TREATMENT OF ACID MINE DRAINAGE AND ACIDIC EFFLUENTS

by

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SUMMARY

The scarcity of water in South Africa is exacerbated by pollution of the surface- and ground- water resources. Typical pollutants of the aquatic environment include acid mine drainage and industrial effluents. AMD and acidic effluents can have detrimental effects on mining infrastructure, water reuse options and environmental discharge. As a result, some form of treatment is required at many mine sites. Unless treated, acid water cannot be discharged into public water courses. It is therefore important to treat mine drainage and wastewater for recycling in industrial facilities. Wastewater treatment represents one of the last frontiers left to maintain our fresh water supplies. Measures to control acid mine drainage include the treatment of acidic effluents. Acid and sulphate rich waters can effectively be treated for re-use or discharge by applying the integrated limestone technology followed by desalination with the DesEl process.

This study investigated the chemical aspects of the limestone neutralisation process. One conclusion was that the limestone particle size is an important parameter in the process. It was shown that the smaller the particle size, the faster is the rate of neutralisation. Finer limestone particle size also resulted in faster settling rates and lower sludge volumes.

Due to the capital and running cost associated with poor sludge settling, the production of high quality sludge is another important parameter of limestone process. It was shown that the sludge settling rate is significantly influenced by:

- the feed water acid- and sludge concentration as a result of gypsum precipitation,
- the way the limestone is added to the acid water,
- the addition of a flocculant

Neutralisation is generally the first step in the treatment of acid mine water. With the limestone neutralisation process, acidity is removed and only partial sulphate (up to 1200 mg/L) and metal removal are achieved. Further treatment for sulphate (to less than 400 gm/L) and metal removal are needed to make the limestone neutralised water suitable for re-use or discharge into waterways. Encouraging results obtained from laboratory studies showed that the DesEl process can be used effectively to lower sulphates from 3700 mg/L to less than 400 mg/L from limestone neutralised acid water. Operating costs amounts to 1.29 R/m^3 feed water treated.

Traditionally acid mine water is neutralised with lime. Limestone is a cheaper alternative for such applications. A case study showed that limestone can be used effectively to replace lime for the neutralization of arsenic rich acid water. The cost of limestone treatment is 45.8% less than that of lime. The acidity can be removed from 33.5 to 0.06 g/l (as $CaCO_3$). The study also showed no significant differences in the TCLP characteristics of the resultant sludge when water is treated with lime or with limestone. Sludge from the limestone treatment process can be disposed of on a non-hazardous landfill site.

SAMEVATTING

Die besoedeling van bo- en ondergrondse waterbronne dra grootliks by tot die ernstige tekort aan vars water in Suid Afrika. Suur mynwater en industriële uitvloeisels is tipiese voorbeelde wat hierdie waterbronne besoedel. Suurwater kan uiters negatiewe gevolge hê op onder andere myninfrastrukture, waterherwinning en varswater bronne. Dit is belangrik om suur mynwater en afvalwater te behandel vir hergebruik deur industrieë, aangesien die storting van suurwater in die land se vars waterbronne nie toegelaat word nie. Afvalwaterbehandelling is een van die laaste oorblywende fronte wat dit moontlik kan maak om ons varswatervoorrade op 'n volhoubare vlak te hantaaf.. Suur en sulfaat ryke afvalwater kan vir hergebruik behandel word deur die geïntegreerde kalksteen tegnologie wat dan gevolg word deur ontsouting met behulp van die DesEl-proses.

Met hierdie ondersoek is gekonsentreer op die chemiese aspekte van die kalksteen-neutralisasieproses. Daar is bevind dat die partikelgrootte van die kalksteen 'n belangrikke rol speel. Dit is getoon dat 'n kleiner partikelgrootte die neutralisasieproses bespoedig. Kleiner partikelsgroottes lei ook tot versnelde besinkings tempo's en laer slyk volumes.

Die produksie van 'n hoë kwaliteit slyk is ook 'n belangrikke faktor in die kalksteen neutralisasieproses. Swak slykbesinking het 'n negatiewe invloed op die kapitaal- en bedryfkostes van die proses. Daar was dan ook gevind dat die slykbesinkingstempo grootliks beïnvloed word deur die volgende faktore:

- Die voerwater suur-en slyk konsentrasies as gevolg van gips neerslag,
- Die metode van kalksteen toevoeging tot die suur-water,
- Die toevoeging van 'n vlokmiddel.

Suur waters word in die algemeen behandel deur die suurinhoud van die water te neutraliseer met 'n alkali. Met die kalksteen neutralisasieproses word die vry suur verwyder maar slegs gedeeltelike sulfaat (tot-en met 1200 mg/L) en metaal verwydering word verkry. Vir storting in die natuur, of vir die hergebruik deur industieë, word verdere behandeling vir sulfaat verwydering (tot minder as 400 mg/L), benodig. Die DesEl proses het, in laboratoriumstudies, bemoediggende resultate gelewer ten opsigte van die verwydering van sulfate vanuit die kalksteen geneutraliseerde

suurwater. Die studies het getoon dat die sulfaat inhoud vanaf 3700mg/L tot 400 mg/L verminder kan word. Die bedryfskoste vir hierdie proses beloop R1.29/m^3 voerwater wat behandel is.

Kalk behandeling is die algemene metode vir neutralisasie van suurwater. Kalksteen is egter 'n goedkoper alkali wat as alternatief vir behandeling gebruik kan word. 'n Studie het getoon dat kalksteen baie effektief gebruik kan word, om kalk te vervang, vir die behandelling van arseenryke suurwater. Die koste van die kalksteen behandellings proses is 45.8% laer as die van kalk behandeling. Die suurvlak van die behandelde water is verlaag van 33.5 g/L tot 0.06 g/L (as $CaCO_3$). Die studie het dan ook getoon dat daar geen merkwaardigge verskil is in die *TLCP*-karakterestieke van die slyk, wanneer die water behandel word met kalk of kalksteen, nie. Slyk, vanaf die kalksteenproses, kan ook gestort word in enige nie-gevaarhoudende stortterrein, soos in die geval van die kalkproses.

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CHAPTER 1 INTRODUCTION

Background

Water is the backbone of our economy. Safe and adequate supplies of water are vital for agriculture, industry, recreation and domestic uses. The sustained growth in human population, economic development and the urgent need to supply water to millions of people without essential services in South Africa, has led to an increasing demand for water. Being largely an arid country, South Africa is fast approaching the limits of its available water supply, threatened in terms of both quantity and quality. To compound the problem the average rainfall is less than half of the world's average and is unevenly distributed across the country resulting in very dry western regions. It has been postulated that the country's fresh water resources will be fully utilized within the next twenty to thirty years if the current growth in water demand and use (or abuse) are not curbed or altered (Van Niekerk *et. al.*, 2001). The three major factors causing increasing water demand over the past century are population growth, industrial development and the expansion of irrigated agriculture. The damming of rivers has traditionally been one of the main ways to ensure adequate water resources for irrigation, hydropower generation and domestic use.

Water is essential for life on our planet. The population is increasing while the water supply is finite. We drink water to sustain life, generate electricity with it and grow our crops with it. Few natural resources are as critical as water, yet the problems of water pollution and availability are reaching catastrophic levels. Water quality problems can often be as severe as those of water availability but less attention has been paid to them. A prerequisite for sustainable development is to ensure uncontaminated streams, rivers, lakes and oceans. We often take the presence of clean water for granted, forgetting its importance and assuming that it is always available. Increasingly, human activities threaten the water sources on which we all depend. Mining is one such activity, which by its nature consumes, diverts and can seriously pollute water resources. Mine drainage is one of the main chemical threats to groundwater and surface water quality (Van Zyl *et.al.*, 2000). It is, therefore, important to treat mine drainage and wastewater for recycling. Wastewater treatment represents one of the last remaining frontiers to maintain our fresh water supplies. Water conservation would be much more effective if industries treated and recycled their process water, instead of purchasing and wasting more water from their local providers (Metcalf, 1991).

Mining and Water Pollution

The scarcity of water in South Africa is exacerbated by pollution of the surface- and ground- water resources. Typical pollutants of the aquatic environment include acid mine drainage and industrial effluents (Wangnick, 2002). Sources of water pollution originate from underground and open cast mining, metallurgical plants, mining infrastructure and mine residue deposits. The coal mining industry, which is still very important to the South African economy (via electricity generation and export revenue), uses or contaminates millions of megalitres of water annually. The production of acid mine drainage (AMD) in the mining industry has always been a key pollution issue and is the mining industry's greatest environmental problem. The potential for a mine to generate acid and release contaminants is dependant on many factors and is site specific. AMD contains high concentrations of heavy metals, iron, sulphate and has a low pH (<2.5).

