

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.

Keywords: ABC Desalination process, AMD treatment, Barium carbonates, Barium sulphate precipitation, Sulphate removal,

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LIST OF SYMBOLS

Symbol	Description	Units
$[\text{SO}_4^{2-}]$	Sulphate concentration	mg/l
E	Activation energy	J/mol
EC	Electrical conductivity	$\mu\text{S/cm}$
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
$r_{\text{SO}_4^{2-}}$	Reaction rate	mg/ l min
T	Temperature	$^{\circ}\text{C}$ 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
$3\text{CaO}\cdot 3\text{CaSO}_4\cdot \text{Al}_2\text{O}_3\cdot 31\text{H}_2\text{O}$	Ettringite
$\text{Al}(\text{OH})_3$	Aluminium tri-hydroxide
$\text{Ba}(\text{OH})_2$	Barium hydroxide
BaCO_3	Barium carbonate
BaS	Barium sulphide
BaSO_4	Barium sulphate or barite
$\text{Ca}(\text{OH})_2$ or $2\text{OH}^+(\text{Ca}^{2+})$	Calcium hydroxide or lime
CaCO_3	Calcium carbonate or limestone
CaSO_4 or $\text{Ca}^{2+}(\text{SO}_4^{2-})$ or $\text{SO}_4^{2-}(\text{Ca}^{2+})$	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 $2\text{H}^+(\text{SO}_4^{2-})$	Sulphuric acid
MgSO_4	Magnesium sulphate
Na_2SO_4	Sodium sulphate
O_2	Oxygen
OH^-	Hydroxyl
$\text{R}_2\text{-Ca}$	Calcium - resin compound
$\text{R}_2\text{-SO}_4$	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 ($[\text{Ba}^{2+}]/[\text{SO}_4^{2-}] > 1$).
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. ($[\text{Ba}^{2+}]/[\text{SO}_4^{2-}] = 1$).
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. ($[\text{Ba}^{2+}]/[\text{SO}_4^{2-}] < 1$).
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

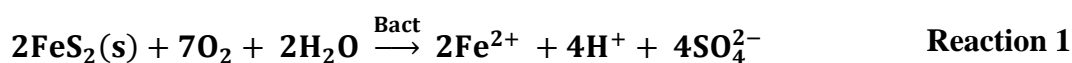
Large quantities of AMD are released into the environment and have a serious negative environmental impact. Figure 1 shows an example of the impact and effects AMD has on the environment.



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).



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).

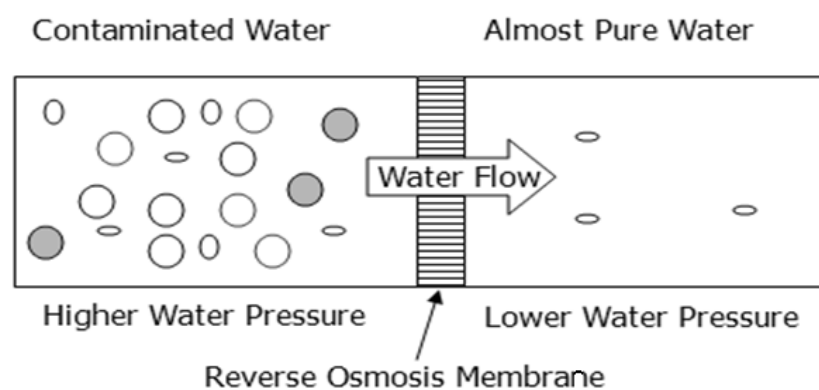


Figure 2: Schematic diagram of an RO membrane (GTAWater 2004)

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 ($< 100 \text{ mg}/\ell$) and low sulphate concentration ($< 700 \text{ mg}/\ell$), 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 m³/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.

