuracy of ± 1 % of the reading or ± 1 µS/cm (whichever the greater). The pH sensor (HI 769828-0) was equipped with a glass membrane. The measuring range was 0.00-14.00 with ± 0.02 accuracy. The temperature sensing thermocouple could measure from - 5.00°C up to 55.00°C (268.15 K-328.15 K) with an accuracy of ± 0.15°C (Hanna Instruments). The probe, equipped with all three sensors, was calibrated once a day before the first experiment was conducted.

A.2.4. Scanning electron microscopy (SEM)

The SEM imaging was done at the University of Pretoria, Faculty of Natural and Agricultural Sciences. This showed the crystal surface structure of the barium carbonate particles.

Strips of black double-sided tape were dipped in the barium carbonate sample and mounted on a microscope stub covered with carbon tape. The samples were coated with gold before it was viewed under the SEM (JEOL-840) at an acceleration voltage from 5 kV to 15 kV.

A.2.5. Overhead stirrer

The overhead stirrer used in the experimental setup was an IKA RW 20.n. mixer. It is suitable for liquids with a low or a high viscosity and can successfully mix up to 20 ℓ at a time (IKA Works Inc 1995).

The mixing speed can be accurately adjusted between 60 min^{-1} and 2 000 min^{-1} at 50Hz AC or 72 $min^{-1}$and 2 400 min^{-1} at 60Hz AC. The power output, torque and rotational speed of the mixer were regarded as constant with a measuring fault of ± 0.5% (IKA Works Inc 1995).

A.2.6. Temperature bath

A Labotech temperature bath (Model 132 A) equipped with a Labotech Circulating Thermostat (Model 100) was used to control the temperature of the 3 ℓ reactor (16 cm diameter). The reactor was positioned in the water bath such that the water level of the heated water was high enough to ensure maximum heat transfer to the reactor.

This temperature bath could maintain the temperature of the reactor with an accuracy of ± 1.5°C, at a temperature between ambient temperature plus 10°C and 100°C, depending on the initial temperature of the water poured into the bath. The capacity of the pump used to circulate the heated water was 6 ℓ/min to insure uniform temperature distribution.

A.3. CONCLUSION

All the measuring instruments used during the experimental work, as well as the analytical work done by the accredited laboratories were reliable and accurate.

APPENDIX B:

EC-SO$_4^{2-}$ CONCENTRATION CORRELATION

B.1. INTRODUCTION

A correlation exists between the EC measurements and the sulphate concentration of the reaction fluid. This was observed in the results shown in Chapter 4 (Paragraph 4.3.1).

B.2. MATHEMATICAL MODELS

Different empirically mathematical models were derived by using Microsoft Excel (version 2007). The EC values were plot against sulphate concentration and the empirical equation of the trend line was used as a model. Different polynomial orders equations were used as trend lines and the mathematical correlations are given in Equation B1 to Equation B6. These equations were compared to each other in order to find the best correlation. The results are summarised in Table B1.

$$[SO_4^{2-}] = (-5\times10^{-17})\,EC^6 + (5\times10^{-13})\,EC^5 - (2\times10^{-9})\,EC^4 + (4\times10^{-6})\,EC^3 - 0.0036\,EC^2 + 1.693EC - 189.8 \qquad \textbf{Equation B1}$$

$$[SO_4^{2-}] = (1\times10^{-13})\,EC^5 - (9\times10^{-10})\,EC^4 + (2\times10^{-6})\,EC^3 - 0.002\,EC^2 + 1.1095EC - 120.19 \qquad \textbf{Equation B2}$$

$$[SO_4^{2-}] = (8\times10^{-11})\,EC^4 - (4\times10^{-7})\,EC^3 + (9\times10^{-4})\,EC^2 - 0{,}223\,EC + 73.683 \qquad \textbf{Equation B3}$$

$$[SO_4^{2-}] = (2 \times 10^{-8})\, EC^3 + (3 \times 10^{-5})\, EC^2 + 0{,}3678EC - 37.877$$ **Equation B4**

$$[SO_4^{2-}] = (9 \times 10^{-5})\, EC^2 + 0{,}2895EC - 17.231$$ **Equation B5**

$$[SO_4^{2-}] = 0{,}5662EC - 143.03$$ **Equation B6**

Table B1: Mathematical correlations

Mathematical equation		**B1**	**B2**	**B3**	**B4**	**B5**	**B6**
Order of polynomial equation		6	5	4	3	2	1
EC	Initial (µS/cm)	2717	2717	2717	2717	2717	2717
	Final (µS/cm)	192	192	192	192	192	192
Calculated SO_4^{2-}	Initial (mg/ℓ)	2990	-5995	2448	1584	1434	1395
	Final (mg/ℓ)	28	32	61	34	42	-34
	SO_4^{2-} (%)	99.1	100.5	97.5	97.9	97.1	102.4
Measured SO_4^{2-}	Initial (mg/ℓ)	1600	1600	1600	1600	1600	1600
	Final (mg/ℓ)	36	36	36	36	36	36
	SO_4^{2-} (%)	97.8	97.8	97.8	97.8	97.8	97.8
R^2		0.9956	0.9955	0.9943	0.9931	0.993	0.9821
% Error	Initial (mg/ℓ)	46.5	126.7	34.6	-1.0	-11.6	-14.7
	Final (mg/ℓ)	-27.4	-12.5	41.0	-5.9	14.3	205.9
	SO_4^{2-} (%)	1.3	2.8	-0.2	0.1	-0.7	4.6

In Table B1 the calculated and measured values are compared. Six mathematical models were used to calculate the initial and final sulphate concentrations from the measured EC values. The percentage sulphate removed was then determined from these calculated values. The measured sulphate concentration values were used to determine the sulphate removal percentage. The percentage error was calculated between the initial sulphate concentration, the final sulphate concentration and the percentage sulphate removal. From the table it was found that the third order polynomial equation (Equation B3) was the best, since the percentage error for the initial and finale sulphate concentration were 1.0% and 5.9%, respectively, and the error between the two sulphate removal percentages was 0.1%.

B.3. CONCLUSION

A third order polynomial equation gave the best correlation between the EC measurement and the sulphate concentration. A 0.1% error exists between the measured and calculated sulphate removed concentrations.

APPENDIX C:
REACTION KINETICS

C.1. INTRODUCTION

A kinetic study was conducted in order to determine the reaction rate constants. The assumption was made that the reaction was first order according to the literature (Hlabela et al. 2007, Motaung et al. 2008). The MATLAB software program was used to determine the reaction rate constant of the sulphate removal reaction.

C.2. KINETIC STUDY

The sulphate removal reaction is irreversible due to the insolubility of the products, barium sulphate and calcium carbonate. The reaction rate equation is given by Equation C1. It was assumed that the reaction is dependent on the sulphate concentration in the sulphate-rich water and not on the barium concentration as explained in the next paragraph.

$$-r_{SO_4^{2-}} = k[SO_4^{2-}]^n$$ **Equation C1**

Barium carbonate is only slightly soluble. It is assumed that there was only a small amount of barium carbonate in solution at all times. The barium carbonate solids dissolved at the same rate as the barium ions reacted with the sulphate ions. Thus, the barium ion concentration stayed relatively constant (± 0.04 mg/ℓ) over time until all the barium carbonate had dissolved. This assumption was supported by barium analyses carried out over time as shown in Figure C1.

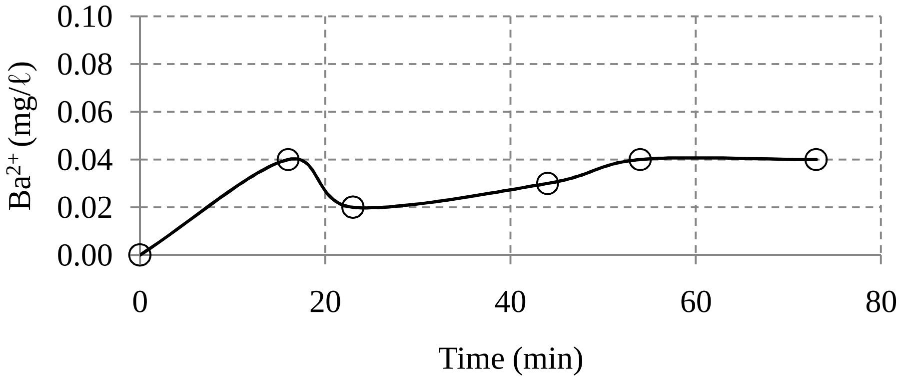

Figure C1: Barium concentration

From the literature it was found that the reaction order (n) is equal to unity (one) (Hlabela et al. 2007, Motaung et al. 2008). The reaction kinetic equation was fitted to the experimental data by using MATLAB software, as shown in Figure C2. It was found that the reaction rate constant (k) for the sulphate removal reaction is 0.03751 min^{-1}, as given in Equation C2.

$$-r_{SO_4^{2-}} = 0.0375[SO_4^{2-}]^1$$ **Equation C2**

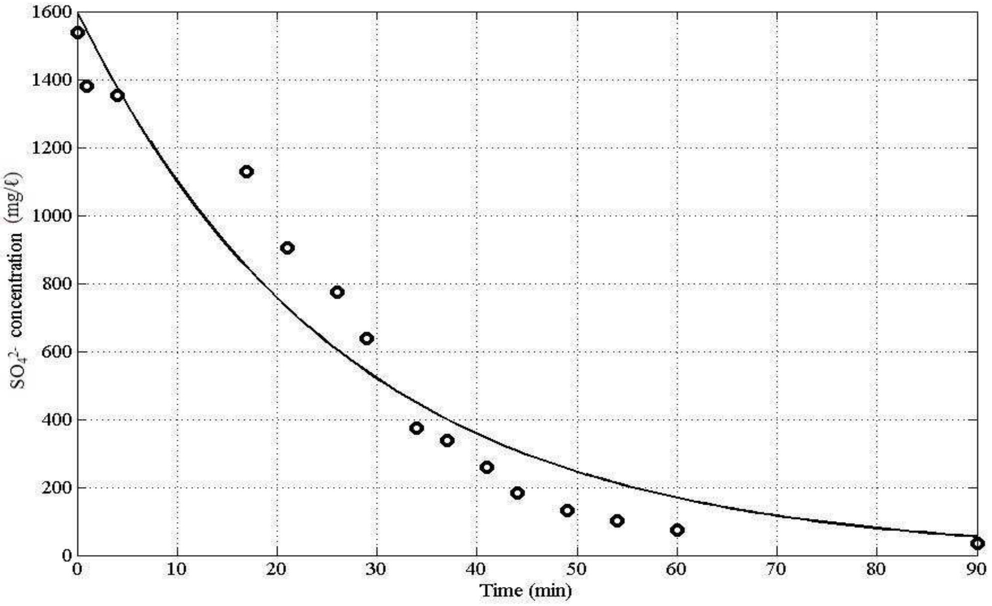

Figure C2: Kinetic equation curve fit of experimental data

The experimental parameters for this experiment were as follows. The initial sulphate concentration in the sulphate-rich water was 1 600mg/ℓ and the mixing rotational speed was

350 min^{-1}. The reactor temperature was constant at ambient temperature (21°C ± 1.5°C). Laboratory produced barium carbonate was used and the dosing ratio was stoichiometrically equal to the sulphate present in the solution. After 90 min. the sulphate concentration was lowered by 97.7% (36 mg/ℓ) according to sulphate analyses.

C.3. TEMPERATURE DEPENDENCY

The rate constant depends on temperature (in K) according to Equation C3 (Levenspiel 1999). The experiment described in paragraph C.2, was conducted at 21°C (294 K). The reaction rate constant was 0.03751 min^{-1}.

$$k = k_o e^{\left(\frac{-E}{RT}\right)} \qquad \textbf{Equation C3}$$

When the same experiment was conducted at a higher temperature (33°C), the reaction rate constant (k) changed. Though k_o (frequency factor) stays constant, and so does the E/R ratio (with E the activation energy of the reaction and R the ideal gas constant (8.314 J/mol K)) (Levenspiel 1999).

In Chapter 4, three experiments were done at three different temperatures. The data from these three experiments are given in Table C1. With the help of Equation C4, that applies to first order reactions, the activation energy of the sulphate removal reaction was determined (Levenspiel 1999).

$$ln\left(\frac{r_2}{r_1}\right) = ln\left(\frac{t_1}{t_2}\right) = -\left(\frac{E}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \textbf{Equation C4}$$

Table C1: Activation energy calculation

	t_1 (min)	**t_2 (min)**	**T_1 (°C)**	**T_1 (K)**	**T_2 (°C)**	**T_2 (K)**	**E (J/mol)**
1	40	120	33	306.15	21	294.15	68 545.09
2	120	180	14	287.15	21	294.15	40 676.46
3	40	180	33	306.15	14	287.15	57 858.84
	Average						55 693.46

Thus for T at 21°C (294.15 K) with a rate constant value of 0.03751 min^{-1}, the reaction rate equations changed as follow (Equation C5 to Equation C8):

$$k = k_o e^{\left(\frac{-E}{RT}\right)}$$
Equation C5

$$0.0375 = k_o e^{\left(\frac{-55\ 693.46}{(8.314)294.15}\right)}$$
Equation C6

$$0.0375 = k_o(1.287 \times 10^{-10})$$
Equation C7

$$k_o = (2.91 \times 10^{8})\ min^{-1}$$
Equation C8

Thus for temperatures of 33°C (306.15 K) and 14°C (287.15 K), the reaction rate constants were calculated (Equation C9 and Equation C10):

$$k_{33} = (2.91 \times 10^{8}) e^{\left(\frac{-55\ 693.46}{(8.314)306.15}\right)} = 0.0915\ min^{-1}$$
Equation C9

$$k_{14} = (2.91 \times 10^{8}) e^{\left(\frac{-55\ 693.46}{(8.314)287.15}\right)} = 0.0215\ min^{-1}$$
Equation C10

Thus the reaction rates for the three different temperatures were given in Equation C11 to Equation C13 (at 50% sulphate removal at a concentration of 800 mg/ℓ):

$$-r_{SO_4^{2-}}|_{33} = 0.0915\ [SO_4^{2-}]^1 = 0.0915\ [800]^1 = 73.2\ mg/\ell\ min$$
Equation C11

$$-r_{SO_4^{2-}}|_{21} = 0.0375[SO_4^{2-}]^1 = 0.0375[800]^1 = 30.0\ mg/\ell\ min$$
Equation C12

$$-r_{SO_4^{2-}}|_{14} = 0.0215[SO_4^{2-}]^1 = 0.0215[800]^1 = 17.2\ mg/\ell\ min$$
Equation C13

C.4. CONCLUSION

Thus the sulphate removal occurs much faster at higher temperatures, as can be expected from literature, and mentioned in Chapter 4 (Levenspiel 1999). At 14°C the reaction rate was 17.2 mg/ℓ min., at 12°C it was 30.0 mg/ℓ min. and at 33°C 73.2 mg/ℓ min.

APPENDIX D:
EXPERIMENTAL DATA

The raw data collected during the experimental work are available on the CD (included in the CD pouch). This data were used to generate the graphs and tables showed in Chapter 4.

An electronic copy (PDF format) of this dissertation is also available on this CD.

CD with raw experimental data

Sulphate removal from industrial effluents through barium sulphate precipitation

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B.Eng (Hons)

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ABSTRACT

The pollution of South Africa’s water resources puts a strain on an already stressed natural resource. One of the main pollution sources is industrial effluents such as acid mine drainage (AMD) and other mining effluents. These effluents usually contain high levels of acidity, heavy metals and sulphate. A popular method to treat these effluents before they are released into the environment is lime neutralisation. Although this method is very effective to raise the pH of the effluent as well as to precipitate the heavy metals, it can only partially remove the sulphate. Further treatment is required to reduce the sulphate level further to render the water suitable for discharge into the environment.

A number of sulphate removal methods are available and used in industry. These methods can be divided into physical (membrane filtration, adsorption/ion exchange), chemical (chemical precipitation) and biological sulphate reduction processes. A literature study was conducted in order to compare these different methods.

The ABC (Alkali - Barium - Calcium) Desalination process uses barium carbonate to lower the final sulphate concentration to an acceptable level. Not only can the sulphate removal be controlled due to the low solubility of barium sulphate, but it can also produce potable water and allows valuable by-products such as sulphur to be recovered from the sludge. The toxic barium is recycled within the process and should therefore not cause additional problems. In this study the sulphate removal process, using barium carbonate as reactant, was investigated.

Several parameters have been investigated and studied by other authors. These parameters include different barium salts, different barium carbonate types, reaction kinetics, co-precipitation of calcium carbonate, barium-to-sulphate molar ratios, the effect of temperature and pH. The sulphate removal process was tested and verified on three different industrial effluents.

The results and conclusions from these publications were used to guide the experimental work. A number of parameters were examined under laboratory conditions in order to find the optimum conditions for the precipitation reaction to take place. This included mixing rotational speed, barium-to-sulphate molar ratio, initial sulphate concentration, the effect of

temperature and the influence of different barium carbonate particle structures. It was found that the reaction temperature and the particle structure of barium carbonate influenced the process significantly. The mixing rotational speed, barium-to-sulphate dosing ratios and the initial sulphate concentration influenced the removal process, but not to such a great extent as the two previously mentioned parameters. The results of these experiments were then tested and verified on AMD from a coal mine.

The results from the literature analysis were compared to the experiments conducted in the laboratory. It was found that the results reported in the literature and the laboratory results correlated well with each other.

Though, in order to optimise this sulphate removal process, one has to understand the sulphate precipitation reaction. Therefore it is recommended that a detailed reaction kinetic study should be conducted to establish the driving force of the kinetics of the precipitation reactions. In order to upgrade this process to pilot-scale and then to a full-scale plant, continuous reactor configurations should also be investigated.

The sulphate removal stage in the ABC Desalination Process is the final treatment step. The effluent was measured against the SANS Class II potable water standard and was found that the final water met all the criteria and could be safely discharged into the environment.

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS

Symbol	**Description**	**Units**
$[SO_4^{2-}]$	Sulphate concentration	mg/ℓ
E	Activation energy	J/mol
EC	Electrical conductivity	µS/cm
k	Reaction rate constant	min^{-1}
k_o	Frequency factor	min^{-1}
k_{sp}	Solubility constant	dimensionless
n	Reaction order	dimensionless
R	Ideal gas constant	J/mol K
$r_{SO_4^{2-}}$	Reaction rate	mg/ ℓ min
T	Temperature	°C and K

LIST OF ABBREVIATIONS

ABC Desalination	Alkali - Barium - Calcium Desalination
AC	Alternating current
AMD	Acid Mine Drainage
aq	Aqueous
Bact	Bacteria
CESR	Cost effective sulphate removal
CSIR	Council for Scientific and Industrial Research (South Africa)
CSTR	Continuous stirred tank reactor
DEAT	Department of Environmental Affairs and Tourism
DO	Dissolved oxygen
DWA	Department of Water Affairs
DWAF	Department of Water Affairs and Forestry
EC	Electrical conductivity
ED	Electro dialyses
EDR	Electro dialyses reversal
FWS wetland	Free water surface wetland
g	Gas
HiPRO	Hi recovery Precipitating Reverse Osmosis
l	Liquid
MBO	Magnesium Barium Oxide
ORP	Oxidation-reduction potential
RO	Reverse osmosis
s	Solid
SANAS	South African National Accreditation System
SANS	South African National Standards
SEM	Scanning electron microscopy
SF wetland	Subsurface flow wetland
SPARRO	Slurry precipitation and recycle reverse osmosis
SRO	Seeded reverse osmosis
TDS	Total Dissolved Solids
WHO	World Health Organisation
XRD	X-ray diffraction

LIST OF CHEMICALS

Formula	**Name**
$3CaO.3CaSO_4.Al_2O_3.31H_2O$	Ettringite
$Al(OH)_3$	Aluminium tri-hydroxide
$Ba(OH)_2$	Barium hydroxide
$BaCO_3$	Barium carbonate
BaS	Barium sulphide
$BaSO_4$	Barium sulphate or barite
$Ca(OH)_2$ or $2OH^-(+Ca^{2+})$	Calcium hydroxide or lime
$CaCO_3$	Calcium carbonate or limestone
$CaSO_4$ or $Ca^{2+}(+SO_4^{2-})$ or $SO_4^{2-}(Ca^{2+})$	Calcium sulphate or gypsum
CO_2	Carbon dioxide
Fe^{2+}	Iron (II) ion
FeS_2	Iron sulphide or pyrite
H^+	Hydrogen ion
H_2CO_3	Carbonic acid
H_2O	Water
H_2S	Hydrogen sulphide
H_2SO_4 or $2H^+(+SO_4^{2-})$	Sulphuric acid
$MgSO_4$	Magnesium sulphate
Na_2SO_4	Sodium sulphate
O_2	Oxygen
OH^-	Hydroxyl
R_2-Ca	Calcium - resin compound
R_2-SO_4	Sulphate - resin compound
R-H	Strong acid cation resin
R-OH	Weak base anion resin
SO_4^{2-}	Sulphate ion

GLOSSARY

ABC (Alkali - Barium - Calcium) Desalination:	A process developed and patented by the CSIR to treat AMD. This process can produce potable water and valuable by-products can be recycled/sold.
Acid Mine Drainage (AMD):	Wastewater, coupled with mining activities, that contains high levels of acidity, heavy metals and sulphates. Caused when pyrite is oxidised and produces sulphuric acid and sulphate.
Aerobic:	In the presence of oxygen.
Anaerobic:	In the absence of oxygen.
Anoxic:	Water in which the dissolved oxygen is partially depleted.
Barite formation:	Barium sulphate precipitation.
Batch reactor:	A reactor with no inflow or outflow streams for the duration of the chemical reaction. The reactor is a standalone unit.
Bioreactors:	A reactor for biological reactions.
Brine:	Wastewater, associated with membrane and filtering processes, that contains high salt concentrations.
Carbonation process:	A process where carbon dioxide gas is dissolved into water in order for the carbonate ions to react with other chemical species such as barium ions.
Class II potable water standards:	A class of potable water as defined by South Africa National Standards (SANS).
Contact time:	The time allowed for the chemicals to come into direct contact with each other.
Continuous reactor:	A reactor with an inflow stream from one unit and an outflow stream to another unit for the duration of the chemical reaction.
Continuous stirred tank reactor (CSTR):	A continuous agitated-tank reactor.
Cost Effective Sulphate Removal (CESR):	A sulphate removal process based on ettringite precipitation. In addition to sulphate removal it also effectively removes dissolved metals.

CSTRs in series:	More than one CSTR in a row operating in a series configuration.
Electrical conductivity (EC):	The measurement of a material's ability to conduct an electrical current. In the case of liquids, the ion charge within the solution.
Electro dialyses (ED):	A membrane process where an electrical potential is used to force dissolved ions through the membrane.
Electro dialyses reversal (EDR):	An ED membrane process where the flow direction through the membrane can be reversed.
Fluidised bed reactors:	A reactor where fluid (gas or liquid) is passed through a granular solid material. The fluid flowrate is high enough to suspend the solid particles and cause it to behave like a fluid.
Free water surface (FWS) wetlands:	The water flows over a vegetated subsurface from one side to the other. These engineered wetlands are generally shallow and a subsurface barrier prevents seepage.
Gas lift reactor:	A reactor where gas is injected through a tubing-casing annulus. The injected gas aerates the fluid and reduces its density. The formation pressure lifts the fluid and forces it upwards.
GYP-CIX process:	An ion-exchange technology for the removal of ions from the wastewater rich in sulphate and calcium ions.
HiPRO process:	A high recover desalination process.
Industrial effluent:	Wastewater generated by different industrial activities. This include AMD and other mining waste streams, plating industry waste, tannery waste, etc.
Lime neutralisation:	Lime or limestone is added to the acidic wastewater in order to neutralise it. This results in heavy metal precipitation and partial sulphate removal.
Magnesium Barium Oxide (MBO):	A sulphate removal process that uses barium hydroxide as barium salt source.

Over-dose:	When barium ions (in molar units) are added to a solution in excess of the sulphate ions (in molar units) present ($[Ba^{2+}]/[SO_4^{2-}] > 1$).
Packed bed reactor:	A reactor filled with solid particles.
Potable water:	Drinking water.
Reactive barium carbonate:	Barium carbonate that reacts quickly (relative to other barium carbonate types) with calcium sulphate under controlled conditions. This results in a fast sulphate removal process.
Reverse osmosis (RO):	A membrane process that uses high pressure to force the water-part of a solution through the membrane while retaining the dissolved ions.
Salinity:	High salt concentration.
SAVMIN:	A process during which sulphate removal is achieved through ettringite precipitation.
Scanning electron microscopy (SEM):	A type of electron microscope that photographs a sample by scanning it with a high-energy beam of electrons. This produces photographs of the crystal structure of the sample.
Seeded reverse osmosis (SRO):	An RO membrane process that involves a suspension of seed crystals being introduced into the effluent through recycling of the waste slurry.
Sludge blanket reactor:	A reactor where the wastewater enters the reactor from the bottom, and flows upward. A suspended sludge blanket forms that acts as a filter.
Slurry precipitation and recycle reverse osmosis (SPARRO):	An RO membrane process where seed crystals are recycled from the concentrate to the feed water.
Stoichiometric ratio dose:	The barium ions (in molar units) added to the solution is equal to the sulphate ions (in molar units) present in the solution. ($[Ba^{2+}]/[SO_4^{2-}] = 1$).
Subsurface flow (SF) wetlands:	This type of wetland holds an appropriate medium in a bed or channel. The water level remains below the bed surface covered with emergent vegetation.