Mine water and industrial effluents are occasionally discharged into local streams, resulting in acidification and regional salination of surface waters (Van Niekerk *et.al.*, 2001). This can be prevented by treating mine drainage and effluents to a quality where it can be re-used as process water. For re-use, the water needs to be neutral and under-saturated with respect to gypsum while for discharge into the sewer system the water needs to meet certain quality requirements in accordance with environmental legislation (Van Zyl *et.al.*, 2000). For irrigation, livestock-watering or aquaculture, heavy metals need to be removed from mining effluent in order to render the water suitable for agricultural uses.

As mining technologies are developed to make it more profitable to mine low-grade ore, even more waste will be generated in future. As a direct result of activities associated with mining, acid drainage can become an environmental, social and economic liability long into the future if left unchecked. If discharge, AMD can effectively sterilize an entire water system for generations to come - turning it into a biological wasteland and a huge economic burden.

Acid mine drainage from coal and mineral mining operations is a difficult and costly problem to solve. In addition to the acid contribution to surface waters, AMD may be the source of toxic elements such as arsenic, cadmium, copper and zinc. The metal load leads to environmental problems, and is of greater concern than the acidity in environmental terms.

Acid Mine Drainage (AMD)

The Origin of Acid Mine Drainage

Acid Mine Drainage (AMD) is water that has become contaminated as the result of passage through a physical environment created by coal mining activities. The contamination can occur in the underground voids created by deep or underground mining or it can occur by water passing through coal mining refuse on the surface. This drainage is typically highly acidic with elevated levels of sulphate and dissolved metals. The metals remain in solution until the pH rise to a level where precipitation occurs. Acid drainage from waste rock, tailings, pits and underground workings is a function of the mineralogy of the rock and the availability of water and oxygen.

The formation of AMD is primarily a function of the geology, hydrology and mining technology employed at the mining site. AMD is formed by a series of complex geo-chemical and microbial reactions that occur when water comes into contact with acidic material in coal, refuse or the overburden of a mining operation (Barnes *et.al.*, 1968). There are many types of sulphide minerals. Iron sulphides are most common; however other metal sulphide minerals may also produce AMD. The iron-sulfide mineral, pyrite, (called fool's gold), is often found near subsurface coal seams along with compounds containing manganese, aluminium, and other metals. Mining coal inevitably involves exposing these pyritic materials to oxygen and water, forming sulphuric acid and dissolved iron in a highly acid run-off. In deep mines, these sulphur-bearing materials are exposed in the voids created by the mining process. It is also brought to the surface as a waste product along with the coal, where these and other unwanted materials are separated from the coal and put in mine dumps. Upon infiltration by rainwater, leach highly acidic acid mine drainage that mobilizes toxic metal species and contaminates ground waters (Kleinmann *et.al.*, 1979). Due to the extremely low pH of AMD many metals such as Fe and Al are present in toxic concentrations. Sulphate is also present at unacceptably high concentrations. Metal contamination associated with acidic, sulphate-rich drainage depends on the type and amount of sulphide mineral oxidised, and the type of minerals in the rock.

While the oxidation of sulphide minerals and the subsequent conversion to acidity occurs through several chemical reactions to contaminate water, the net result of these reactions can be summarized as follows:

$$\mathbf{FeS + H_2O + 3O_2 \rightarrow H_2SO_4 + Fe(OH)_3} \qquad \textbf{(Reaction 1)}$$

Sulphuric acid (H_2SO_4), a product of this reaction, is a strong acid having devastating environmental consequences for plants and animals. ($Fe(OH)_3$), also known as Yellow boy , forms an orange or yellow sludge coating the bottoms of streams, effectively smothering aquatic life.

The primary ingredients for acid generation are:

- sulphide minerals,
- water or a humid atmosphere, and
- an oxidant, particularly oxygen from the atmosphere or from chemical sources.

In most cases, bacteria play a major role in accelerating the rate of acid generation and the inhibition of bacterial activity in these cases will lessen the rate of acid generation.

The nature of AMD contamination varies greatly from site to site, as its formation is dependent on a variety of factors. AMD lowers water quality and impairs aquatic life, and is characterized by one or more of the four major components:

- Low pH (high acidity)
- Elevated sulphate levels
- High metal concentrations (iron is the most common)
- Excessive suspended solids and/or siltation

Basic chemistry of Acid Mine Drainage

The complex series of chemical weathering reactions are spontaneously initiated when surface mining activities expose spoil materials to an oxidizing environment. The mineral assemblages contained in the spoil are not in equilibrium with the oxidizing environment and weathering and mineral transformations begin almost immediately. The reactions are analogous to "geological weathering" which takes place over extended periods of time (i.e., hundreds to thousands of years) but the rates of reaction are orders of magnitude greater than in "natural" weathering systems (Barnes *et.al.*, 1968). The accelerated reaction rates release damaging quantities of acidity, metals, and other soluble components into the environment.

There are four chemical reactions that represent the chemistry of pyrite weathering to form AMD. The pyrite oxidation process has been extensively studied and reviewed by Barnes *et.al.* (1968). The reactions of acid generation are illustrated by examining the oxidation of pyrite (FeS) which is one of the most common sulphide minerals.

The first reaction in the weathering of pyrite includes the oxidation of the sulphide mineral into dissolved iron (Fe^{2+}), sulphate (SO_4^{2-}) and hydrogen (H^+) by oxygen.

$$4FeS_{(s)} + 14O_{2(g)} + 4H_2O_{(l)} \rightarrow 4Fe^{2+}_{(aq)} + 8SO_4^{2-}{}_{(aq)} + 8H^+_{(aq)} \quad \textbf{(Reaction 2)}$$

Equation 2 describes the initial reaction of pyrite with water and oxygen to form ferrous ions. Ferrous ions and acidic hydrogen ions are released into the waters that run off through the mine tunnels or refuse piles. The pH of the water will decrease because this reaction generates two moles of acidity for each mole of pyrite oxidized. Dissolved, ferrous iron ($Fe^{2+}_{(aq)}$) and sulphate ions ($SO_4^{2-}{}_{(aq)}$) are colourless. The water may actually look crystal clear. In some AMD discharges, this is the condition of the water as it makes its way to the surface. The metals remain in solution below ground due to the lack of oxygen. When the water emerges from the mine or borehole it reacts with atmospheric oxygen and deposits iron, manganese and aluminium on rocks and the streambed.

If the surrounding environment is sufficiently oxidising (dependent on O_2 concentration, pH and bacterial activity), much of the ferrous iron will oxidise to ferric iron. The second step in the process is for the ferrous iron to be oxidized to ferric iron as shown in the following reaction:

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O_{(l)} \quad \textbf{(Reaction 3)}$$

Aqueous ferrous (Fe^{2+}) ions react with oxygen and acidic hydrogen ions to form ferric (Fe^{3+}) ions and water. Note, that oxygen needs to be present for this reaction to take place. Often this reaction doesn't occur to any great extent underground because of limited available oxygen. The conversion of ferrous iron to ferric iron consumes one mole of acidity. The reaction rate is pH dependant with the reaction proceeding slowly under acidic conditions (pH 2-3) with no bacteria present and several orders of magnitude faster at pH values near 5. This reaction is referred the rate determining step in the overall acid-generating sequence. Certain bacteria increase the rate of oxidation from ferrous to ferric iron.

The third step involves the hydrolysis of ferric iron with water to form the solid ferric hydroxide (ferrihydrate) and the release of additional acidity.

$$4Fe^{3+}_{(aq)} + 12\ H_2O_{(l)} \rightarrow 4Fe(OH)_{3(s)} + 12H^+_{(aq)} \quad \textbf{(Reaction 4)}$$

Equation 4 describes the hydrolysis and precipitation of ferric hydroxide. Hydrolysis is a reaction in which the water molecule is split. This process releases more hydrogen ions into the aquatic environment as three moles of acidity are generated. The formation of ferric hydroxide precipitate (solid) is pH dependant. Under very acid conditions of less than about pH 3.5, the solid mineral does not form and ferric iron remains in solution. At pH values above 3.5, a precipitate of ferric hydroxide forms. As $Fe(OH)_3$ and jarosite, leaving little Fe^{3+} in solution while lowering the pH.

The ferric hydroxide formed in this reaction is also called "yellow boy", a yellowish-orange precipitate that turns the acidic runoff in the streams to an orange or red colour and covers the streambed with a slimy coating. Aquatic life on the bed of the stream is soon killed off.

Based on the simplified basic reactions, acid generation produces iron that eventually precipitates as $Fe(OH)_3$ may be represented by a combination of reaction (2), (3) and (4) and the net effect is summarized in reaction 5.

$$\mathbf{4FeS_{(s)} + 15O_{2(g)} + 14H_2O_{(l)} \rightarrow 4Fe(OH)_{3(s)} + 8SO_4^{2-}{}_{(aq)} + 16H^+{}_{(aq)}} \quad \textbf{(Reaction 5)}$$

The sulphate ions associate with hydrogen ions to form sulphuric acid and with calcium ions to form gypsum sludge.