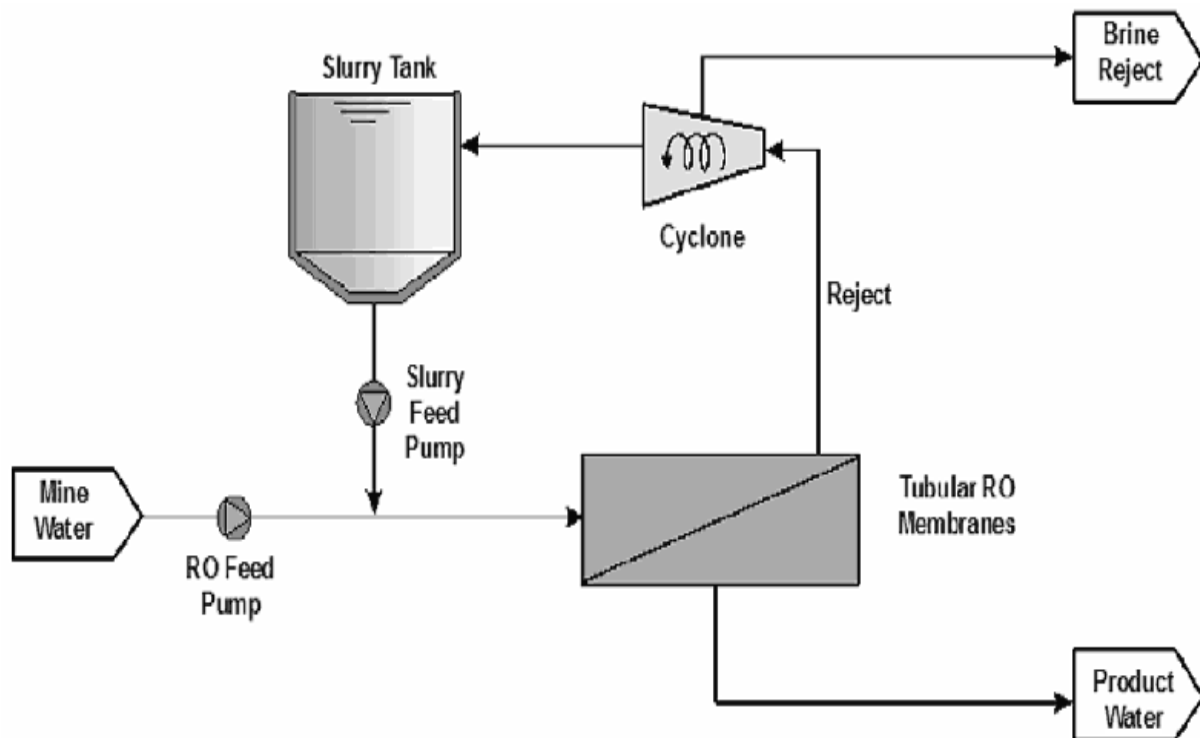


Figure 3: SPARRO process flow diagram (INAP 2010)

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.

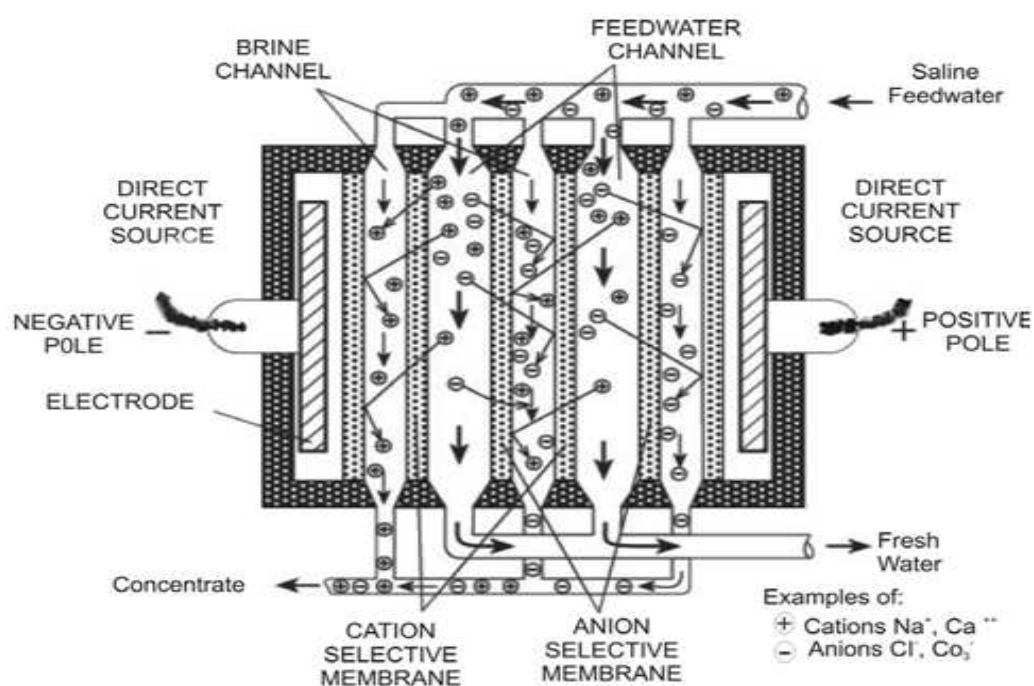


Figure 4: ED or EDR cell (UNEP 1998)

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).