Synthetic sulphate water:	Calcium sulphate is dissolved into distilled water to produce a sulphate-rich solution of which the concentration is known.
Turbidimetric method:	Standard analytical method to measure sulphates in a solution.
Under-dose:	The barium ions (in molar units) added to the solution is less than the sulphate ions (in molar units) present in the solution. ($[Ba^{2+}]/[SO_4^{2-}] < 1$).
Unreactive barium carbonate:	Barium carbonate that reacts very slowly (relative to other barium carbonate types) with calcium sulphate under controlled conditions. This results in a slow sulphate removal process.

CHAPTER 1: INTRODUCTION

Chapter 1 provides the background of this study. The problem statement and the objective of the investigation are presented.

1.1. INTRODUCTION

The water scarcity in South Africa is exacerbated by the pollution of its water resources (Morgan et al. 2008). It is a legal requirement in terms of the National Water Act (RSA 1998) that treated effluent must be returned to the water resource (Section 22(2)(e)) while also reducing or preventing pollution and degradation of water resources (Section 2(h)). According to the Department of Water Affairs (DWA), the quality of South African water resources is deteriorating mainly due to salinity coupled with effluent discharges (DWAF 2004). Effluents originating from or as a result of mining activities usually contain high levels of acidity, heavy metals and sulphates as well as low concentrations of organic material (Roman et al. 2008, Bell et al. 2006). The high sulphate concentration in mining effluent is of specific concern to water quality managers in South Africa (DWAF 2002).

The most widespread treatment method applied to acid mine drainage is lime neutralisation. Lime ($Ca(OH)_2$) is added to raise the pH, resulting in the precipitation of dissolved metals as metal hydroxides while partial sulphate removal (up to 1 200 mg/ℓ) is achieved. However, further treatment is required to lower the sulphate level to below 500 mg/ℓ, the acceptable concentration for discharge into the environment.

One such treatment technology, known as the ABC Desalination Process, developed and patented by the CSIR, uses barium carbonate to achieve this. Barium ions react with the sulphate ions to form barium sulphate. This compound is not very soluble and will precipitate out of the solution, leaving few sulphate ions in the solution (Maree et al. 2004b, Maree et al. 2004a).

1.2. BACKGROUND

Large quantities of AMD are released into the environment and have a serious negative environmental impact. Figure 1 shows an example of the impact and effects AMD has on the environment.

Figure 1: Environmental impact of AMD (Ferreira 2010, Herskovitz 2011)

The high sulphate concentration in AMD originates from a natural oxidation process. Sulphide oxidation is a common phenomenon which occurs in mine effluent. The most common source of sulphate is due to the oxidation of an iron sulphide mineral known as pyrite (FeS_2), a natural substance in the earth's crust (Oxford 2009). Pyrite containing ore is a very rich sulphuric acid source since every ton of ore with 1% pyritic sulphur can produce more than 15 kg of ochre and 30 kg of sulphuric acid (Bowell 2004).

The conversion of pyrite to sulphuric acid (H_2SO_4) and sulphate ions (SO_4^{2-}) is brought about by sulphur oxidation bacteria under aerobic conditions; the chemical reaction is shown in Reaction 1 (Sawyer et al. 2003). The products of this chemical reaction pollute the water due to the increase in acidity, heavy metals and dissolved salts (Bell et al. 2006, Sawyer et al. 2003).

$$2\mathrm{FeS_2(s)} + 7\mathrm{O_2} + 2\mathrm{H_2O} \xrightarrow{\mathrm{Bact}} 2\mathrm{Fe^{2+}} + 4\mathrm{H^+} + 4\mathrm{SO_4^{2-}} \qquad \textbf{Reaction 1}$$

High acid and sulphate levels in the wastewater cause the water to be corrosive to equipment and piping, and can cause scaling problems in pipes and filters. It also increases the salinity of the receiving water bodies. The consumption of drinking water containing a sulphate concentration in excess of 500 mg/ℓ commonly results in laxative effects in humans (WHO 2004b). The taste threshold for the most prevalent sulphate salts ranges from 250 mg/ℓ to 500 mg/ℓ (WHO 2004b). Though the World Health Organisation (WHO) does not stipulate a health-based guideline for the sulphate level in potable water, it does recommend the health authorities are notified if the concentration exceeds 500 mg/ℓ (WHO 2004b). Accordingly, most countries in the world recommend a potable water standard for sulphate between 250 mg/ℓ and 500 mg/ℓ. This is based on the secondary drinking water recommendations of 500 mg/ℓ (INAP 2010).

The effect of high sulphate concentration in water was not always considered to be a problem because sulphate has a low impact on the environment in comparison with the acidic and heavy metal content of AMD. It therefore received little attention in many of the regulatory jurisdictions in comparison to the control of dissolved metals and acidity. The concern over an elevated sulphate level in effluents is increasing at regulatory agencies due to the impact it has on the salinity of receiving water bodies. Therefore, sulphate is being considered a significant long term water quality issue, particularly in water scarce countries such as South Africa (INAP 2003).

1.3. PROBLEM STATEMENT

The high sulphate level in acidic mine drainage (AMD) and industrial effluents released into the environment is problematic for various reasons:

- It causes scaling in pipes and filters and is corrosive to equipment.
- It has a purgative effect in humans when the sulphate concentration in potable water is higher than 500 mg/ℓ (WHO 2004b).
- Saline water can lead to the salinisation of irrigated soils, diminished crop yield and changes in biotic communities (DEAT 2006).

1.4. TREATMENT OPTIONS

A number of sulphate removal methods are available and most of them are implemented on full-scale. These methods include:

- Membrane filtration such as reverse osmosis and electro dialysis.
- Adsorption/ion-exchange.
- Biological degradation.
- Chemical precipitation such as lime/limestone addition to form gypsum, precipitation of ettringite and barite formation.

1.5. RESEARCH OBJECTIVE

Although a number of sulphate removal methods are available to industry, it was decided to investigate the barium sulphate precipitation method. The objective was to demonstrate that barium carbonate can be successfully used to achieve very nearly complete sulphate removal from AMD.

1.6. HYPOTHESIS

Barium carbonate, irrespective of its source, is capable of effective sulphate removal from acidic mine effluents as well as industrial effluents.

1.7. METHOD OF INVESTIGATION

A variety of methods exist to remove sulphate from industrial water and AMD. Therefore it was necessary to start off with a literature study. In this literature study different sulphate removal methods were compared to decide whether a specific method was suitable for solving a particular problem.

Once a sulphate removal method was chosen, a detailed literature study that focused specifically on this method was conducted. The results and conclusions found in the literature were used to guide the experimental work.

A reactor setup, where barium carbonate is used as barium source, to remove sulphate from AMD was analysed with purpose of improvement. Experiments were conducted to aid in the understanding of the conditions required for this precipitation process. A number of parameters which included the effects of temperature, mixing rotational speed, initial sulphate concentration, barium-to-sulphate molar ratio and different barium carbonate sources were considered. The results were tested and verified on industrial process water.

1.8 CONCLUSION

AMD and some industrial effluents are rich in sulphate ions and should not be released untreated into the environment. The high sulphate level in the water causes problems in industry such as equipment and piping damage due to corrosion and scaling. It also has a laxative effect in humans when the sulphate concentration in the consumed water is higher than 500 mg/ℓ.

A number of sulphate removal methods are used in industry such as membrane filtration (reverse osmosis and electro dialysis), adsorption/ion-exchange, biological degradation, chemical precipitation (lime/limestone addition to form gypsum, precipitation of ettringite and barite formation).

CHAPTER 2: LITERATURE SURVEY ON SULPHATE REMOVAL TECHNOLOGIES

2.1. INTRODUCTION

A literature study was conducted to investigate the different, generally available methods to remove sulphate from industrial wastewater. A short explanation of the operating principles of each of these methods is given. These methods can be divided into physical processes such as membrane filtration, chemical treatment such as precipitation methods and biological sulphate reduction (INAP 2003, Bowell 2000, Harries 1985, Akcil et al. 2006, Herlihy et al. 1989, Jiménez-Rodríguez et al. 2010, Aubé 2004).

2.2. PHYSICAL SULPHATE REMOVAL METHODS

2.2.1. Membrane filtration

Two important water treatment methods use membranes. These two methods are ED (electro dialysis) and RO (reverse osmosis). In ED, an electrical potential is used to force dissolved ions through the membrane (1 nm to 2 nm pore size), leaving behind pure water (Fell 1995). The RO on the other hand uses high pressure to force the water-part of the solution through the membrane (0.1 nm to 5 000 nm pore size, depending on filter type) while retaining the dissolved ions (INAP 2003, Fell 1995).

The two most important factors contributing to the operating costs are the membrane efficiency and the energy requirements. The membrane life is greatly affected by mechanical failure and fouling. The major advantage of all the membrane treatment processes is the production of high-quality water that can be used or sold as potable water. A major disadvantage is the production of brine that requires disposal and incurs additional costs (INAP 2003).

RO (Reverse osmosis)

The driving force for RO is the difference in pressure across the selective permeable membrane where an external hydraulic pressure is applied on the saline brine side of the membrane. Therefore the water is forced through the membrane against osmotic pressure (Fell 1995). A schematic diagram is shown in Figure 2. The discharge water or brine is the primary waste product (Letterman 1999).

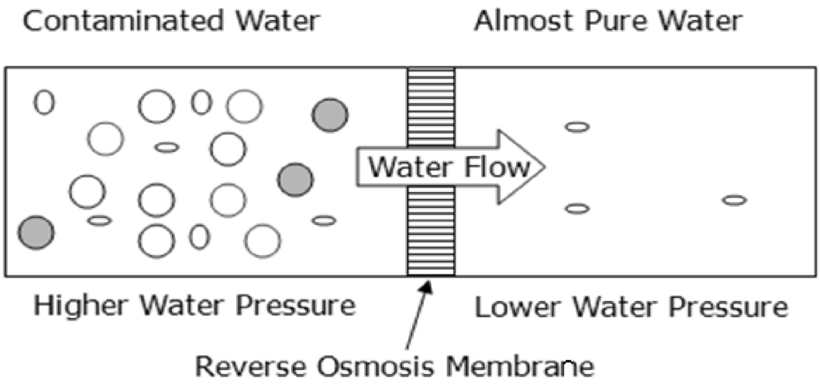


Figure 2: Schematic diagram of an RO membrane (GTAwater 2004)

An RO system consists of four basic stages, namely, pre-treatment, high-pressure pumping, membrane assembly and post-treatment. The pre-treatment prevents membrane fouling from suspended solids, mineral precipitation or microbial growth. It generally involves filtration and/or chemical treatment. A high-pressure pump is required to supply sufficient pressure to force the water through the semi-permeable membrane. This high-pressure pumping is the major contributor to the energy required for this process. Post-treatment involves conditioning of the treated water. This will include pH, alkalinity and hardness adjustments as well as hydrogen sulphide gas removal (INAP 2003). In cases where the water has a low calcium concentration (< 100 mg/ℓ) and low sulphate concentration (< 700 mg/ℓ), RO can be used as treatment method. At higher concentrations membrane scaling will occur (Bowell 2004).

HiPRO (Hi-recovery Precipitating Reverse Osmosis) process

A high recovery desalination process known as the HiPRO process has been developed by Keyplan (Pty) Ltd. Ultra high water recoveries (greater than 97%) are consistently achieved. The final products from this process are potable water (25 000 m^3/d) that is sold to the local municipality, a liquid brine stream (less than 3.0% of the total feed) and solid waste. The solid waste products are calcium sulphate of saleable grade (100 t/d) as well as a calcium and metal sulphates product. A full scale plant has been operating at full capacity since September 2007 (Blueprint 2009, Randall et al. 2011).

SPO (Seeded Reverse Osmosis)

A modified RO process known as seeded reverse osmosis (SRO), is used to treat mine water in South Africa (Harries 1985). The SRO process actively promotes precipitation of calcium sulphate prior to membrane treatment, reducing membrane deterioration and fouling by salt precipitation. This pre-treatment method involves a suspension of seed crystals being introduced into the effluent through recycling of the waste slurry. A number of disadvantages exist with this modified process, despite its advantages that include high salt and water recovery at reduced cost. The disadvantages include the high energy consumption and poor calcium sulphate seed control (Harries 1985). Redevelopment of the SRO process contributed to the patent on the slurry precipitation and recycle reverse osmosis (SPARRO) process (Bowell 2004).

SPARRO (Slurry Precipitation and Recycle Reverse Osmosis)

Water with high levels of calcium and sulphate severely limits water recovery in conventional RO treatment systems. Then again, SRO is particularly attractive for this type of water. Gypsum seed crystals are added to the feed water to serve as nucleation sites for the crystallisation and precipitation of gypsum and other minerals. This prevents mineral precipitation, that causes clogging and fouling, on the membranes. When the seed crystals are recycled from the concentrate to the feed water, the process is called the SPARRO process. The design incorporates three major improvements in comparison to the conventional RO process. These include lower energy consumption, independent control of gypsum seed and concentrate blow-down as well as the utilisation of a novel pumping system (INAP 2003). A flow diagram of the SPARRO process is shown in Figure 3.

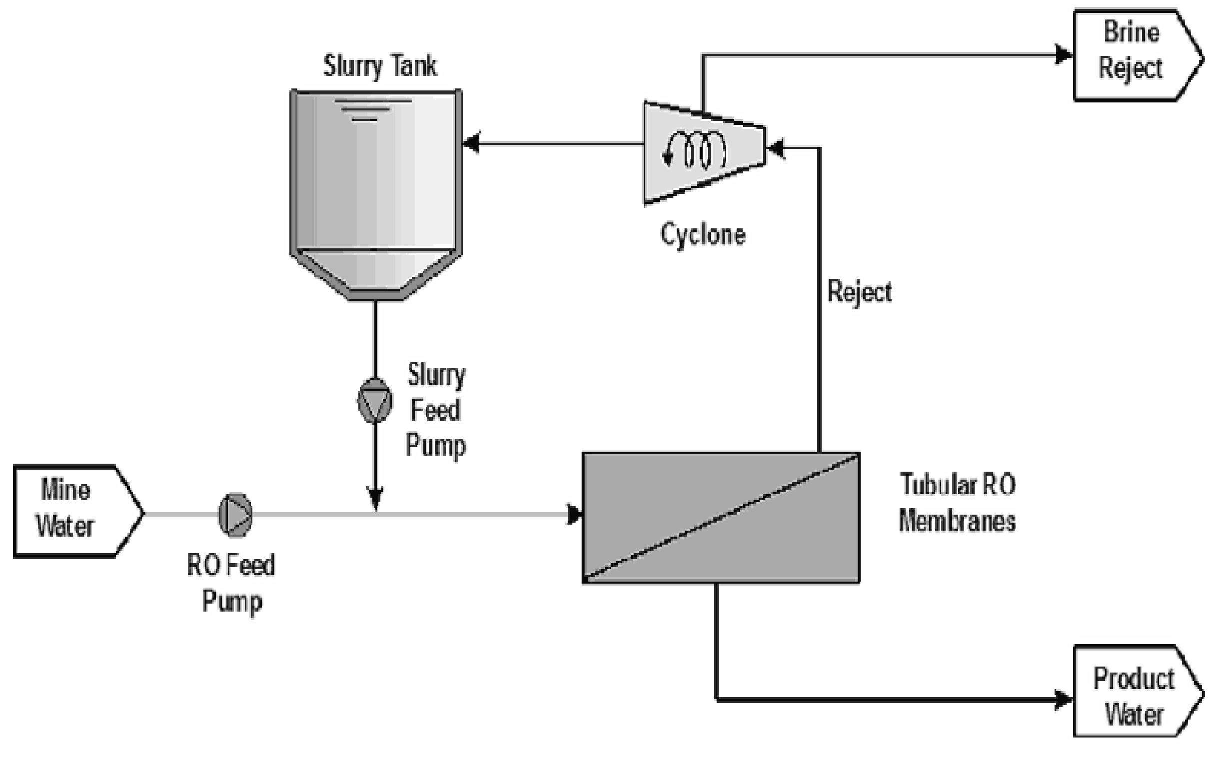


Figure 3: SPARRO process flow diagram (INAP 2010)

ED (Electro Dialysis) and EDR (Electro Dialysis Reversal)

The ED process uses direct electrical current across a stack of alternating cation and anion selective membranes. Anions in the effluent are attracted to the anode but cannot pass through the anion impermeable membranes and are thus concentrated. Cations move in the opposite direction and are obstructed by cation impermeable barriers. In this process the initial feed solution is rid of salts and clean water can be extracted.

The anode and cathode can be changed periodically, a process known as EDR. This could occur several times an hour. This reversing of the anode and cathode reduces the potential for membrane fouling and facilitates regeneration of the membrane by self-cleaning. A major advantage of EDR is that the system is not sensitive to effluent temperature or pH. Capital and working costs are reduced due to lower working pressures. However, calcium sulphate scaling can occur due to inadequate pre-treatment (Strathmann 1995). The internal construction of an ED or EDR cell is shown in Figure 4.

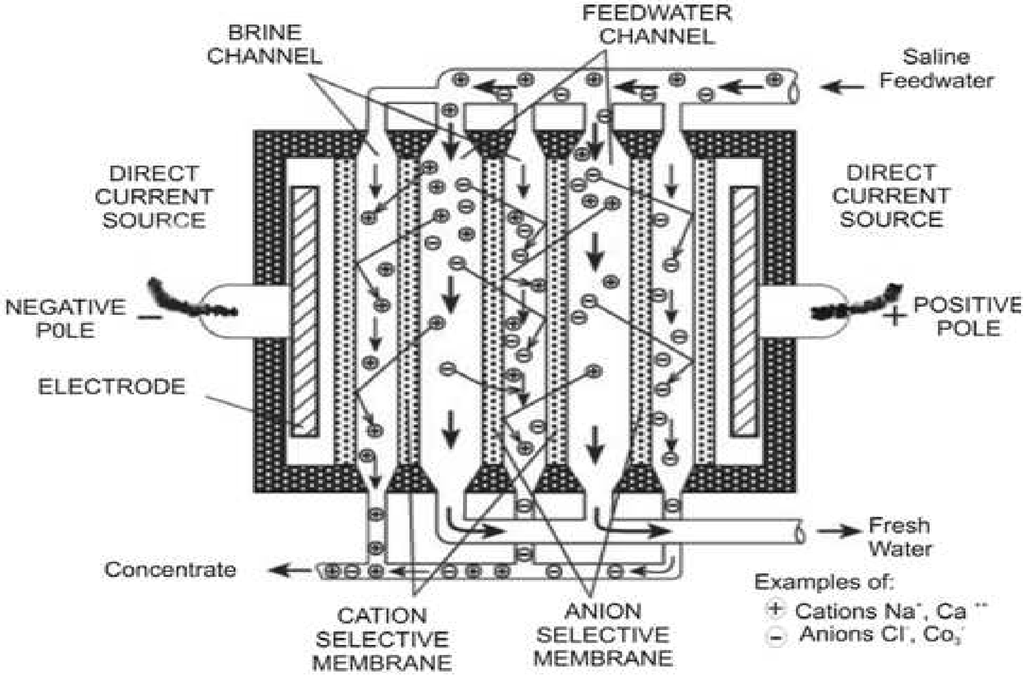


Figure 4: ED or EDR cell (UNEP 1998)

The basic ED and EDR units consist of several hundred cell pairs connected to electrodes, known as membrane stacks (INAP 2003). An EDR unit consists of five basic components: pre-treatment, the membrane stack, low-pressure pumps, power supply for direct current and post-treatment. The pre-treatment is necessary to prevent material that could cause damage to the membranes or clog the channels inside the cells to enter the membrane stacks. The low-pressure pump is necessary to ensure that water circulates through the membrane stack, which is in turn powered by the direct current. Post-treatment involves water conditioning such as the adjustment of pH, alkalinity and hardness (INAP 2003).

2.2.2. Adsorption/ion-exchange

The ion-exchange process operates on the basis of absorption of ions in the solution onto an ion-exchange resin. Ion-exchange resins contain large polar exchange groups. Therefore, this process involves the exchange of ions or molecules between the solid phase and the liquid phase with no substantial change to the solid ion-exchange resin structure. One of the targeted ions is removed from the liquid phase and attached to the solid structure in exchange for another ion. This ion is typically a hydrogen ion (H^+) or a hydroxyl ion (OH^-), thus rendering the target ion immobile (Metcalf 2003).

In the case of calcium sulphate, the anionic sulphate ion would be exchanged for a hydroxyl ion on a positively charged resin. While the cationic calcium ion would be exchanged for a hydrogen ion and so be attached to a negatively charged resin. In this process calcium sulphate scaling is a common problem. To overcome the scaling problem, a modified ion-exchange process has been developed specifically for calcium sulphate water. This process is known as the GYP-CIX process (Bowell 2004).

GYP-CIX Process

The GYP-CIX process is a low-cost ion-exchange technology for the removal of ions from wastewater such as those rich in sulphate and calcium (Wood 2003). This is based on the use of ion-exchange resins that uses cheap regeneration reagents such as lime and sulphuric acid (Akcil et al. 2006). These resins have been designed to target calcium and sulphate so as to reduce gypsum levels in effluent. By achieving this, the TDS (Total Dissolved Solids) levels in effluent are reduced and the corrosion potential limited.

Additionally, a pure gypsum product is produced from both cationic and anionic exchange (Wood 2003). Therefore, the GYP-CIX process is suitable for the treatment of scaling mine water that is high in sulphate and calcium (INAP 2003).

The process flow diagram of the GYP-CIX process is shown in Figure 5. The sulphate removal process is illustrated to the left of the figure while the cationic and anionic regeneration steps are shown on the right.

The principle of operation of the GYP-CIX process is as follows. The untreated wastewater is pumped into the cation loading section where it passes through fluidised contact stages. Calcium ions and other cations are removed from the feed water through cation-exchange with strong acid cation resin (R-H). This is demonstrated in Reaction 2 (INAP 2003).

$$2R - H + \ Ca^{2+}(+SO_4^{2-}) \rightarrow R_2 - Ca + 2H^{+}(+SO_4^{2-}) \qquad \textbf{Reaction 2}$$

After the wastewater has flown through the cation resin contactor, the water is pumped to a degassing tower to remove carbonate alkalinity. Next the water is pumped into the anion loading section where it passes through fluidised contact stages. Anions such as sulphate ions are then removed from the wastewater through anion-exchange with a weak base anion resin such as lime (R-OH). This is shown in Reaction 3 (INAP 2003).

$$2R - OH + SO_4^{2-}\ (+Ca^{2+}) \rightarrow R_2 - SO_4 + 2OH^-(+\ Ca^{2+})$$ **Reaction 3**

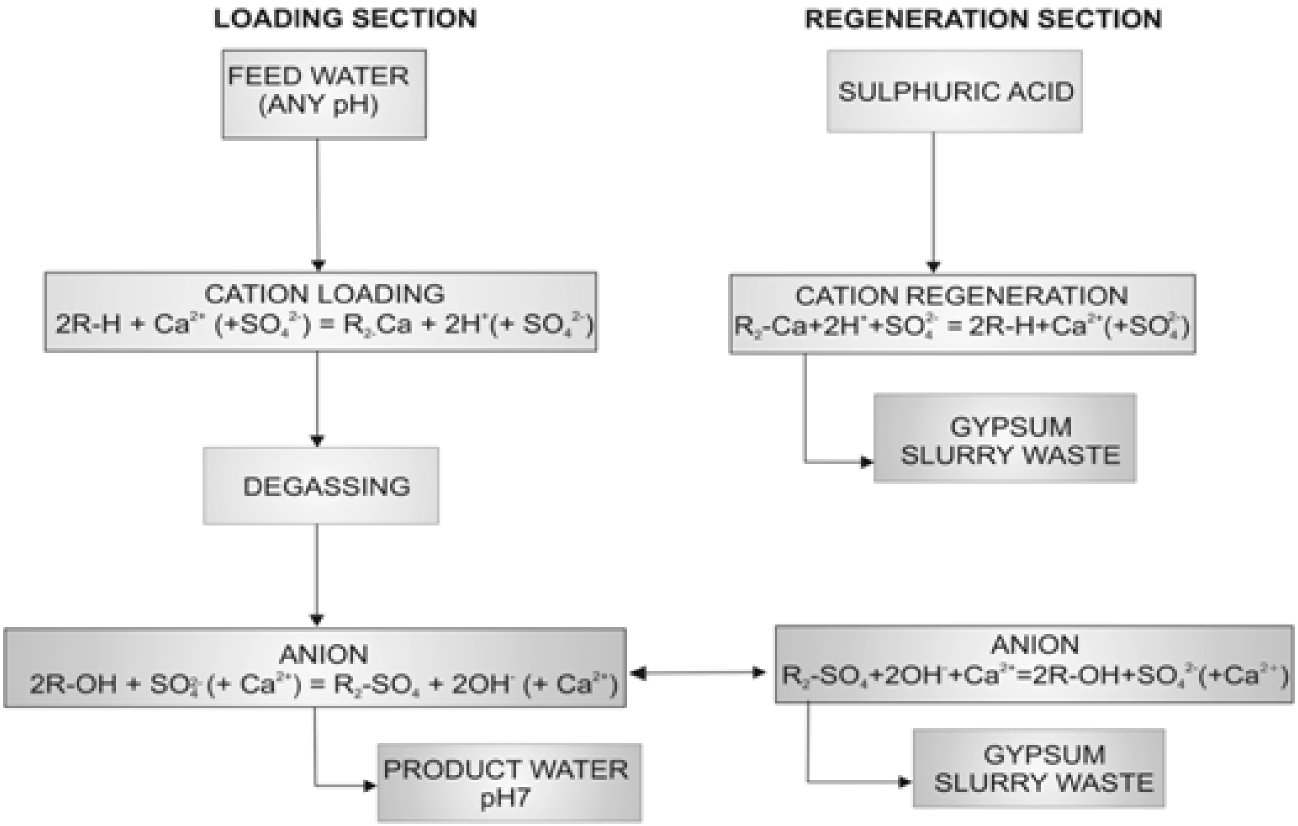


Figure 5: GYP-CIX process (McNee 2003)

The treated water has a neutral pH, and is also low in dissolved calcium, sulphate and other dissolved substances including metals (INAP 2003).