The overall pyrite reaction series is among the most acid-producing of all weathering processes. As mentioned above, this process occurs naturally, however, mining promotes AMD generation simply by increasing the quantity of sulphides exposed. Naturally occurring bacteria accelerate AMD by assisting in the breakdown of sulphide minerals, air and water being the essential agents. Without air and water, AMD will not form. Overall, pyrite is oxidized releasing acidic hydrogen ions into the water and coating the streambed with "yellow boy".

The above reactions give a fair representation of how pyrite reacts to give rise to acid and sulphate pollution. However, a number of other reactions are also possible, mostly leading to the same products. If the ferric ion is formed in contact with pyrite, the following reaction can occur, dissolving the pyrite. The fourth step involves the oxidation of additional pyrite by ferric iron.

$$\mathbf{2FeS_{(aq)} + 14Fe^{3+}{}_{(aq)} + 8H_2O_{(l)} \rightarrow 15Fe^{2+}{}_{(aq)} + 2SO_4^{2-}{}_{(aq)} + 16H^+{}_{(aq)}} \quad \textbf{(Reaction 6)}$$

The ferric iron is generated in reaction (2) and (3). Any Fe^{3+} from reaction (3) that does not precipitate from solution through reaction (4) may oxidize additional pyrite. In this reaction iron is the oxidizing agent, and no oxygen is required. This reaction generates more acid. The dissolution of pyrite by ferric iron, in conjunction with the oxidation of the ferrous ion constitutes a cycle of dissolution of pyrite. This cyclic propagation of acid generation by iron takes place very rapidly and continues until either ferric iron or pyrite is depleted.

The overall reaction for stable ferric iron that is used to oxidize more pyrite (combinations of Reactions (2), (3) and (6)) is:

$$\mathbf{FeS + 15/8\ O_2 + 13/2\ Fe^{3+} + 17/4\ H_2O \rightarrow 15/2\ Fe^{2+} + 2\ SO_4^{2+} + 17/2\ H^+} \quad \textbf{(Reaction 7)}$$

The Role of Bacteria in AMD formation

The pyrite weathering process is a series of chemical reactions, but also has an important a microbiological component. What happens in any particular environment is largely dependant on the prevailing conditions. One factor is the presence of bacteria, known as *Thiobacillus ferroxidans* which are acidophilic and can greatly enhance the rate of oxidation of iron and sulphur containing compounds. The conversion of ferrous to ferric iron in the overall pyrite reaction sequence has been described as the rate determining step (Lundgren *et.al.*, 1972). *T. ferroxidans* and several other species involved in pyrite weathering are widespread in the environment. This bacterium has been shown to increase the iron oxidation rate by a factor of hundreds to as much as 10^6 times (Silverman *et.al.* 1967).

For bacteria to thrive, environmental conditions must be favourable. The activity of *T. ferrooxidans* is pH dependent with optimal conditions in the range of pH 2 – 3 (Barron & Luecking, 1990). If conditions are not favourable, the bacterial influence on acid generation will be minimal. Thus, once pyrite oxidation and acid production has begun, conditions are favourable for bacteria to further accelerate the reaction rate. At pH values of about 6 and above, bacterial activity is thought to be insignificant or comparable to abiotic reaction rates. The catalyzing effect of the bacteria effectively removes constraints on pyrite weathering and allows the reactions to proceed rapidly. The role of microbes in pyrite oxidation is described in more detail by Kleinmann et al. (1997).

Impact of Acid Mine Drainage on Water Resources

Contaminated water seeping from abandoned coalmining areas is the most common and severe water pollution problem in the coal industry. There are many possible contaminants in and around mine sites. These contaminants in sufficiently high concentrations can have a variety of negative effects. AMD pollution degrades habitats, causes safety problems, ruins the natural aesthetics, and has a negative economic impact in general. Each of the chemical characteristics of acid mine drainage (AMD) is toxic to fish and aquatic insects, even in moderate concentrations. At high concentrations all plant life is destroyed (Hoehn & Sizemore, 1977)).

AMD is responsible for depositing a huge acid load to a large number of streams in a coal producing region. This acid is responsible for lowering the pH and degrading the quality of the waterway. As the pH is lowered, less and less living things can tolerate these harsh conditions. At sufficiently low pH, a stream is effectively dead. The corrosive acid also attacks culverts and bridge abutments, resulting in a shorter than normal life span for concrete infrastructure.

The problems of AMD are not only from acidity but toxicities of certain metals can also cause water quality problems. The acidity generated by the pyrite oxidation reactions dissolves other minerals and are responsible for depositing a large load of heavy metals into watercourses. The contaminated water may thus carry a variety of pollutants. Iron, aluminium, and manganese are the principal metals deposited as a result of coal mining activities, but others are also possible. The effects of iron are usually visible in a stream running orange or with an orange coating on the bottom. Here iron is present in the compound yellow-boy smothering aquatic plant and animal life and disrupting the food chain. Dissolved iron and iron precipitate, for example, can kill the aquatic biota that fish feed on, thus reducing the overall fish population. Iron precipitate can also clog the gill structures of fish, eventually leading to their death. In addition, precipitation of iron in the stream also wipes out the aquatic food chains and adversely affects fish populations. When present, aluminium may be seen as white compound called gibbsite. It is toxic to many aquatic organisms and humans. For some plants, aluminium limits or inhibits root development. As a result, plants cannot absorb water and nutrients and exhibit deficiency symptoms. Manganese can interfere with normal growth processes in aerial plant parts, which stunt the plant, discolour it, and cause poor yields.

AMD through acid and metal loading can render a watercourse unsuitable for a variety of uses including human, agricultural, industrial and recreational. Another significant threat to water quality and aquatic organisms also comes from eroding soils at abandoned mining sites. Tiny fly nymphs, insect larvae, and other organisms that form the base of aquatic food chains can be wiped out by heavy accumulations of soil and mine waste particles that wash into streams after rain. Suspended silt particles can clog the gills of fish and smother eggs on the stream bed.

Acid drainage can also have significant impacts on the operational economics of a mining operation. This is largely due to the effects of acid water on the piping and pumping infrastructure, plant equipment and the limitations it places on water reuse and discharge.

Objective of the study

The majority of AMD problems stem from the reactions of sulphide minerals with water and oxygen. A series of chemical reactions creating the pollutants that appears in our waterways. The specifics of where and how these reactions occur are dependent on the specifics of the geology and hydrology of the particular site. No two AMD discharges are chemically exactly alike. The individual impacts and the options for treating discharges have much variability. AMD can have detrimental effects on mining infrastructure, water reuse options and environmental discharge. As a result, some form of treatment is required at many mine sites. Unless treated, acid water cannot be discharged into public water courses.

AMD polluted water is typically highly acidic with elevated levels of sulphate and dissolved metals and iron. The main purpose of treatment systems are:

- to lower the total acidity by neutralizing the acid by adding alkalinity to raise the pH of the water
- to lower the toxicity of metals and sulphate by desalination methods before they are allowed to enter streams and waterways.

Successful treatment relies on:

- a clear understanding of the reason for treatment (e.g. water reuse or infrastructure protection, environmental discharge requirements, pH correction, reduction of metal toxicity)
- the selection of the appropriate technology and/or reagent to address the water quality issue identified

- the correct implementation of the chosen technology.

Identifying the best option for treatment is dependant upon a number of factors including initial water chemistry (eg pH, acidity, acid load, and metal concentrations), water quality objectives, flow rates, site logistics and economics.

Economics are a key consideration for water treatment, and both capital as well as operational costs must be considered. While cost and ease of implementation play a major role, the chemistry and volume of the acid water should ultimately influence the selection and viability of the particular technology. The water chemistry of the acid water determine which treatment processes would be most effective. The dominant anion species in AMD is sulphate and the major cat ion is iron. High concentrations of dissolved heavy metals are also characteristic of acid waters.

Cost effective treatment processes are needed for treatment of AMD and industrial effluents for the recovery of re-usable water. Active treatment involving pH control with neutralization reagents are and will remain the most widely used and lowest cost approach to AMD treatment for neutralization. The largest single cost component in most active treatment systems is the reagent cost. Efforts are therefore needed to be directed at the development of technologies that improve the efficiency of reagent use. For lime-based reagents, key strategies should include minimizing the armouring of reagents with precipitates, and preventing saturation of the reagent during dispensing. Limestone is likely to be the prime choice for acid water neutralization in future due to its widespread availability, non-proprietary nature, ease of application and cost-effectiveness.

The objectives of the studies described in this thesis were the following:

- To investigate the chemical aspects of the integrated limestone neutralisation process.
- To determine the suitability of the DesEl process for the desalination of neutralised acid water.
- To conduct a case study to remove arsenic from an acid water with the Integrated Limestone Neutralisation Process.