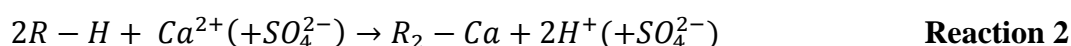
GYP-CIX Process

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).



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).

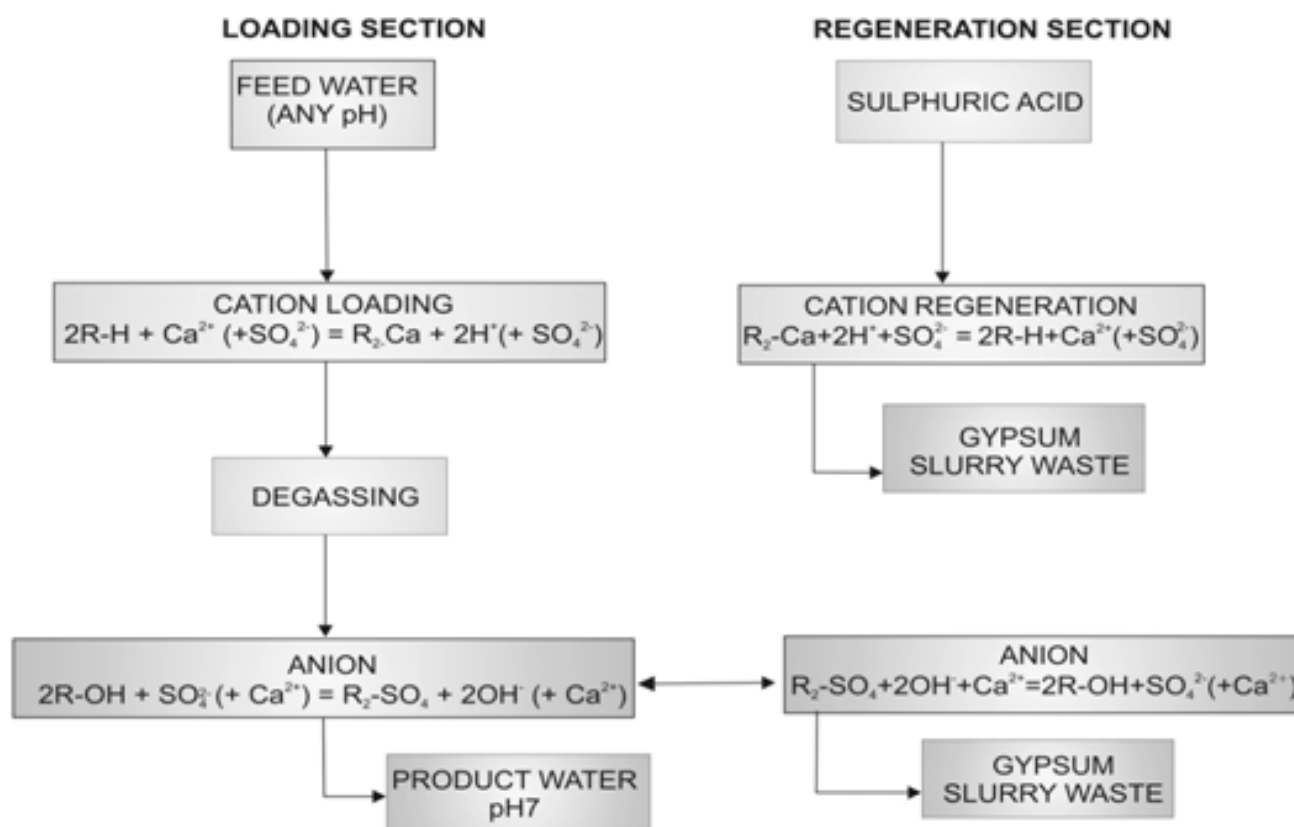
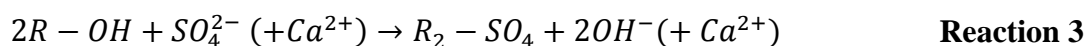


Figure 5: GYP-CIX process (McNee 2003)

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.