2.3. BIOLOGICAL SULPHATE REMOVAL METHODS

There are a number of biological processes to remove sulphate from wastewater. These include bioreactors and constructed wetlands (INAP 2003, Herlihy et al. 1989, Jiménez-Rodríguez et al. 2010).

2.3.1. Bioreactors

The use of bioreactors is one method to biologically reduce the sulphate concentration of wastewater. In the development and use of these reactors several problems occurred that needed special attention, in order to develop a successful sulphate removal process. These issues included the type of substrate used in the reactor, the toxicity of the wastewater and the type/design of the bioreactor (INAP 2003).

What happens inside the bioreactors is complex. In short, the reactors usually operate under anoxic conditions. The sulphate is then removed as stable sulphide precipitate. In the case where a reactor operates under anaerobic conditions, the sulphate is converted to hydrogen sulphide gas. This transformation is brought about by specialised, strictly anaerobic bacteria (Herlihy et al. 1989, Jiménez-Rodríguez et al. 2010).

A large selection of bioreactors is currently available including CSTRs (continuous stirred tank reactors), packed bed reactors, fluidised bed reactors, sludge blanket and gas lift reactors. The most significant progress in bioreactor design was made in 1988 where a continuous flow, fluidised bed reactor was used for the first time (INAP 2003). The hydrogen sulphide gas generated in the reactor was stripped with an inert gas. This stripped hydrogen sulphide gas was then used in a separate reactor to precipitate the metals out of the AMD. Thus the sulphate removal and the metal removal occurred in two different reactors.

The advantage of the reactor setup is that the bacteria are no longer exposed to potential toxins coupled with the wastewater to be treated. Also, the waste stream loading occurs in a separate reactor and is no longer dependent on the biomass retention. This implies that smaller reactors can be used as well as a greater variety of substrates. The metal sulphide precipitation can be controlled in such a manner that it is possible to control the successive precipitation of the different metal sulphides in separate reactors. This allows recovery of individual metals from the AMD (INAP 2003).

The use of bioreactors appears to be one of the most efficient biological treatment processes for sulphate removal. Operating costs of the bioreactor are high owing to the expensive carbon and energy sources required as nutrients for the microorganisms (INAP 2003). A typical bioreactor setup for sulphate removal is shown in Figure 6.

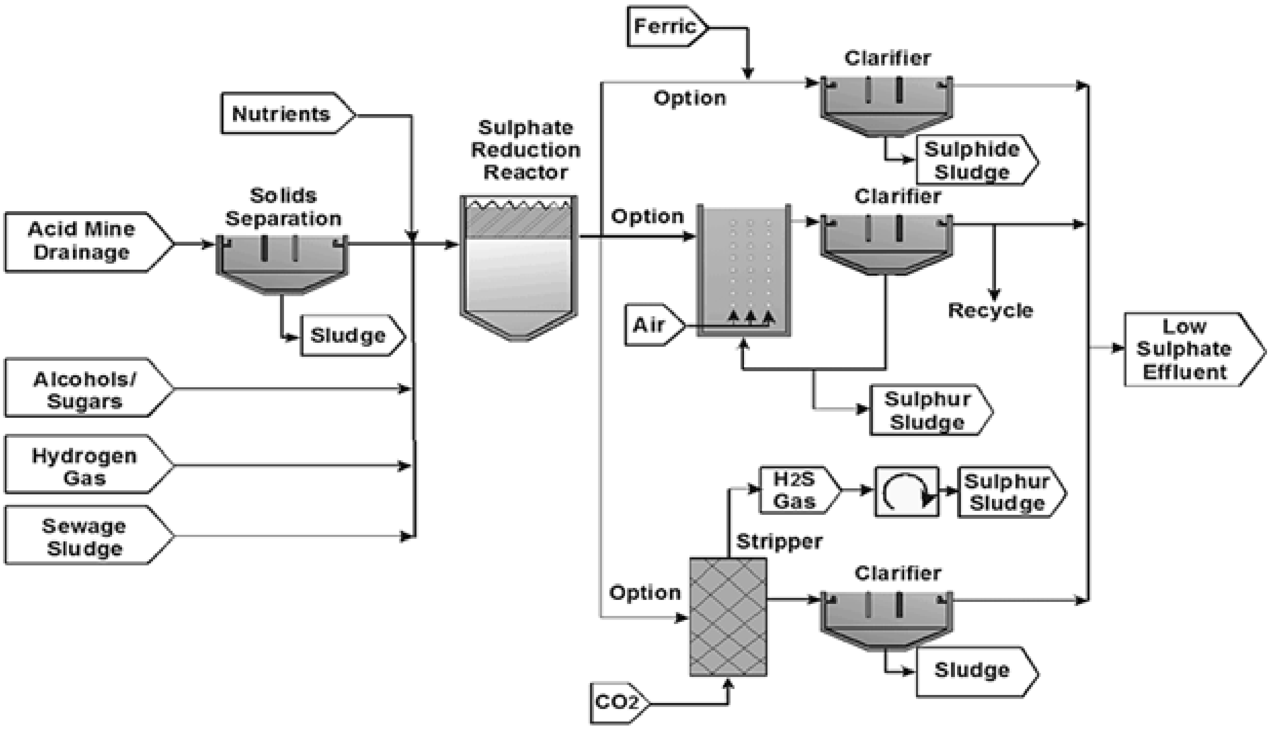


Figure 6: Typical bioreactor setup for sulphate removal (INAP 2010)

2.3.2. Constructed wetlands

Two main categories exist for constructed wetlands, namely, free water surface (FWS) wetlands and subsurface flow (SF) wetlands. The majority of natural wetlands are classified as FWS wetlands. In this type of wetland, the water flows over a vegetated subsurface from one side to the other. These wetlands are generally shallow and a subsurface barrier prevents seepage. An example is shown in Figure 7.

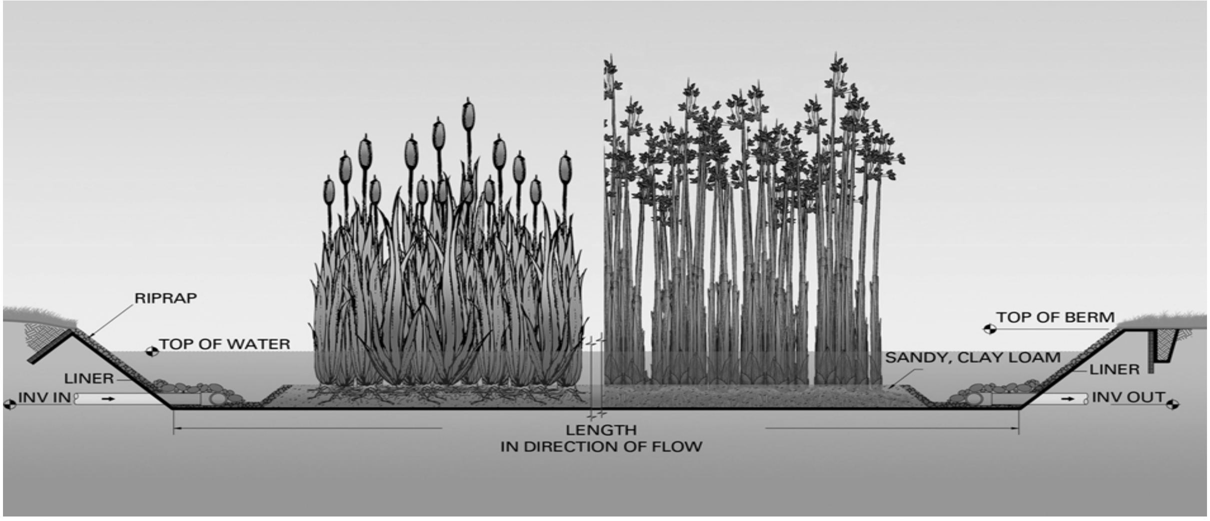


Figure 7: Schematic diagram of a FWS wetland (NSI 2011)

An SF wetland, on the other hand is designed for water treatment. This type holds an appropriate medium in a bed or channel. The water level remains below the bed surface covered with emergent vegetation. An example of such a wetland is shown in Figure 8. The volume of medium used in SF wetlands is generally larger than that in FWS wetlands. For biological sulphate removal FWS wetlands are more suitable than SF wetlands (INAP 2003).

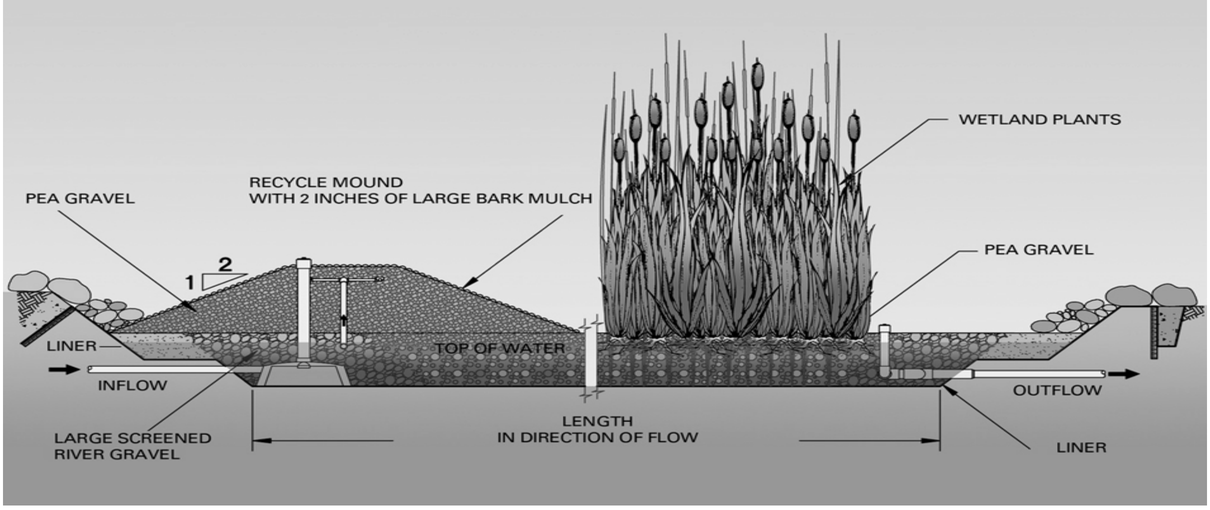


Figure 8: Schematic diagram of a SF wetland (NSI 2011)

The FWS wetlands are either aerobic or anaerobic. Aerobic wetlands are used because they provide sufficient residence time and aeration to enhance the metal precipitation through biotic and abiotic oxidation. Anaerobic wetlands are often used for the treatment of acidic water. The alkalinity used in the neutralisation of the wastewater is obtained from the dissolution of limestone and results in the reduction of sulphate in the subsurface (INAP 2003).

2.4. CHEMICAL PRECIPITATION SULPHATE REMOVAL METHODS

Chemical treatment processes that are used in conjunction with mineral precipitation processes include the addition of lime or limestone to form gypsum, addition of barium salts for barium sulphate precipitation and the SAVMIN process that is based on ettringite precipitation (Bowell 2004, INAP 2003, Aubé 2004).

2.4.1. Gypsum precipitation

Sulphate removal via lime/limestone addition is achieved by means of calcium sulphate saturation. In essence this means that the pH of the raw water is raised to a point where the metals that are of concern are no longer soluble. In turn these metals precipitate out as hydroxides resulting in a clear effluent which is in accordance with regional criteria (Aubé 2004).

The addition of lime/limestone seems to be one of the most suitable sulphate removal methods in the treatment of AMD. The limitation of this process is that it can only lower the sulphate concentration to 1 200 mg/ℓ. But, since it is a simple and inexpensive process, it can be used successfully as pre-treatment for other more expensive processes that lower the sulphate concentration to 500 mg/ℓ or less (INAP 2003).

This process is traditionally used in neutralising AMD where lime ($Ca(OH)_2$) and/or limestone ($CaCO_3$) is added to the effluent. These chemicals can also be used for partial removal of sulphate through gypsum ($CaSO_4$) precipitation. These reactions are shown in Reaction 4 and Reaction 5 (INAP 2003).

$$\mathrm{Ca(OH)_2}\ (s) + \mathrm{H_2SO_4} \rightarrow \mathrm{CaSO_4}\ \mathrm{2H_2O}\ (s) \qquad \textbf{Reaction 4}$$

$$CaCO_3\ (s) + H_2SO_4 + H_2O \rightarrow CaSO_4\ 2H_2O + CO_2\ (g) \qquad \textbf{Reaction 5}$$

The solubility of gypsum depends on the composition and ionic strength of the solution. This solubility ranges between 1 500 mg/ℓ and 2 000 mg/ℓ and it controls the level and extent to which sulphate concentration can be reduced. This process consists of the following three steps.

First, the pH is raised which results in the production of carbon dioxide gas and gypsum precipitation. Second, the pH is raised to 12 by adding more lime to the wastewater to induce gypsum crystallisation and, if the waste contains magnesium, to precipitate it as magnesium hydroxide. Third, the pH is adjusted to 7 by adding carbon dioxide gas that is recovered from step one, and causes calcium carbonate to precipitate (INAP 2003).

The waste products from this process are gypsum and limestone sludge. This is relatively pure limestone sludge and can therefore be recycled back to the first step (INAP 2003). A flow diagram of the lime/limestone addition process is shown in Figure 9.

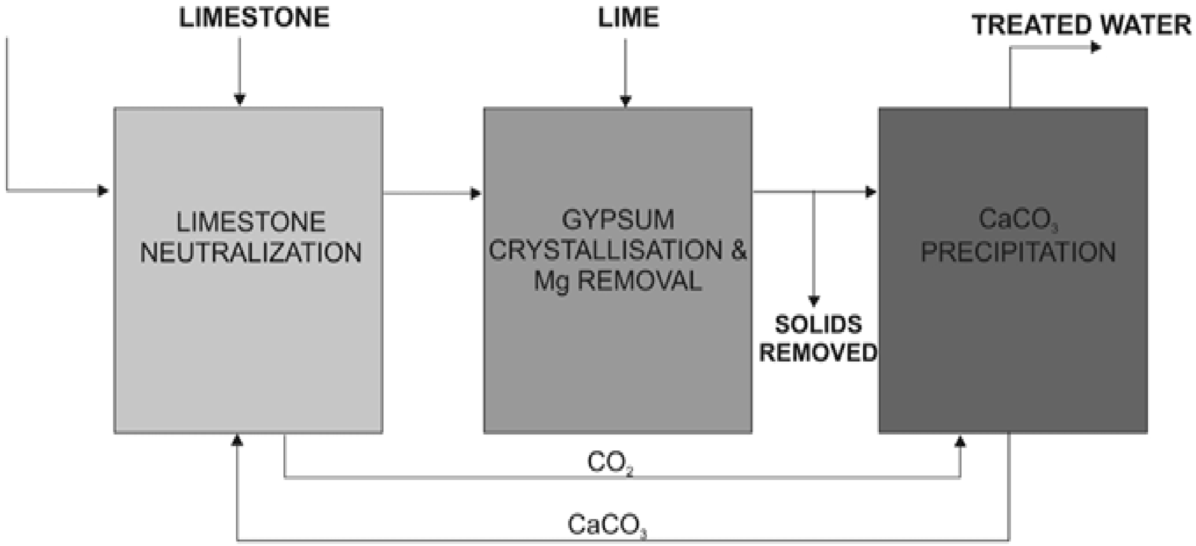


Figure 9: Gypsum precipitation process via lime/limestone addition (Geldenhuys 2004)

2.4.2. Ettringite precipitation

SAVMIN

This is a process during which sulphate removal is achieved through ettringite precipitation. This is a four-stage process as depicted in Figure 10. First, lime addition as pre-treatment removes metals as metal hydroxides. The second stage is the removal of gypsum through seed crystallisation. Stage three, is the addition of aluminium hydroxide in order to form insoluble ettringite ($3CaO.3CaSO_4.Al_2O_3.31H_2O$). The last step, before discharging the water, is to reduce the pH by the addition of carbon dioxide gas and simultaneously precipitate pure calcium carbonate. The ettringite that forms may be handled in one of two ways. One is to dispose of it as a waste product.

The other, is more profitable and requires the ettringite to be dissolved in sulphuric acid in order to recycle the aluminium tri-hydroxide. The process of recycling the aluminium tri-hydroxide complicates the process. Aluminium tri-hydroxide is also not very expensive and makes this option less attractive financially (Usinowicz et al. 2006). There are reports where plants have successfully treated 500 m^3 of wastewater that had a sulphate concentration of 800 mg/ℓ and reduced the concentration to less than 200 mg/ℓ (Bowell 2004).

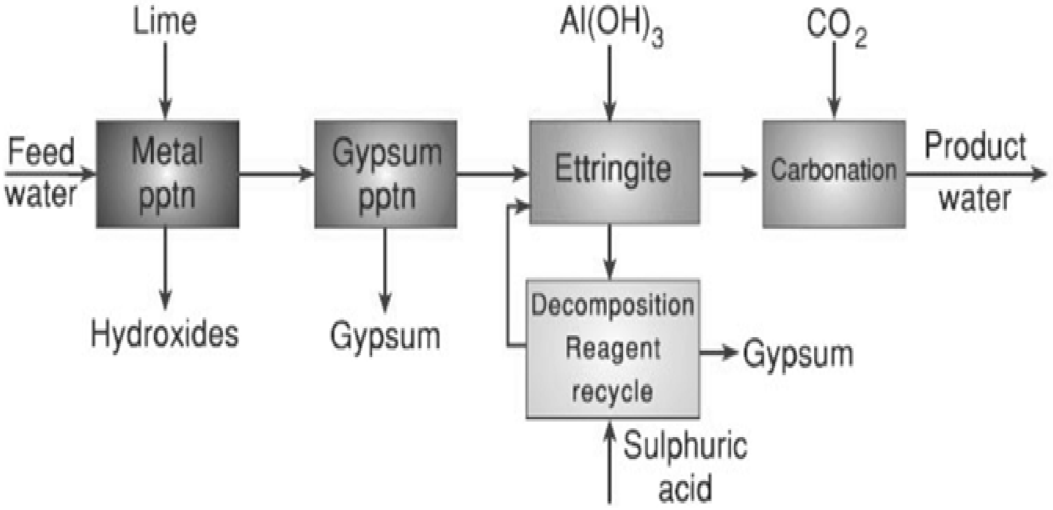


Figure 10: Flow diagram of the SAVMIN Process (McNee 2003)

"pptn" = precipitation

CESR (Cost Effective Sulphate Removal)

The CESR (Cost Effective Sulphate Removal) process is similar to the SAVMIN process since it is also based on ettringite precipitation. In addition to sulphate removal it also removes dissolved metals effectively (INAP 2003).

The process consists of three steps. First, hydrated lime is added to the feed water to induce gypsum precipitation. The pH of the wastewater is maintained at a level where metal precipitation is restricted and therefore the metal rich sludge volume is kept to a minimum. The non-hazardous gypsum sludge is separated from the water by dewatering and filtration. Second, additional lime is added to the water to raise the pH to 10.5 where metal hydroxide precipitation and additional gypsum formation will occur. In the final step the dissolved sulphate is removed. After adding more lime to raise the pH to 11.5, a proprietary reagent is added to precipitate ettringite (INAP 2003).

The more expensive SAVMIN process can reduce sulphate concentrations to very low levels; it can also remove trace metals from the AMD. The CESR processes are probably the most expensive and produce the largest amount of sludge. The primary difference between the SAVMIN process and CESR process is that the SAVMIN process uses aluminium hydroxide in the third step instead of the proprietary reagent used in the CESR process. Unlike the SAVMIN process, CESR does not recycle the ettringite (INAP 2003).

2.*4.3.* *Barite (barium sulphate) formation*

The removal of sulphate ions in the form of barium sulphate was first demonstrated to be effective more than 30 years ago (Kun 1972). Barite ($BaSO_4$) is highly insoluble with a k_{sp} value of 1.08×10^{-10} at 25°C (2.45 mg/ℓ), making it an excellent candidate to remove sulphate ions from wastewater (Kotz & Treichel, 2003). In this process barium salt is added to the sulphate-rich water. The barium salts commonly used include barium carbonate, barium sulphide and barium hydroxide. The reactions that take place are shown in Reaction 6, Reaction 7 and Reaction 8 (INAP 2003).

$$BaCO_3\,(s) + H_2SO_4 \rightarrow BaSO_4\,(s) + H_2CO_3 \qquad \textbf{Reaction 6}$$

$$Ba(OH)_2\,(s) + H_2SO_4 \rightarrow BaSO_4\,(s) + 2H_2O \qquad \textbf{Reaction 7}$$

$$BaS\,(s) + H_2SO_4 \rightarrow BaSO_4\,(s) + H_2S(g) \qquad \textbf{Reaction 8}$$

A greater quantity of sulphate is recovered when barium sulphide is used, but not as much gypsum is produced. However, hydrogen sulphide gas that has an unpleasant odour is produced (INAP 2003). The use of barium hydroxide is proposed for solutions where most metals have already precipitated as metal hydroxides (Bowell 2004).

Barium salts are expensive, thus, the barium sulphate sludge is often recycled and treated to reduce the costs. Additional income could be generated by selling the sulphur that can be recovered (INAP 2003).

2.5. CONCLUSION

A number of sulphate removal methods are available to industry. These include:

- Physical processes such as membrane filtration (RO, HiPRO, SPO, SPARRO, ED and EDR) and adsorption/ion-exchange processes (GYP-CIX Process),
- Biological processes (bioreactors and constructed wetlands), and
- Chemical precipitation (Barite formation, Gypsum and Ettringite precipitation).

For the present study, the barite precipitation method was chosen because the final sulphate concentration in the treated water can be controlled due to the low solubility of barium sulphate. As a consequence the final sulphate level can be reduced to less than 0.02 mg/ℓ.

CHAPTER 3: LITERATURE SURVEY ON BARIUM SULPHATE PRECIPITATION

3.1. INTRODUCTION

Barium sulphate precipitation as a sulphate removal method was effectively demonstrated more than 30 years ago (Kun 1972). Three main problems were identified with this method on an industrial scale: the requirement for more soluble barium in solution than is required stoichiometrically, long retention time and the high cost of barium salts. All three problems were solved.

The barite formation method forms part of the process developed and patented by the CSIR (Council for Scientific and Industrial Research) called the ABC (Alkali - Barium - Calcium) Desalination Process.

This process consists of two stages, namely the water-stage and the sludge handling-stage. In the sludge handling-stage the barium sulphate that is produced in the water-stage is converted to barium carbonate, which is then recycled back to the water-stage. The water-stage consists of three main processes. First the raw AMD undergoes a neutralisation and metal removal process. Second, gypsum crystallisation is induced by adding lime to the AMD. Partial sulphate removal occurs here and if the AMD contains magnesium, it will precipitate. In the final step the barium carbonate, recycled from the sludge handling-stage, is used to remove the residual sulphate still present in the treated AMD via barium sulphate precipitation or barite formation. The final product of the ABC Desalination Process is potable water. Most of the by-products generated can be recycled to a different part in the process, used in another process or sold. A flow diagram of this process is shown in Figure 11.

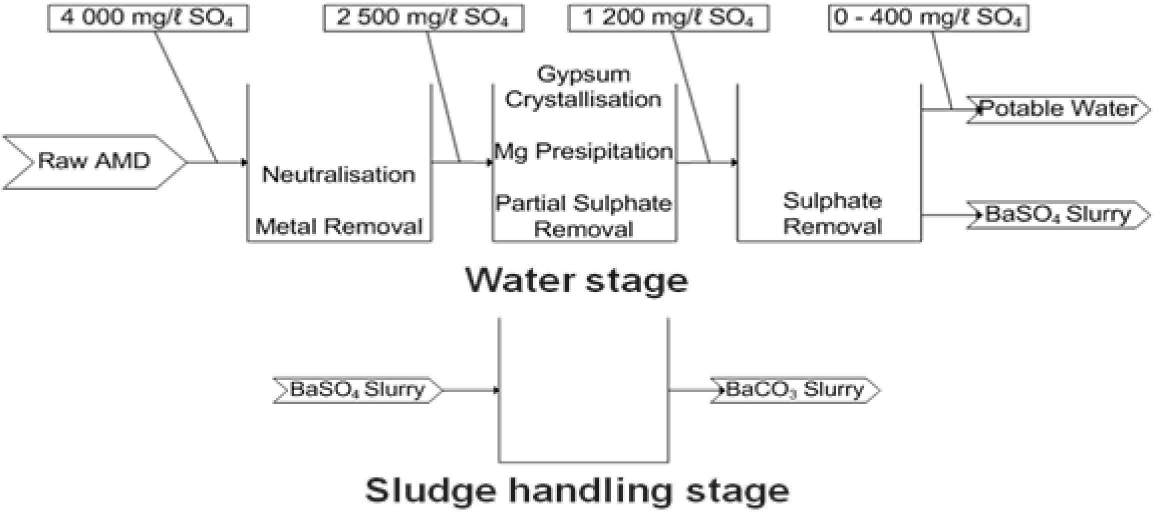


Figure 11: ABC Desalination Process flow diagram (Swanepoel 2011)

3.2. BATCH STUDIES

A number of parameters have been investigated and studied by other authors and are summarised in the following section.