Brief overview of thesis.

The background of acid mine drainage and the impact of acidic effluents on water scarcity and water demand were discussed in the Introduction (Chapter 1). A literature survey of current water treatment technologies for neutralisation and desalination is the subjects of Chapter 2.

The body of the thesis details the work done on the integrated limestone neutralisation process. The characteristics of a reactive limestone are a high neutralising rate. Particle size is an important parameter in this process. In Chapter 3 work on the effect of the limestone particle size on the limestone neutralisation rate is described.

In addition to the neutralisation rate, the production of high quality sludge is also important. Due to the capital and running costs associated with poor sludge settling in the limestone neutralisation process, ways whereby the sludge settling rate and sludge density could be increased (or sludge volume reduced), were also investigated. The sludge characteristics are of great importance in the final design of a treatment plant, and further research was required and is described in Chapter 3.

Neutralisation is generally the first step in the treatment of acid mine water. With the limestone neutralisation process, acidity is removed but only partial sulphate and metal removal are achieved. Further treatment for sulphate and metal removal are required to make the limestone neutralised water suitable for re-use or discharged. The purpose of the study described in Chapter 4 was to investigate the suitability of the DesEl process for desalination of neutralised process water.

The Integrated Limestone Neutralisation Process is used for treating acid, iron and sulphate-rich water with limestone. Chapter 5 describes a case study where results from Chapter 3 were implemented in the limestone neutralisation of arsenic rich process water from a gold mine.

Conclusions on the limestone neutralisation technology, followed by desalination with the DesEl process are to be found in chapter 6.

CHAPTER 2 LITERATURE SURVEY OF WATER TREATMENT TECHNOLOGIES

Neutralisation of acid mine water

AMD is a serious problem since mixing of acidic mine water with natural waters in rivers and lakes can cause severe degradation in the quality of the natural water bodies. This can be ascribed to the fact that both the acid and the dissolved metals are toxic to aquatic life. Such polluted waters are unsuitable for human consumption and industrial use. Collecting and treating mine water to a quality where it can be re-used without restrictions can prevent this source of pollution (Maree & Du Plessis, 1994). Traditionally, iron (II) rich acid mine water is treated with lime using the High Density Sludge (HDS) process. Iron (II) is oxidised at a rapid rate through aeration when the pH is raised with lime to pH 7.2 and higher.

Neutralisation is generally the first step in the treatment of acid mine water. The treatment of AMD is currently done by natural means (i.e. AMD streams that pass through alkaline bedrock minerals which posseses neutralization capacity), active treatment (whereby chemicals are added to the AMD) and passive treatment where AMD is passed through constructed wetlands. Treatment technologies are commonly categorised as either passive or active (Benefield *et.al.*, 1982). Different passive and active technologies are available for dealing with acid drainage.

Passive Treatment Technologies

Passive treatment systems do not require continuous chemical inputs, but take the advantage of naturally occurring chemical and biological processes to treat the acid drainage. Passive treatment systems are almost exclusively used for highly reduced (eg low oxygen) waters with low soluble aluminium concentrations, low flow, low acidity and therefore low acid load scenarios. The more oxidised and aluminium-rich waters from operational mines are less suited to sustainable passive treatment approaches. All of the passive treatment systems have an engineered life expectancy. Passive treatments technologies include, oxic limestone drains, anoxic limestone drains, limestone diversion wells, various reducing and alkalinity producing systems, pyrolusite limestone beds, aerobic and anaerobic wetlands, permeable reactive barriers, slag leach beds and gas redox and displacement systems (Pulles, 2000).

Mine water has high levels of acidity and consequently a low pH. Adding alkalinity will raise the pH. For passive treatment systems, limestone is the widely preferred neutralizing agent. Having mine water in contact with limestone neutralizes the acidity with an increase in pH. If the water also contains iron, particularly ferric iron and the pH rises above 3.5, the ferric iron precipitates as yellow-boy ($Fe(OH)_3$). The yellow-boy deposit on the limestone passivates it and prevents further dissolution, rendering it ineffective in further neutralization because of the coating, also known as armouring. Armouring is a failure mode of some passive treatment systems.

When pyrite initially reacts with oxygen and water, one of the products is ferrous iron. For ferrous to be oxidised to ferric iron, more oxygen is needed. The amount of oxygen underground can be very limited, and the conversion may not happen to any significant extent in this oxygen limited environment. Often when polluted mine water emerges at the surface, very little of the iron is in the ferric form because of a lack of oxygen underground. This, however, changes quickly once the mine water is exposed to the atmosphere where plenty of oxygen is available. One passive treatment strategy for mine water having high acidity and virtually all the iron in the ferrous state is to exclude oxygen while it is passed through a channel of limestone rock.

Active Treatment Technologies

Active treatment systems require the continuous or semi-continuous input of energy and/or reagents. Active treatment involving raising the pH with an alkaline is the most common and cost-effective form of acid water treatment. Active treatment technologies can be tailored to suit most applications and can be engineered to treat virtually all types of drainage or effluents. Any pH, flow rate and daily acid load can be accommodated. It has no limitations in respect of acid load or redox potential as is the case with passive treatment systems.

Many mining companies use active chemical treatment methods to comply with legislation. In these treatment systems, the acidity is buffered by the addition of alkaline chemicals such as lime (CaO), limestone ($CaCO_3$), sodium hydroxide ($NaOH$) or anhydrous ammonia (NH_3). Calcium-based alkalies like quicklime (CaO), hydrated lime ($Ca(OH)_2$) and limestone ($CaCO_3$) are the neutralising agents of choice due to their widespread availability. Active treatment systems are generally more expensive to implement and maintain than passive systems, requiring the installation of a plant with agitated reactors, precipitators, clarifiers and thickeners. Chemicals are used raise the pH to acceptable levels and decrease the solubility of dissolved metals, removing major and trace metals through precipitation and adsorption. The metal precipitates that form are settled out. The largest, single cost, component of an active treatment system is the reagent. Additional costs are also associated with the operation and maintenance of the plant as well as the disposal of metal-laden sludges (Van Tonder *et.al.*, 1994).

Lime Neutralisation

Conventional Lime Treatment Process

Conventional lime treatment is a well established technology that is widely practiced. However, the process generates a low density sludge (1-30% solids) which requires relatively large settling areas to clarify the discharge and store the sludge.

A flow-diagram of the conventional process is shown in Figure 1. The process consists of neutralisation followed by solid-liquid separation. The main disadvantage of this process is that sludge with a low density is produced.

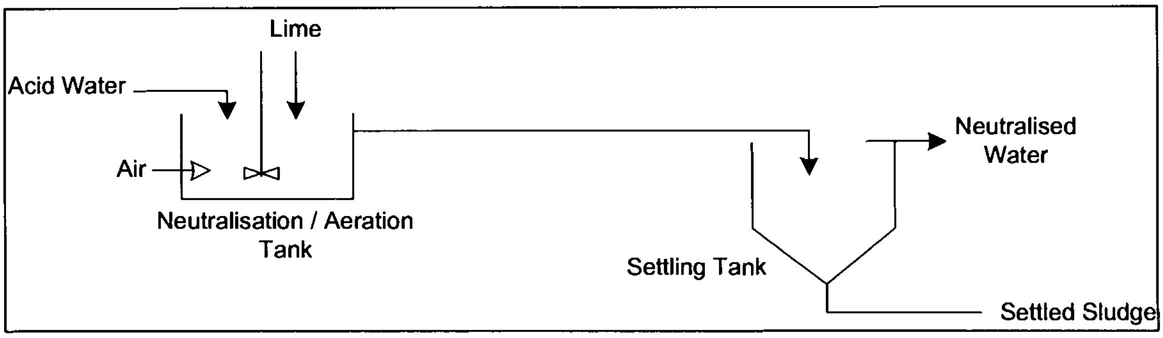


Figure 1. The conventional lime treatment process for acid water neutralization.

Conventional lime treatment involves the controlled addition of lime slurry to a reactor tank. Single or multiple tanks may be used, depending on the quality and quantity of the AMD being treated. Air is frequently added to oxidize the ferrous iron to ferric form. Flocculant is also added to the discharge from the final reactor to enhance settling in the settling pond. The final effluent from the settling pond is released to the receiving environment. Some of the effluent may be recycled to mix the reagent slurry.

High Density Sludge Process

The high density sludge process (HDS) is a modification of the conventional lime treatment process and is used by several mining companies to produce a final sludge with higher solids content than afforded by the conventional lime treatment process. The solids content is generally 10% to 30% higher than conventional lime treatment. The flow diagram of the HDS process is shown in Figure 2 and consists of a pH correction and sludge conditioning stage, aeration and neutralisation stage and a solid-liquid separation stage.

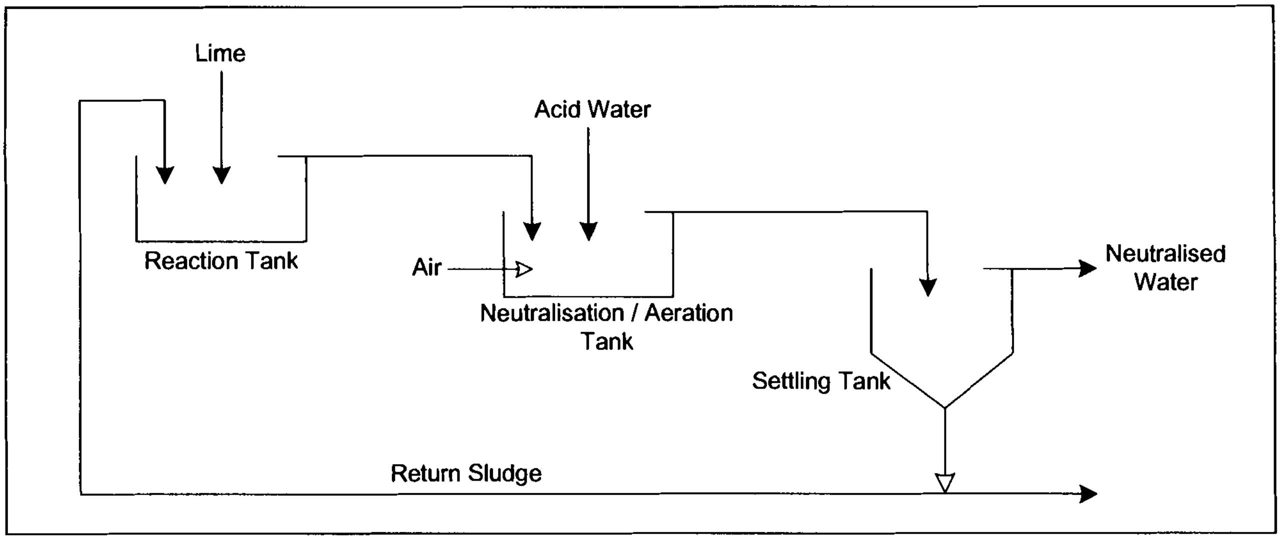


Figure 2. The High Density Sludge process for acid water neutralization.

The process involves utilizing a mixture of lime slurry and recycled sludge as the alkaline reagent for the first reactor tank. This pH correction and sludge conditioning stage consists of a reaction tank for the preparation of a lime solution and a sludge conditioning tank which receives both the recycled, settled sludge from the settling tank underflow and the lime solution. The lime dosage in the conditioning stage is such that the final treated water is between pH 8 and 9.5.

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

The neutralised and oxidised effluent overflows to the thickener where sludge is separated from the liquid. A polyelectrolyte (flocculent) can be dosed to the clarifier to promote flocculation. The flocculent is added to the discharge from the final reactor before it is pumped to a thickener. The thickener underflow is discharged to a sludge storage pond or mixed with the mine tailings. The thickener overflow is discharged to a polishing pond before being released to the receiving environment. The mixing of the lime slurry with recycled sludge causes denser, larger particles to form during the subsequent precipitation.

The HDS process has the following advantages over the conventional process, as highlighted by Osuchowski (1992)

- Sludge with a density 10 times higher than that of the conventional process is produced. As a result less demanding sludge drying facilities are required.
- The sludge settles faster, therefore, a saving on equipment costs can also be realised.

Acid mine water in the industry is generally neutralized with lime by using the above two processes. The conventional neutralization process produces sludge with low solids content. Although the HDS process produces sludge with high solids content, one of the disadvantages of lime treatment is the difficulty to control the process, especially where there is fluctuation in flow rates and acid concentrations. Other disadvantages are the cost of lime and the maintenance of the slaking equipment as well as hazards associated with handling of the alkali.

Typical problems associated with acid mine water treatment processes with lime include (Maree *et.al.*, 1992):

- Corrosion and scaling of equipment.
  When acid water is neutralised with lime, the water often becomes over-saturated with respect to gypsum. This results in scaling of equipment by the unstable water, malfunctioning of dosing equipment and settling of particles in pipelines and valves. The latter causes blockages that result in under-dosage, which in turn leads to acid corrosion.
- High treatment cost.
  Lime is expensive. Should limestone be used, the cost could be reduced significantly. Desalination of neutralized mine water is not generally applied due to high treatment cost. However, desalination treatment will have to be considered when treated acid mine water has to meet more stringent quality requirements for industrial re-use or discharge.
- Sludge disposal.
  Legislation requires that sludge from neutralisation plants be discharged into lined ponds to prevent metal leachate from polluting ground water. Construction of lined ponds is costly. The volume of sludge to be disposed of also influences the cost and processes that produce sludge with a high solids content would be preferred.

Limestone Neutralisation

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

The cost of powdered limestone ($CaCO_3$) in South Africa, a by-product, is 50 - 60% cheaper than lime. The cost of neutralisation can be reduced significantly when lime is replaced with limestone (Maree *et.al.*, 1992).

Iron in mine water can occur in two oxidation states. This can be significant, especially when considering treatment strategies to remove iron. The iron will be either: ferrous (Fe(II)) or ferric (Fe(III)). Ferrous iron is soluble in water at any pH and the water will appear crystal clear. The situation is different with ferric iron. At a pH below about 3.5, ferric iron is soluble. If the pH is higher than 3.5, the ferric iron will precipitate as an orange/yellow compound. Limestone powder was found to react rapidly with free acid, ferric and aluminium salts in AMD, but not in the ferrous containing AMD (Maree & Du Plessis, 1994).

Limestone is not generally used for iron(II) rich, acid water, neutralisation because of the following disadvantages (Du Plessis & Maree, 1994) :

- Rapid oxidation of Fe(II) to Fe(III) occurs only at pH 7 and higher. This pH can be achieved with lime but not with limestone.
- Low reactivity of limestone leads to long residence times being required for complete neutralisation.
- Scaling of limestone particles by iron also known as armouring.

A key problem that greatly reduces the effectiveness of limestone-based treatment systems is the armouring of the limestone by metal hydroxides (eg iron, aluminium, manganese) and gypsum ($CaSO_4.2H_2O$). Such armouring retards the reactivity of the limestone. Armouring can be partially overcome by approaches that minimise the presence of oxygen within the treatment system, maximise the available surface area of the limestone and or provide sufficient agitation within the system for the continuous abrasion of armoured surfaces. When crushed or mined limestone is used, a biological iron(II)-oxidation process is needed upstream due to scaling of the limestone particles with gypsum and ferric hydroxide (Maree *et.al.*, 1998).

Over the past years, the CSIR has developed a limestone neutralisation technology for treatment of acidic effluents. Further research was needed to investigate methods to improve the settling rates of the sludge produced from the integrated limestone process. This process is used for treating acid, iron and sulphate-rich water with powdered calcium carbonate. The CSIR neutralization technology is patented in South Africa under the following patent numbers (Maree, 1997):

- RSA Patent No 91/5516 - Limestone neutralization in a fluidized-bed reactor

- RSA Patent No 98/5777 -Treatment of acid and iron(II)-rich water with powdered calcium carbonate for simultaneous removal of acid and iron(II) and partial removal of sulphate through gypsum crystallization.
- RSA Patent No 2001/7086 - A novel system for dosing powdered calcium carbonate.

The integrated limestone neutralisation process consists of the following stages (Geldenhuys *et.al*, 2001 and Maree *et.al.*, 1997):

- Neutralisation, iron oxidation and gypsum crystallisation stage. During this stage acid water is treated in an aerated sludge reactor with powdered limestone (particle size < 100 μm). The limestone is dosed to a level slightly in excess of stoichiometric requirements.
- Sludge separation stage. For this stage, a clarifier is required from which sludge is returned to the neutralisation reactor to maintain a minimum concentration of suspended solids.

The CSIR limestone neutralisation process, which uses limestone or powdered calcium carbonate or dolomite as the neutralising agent is discussed by Maree and Du Plessis (1992). In the case of the fluidised-bed limestone process, the dosing problem mentioned above is overcome, as limestone will only dissolve provides the water is undersaturated with respect to calcium carbonate. This usually occurs at pH levels below 7.

The benefits associated with neutralisation of acid water with calcium carbonate are the following (Du Plessis & Maree, 1994):

- Direct savings on the cost of neutralisation agent.
- Limestone is readily available.
- Simplified process control. No pH-control is required as limestone and dolomite dissolution occur mainly at pH-values below 7. Since the flow rates of plant effluents may vary by a factor of 10 as shown by Pulles (2000), lime/soda ash systems can only function well if their dosing rates are adjusted accordingly.
- Minimisation of material wastage, which would occur as a result of over-dosage.
- Elimination of hazardous chemicals used for neutralisation (limestone in non-hazardous).
- Simplified bulk chemical storage. Raw material can be stockpiled in the open as the material is not readily soluble in neutral water.
- Utilization of existing equipment at lime neutralisation plants is possible.