3.2.1. Different barium salts

Barium sulphide, barium hydroxide and barium carbonate can be used to remove sulphate from wastewater that contains sulphate and calcium ions. Barium carbonate is favoured above barium sulphide because it does not require stripping of hydrogen sulphide gas from the solution (Hlabela et al. 2007). When barium hydroxide is used, a significant amount of calcium sulphate is (source) produced that increases the volume of sludge (Bowell 2004, Bologo et al. 2009, Bologo et al. n.d.).

The problem when using barium carbonate is that it becomes inactive when the particles are coated with metal hydroxides. Thus, the removal of metals form wastewater is required before sulphate precipitation occurs. It also required the separation of the barium sulphate from the calcium carbonate that co-precipitates in this process (Maree et al. 2004b).

Another compound that can be used to remove sulphate from wastewater is barium sulphide. In this process two by-products are produced, namely, sulphur and calcium carbonate (Bosman et al. 1990). A sulphate reduction of 95% is obtained and a variety of metals such as iron, nickel, cobalt and manganese are removed during experiments done at ambient temperature. The industrial water used to test this process was from the uranium process raffinate and AMD from a coal mine. Initially, this water was neutralised with lime/limestone and clarified before the sulphate was removed. The final sulphate content was reduced to less than 200 mg/ℓ (Bosman et al. 1990).

The barium sulphide process consists of the preliminary treatment with lime, sulphate precipitation as barium sulphate, hydrogen sulphide gas stripping, gypsum crystallisation and finally, the recovery of barium sulphide. During the lime neutralisation step, the sulphate concentration was reduced from 2 800 mg/ℓ to 1 250 mg/ℓ by means of gypsum crystallisation. The metals in the effluent were precipitated as metal hydroxides. The barium sulphide treatment stage then lowered the sulphate ions concentration to less than 200 mg/ℓ (Maree et al. 2004b).

The advantage of the barium carbonate process is that the sulphate levels can be reduced to specific values due to barium sulphate's low solubility. The soluble barium salts such as barium sulphide can be recovered as well. Three problems were identified with this process. First, a long retention time is required; second, the high concentration of soluble barium remaining in the treated water after the barium carbonate was over-dosed relative to the stoichiometric requirements of the reaction and, thirdly the high cost of the barium salt. To overcome the high cost problem, it was demonstrated that the barium sulphate can be reduced efficiently and economically with coal under high temperatures (± 1 050°C) to barium sulphide. This barium sulphide can then be either used directly on site or be converted to barium carbonate (Maree et al. 2004b).

Another study was done where barium sulphide was used. In this study lime treatment was incorporated as pre-treatment where the sulphate concentration decreased from 2 650 mg/ℓ to 1 250 mg/ℓ during work done at ambient temperature. During the barium sulphide treatment the sulphate concentration was lowered to 1 000 mg/ℓ (Maree et al. 2004b, Maree et al. 2004a).

Barium hydroxide can also be used. The Magnesium Barium Oxide (MBO) process consists of three steps: the metal removal stage, that uses magnesium hydroxide followed by the magnesium and sulphate removal stage, using barium hydroxide, and lastly, the calcium removal stage using carbon dioxide gas. The raw materials used in this process, magnesium hydroxide and barium hydroxide, can be recovered from the waste sludge that is produced, namely barium sulphate and magnesium hydroxide sludge. In this process the sulphate can be reduced to low concentrations (Bologo et al. 2009, Bologo et al. n.d.).

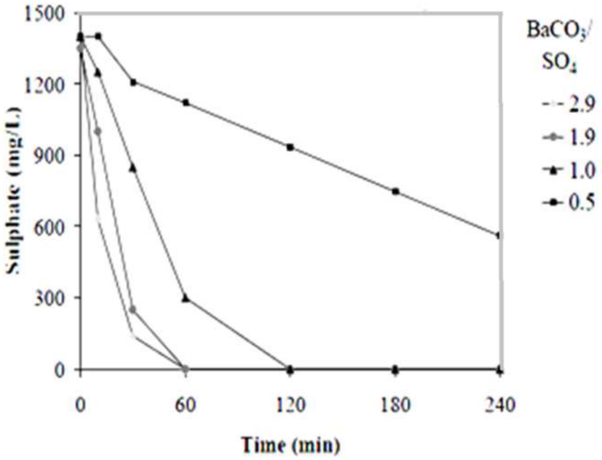
In the case where the MBO Process was used to treat a coal mine effluent, the sulphate levels were lowered from 2 493 mg/ℓ to 181 mg/ℓ by means of barium sulphate precipitation at ambient temperature. In the case where sulphates were removed from gold mine effluents the concentration remained unchanged during magnesium hydroxide treatment because of the high solubility of magnesium sulphate. During the next step in the MBO Process, barium hydroxide treatment takes place at a pH of 12. Most of the magnesium in the wastewater precipitated and only 1 mg/ℓ magnesium remained. Simultaneously, the sulphate concentration was lowered from 4 398 mg/ℓ to 24 mg/ℓ at ambient temperature by means of barium sulphate precipitation (Bologo et al. n.d.).

3.2.2. Different barium carbonate types

Two different types of barium carbonate were used to remove sulphate ions from sulphate-rich water. One was commercial barium carbonate imported from China and the other a barium carbonate produced in the laboratory. The commercial barium carbonate exhibited much slower reaction rates compared to the barium carbonate produced in the laboratory. The reasons for the differences in removal efficiency were not investigated (Motaung et al. 2009).

3.2.3. Kinetics

Reaction kinetic studies were reported in two different publications (Hlabela et al. 2007, Motaung et al. 2008). The sulphate concentrations of the samples taken over time that were used to determine this kinetics are shown in Figure 12. The reaction order of the sulphate removal process was determined by plotting the sulphate removal reaction rates against the barium carbonate concentrations on a log-log graph as shown in Figure 13. A reaction order of unity was found because the graph resulted in a straight line (Hlabela et al. 2007, Motaung et al. 2008).



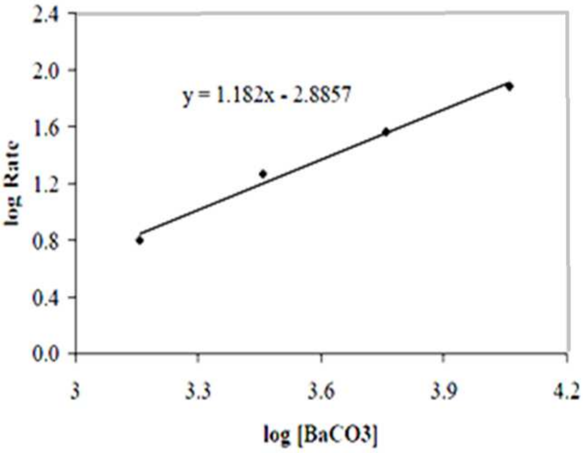


Figure 12: Sulphate removal profiles (for reaction kinetics) (adapted from Hlabela et al. 2007)

Figure 13: Log of SO_4^{2-} vs. log $BaCO_3$ concentrations (adapted from Hlabela et al. 2007)

3.2.4. Co-precipitation of calcium carbonate

A study was conducted with the aim of comparing sulphate removal efficiency when different sulphate salts are present in the effluent. Two different sulphate salts were used namely calcium sulphate and sodium sulphate. The sulphate concentration profiles as the sulphate is removed from the feed water are shown in Figure 14.

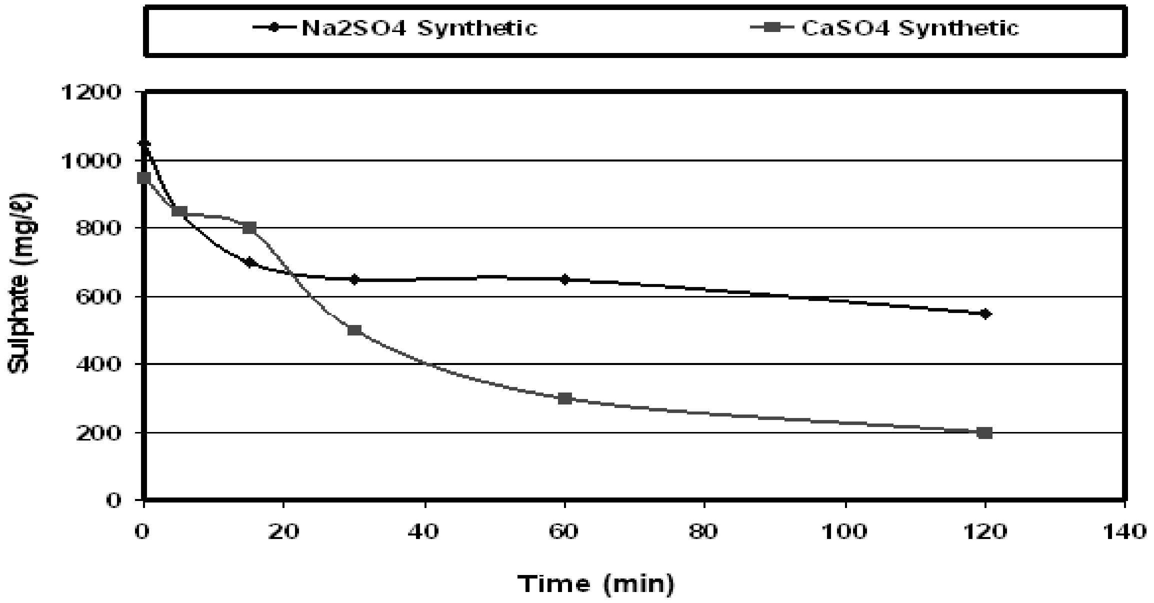


Figure 14: Different sulphate salts as sulphate sources (Motaung et al. 2009)

In the scenario where calcium sulphate was used in the solution the reaction proceeded quicker than in the case where sodium sulphate was used. The conclusion was reached that the cation coupled with the sulphate ion influenced the rate and amount of the sulphate being removed when barium carbonate is used (Motaung et al. 2009).

Another study indicated that sulphate can only precipitate as barium sulphate when barium carbonate is used after the magnesium ions are removed from the solution (Trusler et al. 1988). An investigation was launched to determine the effect on sulphate removal when the sulphate ions in solution were coupled with magnesium ions and when they were not. In the experiments where the magnesium was coupled with the sulphate ions, only the sulphate ions that were not coupled with magnesium, those coupled with calcium were removed.

The results are shown in Figure 15. In the experiments where the sulphate ions were not coupled with magnesium, almost complete sulphate removal was achieved irrespective of the magnesium concentration, as indicated in Figure 16. The conclusion was that the magnesium concentration only influenced the sulphate removal if it was coupled with sulphate ions; if not, then it will not interfere with the sulphate removal process (Hlabela et al. 2007, Hlabela et al. 2005). In short, the formation of magnesium sulphate ion pairs retards the rate of sulphate removal due to the greater solubility of magnesium carbonate (Trusler et al. 1991).

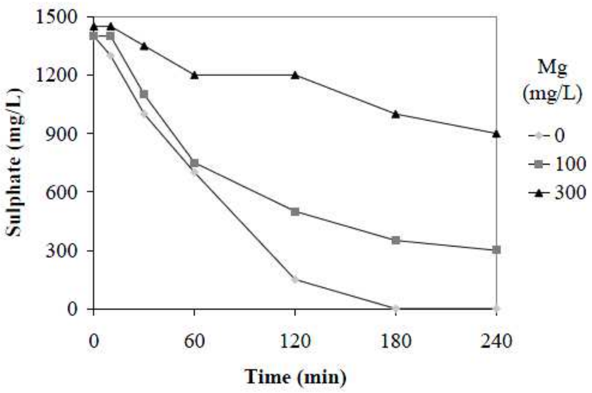


Figure 15: Magnesium-sulphate association (Hlabela et al. 2007)

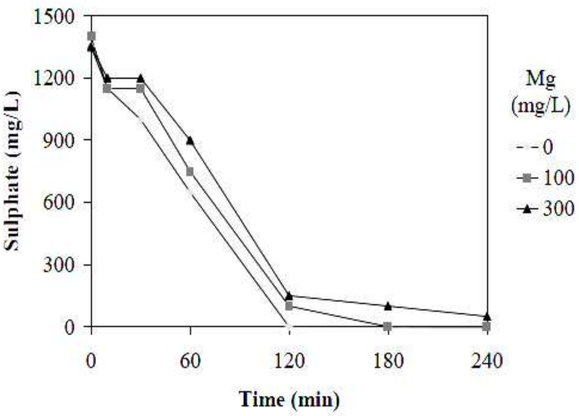


Figure 16: No magnesium-sulphate association (Hlabela et al. 2007)

The above was explained by Hlabela et al. (2007) as follows. The ionic compound, barium carbonate, dissolves partially, releasing barium ions to bind with the sulphate ions in the solution to precipitate as barium sulphate. Due to barium carbonate's low solubility, both the barium ions and the carbonate ions in the solution have to be removed, before the dissolution of the remainder solid barium carbonate particles can occur. The barium ions in the solution are removed through barium sulphate precipitation while the carbonate ions are removed through calcium carbonate precipitation (Hlabela et al. 2007, Hlabela et al. 2005).

3.2.5. Barium-to-sulphate molar ratios

The kinetics of the sulphate removal process is influenced by the amount of barium carbonate that is dosed into the feed water. The sulphate removal occurs faster when excess barium carbonate is used (Hlabela et al. 2007, Hlabela et al. 2005). In experimental work the sulphate level in the wastewater can be removed to a concentration lower than 200 mg/ℓ (at ambient temperature) in less than one hour (Motaung et al. 2009). Although the fast sulphate removal is favourable, it causes additional problems due to the fact that barium is toxic. Over-dosing of barium carbonate will result in excess barium in the final water product.

However, it takes about two hours to reduce the sulphate concentration to less than 200 mg/ℓ (at ambient temperature) when the barium carbonate was under-dosed. In both these cases the initial sulphate concentration in the feed water was 1 000 mg/ℓ. Taking the toxicity of barium into consideration, it is preferred to use a barium-to-sulphate ratio that is less than stoichiometric (Motaung et al. 2009).

3.2.6. Effect of temperature

Only one author mentioned the importance of temperature on the sulphate precipitation process. In general the higher the reactor temperature, the faster the sulphate removal rate became. Thus, the increase in the reaction rate at higher temperatures was significant in this process (De Beer et al. 2010).

3.2.7. pH effect

Sulphate removal is only slightly influenced by the pH of the process water (Herskovitz 2011, Hlabela et al. 2005). The removal rate decreases slightly with increased pH. This is due to the solubility of barium carbonate that decreases with increased pH (Hlabela et al. 2007, Hlabela et al. 2005).

Barium carbonate, with a solubility product (k_{sp}) of 2.58×10^{-9}, is scarcely soluble in water. For sulphate precipitation to occur when barium carbonate is added to the feed water, the barium carbonate should be dissociated. The dissociation of barium carbonate is dependent on the solution pH as shown in Figure 17. The lower the pH of the solution, the more barium carbonate dissociates and becomes available for the sulphate removal process (Motaung et al. 2009). Thus, it is expected that the sulphate removal rate will be slower at a higher pH because of the lower barium ion concentration (Motaung et al. 2008). This is supported by the results illustrated in Figure 18.

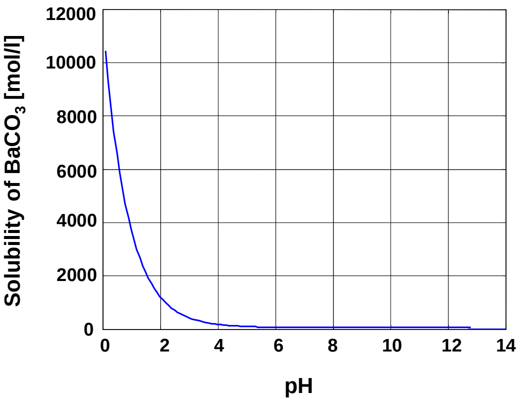


Figure 17: pH dependency of $BaCO_3$ solubility (Motaung et al. 2009)

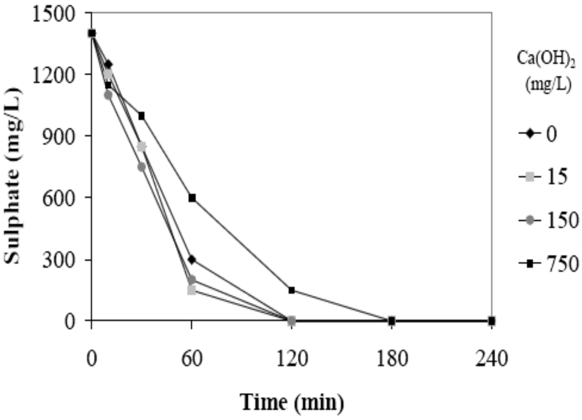


Figure 18: Effect of pH on sulphate removal (Hlabela et al. 2005)

3.3. CASE STUDIES

Three case studies are discussed in this section. The sulphate removal process was tested and verified on AMD, zinc plant effluent and power station cooling-water effluent.

The sulphate removal from AMD using commercial barium carbonate was carried out before the magnesium was removed. Sulphate ions were removed from the AMD that contained 120 mg/ℓ magnesium. The sulphate concentration in the feed water was reduced from about

2 000 mg/ℓ to 500 mg/ℓ with a stoichiometric barium-to-sulphate molar ratio and a four hours run time. But, when synthetic barium carbonate was used on the feed water from which the magnesium had been removed, a significant amount of sulphate was removed. The sulphate was reduced from 2 000 mg/ℓ to less than 500 mg/ℓ even when the barium carbonate was under-dosed (Motaung et al. 2009).

In the second case study, it was seen that by treating zinc plant effluent with barium carbonate the effluent was effectively neutralised. Also, all the zinc and most of the calcium and manganese were removed. The sulphate concentration could not be sufficiently reduced from this feed water within the three-hour experimental run time. But when this effluent was treated with lime prior to the barium carbonate dosing stage, the sulphate, zinc and cadmium in the feed water were almost completely removed (Trusler et al. 1991).

In the last case study, the sulphate removal from power station cooling-water was investigated. In contrast to AMD, the sulphate removal with barium carbonate was less effective if lime was added. Reducing the pH of the feed water with sulphuric acid appeared to aid the sulphate and calcium removal process. It appeared as though some additives to the power station cooling-water, such as anti-scalants and/or anti-bacterial agents, had a significant impact on the sulphate removal process (Trusler et al. 1991).

3.4. CONCLUSION

The sulphate removal literature based on barite formation was investigated. This sulphate removal method is part of the process developed and patented by the CSIR known as the ABC Desalination Process. In this process the sulphate in the AMD is removed by barium sulphate precipitation when a barium carbonate is added to the effluent. The sulphate removal can be controlled due to the very low solubility of barium sulphate. It can even be removed completely if required.

A number of experiments have previously been carried out and these results and conclusions were documented. These investigations covered parameters such as:

- Different barium compounds such as barium sulphide, barium hydroxide and barium carbonate,
- Different barium carbonate types such as commercial imported barium carbonate form China and laboratory-produced, synthetic barium carbonate,
- The kinetics of the sulphate removal process,
- Co-precipitation of calcium carbonate,
- Barium-to-sulphate molar ratios,
- The effect of temperature on the sulphate removal process, and
- The effect of pH on the sulphate removal process.

Three case studies were discussed where the sulphate removal process was tested and verified on AMD, zinc plant effluent and on power station cooling-water.

CHAPTER 4: SULPHATE REMOVAL EXPERIMENTS

4.1. INTRODUCTION

Barium salts are successfully used to remove sulphate from AMD. When barium carbonate is added to the AMD, a white precipitate will form. The precipitate is barium sulphate and calcium carbonate, both insoluble compounds. The operating parameters were investigated.

These parameters were all tested using a batch reactor setup. The results of these experiments were then tested and verified on AMD. The sulphate removal reaction that takes place is given by Reaction 9.

$$CaSO_4(aq) + BaCO_3(s) \rightarrow CaCO_3(s) + BaSO_4(s)$$ **Reaction 9**

4.2. EXPERIMENTAL METHOD

4.2.1. Chemicals and equipment

The chemicals and equipment used during the experimental work are listed in Table 1. Calcium sulphate (Merck) was used to prepare synthetic sulphate feed water. Three different types of barium carbonate were used to remove the sulphate from the sulphate-rich water as listed in Table 1. AMD from a coal mine was used to verify the results from the synthetic feed water experiments. The experimental setup is described in more detail in Paragraph 4.2.4.

Table 1: Chemicals and Equipment for experimental work

Chemicals	**Equipment**
• $BaCO_3$ (Imported from China (CIF Durbsan)) • $BaCO_3$ (Produced in the laboratory) • $BaCO_3$ (Recycled from the ABC Desalination Process) • $CaSO_4$ (Merck) • Distilled Water • Process water (AMD from a coal mine)	• 100 ml Glass beaker • 100 ml Measuring cylinder • 1ℓ Measuring cylinder • 2ℓ Measuring cylinder • Computer (download data from Multimeter datalogger) • Funnels • Magnetic stirrer with magnetic bar • Multimeter Datalogger with measuring probe • Overhead agitator with impeller • Perspex reactor with baffles (3 ℓ) • Pipette for sampling • Sample bottles • Stop watch • Whatman nr 1 filter paper

4.2.2. Synthetic sulphate water

Several laboratory experiments were conducted where barium carbonate was used to remove sulphate ions from sulphate-enriched water. Synthetic sulphate water was prepared by dissolving calcium sulphate in distilled water to determine the effect that different parameters have on this process. All of these experiments were done in a batch reactor configuration on laboratory scale. After the optimum operation conditions were determined, this sulphate removal method was tested on AMD. The parameters that were investigated included:

- The effect of mixing on sulphate removal,
- The effect of initial sulphate concentration in the feed water,
- The barium (Ba^{2+}) (dosed as barium carbonate) to sulphate (SO_4^{2-}) (present in the feed water) molar ratio,
- The effect of temperature on the entire sulphate removal process, and
- Barium carbonate morphology.

4.2.3. Barium carbonate

Barium carbonate from two different sources was used to determine whether the barium carbonate characteristics, such as its crystal surface structure or morphology, had an effect on the sulphate removal process. One source of barium carbonate is commercially available and was imported from China. The other barium carbonate source was prepared in the laboratory.

In an effort to confirm the importance of the barium carbonate crystal structure used to remove sulphate from water, a separate set of experiments was conducted. In these experiments barium carbonate was produced through a carbonation process where barium sulphide is carbonated with carbon dioxide gas. Different batches of barium carbonate were produced each under a unique set of conditions; this ensured that each batch of barium carbonate had a different crystal structure and surface area. The investigation was aimed at confirming whether or not all barium carbonate is equally effective in removing sulphate ions from sulphate enriched water and whether certain crystal characteristics are more favourable than others.

4.2.4. AMD (Acid Mine Drainage)

The AMD was collected from a coal mine. The selected sulphate removal method was used to determine how the optimised parameters, from the synthetic sulphate-enriched water experiments, would work on authentic industrial effluents. An industrial effluent, at different pH levels, was used to confirm whether this method was applicable to industrial water.

4.2.5. Batch reactor

For the batch experiments, a 3 ℓ reactor equipped with baffles was used together with an overhead agitator. First the required amount of calcium sulphate was dissolved in distilled water to prepare a sulphate-rich solution. During the experiments, sulphate ions were removed in order to determine to what extent the sulphate could be precipitated under the specific operating conditions. Barium carbonate slurry (approximately 100 ml) was simultaneously prepared in a small beaker adjacent to the reactor. Barium carbonate has a low solubility, and approximately 10 min. mixing time was required to ensure that the maximum amount of barium carbonate had dissolved into the distilled water before it was added to the sulphate-rich solution, as experimentally determined beforehand. The concentration of the barium carbonate slurry, after adding it to the sulphate-rich water, depended on the sulphate concentration of the sulphate-rich water.

After sufficient mixing of the barium carbonate slurry, it was added to the sulphate-rich solution to initiate the sulphate removal process. During this process the pH, temperature and electrical conductivity (EC) were continuously measured using a multiple parameter probe that recorded and stored the data. At EC-dependent time intervals, samples were collected for sulphate and barium analysis (Turbidimetric method) (APHA 1992). Figure 19 is a photograph of the reactor setup in the laboratory before the addition of barium carbonate.