Fluidised-bed neutralisation process

In this process, crushed limestone (particle size < 4 mm) is used for neutralization of acid water in a fluidised-bed reactor after iron (II) has been oxidised to iron (III) at low pH. This oxidation process is needed as limestone particles are scaled with a layer of ferric hydroxide and gypsum when iron (II) rich water is fed directly to the limestone neutralization plant.

Complete neutralisation of discard leachate containing, 10 g/L $CaCO_3$ and 4 g/L iron (II) can be achieved in a limestone neutralisation fluidised-bed reactor, provided that the iron (II) is oxidised beforehand (Maree & Van Tonder, 2000). This can be achieved through biological iron (II) oxidation at low pH. It was shown that the iron (II) oxidation rate is related to the surface area of the biomass support medium: when plastic medium (surface area 200 m^2/m^3) was used a reaction time of 18 h is required to oxidise 4 g/l iron (II) to iron (III) (Maree *et.al.*, 1998).

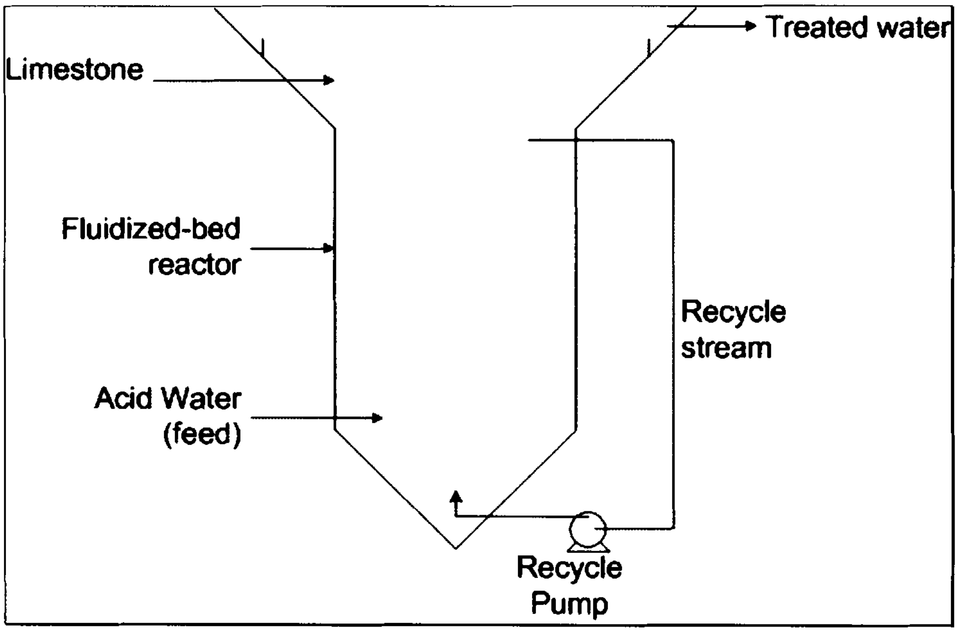


Figure 3. Schematic diagram of the fluidised-bed reactor for acid water neutralisation.

A schematic diagram of the fluidised-bed reactor technology is shown in Figure 3. In this process, crushed limestone is dosed to a column reactor. The particles are kept in suspension by controlling the up-flow velocity by means of a recycle pump. Accurate control of the limestone dosage is not required, because limestone only dissolves as long as the water is under-saturated with respect to $CaCO_3$. This usually occurs below pH 7. Load cells, that measure mass, are used to control the feed-rate of limestone. Chemical sludge, ferric hydroxide and gypsum, are washed out with the treated water and separated from the water in a clarifier.

By using the fluidised bed reactor for limestone neutralisation, the main disadvantage of limestone (low reactivity, scaling of limestone particles) are overcome. The problem of long reaction times due to the low reactivity of limestone, are solved with the fluidised bed technology because an excess amount of limestone is in contact with the acid water. Scaling of limestone particles with compounds such as gypsum or aluminium hydroxide is prevented by the attrition between particles under fluidised conditions. Sludge of higher density is also produced when compared to that of the conventional lime treatment process.

A limitation of the fluidised-bed process is that iron(II) rich effluent cannot be treated directly (Van Tonder et.al., 1994). Iron(II) passes through the fluidised-bed reactor. When aeration is applied to oxidise iron(II), the limestone particles become coated with ferric hydroxide which prevents dissolution of the limestone particles. For ferrous rich acid mine water, a biological iron(II)-oxidation process is needed upstream of the fluidised-bed neutralisation process where iron(II) is oxidised to iron(III). The disadvantage of the multi-stage limestone treatment process for acid mine water is that the capital cost is unacceptably high.

Integrated iron (II) oxidation and limestone neutralisation process

Maree et.al. (1998) showed that powdered calcium carbonate can be used in an integrated process for treatment of acid water. In this process, the calcium carbonate is used for neutralisation, facilitating precipitation of Fe^{3+} and Al^{3+}, and gypsum crystallization, in the same reactor. The novelty of this development lies in the conditions that were identified where ferrous iron can be oxidised at pH 5.5 by the addition of $CaCO_3$. Previously, lime was used to raise the pH to 7.2 where the rate of iron oxidation is rapid.

In this process, powdered calcium carbonate together with aeration is used to oxidise iron (II) to iron (III), to neutralize acid water and to allow for gypsum crystallization in a single completely mixed reactor system (Maree, *et al.*, 1999). Milled limestone (particle size < 0.1 mm) or the precipitated calcium carbonate, can be used as neutralisation agent.

Maree *et.al* (1998) showed in tests where synthetic discard leachate was treated with calcium carbonate that the leachate was neutralised effectively, sulphate was reduced and ferrous iron was completely oxidised. This showed that partial sulphate removal could be achieved by using a cheap neutralising agent. In the absence of sodium and magnesium, sulphate can be removed to 1 500 mg/L, which was still higher than the target of 500 mg/L, calcium carbonate neutralisation, therefore, can be applied effectively as pre-treatment prior to further treatment for sulphate removal below 500 mg/L.

Desalination of Saline Waters

In recent years, desalination has increasingly been used throughout the world to produce potable water from brackish groundwater and seawater, to improve the quality of fresh water for drinking and industrial use, and to treat industrial wastewater prior to discharge or reuse. The use of desalination technologies for treating water supplies will continue to increase because of increasing shortage of useable surface and ground water in many parts of the world (Abbas, 2005).

Mining and smelting industries are faced with numerous environmental issues regarding wastewater containment and disposal. Some industries have large holding ponds containing mining wastes while other operations may have contaminated groundwater supplies. Industries also have wastewater streams that often do not meet increasingly stringent discharge limits. All these water sources can be treated with desalination technologies to produce high quality water for reuse. In some cases, valuable mining by-products can also be recovered for sale or reuse.

Acid water from mining activities require treatment for both neutralization and desalination. Neutralization can be used as pre-treatment to desalination processes. In South Africa, the emphasis for desalination is placed on the removal of sulphate from acid mine waters to minimised salination of surface water. In countries like the USA more emphasis is placed on the removal of heavy metals due to the toxicity. Although some substances dissolved in water, such as calcium, sulphate, carbonate, iron, aluminium etc. can be removed by chemical treatment (concurrently with neutralisation) with limestone and lime, other common constituents, like sodium and chloride, require more technically sophisticated methods for removal, such as desalination.

Desalination is a separation process used to reduce the total dissolved solids (TDS) content of water to usable levels. It provides a means of upgrading poor quality, saline waters, and refers to all technologies designed to produce freshwater from saline sources. The term is therefore usually confined to any process for making fresh water out of saline or polluted water. Although fresh water is usually the objective of desalination, the same techniques can be used for recovery of dissolved salts and metals. All desalination processes involve three liquid streams. The saline feed water, which is separated by the desalination process into two output streams, namely the low-salinity product water and the very saline concentrated brine stream. The product water of the desalination process is generally water with less than 500 mg/l TDS, which is suitable for most domestic, industrial, and agricultural uses. The by-product of desalination is brine, a concentrated salt solution that must be disposed of.

Desalination Technologies

A number of technologies have been developed for desalination, including reverse osmosis (RO), electro-dialysis (ED), reverse electro-dialysis (EDR), ion exchange (IX) and the DesEl process. The major factors that determine which type of treatment is best suited to a particular application include the levels of salinity and temporary hardness, the presence of colloidal suspended matter, dissolved metal ions, oxidizing agents, and hydrogen sulphide, and temperature of the feed water, etc. (Crossley, 1983).

Reverse Osmosis (RO)

Reverse osmosis is a membrane process that relies on the tendency for fresh water to diffuse through a semipermeable membrane into a salt solution, thereby diluting the more saline water. The fresh water migrates through the membrane as though there were pressure on it, and the effective driving force is called osmotic pressure. By applying pressure to saline water on one side of a semipermeable membrane, fresh water can be driven through in the direction opposite to the osmotic flow. This process is called reverse osmosis (Crossley, 1983). Relatively pure water is thus "squeezed" out of the stronger solution. Even with an applied pressure that is double the osmotic pressure, the flow rate is very low.

RO plants produce a product stream (pure water) and waste stream (brine). The water recovery through a RO plant is defined as the percentage of treated water (pure water) to the feed water flow. Normally it is desirable to recover as much as possible, thereby maximising production and minimising the quantity of brine that requires disposal. In reality however there are many factors that restrict the maximum recovery that can be achieved through a RO plant. The main factors are membrane scaling, maintaining minimum brine flows, achieving satisfactory pure water quality, maintaining acceptable membrane flux rates, and not exceeding membrane operating pressure.

For the preservation of the effectiveness and life span of a reverse osmosis (RO) installation, a sufficient pre-treatment of the feed water is required. This greatly influences the performance of the installation. The incoming feed water is pre-treated to be compatible with the membranes by removing suspended solids, adjusting the pH, and adding a threshold inhibitor to control scaling caused by constituents such as calcium sulphate.

The performance of RO desalination processes are affected by the following factors: (Schoeman & Steyn, 2003)

- The condition of the raw water and the effectiveness of the pre-treatment procedures
- Membranes: type, size and the number of modules used and their arrangement.
- The rate and degree of fouling and cleaning ability.
- Operating conditions, such as feed pressure, temperature and permeate recovery.
- The efficiency of pumps (high pressure and booster pumps) and energy recovery systems.

Scaling is the accumulation of partially insoluble salts on a membrane. When a reverse osmosis installation has a recovery of 50%, the concentration of salts in the concentrate flow is double the concentration of salts in the feed water flow. When recovery increases, the chances of scaling increase also. Because of this it is of great importance that the saturation limits of the partially insoluble salts are not exceeded. Substances that cause problems in a reverse osmosis system are mainly calcium carbonate ($CaCO_3$), calcium sulphate ($CaSO_4$) and silica, but also calcium fluoride (CaF_2), barium sulphate ($BaSO_4$) and strontium sulphate ($SrSO_4$).

Over the last 40 years, tremendous advance have been made in the field of membrane technologies. In fact, RO represents the fastest growing segment of the desalination market (Wangnick, 2002).

Elecro-dialysis (ED)

Electro-dialysis (ED) is an electrochemical separation process in which mineral salts and other ionic species are transported through ion-selective membranes from one solution into another under the driving force of a direct current (DC) electrical potential. The key to the process are the ion-selective membranes which are essentially ion-exchange resins cast in sheet form (Hell *et.al.*, 1998). Ion exchange membranes, which allow passage of positively, charged ions (such as sodium and potassium) are called cation membranes. Membranes that allow passage of negatively charged ions (such as chloride and phosphate) are called anion membranes.

To demineralise a solution using ED, cation and anion membranes are arranged alternately between plastic spacers in a stacked configuration with a positive electrode (anode) at one end and a negative electrode (cathode) at the other. When a DC voltage is applied, the electrical potential created becomes the driving force to move ions, with the membranes forming barriers to ions of opposite charge. Therefore, anions attempting to migrate to the anode will pass through the adjacent anion membrane but will be stopped by the first cation membrane they encounter. Cations trying to migrate to the cathode will pass through the cation membrane but will be stopped by the anion membrane. Hence, the membranes form ion diluting compartments and ion concentrating compartments. The concentrated saltwater flow is circulated until it has reached a value that enables precipitation. At this point the flow is discharged. The standard configuration of a desalting process utilizing the electro-dialysis principle is shown in Figure 4. In ED applications, hundreds of positively and negatively charged cell pairs are assembled in a stack to achieve a practical module (Lee & Karos, 2002).

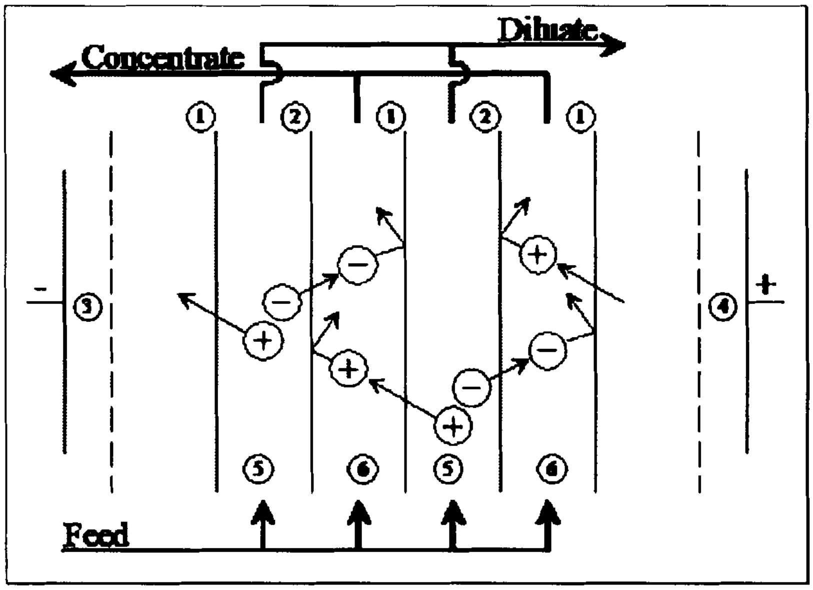


Figure 4. Principle of a simple electro-dialysis process.

Diagram shows the membrane configuration with alternating cation-selective (1) and anion-selective (2) membranes between two electrodes ((3) and (4)), one at each end of the stack.

Pre-treatment is necessary before electro-dialysis can take place. Suspended solids with a diameter that exceed 10 µm need to be removed, or else they will plug the membrane pores. There are also substances that are able to neutralize a membrane, such as large organic anions, colloids, iron oxides and manganese oxide. These disturb the selective effect of the membranes. Pre-treatment methods, which aid the prevention of these effects, are active carbon filtration (for organic matter), flocculation (for colloids) and filtration techniques.

Typical recovery rates using the electro-dialysis process range from 80% to 90% of the volume of feed water (Hell *et.al.*, 1998). This process uses energy at a rate directly proportional to the quantity of salts to be removed and for this reason, is usually used for the treatment of low TDS water. This technology is very cost effective for salinities up to 10 000 mg/l, but is not well suited for desalinating high salinity seawater.

Electro-dialysis reversal (EDR)

One of the problems in membrane desalination processes is that membranes and other active surfaces tend to become fouled or scaled over time with inorganic and organic substances. Electro-dialysis reversal (EDR) was developed with the ED technology as the basis. EDR operates according to the same principles as ED, but periodically reverses the polarity of the system to reduce scaling and membrane clogging. Electro-dialysis represents approximately three percent of worldwide desalination capacity (Wangnick, 2002).

The same membranes as in the ED process are used to provide a continuous self-cleaning electro-dialysis process which uses periodic reversal of the DC polarity to allow systems to run at higher recovery rates. Polarity reversal causes the concentrating and diluting flow streams to switch after every cycle. Any fouling or scaling constituents are removed when the process reverses, sending fresh product water through compartments previously fill with concentrated waste streams. Therefore, EDR systems operate with higher concentrations in the brine with less flow to waste.

EDR treatment is rarely used in SA and very little information is available for performance and maintenance requirements. In contrast there is extensive experience with RO. An advantage of EDR over RO is that the volume of waste stream is smaller. Because of its rugged membranes and high chlorine tolerance, EDR membranes could be ideal for wastewater reuse.

Ion Exchange (IX)

Ion exchange involves passing saline water over resins that exchange more desirable ions for less desirable dissolved ions. Ion exchange resins substitute hydrogen and hydroxide ions for salt ions. For example, cation exchange resins are used to remove calcium and magnesium from "hard" water. A number of municipalities use ion exchange for water softening, and industries requiring extremely pure water commonly use ion exchange resins as a final treatment following reverse osmosis or electro-dialysis. The primary cost associated with ion exchange is in the regenerating or replacing the resins. The higher the concentration of dissolved salts in the water, the more often the resins will need to be renewed. In general, ion exchange is rarely used for salt removal on a large scale.

Among the several techniques available for desalination, the ion exchange process seems to be the most attractive because of its simplicity, effectiveness and relatively low cost. (Clifford 1993) Although technically and economically effective, the ion exchange process has two inevitable problems. Ion removal by ion exchange are affected by the presence of other species, such as hardness (Ca^{2+} and Mg^{2+}) and sulphate, which compete for the limited ion exchange sorption capacity. For nitrate removal with IX, the first is the trouble caused by sulphate ions. Since conventional anion exchange resins have general selectivity sequences of $SO_4^{2-} > NO_3^- > Cl^- > HCO_3^-$, sulphate ions in the raw water interfere heavily in nitrate removal and results in short service runs. For nitrate removal with ion exchange, selective resins are available (Crossley, 1983) to overcome this problem.