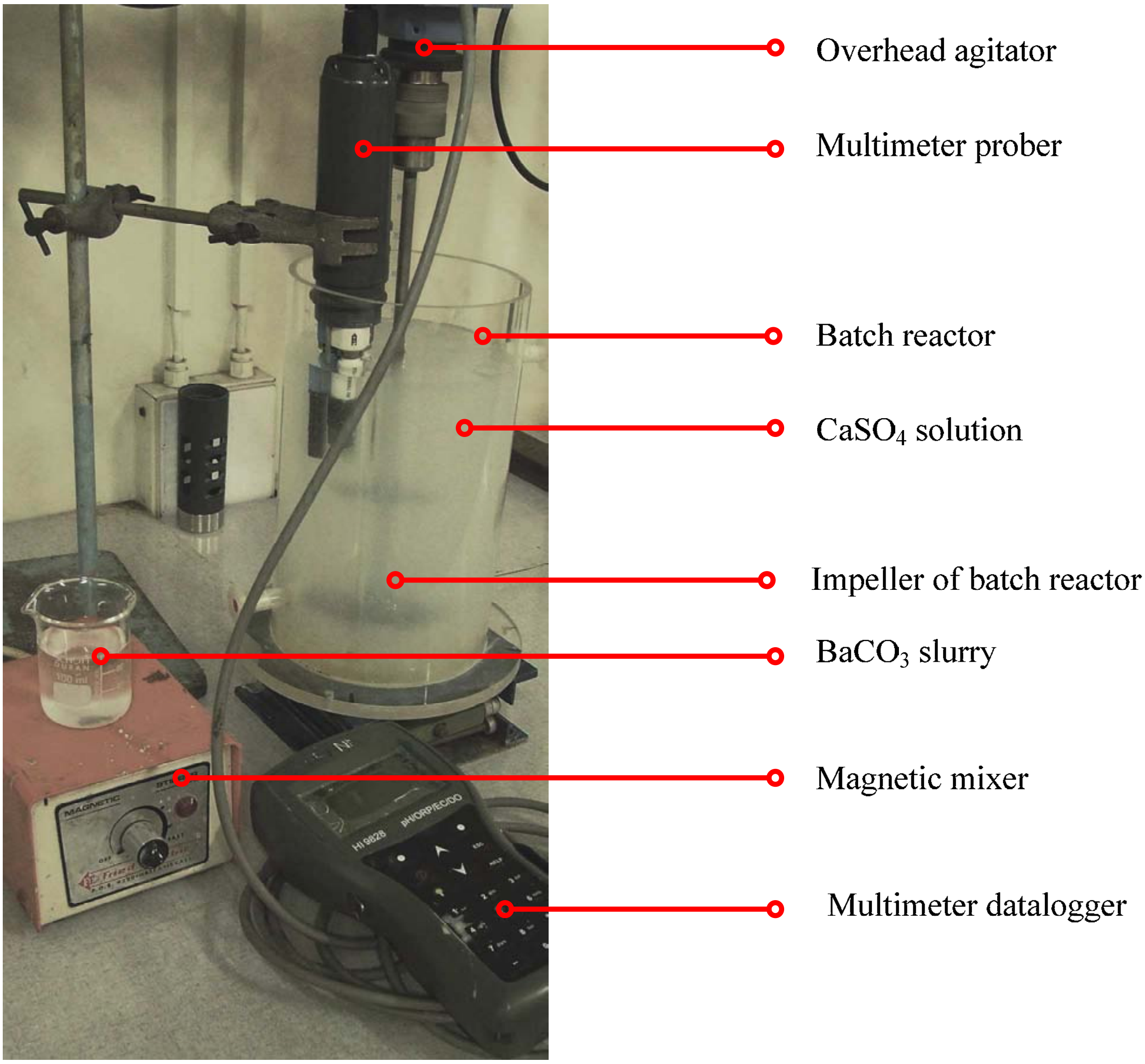


Figure 19: Laboratory setup before barium carbonate addition

A detailed description and the limitations of all the measuring equipment used during the experiments are available in Appendix A.

Numerous experiments were conducted to determine the effect of different parameters on the sulphate removal process. These included:

- Different barium-to-sulphate molar ratios (Ba^{2+}/SO_4^{2-} equal to 0.50, 0.75, 1.00, 1.25 and 1.50, respectively);
- Initial sulphate concentrations (400 mg/ℓ, 800 mg/ℓ, 1 200 mg/ℓ, 1 600 mg/ℓ and 2 000 mg/ℓ, respectively);
- The mixing rotation speed of the impeller (60 min^{-1}, 160 min^{-1}, 260 min^{-1}, 350 $min^{-1}$and 450 min^{-1}, respectively);
- The reactor temperature (commercial barium carbonate: 13°C and 34°C,respectively; laboratory produced barium carbonate: 14°C, 21°C and 34°C, respectively); and
- Using barium carbonate from different sources. These included industrial grade barium carbonate imported from China, recycled barium carbonate from the ABC Desalination Process (De Beer et al. 2010) and barium carbonate produced under different conditions in the laboratory during the carbonation of barium sulphide with carbon dioxide gas.

4.2.6. Electrical conductivity (EC) correlation

The reaction progress of the sulphate ion removal process was followed by electrical conductivity (EC) measurement. Only four chemical compounds were present in the solution during the testing of sulphate removal from synthetic-sulphate water, namely calcium sulphate, barium carbonate, calcium carbonate and barium sulphate. All four of these chemicals are a white powdery substance. The calcium sulphide was the source of sulphate ions. The barium carbonate was added to the sulphate solution in order to precipitate sulphate from the solution. Calcium carbonate and barium sulphate formed as products during the chemical reaction.

Due to the low solubility of barium carbonate, barium sulphate and calcium carbonate it was assumed that these three compounds were present in their solid, crystal form. The assumption was supported by analysing the feed solution for barium ions (< 0.02 mg/ℓ) and sulphate ions (1 600 mg/ℓ). Therefore, the majority of the dissolved ions in the solution originated from the dissolution of calcium sulphate. Since the calcium ions and the sulphate ions were both removed from the solution during the sulphate removal process, it was assumed to be realistic to track the sulphate reduction with EC measurements (Swanepoel et al. 2011).

The above correlation makes sense because the conductivity of a solution is the result of the ion charge within the solution (Perry et al. 1997). Thus, when the EC values stabilise it implies that the reaction could be considered complete, i.e., the sulphate removal process had progressed to a point where no more sulphates could be removed from solution.

An experiment was conducted to establish the correlation between the sulphate concentration in the solution and its EC value. The sulphate removal profile correlated very well with the EC profile, by inspection, as shown in Figure 20.

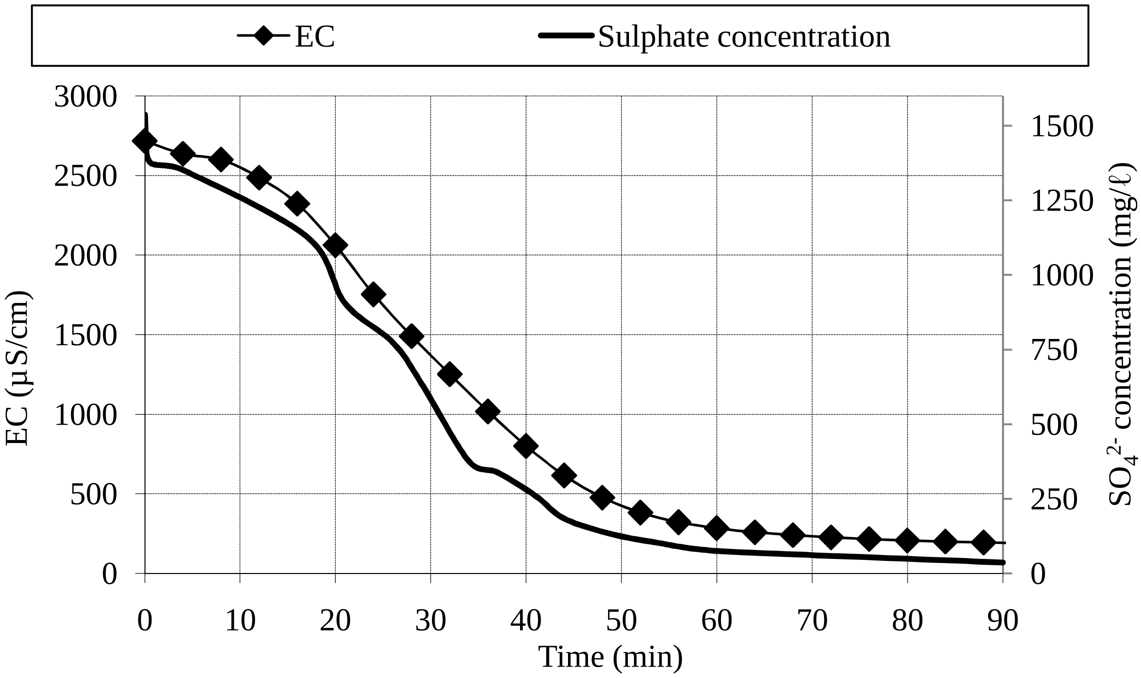


Figure 20: The sulphate concentration and EC profile correlation

The experimental parameters were as follows. The initial sulphate concentration in the sulphate-rich water was 1 600mg/ℓ and the mixing rotational speed was 350 min^{-1}. The reactor temperature was constant at ambient temperature (21°C ± 1.5°C). Laboratory produced barium carbonate was used and the dosing ratio was stoichiometrically equal to the sulphate present in the solution. After 90 min. the sulphate concentration was reduced by 97.7% (36 mg/ℓ) according to sulphate analyses.

Different models were used to find the mathematical relationship between the EC values and the sulphate concentrations. The numerical relation between these two profiles was determined by plotting the EC values against the sulphate concentrations, as shown in Figure 21. The EC measurements (and also the temperature and the pH of the solution) were recorded and stored by a Hanna Data Logger (Hanna Instruments HI 9828). Sulphate analyses were conducted by an SANAS accredited laboratory (Waterlab (Pty) Ltd, Persequor Park, Pretoria). These different models are listed in Appendix B.

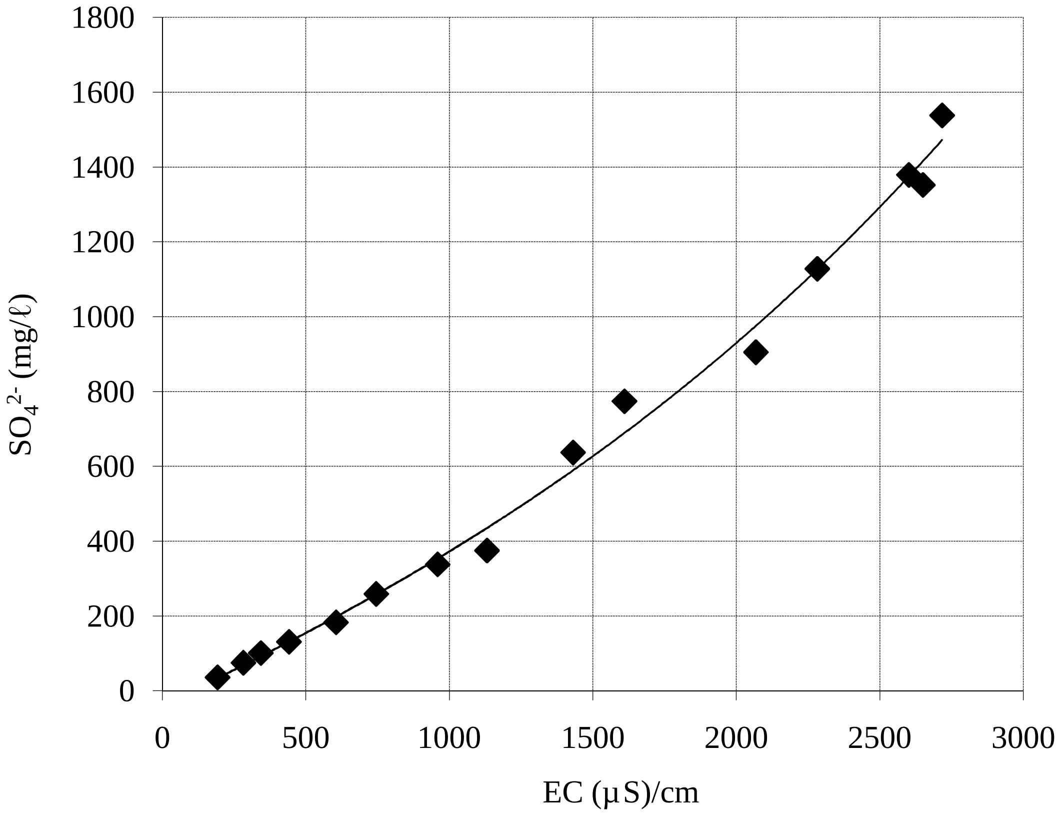


Figure 21: Sulphate concentration – EC correlation

From Figure 21 it was concluded that the relationship between the sulphate concentration changes and the EC changes in the solution are represented by a third order polynomial equation (Equation 1). This empirical formula enabled the sulphate concentration of the solution to be calculated in mg/ℓ from the EC (µS/cm) values.

$$[SO_4^{2-}] = (2 \times 10^{-8})\, EC^3 + (3 \times 10^{-5})\, EC^2 + \; 0.3678\, EC - \; 37.877 \qquad \textbf{Equation 1}$$

The difference between the measured and calculated values was 0.1%. According to the above mathematical expression the sulphate concentration was reduced by 97.9%. The measured and calculated results are given in Table 2.

Table 2: Model comparison

	SO_4^{2-} measured by analysis (mg/ℓ)	**SO_4^{2-} calculated (mg/ℓ)**
Initial value	1538	1584
Final value	36	34
% removal	97.8	97.9

Owing to limited funding granted for this project, the sulphate concentration levels were established by logging the EC values of the solution. Equation 1 was used to calculate the sulphate concentration of the solution instead of sending the samples to a SANAS accredited laboratory.

4.2.7. Repeatability

The repeatability of the sulphate removal process was determined by repeating the same experiment twice under identical conditions within the boundaries of experimental error. The experimental parameters for these experiments were as follows. The initial sulphate concentration in the sulphate-rich water was approximately 1 000mg/ℓ and the mixing rotational speed was 350 min^{-1}. The reactor temperature was constant at ambient temperature (21°C ± 1.5°C). Laboratory produced barium carbonate was used and the dosing ratio was stoichiometrically equal to the sulphate present in the solution.

The repeatability was excellent as can be seen in Figure 22 and Figure 23. The EC profiles for the three separate experiments are shown in Figure 22. From this figure it was evident that the three graphs were superimposed. In Figure 23 the pH profiles of the three experiments are shown and again, by inspection, the three graphs were identical. Statistical analyses were, therefore, performed to confirm this.

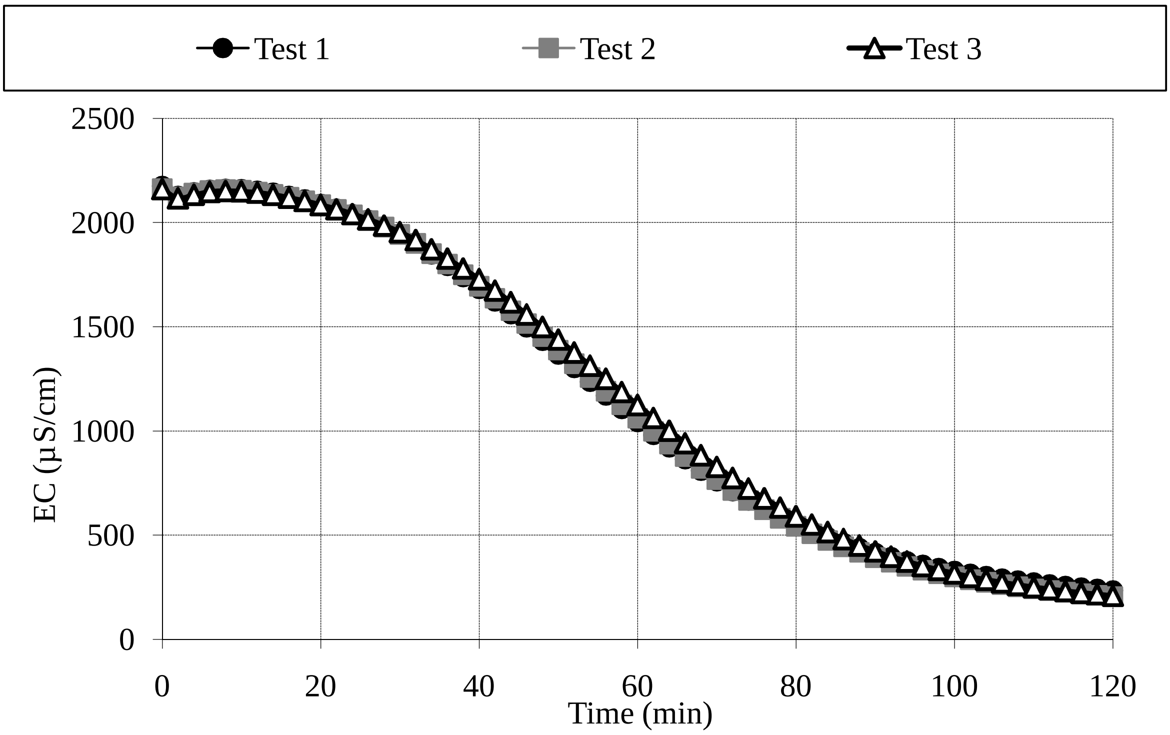


Figure 22: EC profiles tested for repeatability with three replications

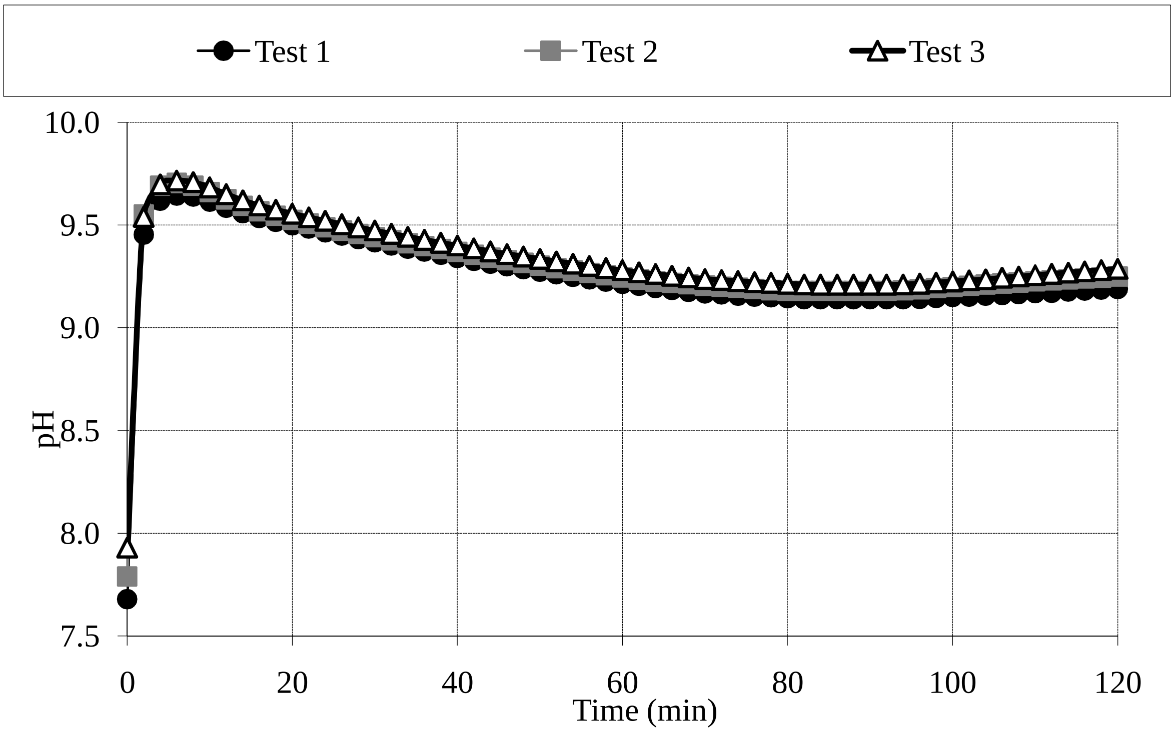


Figure 23: pH profile repeatability after three replications

The calculated initial and final sulphate concentrations for each of these experiments are given in Table 3. The percentage sulphate removal for each experiment was calculated in order to determine the average sulphate concentration as well as the variance.

Table 3: Repeatability of sulphate removal experiment

	Test 1	**Test 2**	**Test 3**	**Standard deviation**	**Variance**
Initial SO_4^{2-} (mg/ℓ)	1037.10	1028.95	1026.91	5.392	29.070
Final SO_4^{2-} (mg/ℓ)	26.15	36.21	35.77	5.685	32.324
% SO_4^{2-} removal	97.4	96.4	96.4	0.577	0.333

The average sulphate removal was 96.7%. The standard deviation was 0.577 and the variance 0.333. The variance gives an indication of the dispersion of the data. Thus, the greater the variance of the data is, the larger the deviation from the mean. The low variance of 0.333 amongst the three tests therefore indicated a small deviation from the average of 96.7%. The standard deviation records the actual distribution of the mean. Even though the test was replicated only three times, the low standard deviation gives proof of consistent test results around the mean. Thus, this process was considered to be repeatable.

4.3. RESULTS AND DISCUSSION

4.3.1. Barium-to-sulphate molar ratios

The ratio of dissociated barium ions from the barium dosed as barium carbonate relative to the sulphate ions present in the feed water will influence the sulphate removal process. This was investigated under laboratory conditions and the results are presented in Figure 24. The initial sulphate concentration was kept constant in these experiments while the barium carbonate slurry concentration added to the feed water was varied (Swanepoel et al. 2011).

The experimental parameters for this experiment were as follow. The initial sulphate concentration in the sulphate-rich water was 1 600mg/ℓ and the mixing rotational speed was 350 min^{-1}. The reactor temperature was kept constant at ambient temperature (20°C ± 1.5°C). Laboratory produced barium carbonate was used. The dosing ratios were varied from an under-dosed 0.5 dosing ratio to over-dosed 1.5 dosing ratio.

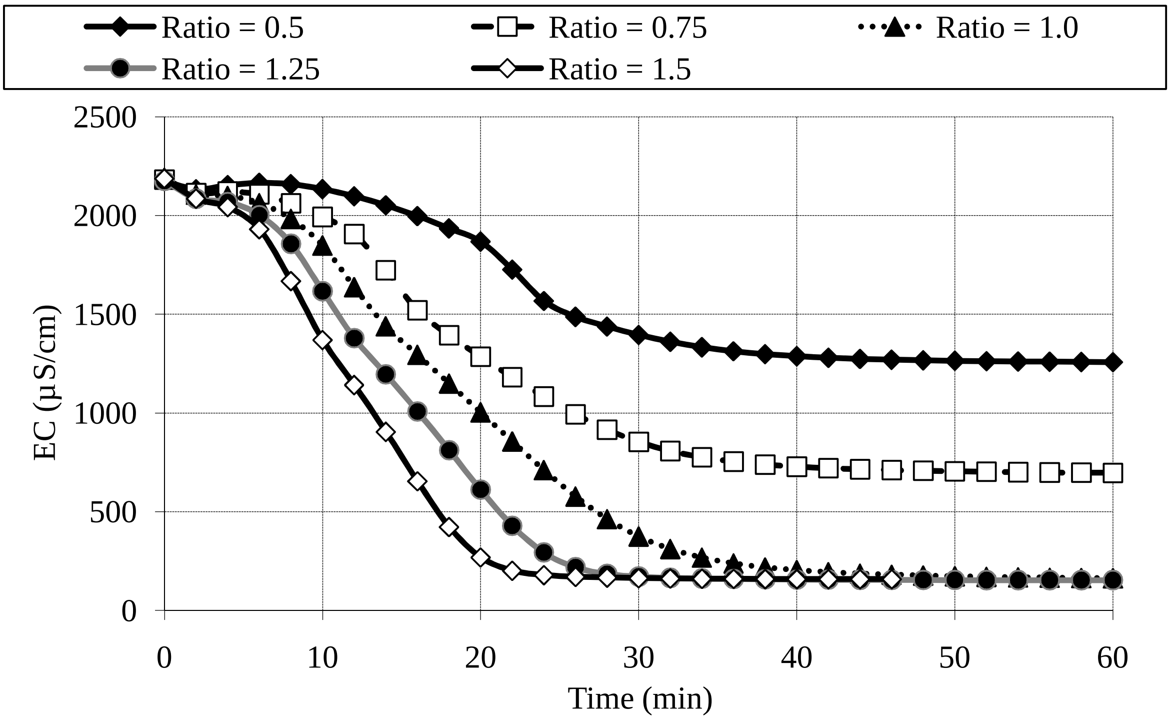


Figure 24: The effect of barium-to-sulphate molar ratio

In the first two experiments the barium ions were under-dosed (i.e., the barium-to-sulphate ratio was less than stoichiometric ($[Ba^{2+}]/[SO_4^{2-}] < 1$)). It was found that only partial sulphate removal could be achieved, because there were not enough barium ions available to react with all the sulphate ions present in the feed water. During the first experiment, of Figure 24, the barium to sulphate dosing ratio was 0.5, which lowered the sulphate concentration by 68.0%. In a second experiment the ratio was set to 0.75. This led to a reduction of the sulphate concentration by 85.8%.

In the last two experiments of Figure 24, the barium ions were over-dosed in comparison with the sulphate ions present in the feed water (i.e., where the barium-to-sulphate ratio was greater than stoichiometric ($[Ba^{2+}]/[SO_4^{2-}] > 1$)). In these cases almost complete sulphate removal was achieved. For the 1.25 dosing ratio and 1.5 dosing ratio the sulphate removals were 98.2% and 98.1%, respectively. The maximum of sulphate that can be removed from the sulphate-rich water is approximately 98% (See Appendix A).

The slopes of the graphs are an indication of how rapidly the reaction took place. Therefore, the steeper the slope of the graph, the shorter the time required to achieve maximum sulphate removal. According to Figure 24, by over-dosing the barium, the sulphate removal process accelerates. This is beneficial since a shorter reaction time requires a smaller reactor (at a constant flowrate), which leads to lower construction costs. However, a major disadvantage of over-dosing is the resulting excess of barium compounds in the end product. This is a major concern and highly undesirable since barium is very toxic to humans and animals (Sciencelab 2010). Barium carbonate is slightly soluble with a k_{sp} value of 2.58×10^{-9} (Kotz et al. 2003), but even at low concentrations the barium in the waste stream may have serious environmental impacts.

When the barium carbonate is dosed in stoichiometric ratio (i.e. $[Ba^{2+}]/[SO_4^{2-}] = 1$), it was found that the sulphate concentration was reduced to about the same final concentration (98.0% sulphate removal) as in the case where barium was over-dosed. The most important advantage is that there is a negligible concentration of barium in the final product stream, 0.04 mg/ℓ according to analysis done by an accredited laboratory (CSIR, CAS) (Swanepoel et al. 2011).

4.3.2. *Effect of initial sulphate concentration*

The initial sulphate concentration of the AMD could influence the sulphate removal process. Therefore, experiments were conducted to determine its effect on the process. The results of these experiments, where the initial sulphate concentration of the feed water were varied whilst a stoichiometric amount of barium as barium carbonate was dosed, are shown in Figure 25.

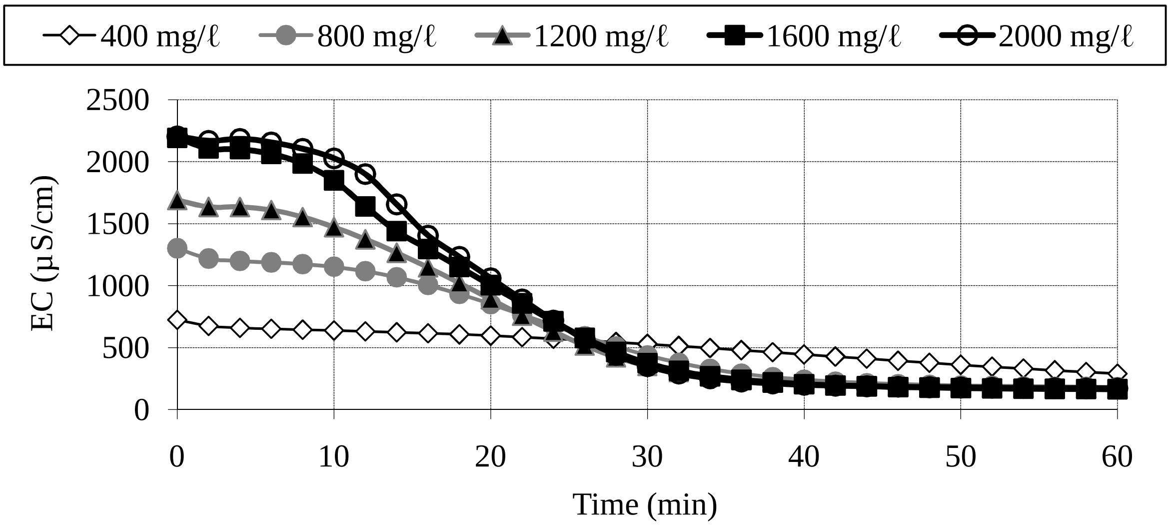


Figure 25: The effect of initial sulphate concentration

The experimental parameters were as follows. The initial sulphate concentration was varied for each experiment. The mixing rotational speed was 350 min^{-1}, while the reactor temperature was constant at ambient temperature (21°C ± 1.5°C). Laboratory-produced barium carbonate was used and the dosing ratio was equal to the stoichiometric relationship.

Only a limited amount of calcium sulphate, also known as gypsum, can be dissolved in distilled water since its solubility constant (k_{sp}) is 4.93×10^{-5} at 25°C. It also depends on the composition and ionic strength of the solution. Thus, gypsum's solubility ranges between 1 500 mg/ℓ and 2 000 mg/ℓ at 25°C (Kotz et al. 2003). This is supported by the fact that the initial EC was the same for experiments with initial sulphate concentrations of 1 600 mg/ℓ and 2 000 mg/ℓ, according to Figure 25 (Swanepoel et al. 2011).

When more gypsum was added to the feed water than the amount that could be immediately dissolved, solid gypsum particles were present in the reactor. The dissolved calcium sulphate reacted with the barium carbonate. As the dissolved gypsum reacted (thus decreasing in concentration), the solid gypsum particles dissolved. Thus, causing the dissolved gypsum concentration to increase until all the solid gypsum particles have dissolved. Up to that point the actual dissolved gypsum concentration in the solution was constant. Only after all the solid gypsum particles had dissolved, could a change in sulphate concentration (and EC values) be observed. This explains the delay in sulphate concentration lowering in the experiments having an initial sulphate concentration of 1 600 mg/ℓ and 2 000 mg/ℓ in Figure 25.

The final sulphate removal percentages for these experiments were 92.8% (400 mg/ℓ SO_4^{2-}), 96.3% (800 mg/ℓ SO_4^{2-}), 97.8% (1 200 mg/ℓ SO_4^{2-}), 98.6% (1 600 mg/ℓ SO_4^{2-}) and 98.7% (2 000 mg/ℓ SO_4^{2-}). From this it was found that the amount of sulphate removed from the effluent was very nearly the same after 45 min, i.e. almost maximum sulphate removal. The only differences seemed to be in the slope of the graphs, and hence the rate at which the sulphate was removed from the water. For higher initial sulphate concentration the sulphate removal rate was faster. Therefore the amount of sulphate removed from the sulphate-rich water was independent of the initial sulphate concentration; only the rate of the sulphate removal process was affected.

4.3.3. Effect of the mixing rotational speed

The effect of reactor stirring rate on sulphate removal is shown in Figure 26. Sulphate removal was affected only at very low mixing rotational speeds (60 min^{-1}). At higher mixing rotational speeds, almost no differences in the sulphate removal profiles were visible. It seemed that a slow mixing rotational speed (60 min^{-1}) was insufficient. The lower sulphate removal using this low stirring rate was probably due to the amount of solids that accumulated beneath the impeller of the overhead agitator, that were not participating in the reaction due to insufficient contact time with the sulphate solution. At the higher mixing rotational speeds all the solid particles had sufficient contact time with the sulphate feed solution, and better sulphate removal occurred.

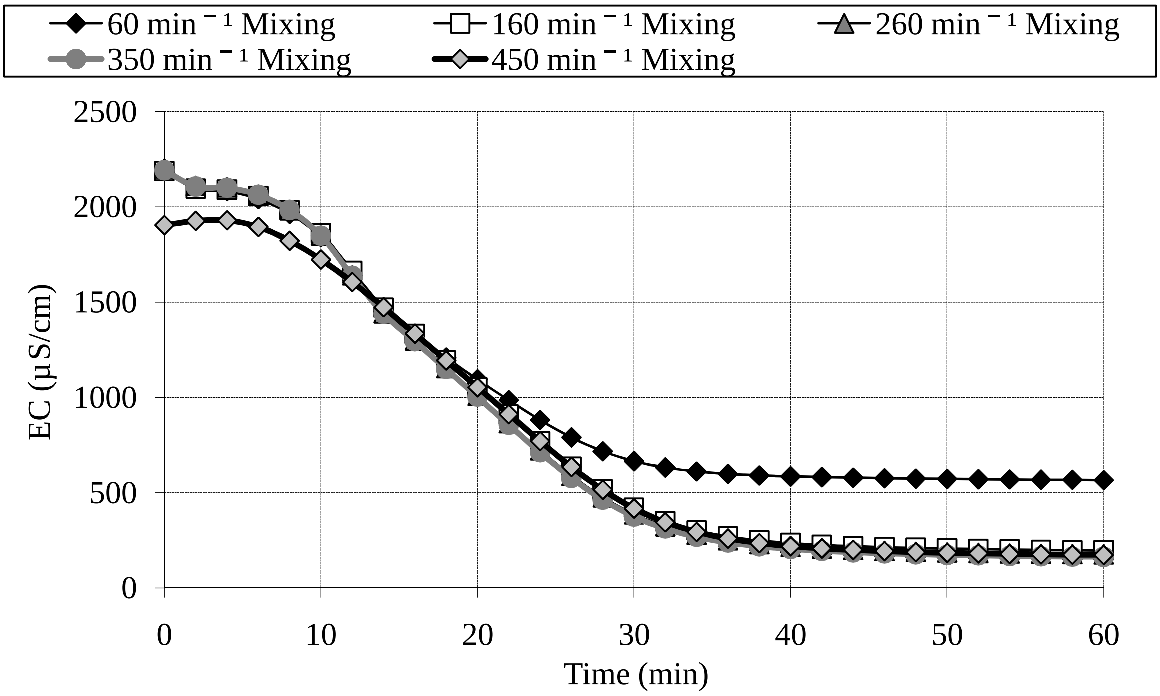


Figure 26: The effect of reactor mixing rotational speed

For these experiments the initial sulphate concentration was 1 600 mg/ℓ. The mixing rotational speed of each experiment was different while the reactor temperature was constant at ambient temperature (20°C ± 1.5°C). Laboratory produced barium carbonate was used and the dosing ratio was equal to the stoichiometric relationship.

Only 88.7% sulphate removal was obtained at a mixing rotational speed of 60 min^{-1} while sulphate removal percentages of 97.8%, 98.3%, 98.6% and 98.3% were obtained for the mixing rotational speeds of 160 min^{-1}, 260 min^{-1}, 350 min^{-1} and 450 min^{-1}, respectively. Thus, the sulphate removal percentage decreased by more than 10% at a mixing rotational speed of 60 min^{-1} in comparison to the higher mixing rotational speeds of 160 min^{-1}.

4.3.4. Effect of temperature

In general it was found that the higher the reactor temperature is, the faster the reaction rates are (Levenspiel 1999). But some reactions are more sensitive to temperature changes than others. This precipitation reaction was found to be very sensitive to temperature changes. Because temperature is a difficult parameter to control on laboratory scale, this investigation was carried out using barium carbonate from two different sources in order to confirm the results. The first barium carbonate was a commercially available material imported from China. The second barium carbonate had been produced in the laboratory where a barium sulphide solution was carbonated as described in Paragraph 4.2. (Swanepoel et al. 2011).

Barium carbonate from China

The effect of temperature on sulphate removal using barium carbonate from China was investigated. The results are shown in Figure 27 and Figure 28. The first experiment was conducted at a temperature of 13°C and the second at 34°C. These two temperatures were the limits of the thermostat bath that was used. The minimum temperature that could be reached and sustained on this particular day with this particular thermostat bath was 13°C and the maximum temperature was 34°C.

The initial sulphate concentration for these two experiments was 1 600 mg/ℓ. The mixing rotational speed was 350 min^{-1}. The dosing ratio of the barium-to-sulphate was equal to stoichiometry.

In Figure 27 the EC profiles of the two experiments are shown while Figure 28 shows the pH profiles. At 34°C the EC curve initially showed a negative slope, which flattened out at approximately 500 µS/cm, after about 150 min. The EC profile of the experiment conducted at 13°C stayed almost constant over the entire duration of the experiment of about 180 min.

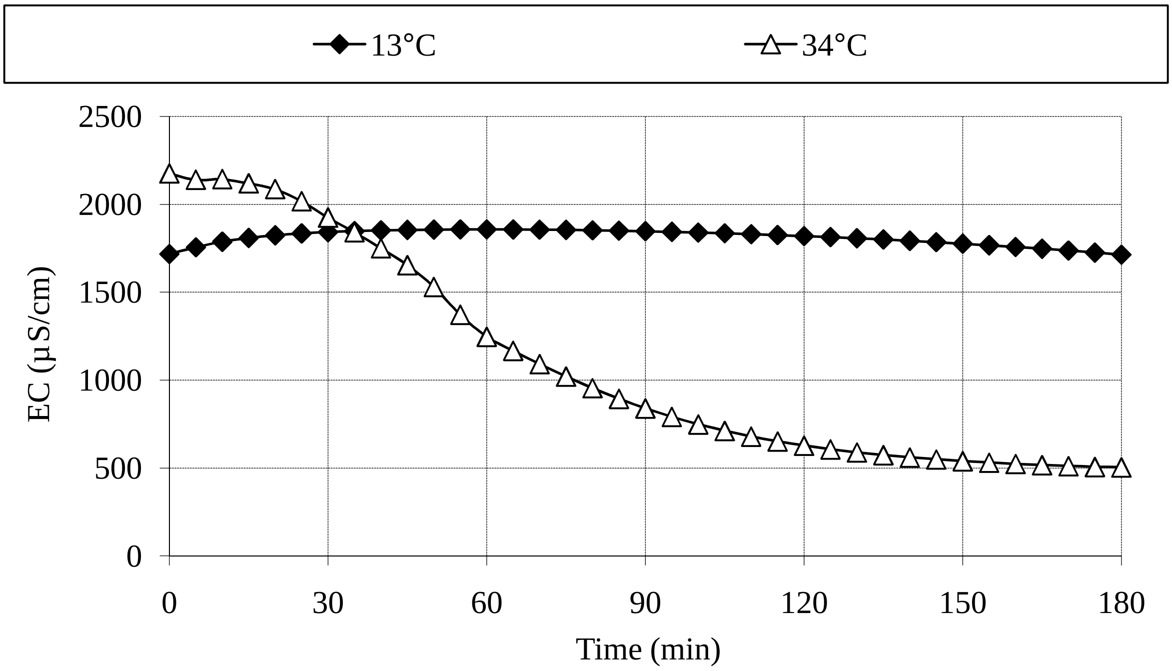


Figure 27: EC profile regarding to different temperatures (commercial barium carbonate)

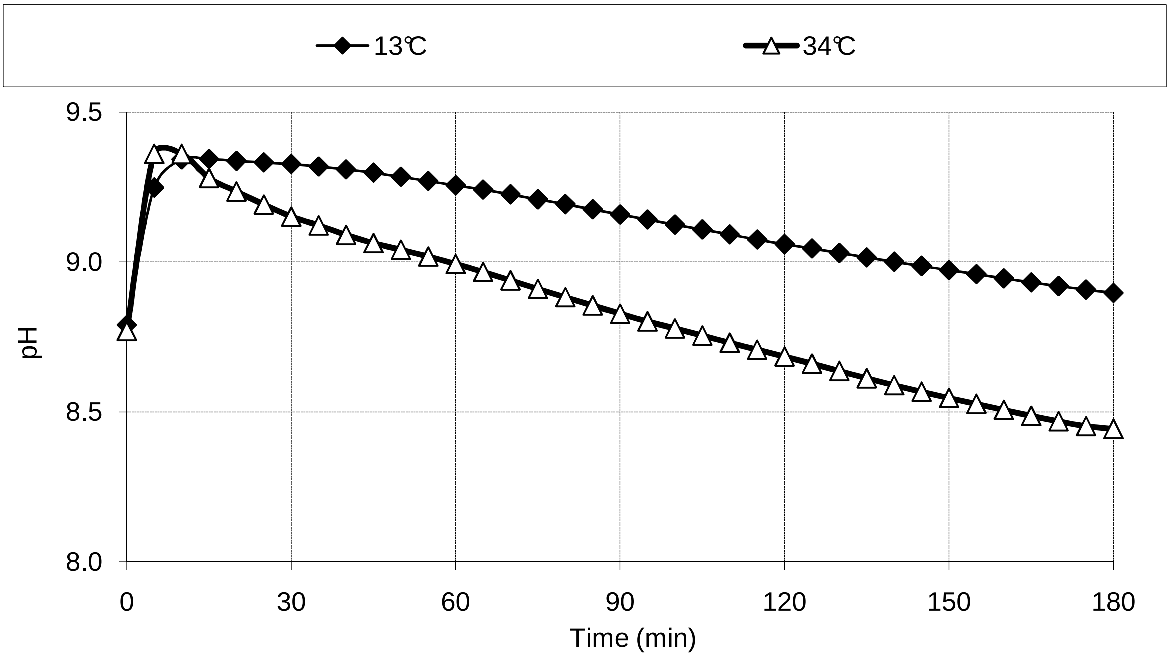


Figure 28: pH profiles corresponding to Figure 27

The final sulphate removal conducted at 13°C was 85.5% while that done at 34°C was 90.2%. Therefore, the higher the temperature of the reactor, the faster the sulphate removal process takes place and the better the sulphate removal from solution is.

Laboratory Produced Barium Carbonate

The effect of reactor temperature was also investigated on barium carbonate prepared in the laboratory as described earlier. The results obtained at three different temperatures (14°C, 21°C and 33°C) are shown in Figure 29 and Figure 30. Again, the minimum and maximum temperatures were chosen to be 14°C and 33°C due to the limits of the thermostat bath. The ambient temperature of the laboratory on this specific day was 21°C and was chosen as the middle temperature. From Figure 29 it is clear what the effect of temperature was. At the highest temperature (33°C) the EC value dropped rapidly to (and then stabilised) a point, in this case, approximately 400 µS/cm.

The experiment carried out at the lowest temperature (14°C) took 180 min. for the EC values to reach 400 µS/cm and eventually stabilised at this value. The sulphate removal experiment at 33°C, in contrast, was completed in about 30 min. The 21°C experiment EC profile fitted between the other two profiles. It took about 100 min. for the 21°C reaction to proceed to completion. In Figure 30 the pH profiles of these experiments are shown. The same trend can be seen as with the EC profiles.

The initial sulphate concentration for these two experiments was 1 600 mg/ℓ. The mixing rotational speed was 350 min^{-1}. The dosing ratio of the barium-to-sulphate was equal to stoichiometry.

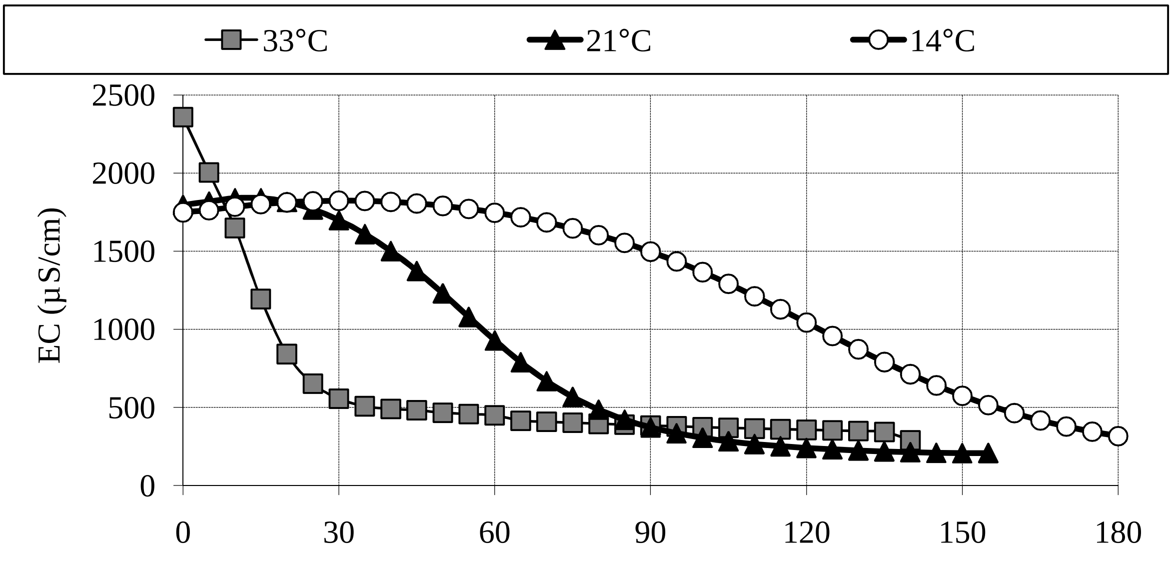


Figure 29: The EC profiles due to the effect of temperature (laboratory barium carbonate)

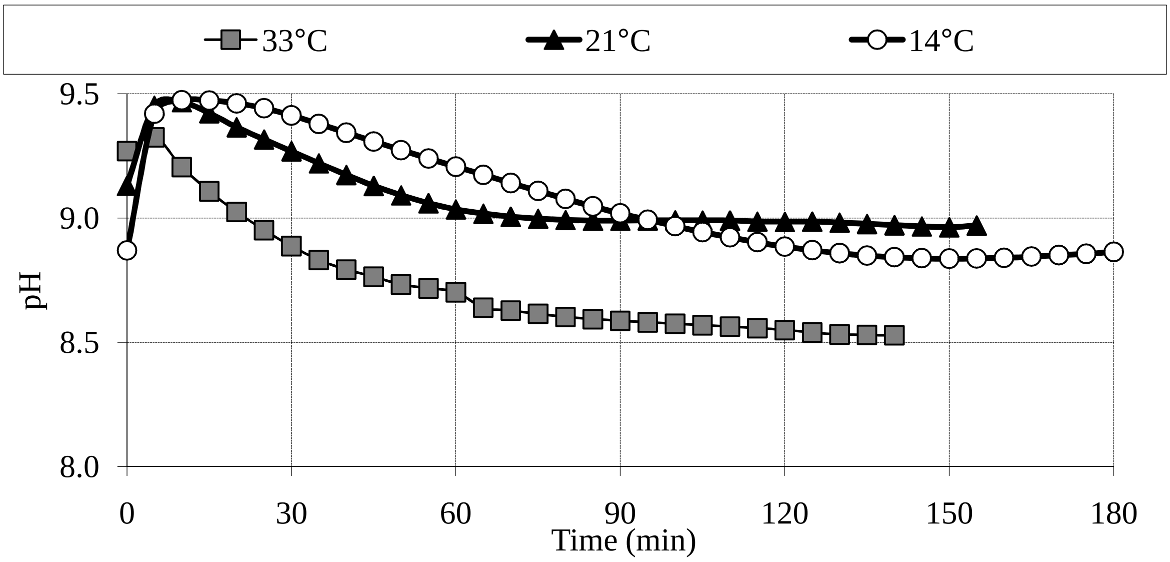


Figure 30: The pH profiles corresponding to Figure 29

The sulphate removal for the 14°C experiment was 98.2% while the sulphate removal for the 21°C experiment was 97.5% and for the 33°C experiment, 94.5%. In all three experiments the sulphate concentration was reduced significantly (on average 96.7%). Though, from Figure 29 it is seen that at 33°C, 90.05% of the initial sulphate was removed after 35 min while at 14°C, 89.95% of the initial sulphate was removed after 155 min. Thus, the reaction time increased with 120 min in order to obtain approximately 90% sulphate removal when the reaction temperature decreased from 33°C to 14°C. Thus, this experiment confirmed that the higher the reactor temperature is, the faster the sulphate removal rate is.

In Appendix C the reaction rates were determined and are given in Equation 12, Equation 13 and Equation 14. These reaction rates were determined at 50% sulphate removal at a concentration of 800 mg/ℓ. See Appendix C for more detailed calculations regarding the reaction kinetics.

$$-r_{SO_4^{2-}}|_{33} = 0.0915\ [SO_4^{2-}]^1 = 0.0915\ [800]^1 = 73.2\ mg/\ell\ min$$ **Equation 2**

$$-r_{SO_4^{2-}}|_{21} = 0.0375[SO_4^{2-}]^1 = 0.0375[800]^1 = 30.0\ mg/\ell\ min$$ **Equation 3**

$$-r_{SO_4^{2-}}|_{14} = 0.0215[SO_4^{2-}]^1 = 0.0215[800]^1 = 17.2\ mg/\ell\ min$$ **Equation 4**

From these two studies it was concluded that a higher reactor temperature led to a faster sulphate removal rate. Even if the initial reactor temperature is just slightly elevated it can result in a significant increase in the reaction rate. The opposite is also true, if the reactor temperature is just slightly cooler than planned, the reaction rate will be much slower and result in a much longer reaction time to remove the sulphate in the process fluid to the desired concentration.

It was observed that there was a marked difference between the curves when the results using imported barium carbonate were compared with the corresponding results using the laboratory-produced barium carbonate. This phenomenon was investigated in more detail.

4.3.5. Different barium carbonate types

The sulphate removal process was investigated using commercially available barium carbonate, imported from China (CIF Durbsan) and the process was repeated, using barium carbonate recycled from the ABC Desalination plant. Both these barium carbonate sources were very pure; approximately 99.95% pure according to XRD analyses.

The experimental parameters for these two experiments were as follows. The initial sulphate concentration in the sulphate-rich water was 1 300mg/ℓ and the mixing rotational speed was 350 min^{-1}. The reactor temperature was constant at ambient temperature (22°C ± 1.5°C). The dosing ratio of the barium-to-sulphate was equal to the stoichiometric relationship.

The results are shown in Figure 31. From this figure it became clear that the origin, and probably the morphology, of the barium carbonate particles is important.

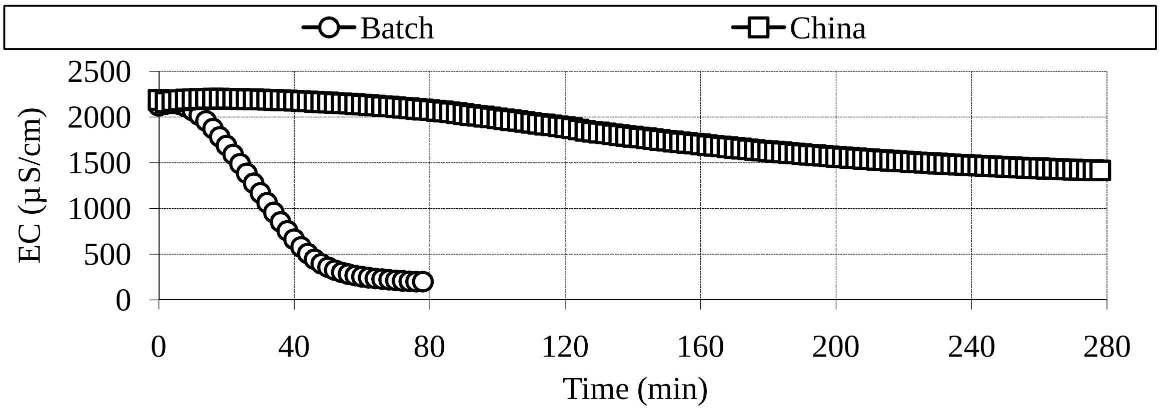


Figure 31: Effect of barium carbonate crystal surface characteristics

From Figure 31 it was seen that the commercial barium carbonate took a long time to remove even small amounts of sulphate from solution. Only 53.8% sulphate removal was obtained after 300 min. In contrast, the recycled barium carbonate removed 97.2% of the sulphate in the solution within 60 min. This phenomenon was confirmed by plotting the sulphate concentration profiles shown in Figure 32.

Since it takes the commercial barium carbonate much longer to remove about 50% of the sulphates in the process water, it is deemed as being *less-reactive* in comparison to the recycled (Batch) barium carbonate. While the Batch barium carbonate takes a short time to remove more than 97% of the sulphates from the process water, it is seen as *reactive* barium carbonate in comparison with the China barium carbonate.

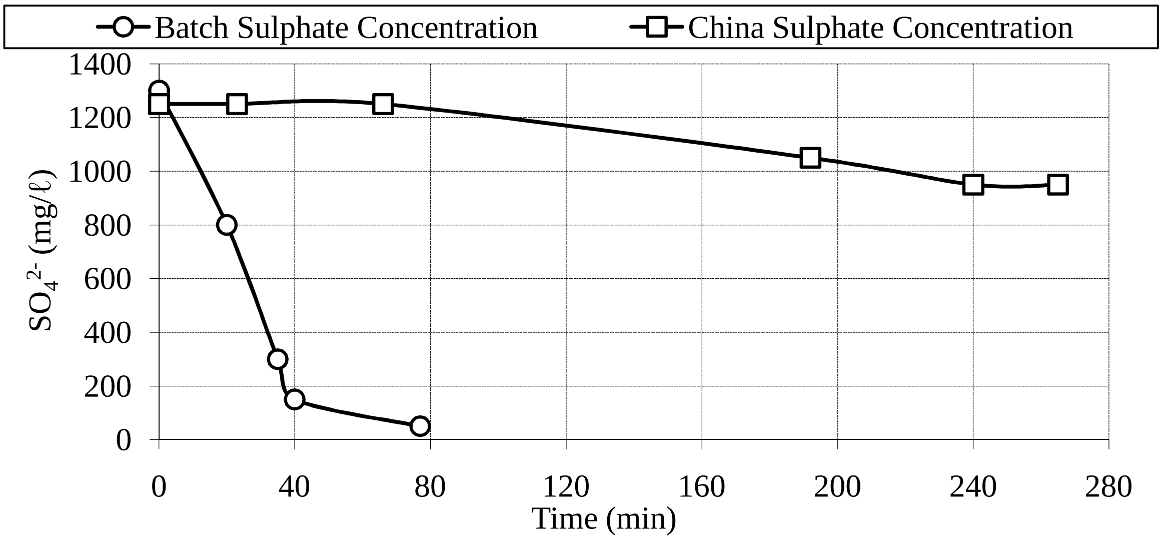


Figure 32: Effect of barium carbonate types

For increased clarity and to easily differentiate between these two barium carbonate types, the Chinese barium carbonate will be called *unreactive barium carbonate*. This description was convenient although not entirely true since this barium carbonate is capable of removing sulphates from the feed solution; it just removes very little sulphate over a long period (53% in 300 min.). The Batch barium carbonate will be denoted *reactive barium carbonate* since it is able to remove almost all the sulphate (97.2%) from the same feed solution within an hour.

The differences in the results using these two different barium carbonate types, needed to be understood. An investigation was initiated to determine the effect that the different barium carbonate types, and therefore the particle shape and size, have on the sulphate removal process.

Three different barium carbonate batches (Batch 1 to Batch 3) were prepared in the laboratory. Each of these batches was prepared differently by the carbonation of barium sulphide solution by carbon dioxide gas. In each case different preparation parameters were used. The differences in the parameters included the carbon dioxide flowrates and its purity as well as the initial barium sulphide concentration in the solution. The details of this work were considered to be beyond the scope of this study. What is important is that each barium carbonate batch was prepared in a unique experiment which resulted in different crystal characteristics as will become evident later (De Beer et al. 2010).

The commercial barium carbonate from China, the original recycled barium carbonate from the ABC Desalination Process, and the three barium carbonate batches were compared. The results are shown in Figure 33.

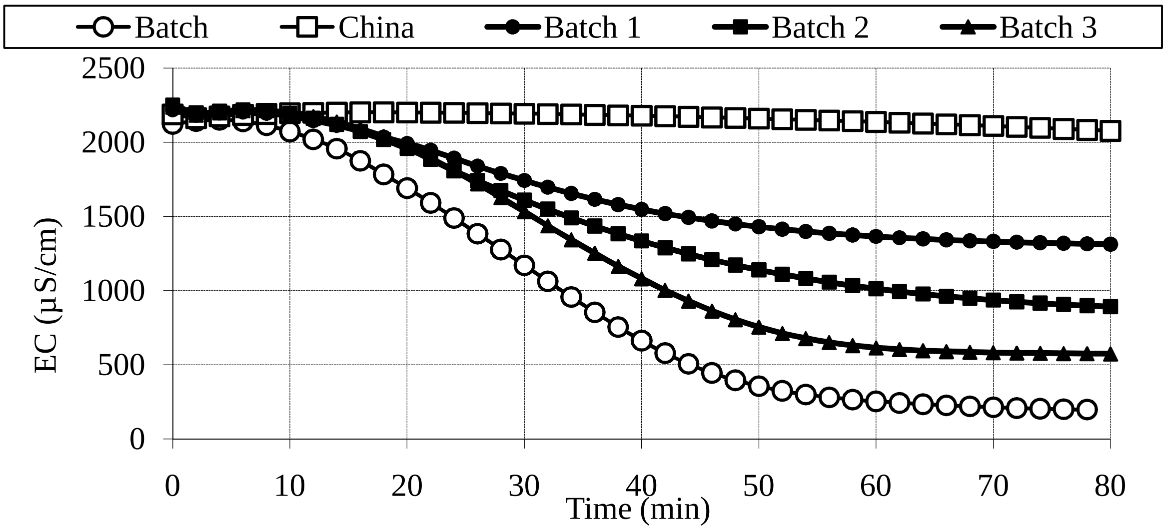
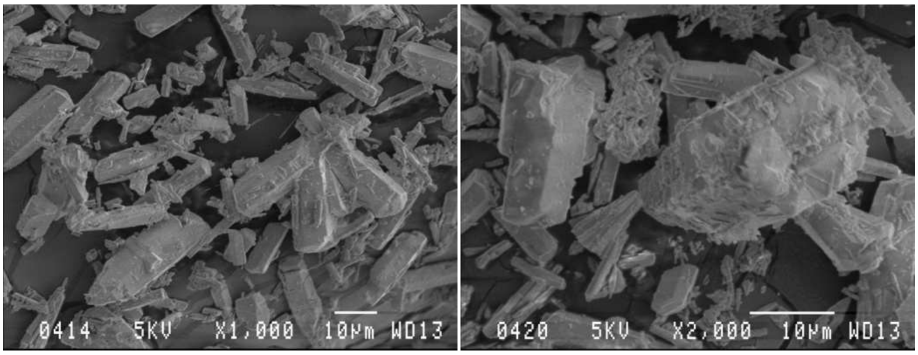


Figure 33: Effect of barium carbonate crystal surface characteristics

From Figure 33 one can see that the different barium carbonate types reacted differently from each other and therefore produced different results. The top graph represents the results from the *unreactive barium carbonate*, while the bottom graph represents the results from the *reactive barium carbonate*. The results from the three additional barium carbonate types are arranged reasonably equally spread between the two “extreme” types where Batch 1 removed 96.8% of the sulphates, Batch 2 removed 77.2% and Batch 3 obtained 59.5% removal.

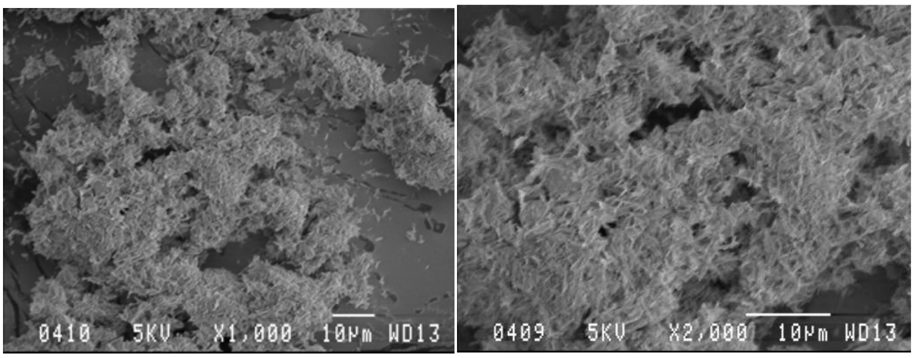
A sample of each of these barium carbonate types was analysed with SEM (scanning electron microscopy) to determine the particle surface structure. These photographs are shown in Figure 34 to Figure 38. The photographs on the left represent the particle shape and size of each of the barium carbonate samples when it is magnified 1 000 times (× 1 000) , while the photographs on the right represents the same barium carbonate sample as on the left, but at 2 000 times (× 2 000) magnification.

The first two photographs (Figure 34) represent the imported barium carbonate, known as the *unreactive barium carbonate*. The second set of photographs (Figure 35) represents the *reactive barium carbonate* recycled from the ABC Desalination process. The remainder of the photographs show the barium carbonate that was additionally prepared for this study in the order of Batch 1 (Figure 36), Batch 2 (Figure 37), and Batch 3 (Figure 38).



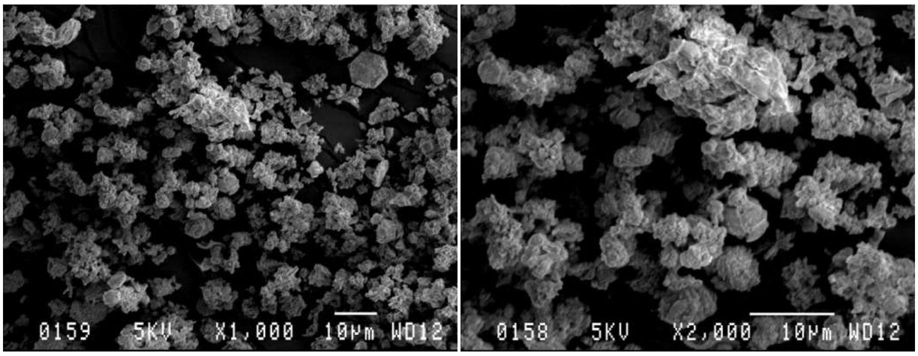
(a) **(b)**

Figure 34: SEM image of *Unreactive barium carbonate* (Chinese barium carbonate) (a) × 1 000 magnification (b) × 2 000 magnification



(a) **(b)**

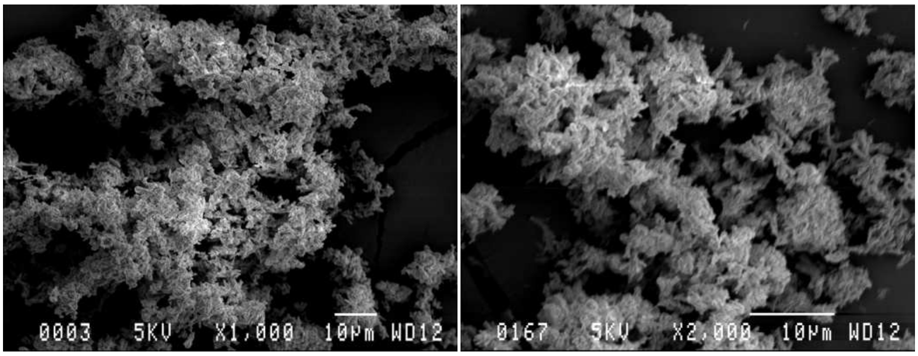
Figure 35: SEM image of *reactive barium carbonate* (recycled barium carbonate) (a) × 1 000 magnification (b) × 2 000 magnification



(a) **(b)**

Figure 36: SEM image of laboratory produced barium carbonate Batch 1

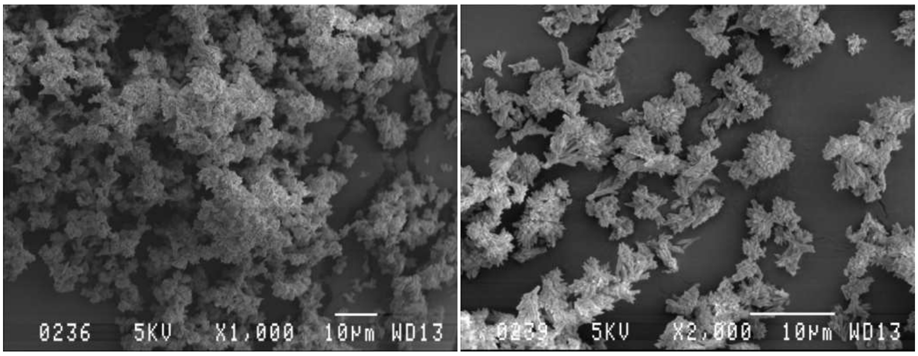
(a) × 1 000 magnification (b) × 2 000 magnification



(a) **(b)**

Figure 37: SEM image of laboratory produced barium carbonate Batch 2

(a) × 1 000 magnification (b) × 2 000 magnification



(a) **(b)**

Figure 38: SEM image of laboratory produced barium carbonate Batch 3

(a) × 1 000 magnification (b) × 2 000 magnification

From these photographs it was seen that the *unreactive barium carbonate* has a large, well-defined crystal structure while the *reactive barium carbonate* almost seems fuzzy with small, fine crystals. Therefore, the conclusion was made that barium carbonate with a small, fine crystal structure is more reactive than barium carbonate that consists of large, well-defined crystals.

From the additional barium carbonate types it seems that this conclusion was valid since the barium carbonate from Batch 1 had larger, better defined crystals than the other two types, while Batch 3 had smaller and finer crystals. The crystals from Batch 2 were intermediate between those of Batch 1 and Batch 3. Figure 33 revealed that, among the three barium carbonate types, Batch 1 was less reactive than the other two; Batch 3 was more reactive, and Batch 2 fell between them with respect to reactivity.

4.3.6. Process water

All of the above experiments were done on synthetic sulphate-rich water. In this section the experiments were conducted on two different types of industrial process water from a coal mine. Both came from the same process but were collected at two different treatment points. The first point was after lime neutralisation and gypsum crystallisation (if the raw AMD contained magnesium, it precipitated here) with a pH of 12. The second collection point was after the water had again been neutralised and had a pH of 7 (Swanepoel et al. 2011).

The experimental parameters for these experiments were as follows. The initial sulphate concentration in the feed water was approximately 2 400mg/ℓ and the mixing rotational speed was 350 min^{-1}. The reactor temperature was constant at ambient temperature (22°C ± 1.5°C). The dosing ratio of the barium-to-sulphate was equal to the stoichiometric relationship.

The gypsum crystallisation step is important if the raw AMD contains magnesium. Barium carbonate can only remove sulphate ions that are coupled with calcium ions, since calcium ions are required to remove the carbonate ions coupled with the barium cations. The sulphates that are coupled with magnesium and sodium will not be removed in this process (Hlabela et al. 2007, Hlabela et al. 2005). Thus, to successfully achieve sulphate removal, the magnesium and sodium ions have to be removed from the solution before sulphate precipitation.

From laboratory tests, as shown in Figure 39, it was clear that this sulphate removal process works well with AMD. In this case, the *reactive barium carbonate* that was recycled from the ABC Desalination Process was used to remove sulphate from the AMD.

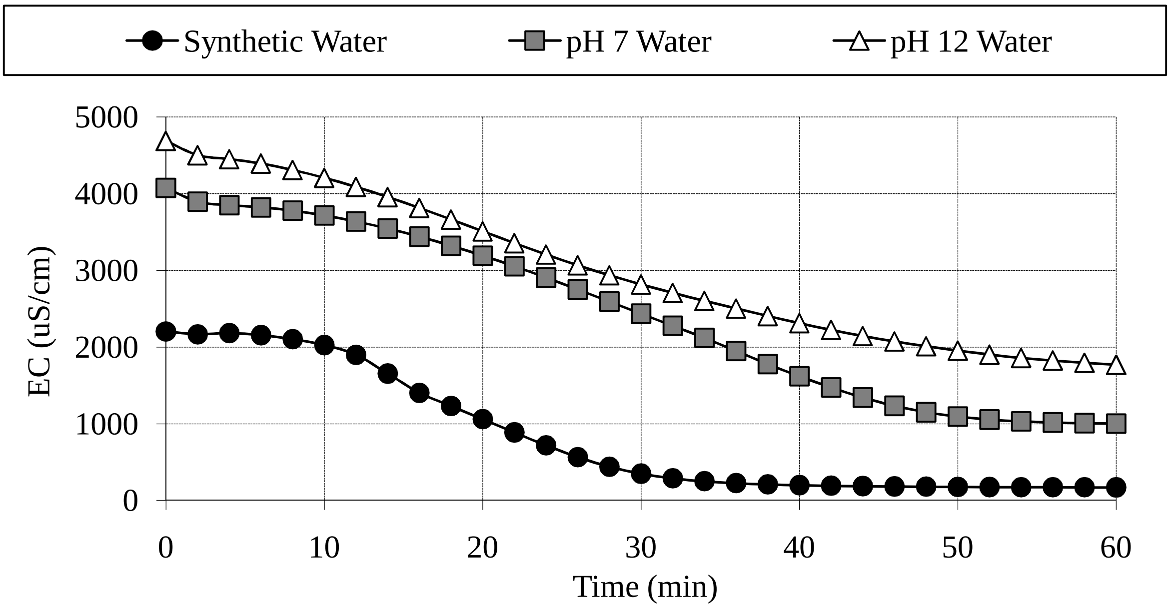


Figure 39: Sulphate removal from different process fluids

The EC of the AMD did not decrease as much as the synthetic sulphate-enriched water, due to other ions being present, such as sodium, magnesium, iron and manganese. The empirical EC-sulphate ion concentration correlation derived earlier could also not, due to the presence of these ions. Thus, samples were sent to a SANAS accredited laboratory for sulphate analysis.

The sulphate concentration for the pH 7 experiment decreased from 2 350 mg/ℓ to less than 50 mg/ℓ (98% sulphate removal), and for the pH 12 experiment it decreased from 2 400 mg/ℓ to 250 mg/ℓ (90% sulphate removal). The sulphate removal percentages for the synthetic water and the pH 7 water correlated well with each other.

The difference in EC values between the pH 7 water and pH 12 water can be explained by the solubility variation of barium carbonate for different pH levels, as explained in Paragraph 3.2.7. In short, barium carbonate is more soluble at lower than at higher pH levels. Thus, at a pH of 7, more barium ions were available to precipitate with sulphate ions, than at pH 12. Therefore it will result in a higher percentage sulphate removal as can be seen from the results (Hlabela et al. 2007, Hlabela et al. 2005).

4.4. WATER QUALITY

To legally discharge water into the environment, the water has to be of a certain quality. In Table 4 the list of parameters and their requirements are presented. These compositions of raw AMD and AMD treated by the ABC Desalination Process were compared. The results are shown in Table 4.

Table 4: Potable water standards (WHO 2004a, DWAF 1995, SANS 2011)

Parameter		Units	Class II Potable Water Standard	Raw AMD	Treated AMD
pH			4 – 10	3.35	7.9
Total Alkalinity	TAlk	mg/ℓ as $CaCO_3$	No Spec.	0	140
Aluminium	Al	mg/ℓ	0.5	2.97	0.01
Sodium	Na	mg/ℓ	400	46.5	53.2
Potassium	K	mg/ℓ	100	4.40	4.8
Calcium	Ca	mg/ℓ	300	205	75
Magnesium	Mg	mg/ℓ	100	124.6	0.98
Total Iron	Fe	mg/ℓ	2	182	0.3
Manganese	Mn	mg/ℓ	1	63.7	0.09
Sulphate	SO_4	mg/ℓ	500	1910	90
Chloride	Cl	mg/ℓ	600	44.5	49.5
Fluoride	F	mg/ℓ	5	5.4	0.07
Silicon	Si	mg/ℓ	No Spec.	11	0.45
Barium	Ba	mg/ℓ	0.7	< 0.02	< 0.02

From Table 4 it is clear that there was a major improvement in the quality of the AMD following treatment. When the treated AMD was compared to SANS Class II potable water standards, the final water quality easily complied with the required standards for all the variables (WHO 2004a, DWAF 1995). Since the potable water standards were met, this wastewater can be safely discharged into the environment (Swanepoel, 2011).

4.5. CONCLUSION

From the experimental work that was conducted, and by studying the results, the conclusions that were made are summarised as follows:

- *Barium-to-sulphate molar ratios:* When the barium (as barium carbonate) was under-dosed relative to the sulphate present in the feed water, only partial sulphate removal could be achieved. When the barium was over-dosed close to complete sulphate removal was achieved (98%). This caused barium to be present in the final product water which should be avoided at all costs due to its toxicity to humans and animals. Therefore the barium-to-sulphate molar ratio equal to the stoichiometric requirement is optimum.

- *Effect of initial sulphate concentration:* A limited amount of calcium sulphate dissolves in distilled water at one instance. This explains the delay in sulphate concentration reduction when the initial sulphate concentration was higher than 1 600 mg/ℓ. The initial sulphate concentration did not influence the final sulphate concentration in the solution (96.8% removal)

- *Effect of mixing rotational speed:* The mixing rotational speed inside the reactor should be high enough (160 min^{-1}, or higher) to ensure that all the solid particles have sufficient contact time with the sulphate feed solution.

- *Effect of temperature:* The sulphate removal process is very sensitive to the reactor temperature. Even if the initial reactor temperature is just 7°C higher than the optimised temperature, it could result in quite an increase in the reaction rate (from 17.2 mg/ℓ min at 14°C to 30.0 mg/ℓ min at 21°C). Therefore, proper temperature control is required for this process.

- *Different barium carbonate types:* It is found that the morphology of the barium carbonate plays an important role in the sulphate removal process. Barium carbonate with a small, fine crystal structure (Figure 35) is more reactive than barium carbonate that consists of large, well-defined crystals, as shown in Figure 34.

- *Process water:* This sulphate removal process works well with AMD. A 98% (pH 7 water) and 90% (pH 12 water) sulphate removal, respectively, was obtained on two different AMD types.

- *Water quality:* A major improvement occurred in the quality of the AMD after it was treated with the ABC Desalination Process. When measured against the SANS Class II potable water standards, it was found that the final water conformed to all the criteria and could be safely discharged into the environment.

The spread-sheets with the raw data of the experiments are available on the DVD included in Appendix D.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1. INTRODUCTION

This chapter consolidates the work done in this research project. All conclusions from the literature surveys and experiments conducted in the laboratory are compared. The outcomes of the project are linked with the original study objectives. Recommendations for potential future studies are given.

5.2. BACKGROUND

Sulphide oxidation in AMD is a common phenomenon, whereby pyrite is oxidised by sulphur oxidation bacteria under aerobic conditions. This result in a deterioration of water quality due to acidity, leached heavy metals and dissolved salt levels (Bell et al. 2006, Sawyer et al. 2003).

Sulphate removal by barite formation can achieve low sulphate concentrations due to the low solubility of barium sulphate. The final sulphate levels can be lower than 0.02 mg/ℓ. This method forms part of the ABC Desalination Process, developed and patented by the CSIR. In this process a barium carbonate is added to the sulphate-rich effluent in order to precipitate barium sulphate.

Barium sulphide, barium carbonate, and barium hydroxide can all be used to remove sulphate from wastewater. Barium carbonate is favoured because it does not require stripping of the foul smelling hydrogen sulphide gas from the main water stream as in the case of barium sulphide (Hlabela et al. 2007, Hlabela et al. 2005). When barium hydroxide is used a significant amount of calcium sulphate is produced, which increases the volume of waste sludge. (Bowell 2004, Bologo et al. 2009, Bologo et al. n.d.). The problem when using barium carbonate is that it becomes inactive when the particles are coated with metal hydroxides. It could also be problematic to separate the barium sulphate precipitate from the calcium carbonate that co-precipitates in this process (Maree et al. 2004b, Maree et al. 2004a).

The original three major problems that were identified with this process are as follows:

- A long retention time is required,
- The high concentrations of soluble barium in the treated water after the barium carbonate is over-dosed relative to the stoichiometric relationship of the reaction, and
- The high cost of the barium salt.

The first problem is solved by producing highly reactive barium carbonate. This study showed that the morphology of barium carbonate is important and that a specific particle structure (small, fine structure) is favoured. The second is solved by dosing the barium in stoichiometric quantities relative to the sulphate concentration in the water. This will result in the absence of barium ions in the final effluent. To overcome the high cost of barium carbonate, it has been demonstrated that the barium sulphate sludge, after dewatering, can be reduced efficiently and economically with coal at high temperatures (1 050°C) to produce barium sulphide. This can then be either used directly on site or be converted to barium carbonate (Maree et al. 2004b).

5.3. BARIUM SULPHATE PRECIPITATION: BATCH PROCESSES

5.3.1. Electrical conductivity (EC) correlation

A correlation was drawn between the reduction of the sulphate concentration and the EC values of the synthetic water being treated. The sulphate removal profile and the EC profile correlated very well with each other and an empirical relationship (Equation 1) was determined to enable the sulphate concentration to be calculated in mg/ℓ from the EC (µS/cm) values. This was discussed in detail in Paragraph 4.2.5.

5.3.2. Repeatability

The same experiment was replicated three times under identical conditions. The average sulphate removed for these three runs was 96.7%. The standard deviation was 0.577 and the variance 0.333. The low variance of 0.333 indicated a small deviation from the average of 96.7%, and the low standard deviation gave proof of consistent test results around the mean. Thus, this process was repeatable. A detailed discussion was given in Paragraph 4.2.6.

5.3.3. Kinetics

Two different reaction kinetics studies have been reported (Hlabela et al. 2007, Motaung et al. 2008). Both reported that the sulphate removal reaction is first-order. A detail discussion was given in Paragraph 3.2.3.

5.3.4. Co-precipitation of calcium carbonate

Two different studies were found in the literature, which investigated the effect of calcium carbonate co-precipitation. The first study used calcium sulphate and sodium sulphate as sulphate salts (Motaung et al. 2009). The second study used calcium sulphide and magnesium sulphate (Hlabela et al. 2007).

In both cases it was found that the sulphate removal process was more successful when calcium sulphate was used as sulphate source instead of sodium sulphate or magnesium sulphate (Trusler et al. 1988). A detailed discussion was given in Paragraph 3.2.4.

5.3.5. Barium-to-sulphate molar ratios

According to the literature the sulphate removal process is influenced by the amount of barium carbonate dosed into the effluent (Hlabela et al. 2007, Hlabela et al. 2005). It was found that it is preferred to under-dose the barium carbonate due to the toxicity of barium (Motaung et al. 2009). A detailed discussion was given in Paragraph 3.2.5.

Experiments were done where the barium carbonate was over-dosed, under-dosed and dosed according to stoichiometric ratio, relative to the sulphate present in the effluent. In the case of under-dosing, only partial sulphate removal could be achieved. Two experiments were conducted; in the first experiment (0.5 dosing ration) 68.0% sulphate removal was achieved and in the second experiment (dosing ratio of 0.75) a sulphate removal of 85.8% was obtained. When barium ions were over-dosed, almost complete sulphate removal was achieved (98.2%). Excess barium was present in the final product stream which should be avoided due to its toxicity.

In the scenario where barium carbonate was dosed in stoichiometric ratio it was found that the sulphate concentration was also lowered by 98.0%, similar to the scenario where barium was over-dosed. The most important advantage was that there was no excess barium in the final product stream. A detailed discussion was given in Paragraph 4.3.1.

5.3.6. Effect of initial sulphate concentration

It was found in the laboratory that the initial sulphate concentration influences the sulphate removal rate to certain extent, but not the final sulphate concentration of the effluent. A detailed discussion was given in Paragraph 4.3.2.

5.3.7. Effect of the mixing rotational speed

During the experimental work it was noted that the sulphate removal was affected only at a very low mixing rotational speed (60 min^{-1}). Only 88.7% sulphate was removed at this mixing rotational speed in comparison with the higher mixing rotational speeds of 160 min^{-1}, (97.8%). Some of the solids accumulated beneath the impeller of the overhead agitator at the lower mixing rotational speed. A detailed discussion was given in Paragraph 4.3.3.

5.3.8. pH effect

The dissociation of barium carbonate is dependent on the pH of the solution; the lower the pH of the solution the more barium carbonate would dissociate (Motaung et al. 2009). Therefore, sulphate removal is slightly influenced by the pH of the process water (Hlabela et al. 2007, Hlabela et al. 2005). A detailed discussion was given in Paragraph 3.2.7.

5.3.9. Effect of temperature

It was confirmed in the literature that the reactor temperature is a key factor in barium sulphate precipitation (De Beer et al. 2010). A detailed discussion was given in Paragraph 3.2.6.

Two different barium carbonate sources were used to investigate this in the laboratory. The sulphate concentration was reduced by 90.2% (34°C) after about 130 min and 85.8% (13°C) after 180 min, when using commercial barium carbonate. When laboratory-produced barium carbonate was used, the final sulphate concentration was reduced by 94.5% (33°C) in about 30 min. at a reaction rate of73.2 mg/ℓ min., 97.5% (21°C) in approximately 100 min at a reaction rate of 30.3 mg/ℓ min., and 98.2% (14°C) after 180 min at a reaction rate of 17.2 mg/ℓ min.

The study confirmed that the sulphate removal process is very sensitive to the reactor temperature. Therefore, proper temperature control is needed for this process. A detailed discussion was given in Paragraph 4.3.4.

5.3.10. Different barium carbonate types

Different types of barium carbonate were used to remove sulphate from sulphate-rich water. It was found that the different barium carbonate types gave different results.

In the literature barium carbonate from two different sources were used, namely, commercial barium carbonate imported from China and barium carbonate that was produced in the researcher's laboratory. It was found that the commercial barium carbonate displayed a much slower reaction rate in comparison with the laboratory produced material. The reason for this was not investigated at that stage (Motaung et al. 2009). A detailed discussion was given in Paragraph 3.2.2.

Experiments were conducted to investigate this phenomenon. The commercial barium carbonate and a recycled barium carbonate from the ABC Desalination plant were used. It was found that the commercial material lowered the initial sulphate concentration (1 300 mg/ℓ) by only 53.8% in 300 min, while the recycled barium carbonate (Batch) removed 97.2% within 30 min.

By conducting SEM analyses, photographs of the particles were obtained of the different barium carbonate types (Figure 34 and Figure 35). It was found that the less reactive, commercial barium carbonate has a large, well-defined crystal structure. The more reactive barium carbonate's structure almost seems fuzzy with small, fine crystals.

Thus, the barium carbonate crystal surface structure does have an influence on the sulphate removal reaction. Barium carbonate with a small, fine crystal structure is more reactive than barium carbonate that consists of large, well-defined crystals. A detailed discussion was given in Paragraph 4.3.5.

5.5. BARIUM SULPHATE PRECIPITATION: CASE STUDIES

Three case studies from the literature are discussed in Paragraph 3.3 where the sulphate removal process is tested and verified on AMD, zinc plant effluent and on power station cooling water effluent. In the first two case studies, the AMD and zinc plant effluent, the ABC Desalination process successfully removed the sulphate from the effluent (Motaung et al. 2009; Trusler et al. 1991). In the third case study it was found that, the sulphate removal from the power station cooling water was not as effective. It appeared as though some additive to the power station cooling water had severe impact on the sulphate removal process (Trusler et al. 1991). A detailed discussion was given in Paragraph 3.3.

Experiments were conducted in the laboratory where the sulphate removal method was tested on two different AMD streams from a coal mine. In both cases the sulphate was successfully removed. The sulphate concentration of the one AMD stream at a pH of 7 was reduced to 50 mg/ℓ (98% sulphate removal), and the sulphates on the second AMD stream at a pH of 12 was decreased to 250 mg/ℓ (90% sulphate removal). Both concentrations were well below the recommended level of 500 mg/ℓ. A detailed discussion was given in Paragraph 4.3.6.

5.6. WATER QUALITY

By comparing the compositions of raw AMD and AMD treated by the ABC Desalination Process, it was found that the quality of the treated AMD had improved. The treated AMD compared well to the SANS Class II potable water standards (SANS 2011), and therefore it had been rendered suitable to be safely discharged into the environment (WHO 2004a, DWAF 1995). A detailed discussion was given in Paragraph 4.4.

5.7. CONCLUSION

Barium carbonate from different sources was used to test its effectiveness in the removal of sulphate from sulphate-rich water. Different results were obtained.

A commercial barium carbonate imported from China (CIF Durbsan), could only reduce the effluent’s initial sulphate concentration with 53.8% while the recycled barium carbonate removed 97.2% of the initial sulphate. Not only did the recycled barium carbonate remove double the sulphates from the effluent, the reaction was also completed 10-times faster (30 min.) than the reaction where commercial barium carbonate was used (300 min.).

From SEM photos (Figure 34 and Figure 35) it was clear that the barium carbonate that was deemed *unreactive* relative to the other barium carbonate types had a large, well-defined crystal structure. The barium carbonate types that were more *reactive* relative to the commercial barium carbonate possessed small crystals with a fine structure.

Nonetheless, all the barium carbonate sources that were used in this study were able to remove the sulphate from the sulphate rich water, although some were more efficient than others. Therefore the hypothesis stated in Chapter 1 was supported, i.e. “barium carbonate, irrespective of its source, is capable of effective sulphate removal from acidic mine drainage and from industrial effluents”.

5.8. RECOMMENDATION

In order to optimise the sulphate removal process, the chemical reaction that takes place inside the reactor has to be completely understood. Therefore it is recommended that a detailed reaction kinetic study should be conducted, in order to find the actual driving force of the reaction kinetics. In other words: What is the limiting step during the sulphate removal reaction? Is it the dissolution of barium carbonate into solution, the precipitation of barium sulphate or calcium carbonate?

Motaung (2011) found that the reaction does not occur in the absence of calcium ions. It is recommended that this phenomenon be investigated as well to understand the dynamics of the chemical reactions that take place. The effect of the initial calcium concentration in the effluent could also be considered.

A study involving a continuous reactor configuration for sulphate removal is recommended in order to upgrade this process first to a pilot-scale, and then to a full-scale plant.

CHAPTER 6: REFERENCES AND BIBLIOGRAPHY

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APPENDIX A:
MEASURING INSTRUMENTS

A.1. INTRODUCTION

The measuring equipment used in the experimental work (described in Chapter 4) is listed. This included pH, temperature and EC sensors, temperature control bath, the Scanning Electron Microscopy (SEM) imaging and the analytical methods used for determining sulphate and barium concentrations.

A.2. INSTRUMENTATION

A.2.1. Sulphate measuring method

Waterlab (Pty) Ltd, a SANAS accredited analytical laboratory, used the Turbidimetric method (Method Number 4500-SO_4^{2-} E) to determine the concentration of sulphate ions in the samples. This method can accurately detect sulphate ions in solution between 1 mg/ℓ and 40 mg/ℓ (APHA 1992).

This is one of the methods recommended by the United States Environmental Protection Agency (USEPA) for sulphate monitoring purposes (APHA 1992).

A.2.2. Barium measuring method

CAS (CSIR), a SANAS accredited analytical laboratory, used an Inductively Coupled Plasma Optical Emission Spectrometer (Varian Vista Pro ICP-OES) to analyse the barium content in the samples. This method is able to determine trace elements in solutions at concentrations below one part per trillion (1 ppt = 1×10^{-12} mg/ℓ). It has the advantages of being fast, precise and sensitive (APHA 1992). The uncertainty of the instrument was 3.7% within a detection limit of 0 mg/ℓ to 5 mg/ℓ at a wavelength of 385.368 nm.

A.2.3. Temperature, EC and pH measuring instrument

A portable data logger known as a Multiparameter instrument (HI 9828 from Hanna Instruments) was used to measure the temperature, pH and EC of the reactor fluid. This instrument can measure up to 12 different parameters, including dissolved oxygen (DO), pH, ORP, conductivity, temperature, atmospheric pressure and seawater specific gravity. Up to 60 000 data points in a 100 different files can be captured on the instrument itself and be downloaded onto a computer. This instrument is shown in Figure A1.

Figure A1: Multiparameter measuring instrument (Hanna Instruments)

The time interval between two sampling points can be controlled. For this study, a pH, temperature and EC measurements were collected every second. This instrument was equipped with a conductivity sensor, a pH sensor and a temperature couple.

The conductivity sensor (HI 769828-3) was a four ring system. This allowed for stable and linear readings. The measuring range for this sensor is between 0.000 mS/cm to 200.000 mS/cm with an accuracy of ± 1 % of the reading or ± 1 µS/cm (whichever the greater). The pH sensor (HI 769828-0) was equipped with a glass membrane. The measuring range was 0.00-14.00 with ± 0.02 accuracy. The temperature sensing thermocouple could measure from - 5.00°C up to 55.00°C (268.15 K-328.15 K) with an accuracy of ± 0.15°C (Hanna Instruments). The probe, equipped with all three sensors, was calibrated once a day before the first experiment was conducted.

A.2.4. Scanning electron microscopy (SEM)

The SEM imaging was done at the University of Pretoria, Faculty of Natural and Agricultural Sciences. This showed the crystal surface structure of the barium carbonate particles.

Strips of black double-sided tape were dipped in the barium carbonate sample and mounted on a microscope stub covered with carbon tape. The samples were coated with gold before it was viewed under the SEM (JEOL-840) at an acceleration voltage from 5 kV to 15 kV.

A.2.5. Overhead stirrer

The overhead stirrer used in the experimental setup was an IKA RW 20.n. mixer. It is suitable for liquids with a low or a high viscosity and can successfully mix up to 20 ℓ at a time (IKA Works Inc 1995).

The mixing speed can be accurately adjusted between 60 min^{-1} and 2 000 min^{-1} at 50Hz AC or 72 $\text{min}^{-1}$and 2 400 min^{-1} at 60Hz AC. The power output, torque and rotational speed of the mixer were regarded as constant with a measuring fault of ± 0.5% (IKA Works Inc 1995).

A.2.6. Temperature bath

A Labotech temperature bath (Model 132 A) equipped with a Labotech Circulating Thermostat (Model 100) was used to control the temperature of the 3 ℓ reactor (16 cm diameter). The reactor was positioned in the water bath such that the water level of the heated water was high enough to ensure maximum heat transfer to the reactor.

This temperature bath could maintain the temperature of the reactor with an accuracy of ± 1.5°C, at a temperature between ambient temperature plus 10°C and 100°C, depending on the initial temperature of the water poured into the bath. The capacity of the pump used to circulate the heated water was 6 ℓ/min to insure uniform temperature distribution.

A.3. CONCLUSION

All the measuring instruments used during the experimental work, as well as the analytical work done by the accredited laboratories were reliable and accurate.

APPENDIX B:
EC-SO_4^{2-} CONCENTRATION CORRELATION

B.1. INTRODUCTION

A correlation exists between the EC measurements and the sulphate concentration of the reaction fluid. This was observed in the results shown in Chapter 4 (Paragraph 4.3.1).

B.2. MATHEMATICAL MODELS

Different empirically mathematical models were derived by using Microsoft Excel (version 2007). The EC values were plot against sulphate concentration and the empirical equation of the trend line was used as a model. Different polynomial orders equations were used as trend lines and the mathematical correlations are given in Equation B1 to Equation B6. These equations were compared to each other in order to find the best correlation. The results are summarised in Table B1.

$$\begin{aligned}[SO_4^{2-}] = {} & (-5\times10^{-17})\,EC^6 + (5\times10^{-13})\,EC^5 - (2\times10^{-9})\,EC^4 \\ & + (4\times10^{-6})\,EC^3 - 0.0036\,EC^2 + 1.693EC - 189.8\end{aligned}$$ **Equation B1**

$$\begin{aligned}[SO_4^{2-}] = {} & (1\times10^{-13})\,EC^5 - (9\times10^{-10})\,EC^4 + (2\times10^{-6})\,EC^3 \\ & - 0.002\,EC^2 + 1.1095EC - 120.19\end{aligned}$$ **Equation B2**

$$\begin{aligned}[SO_4^{2-}] = {} & (8\times10^{-11})\,EC^4 - (4\times10^{-7})\,EC^3 + (9\times10^{-4})\,EC^2 \\ & - 0{,}223\,EC + 73.683\end{aligned}$$ **Equation B3**

$$[SO_4^{2-}] = (2 \times 10^{-8})\, EC^3 + (3 \times 10^{-5})\, EC^2 + 0{,}3678EC - 37.877$$ **Equation B4**

$$[SO_4^{2-}] = (9 \times 10^{-5})\, EC^2 + 0{,}2895EC - 17.231$$ **Equation B5**

$$[SO_4^{2-}] = 0{,}5662EC - 143.03$$ **Equation B6**

Table B1: Mathematical correlations

Mathematical equation		**B1**	**B2**	**B3**	**B4**	**B5**	**B6**
Order of polynomial equation		6	5	4	3	2	1
EC	Initial (µS/cm)	2717	2717	2717	2717	2717	2717
	Final (µS/cm)	192	192	192	192	192	192
Calculated SO_4^{2-}	Initial (mg/ℓ)	2990	-5995	2448	1584	1434	1395
	Final (mg/ℓ)	28	32	61	34	42	-34
	SO_4^{2-} (%)	99.1	100.5	97.5	97.9	97.1	102.4
Measured SO_4^{2-}	Initial (mg/ℓ)	1600	1600	1600	1600	1600	1600
	Final (mg/ℓ)	36	36	36	36	36	36
	SO_4^{2-} (%)	97.8	97.8	97.8	97.8	97.8	97.8
R^2		0.9956	0.9955	0.9943	0.9931	0.993	0.9821
% Error	Initial (mg/ℓ)	46.5	126.7	34.6	-1.0	-11.6	-14.7
	Final (mg/ℓ)	-27.4	-12.5	41.0	-5.9	14.3	205.9
	SO_4^{2-} (%)	1.3	2.8	-0.2	0.1	-0.7	4.6

In Table B1 the calculated and measured values are compared. Six mathematical models were used to calculate the initial and final sulphate concentrations from the measured EC values. The percentage sulphate removed was then determined from these calculated values. The measured sulphate concentration values were used to determine the sulphate removal percentage. The percentage error was calculated between the initial sulphate concentration, the final sulphate concentration and the percentage sulphate removal. From the table it was found that the third order polynomial equation (Equation B3) was the best, since the percentage error for the initial and finale sulphate concentration were 1.0% and 5.9%, respectively, and the error between the two sulphate removal percentages was 0.1%.

B.3. CONCLUSION

A third order polynomial equation gave the best correlation between the EC measurement and the sulphate concentration. A 0.1% error exists between the measured and calculated sulphate removed concentrations.

APPENDIX C:
REACTION KINETICS

C.1. INTRODUCTION

A kinetic study was conducted in order to determine the reaction rate constants. The assumption was made that the reaction was first order according to the literature (Hlabela et al. 2007, Motaung et al. 2008). The MATLAB software program was used to determine the reaction rate constant of the sulphate removal reaction.

C.2. KINETIC STUDY

The sulphate removal reaction is irreversible due to the insolubility of the products, barium sulphate and calcium carbonate. The reaction rate equation is given by Equation C1. It was assumed that the reaction is dependent on the sulphate concentration in the sulphate-rich water and not on the barium concentration as explained in the next paragraph.

$$-r_{SO_4^{2-}} = k[SO_4^{2-}]^n$$ **Equation C1**

Barium carbonate is only slightly soluble. It is assumed that there was only a small amount of barium carbonate in solution at all times. The barium carbonate solids dissolved at the same rate as the barium ions reacted with the sulphate ions. Thus, the barium ion concentration stayed relatively constant (± 0.04 mg/ℓ) over time until all the barium carbonate had dissolved. This assumption was supported by barium analyses carried out over time as shown in Figure C1.

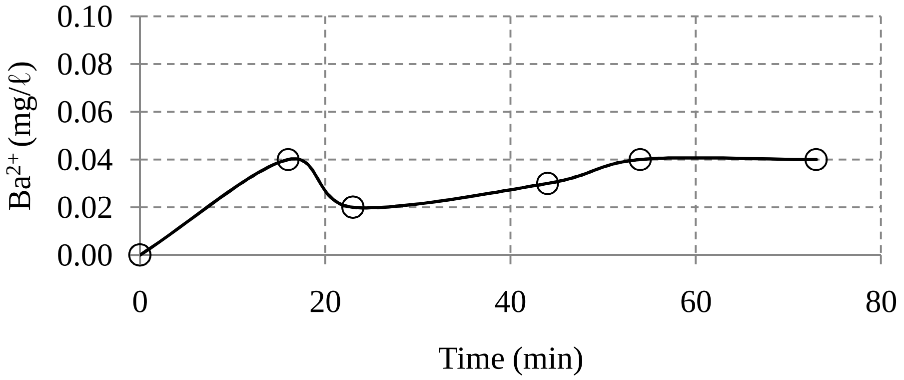

Figure C1: Barium concentration

From the literature it was found that the reaction order (n) is equal to unity (one) (Hlabela et al. 2007, Motaung et al. 2008). The reaction kinetic equation was fitted to the experimental data by using MATLAB software, as shown in Figure C2. It was found that the reaction rate constant (k) for the sulphate removal reaction is 0.03751 min^{-1}, as given in Equation C2.

$$-r_{SO_4^{2-}} = 0.0375[SO_4^{2-}]^1 \qquad \textbf{Equation C2}$$

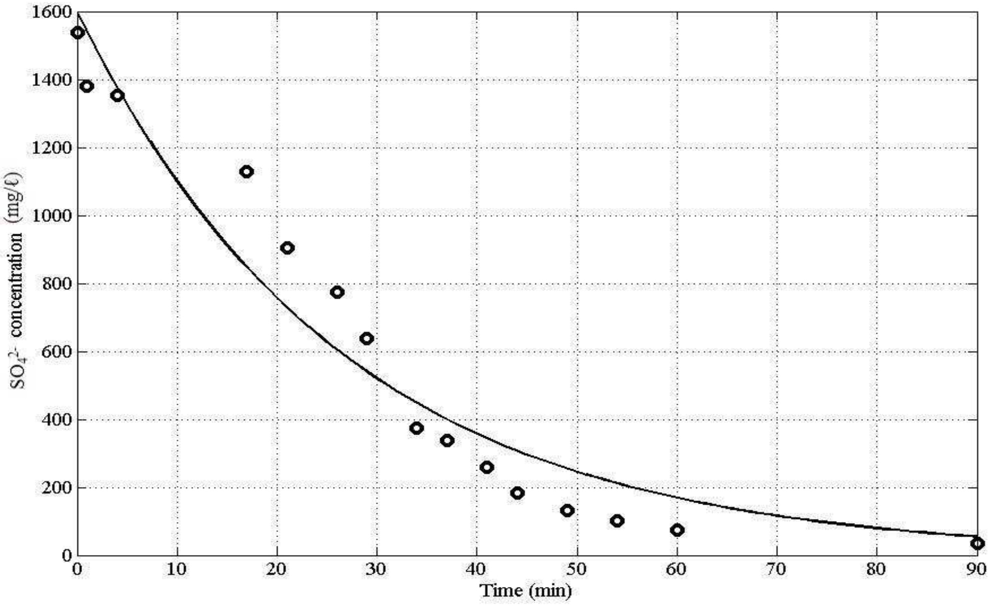

Figure C2: Kinetic equation curve fit of experimental data

The experimental parameters for this experiment were as follows. The initial sulphate concentration in the sulphate-rich water was 1 600mg/ℓ and the mixing rotational speed was

350 min^{-1}. The reactor temperature was constant at ambient temperature (21°C ± 1.5°C). Laboratory produced barium carbonate was used and the dosing ratio was stoichiometrically equal to the sulphate present in the solution. After 90 min. the sulphate concentration was lowered by 97.7% (36 mg/ℓ) according to sulphate analyses.

C.3. TEMPERATURE DEPENDENCY

The rate constant depends on temperature (in K) according to Equation C3 (Levenspiel 1999). The experiment described in paragraph C.2, was conducted at 21°C (294 K). The reaction rate constant was 0.03751 min^{-1}.

$$k = k_o e^{\left(\frac{-E}{RT}\right)} \qquad \textbf{Equation C3}$$

When the same experiment was conducted at a higher temperature (33°C), the reaction rate constant (k) changed. Though k_o (frequency factor) stays constant, and so does the E/R ratio (with E the activation energy of the reaction and R the ideal gas constant (8.314 J/mol K)) (Levenspiel 1999).

In Chapter 4, three experiments were done at three different temperatures. The data from these three experiments are given in Table C1. With the help of Equation C4, that applies to first order reactions, the activation energy of the sulphate removal reaction was determined (Levenspiel 1999).

$$ln\left(\frac{r_2}{r_1}\right) = ln\left(\frac{t_1}{t_2}\right) = -\left(\frac{E}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \textbf{Equation C4}$$

Table C1: Activation energy calculation

	t_1 (min)	**t_2 (min)**	**T_1 (°C)**	**T_1 (K)**	**T_2 (°C)**	**T_2 (K)**	**E (J/mol)**
1	40	120	33	306.15	21	294.15	68 545.09
2	120	180	14	287.15	21	294.15	40 676.46
3	40	180	33	306.15	14	287.15	57 858.84
	Average						55 693.46

Thus for T at 21°C (294.15 K) with a rate constant value of 0.03751 min^{-1}, the reaction rate equations changed as follow (Equation C5 to Equation C8):

$$k = k_o e^{\left(\frac{-E}{RT}\right)} \quad \textbf{Equation C5}$$

$$0.0375 = k_o e^{\left(\frac{-55\,693.46}{(8.314)294.15}\right)} \quad \textbf{Equation C6}$$

$$0.0375 = k_o(1.287 \times 10^{-10}) \quad \textbf{Equation C7}$$

$$k_o = (2.91 \times 10^{8})\,min^{-1} \quad \textbf{Equation C8}$$

Thus for temperatures of 33°C (306.15 K) and 14°C (287.15 K), the reaction rate constants were calculated (Equation C9 and Equation C10):

$$k_{33} = (2.91 \times 10^{8}) e^{\left(\frac{-55\,693.46}{(8.314)306.15}\right)} = 0.0915\,min^{-1} \quad \textbf{Equation C9}$$

$$k_{14} = (2.91 \times 10^{8}) e^{\left(\frac{-55\,693.46}{(8.314)287.15}\right)} = 0.0215\,min^{-1} \quad \textbf{Equation C10}$$

Thus the reaction rates for the three different temperatures were given in Equation C11 to Equation C13 (at 50% sulphate removal at a concentration of 800 mg/ℓ):

$$-r_{SO_4^{2-}}|_{33} = 0.0915\,[SO_4^{2-}]^1 = 0.0915\,[800]^1 = 73.2\,mg/\ell\,min \quad \textbf{Equation C11}$$

$$-r_{SO_4^{2-}}|_{21} = 0.0375[SO_4^{2-}]^1 = 0.0375[800]^1 = 30.0\,mg/\ell\,min \quad \textbf{Equation C12}$$

$$-r_{SO_4^{2-}}|_{14} = 0.0215[SO_4^{2-}]^1 = 0.0215[800]^1 = 17.2\,mg/\ell\,min \quad \textbf{Equation C13}$$

C.4. CONCLUSION

Thus the sulphate removal occurs much faster at higher temperatures, as can be expected from literature, and mentioned in Chapter 4 (Levenspiel 1999). At 14°C the reaction rate was 17.2 mg/ℓ min., at 12°C it was 30.0 mg/ℓ min. and at 33°C 73.2 mg/ℓ min.

APPENDIX D:
EXPERIMENTAL DATA

The raw data collected during the experimental work are available on the CD (included in the CD pouch). This data were used to generate the graphs and tables showed in Chapter 4.

An electronic copy (PDF format) of this dissertation is also available on this CD.

CD with raw experimental data