The most notable unsolved problem is the disposal of spent brine produced during regeneration of exhausted resins (Bae *et.al.*, 2002). The process requires the use of salt solution at saturation concentration to regenerate the ion exchange resins resulting in the production of wastes with high salt content. The high salt consumption require a substantial salt handling, storage and disposal system. Problems related to the disposal of spent brine from regeneration of exhausted resin must be overcome before ion exchange can be applied more widely and economically.

DesEl process

The DesEl process is a novel, electrostatic charging system which acts as a capacitor to reversibly absorb salts and other charged substances dissolved in water. The process was developed by Enpar Technologies in Canada. The lab scale unit used during this study was the first DesEl system in South Africa.

The DesEl process has many advantages over conventional desalination technologies. These advantages include regeneration without chemicals, simplified pre-treatment, consistently pure water without breakthrough or regeneration downtime, and minimal operating costs.

The process operates on the principles of capacitive deionization to remove ionic TDS. The main component of the DesEl System is a novel, electrostatic charging system which behaves as a capacitor and is comprised of inexpensive carbon electrodes. The capacitor is energized using direct current, creating positive and negatively charged surfaces. Ionic compounds such as iron, chloride, arsenic and nitrate are attracted to and electrostatically adsorbed onto the surfaces of the electrodes.

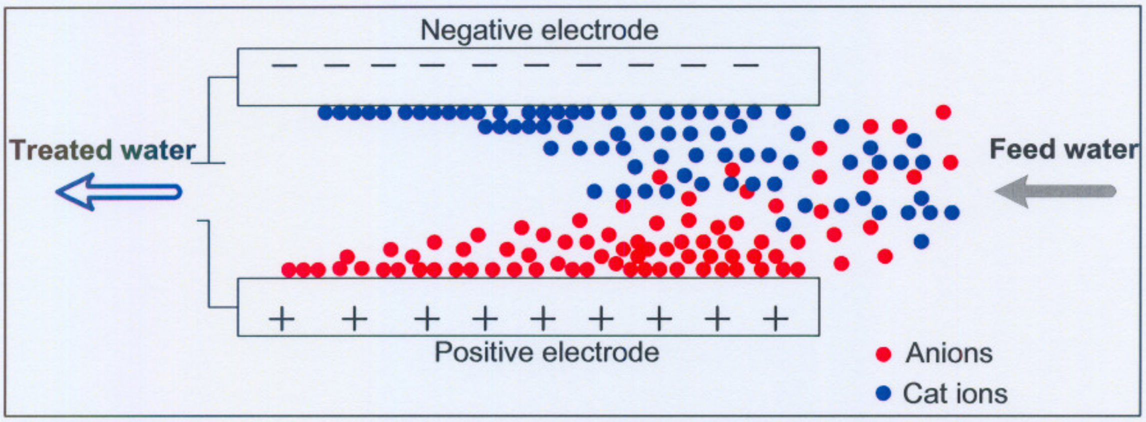


Figure 5. Simple flow through capacitor during the purification cycle.

To regenerate the system, the polarity of the cell is reversed causing the capacitor to release the contaminants into the cell channels. The contaminants are removed from the cell by flushing with a small quantity of liquid forming a concentrated solution. The operating potential is relatively low (approximately 1.3V) such that no electrolysis reactions occur precluding breakdown of the capacitor material and the formation of secondary solid phases. The DesEl unit employs the "Charge Barrier" innovation consisting of ion selective layers. This innovation enables >90% water recoveries for brine with similar potential for seawater.

The main advantages of the DesEl System over conventional water desalination technologies are:

- No sub 15 μm-filtration required.
- No sustained concentrate leading to the formation of precipitates and fouling.
- Extremely high water recoveries coupled with high ion removal efficiencies.
- Long life cycle of capacitor materials.
- Low maintenance

- No continued addition of salts to treated water as with ion exchange.
- Chemically stable components precludes the introduction of foreign materials into the treatment stream
- Readily removes problem contaminants such as nitrate, perchlorate and arsenic
- Can be designed to preferentially remove contaminants without complete deionization of the water stream
- Can be operated at various levels of ion removal and water recovery efficiencies

Due to these advantages, the application of the DesEl technology for desalination of industrial effluents will be discussed in Chapter 5 of this thesis.

Brine Disposal

Desalination and membrane-based water purification technologies do not eliminate the water constituents of concern. Rather, these constituents are concentrated in a fraction of the water, thus improving the water quality of the other fraction. The by-product of desalination processes is brine, a concentrated salt solution that must be disposed of. Designing a desalination plant to minimize production of salt solids is not technologically feasible. However, the volume of water containing concentrated salts can be reduced through various technologies.

The brine must be handled in a manner that minimizes environmental impacts. The best option for concentrate disposal must be selected on a site-specific basis based on economic and environmental considerations (Schoeman & Steyn, 2003). Options for brine disposal include discharge into deep saline aquifers or surface waters with a higher salt content, or the brine can also be diluted with treated effluent and disposed of by spraying on golf courses and/or other open space areas.

CHAPTER 3 CHEMICAL ASPECTS OF THE INTEGRATED LIMESTONE NEUTRALISATION PROCESS

Introduction

The characteristics of a reactive limestone are a high neutralising rate. In addition to the neutralisation rate, other factors should also be considered for the limestone neutralisation process. The production of high quality sludge, three characteristics of the produced sludge are important and were investigated during this study:

- Settling rate
- Sludge volume
- Sludge solids content

Due to high capital and running costs of water treatment plants showing with poor sludge settling it is necessary to explore ways whereby the sludge settling rate and sludge density could be increased (or sludge volume can be reduced). The sludge characteristics are of great importance in the final design of the treatment plant. It was envisaged that the outcome of the proposed investigations would have a direct effect on the equipment required for sludge handling (e.g. clarifiers and filter presses) as:

- The faster the settling rate of the sludge, the smaller the diameter of the clarifier can be.
- The larger the volume of the settled sludge, the more costly the filter press will be.

The objectives of this study were to investigate the following parameters on the sludge settling rate, final sludge volume and sludge solids content:

- Effect of limestone particle size on the rate of neutralisation
- Effect of sludge concentration as a function of feed water acid concentration.
- Effect of limestone source.
- Effect of the limestone addition method (single as opposed to multiple dosages).
- Identification of the most suitable flocculant.
- Effect of limestone neutralisation sludge on required lime dosage to raise the pH to 10.

Materials and Methods

Feed water:

The following acid waters were used as feed water during the study:

- Ticor - mineral separation plant A (8 g/l acidity)
- Namakwa Sands - mineral separation plant B (24 g/l acidity)
- Somchem - acid factory stream (21.5 g/l acidity) and
- Synthetic - artificially prepared acid water (8 g/l acidity).

The chemical compositions of the four different acid waters are presented in Table 1.

Table 1. Chemical composition of acid water samples for neutralisation tests.

Parameter	Unit	Somchem	Ticor	Namakwa Sands	Synthetic
pH		0.5	1.88	1.21	1.32
Acidity	mg/l as $CaCO_3$	21500	4250	24500	19000
Iron(II)	mg/l as Fe	<28	<28	447	<28
Sulphate	mg/l as SO_4	14736	5000	27363	19000

Limestone samples:

Limestone samples from various sources (Table 2) were used for neutralization tests.

Table 2. Characteristics of limestone samples for neutralisation tests.

Name	Particle size	$CaCO_3$ content	Origin
Unimin	As received	98 %	Australia
Sappi Enstra	< 50 µm	69 %	Sappi
Calcitic Lime	2mm (60%) -250µm (40%)	80 %	Saldanha
Shell Lime	-2mm (50%) -500µm (50%)	75 %	Saldanha
Cape Lime	-250µm (100%)	97 %	Klawer

The different limestone samples were separated into various particle size fractions:

- -45µm;
- +45 to -75µm;

- +75 to -106 µm;
- +106 to -150µm;
- +150 to -180µm;
- +180 to -212µm;
- +212 to -300µm
- and +300µm

Lime ($Ca(OH)_2$) was used to increase the pH after limestone treatment.

Operational Procedures.

Batch studies.

Batch studies were conducted at atmospheric pressure to determine the rate of neutralization, iron oxidation and gypsum crystallization. The following procedure was followed:

- The reaction vessels (1000 ml) were filled with acid water.
- Limestone of a specific mass was added at time zero while the acid water was stirred with paddle stirrers.
- Samples were taken, filtered and analysed for pH, acidity-, sulphate-, alkalinity-, and iron(II) concentration as well as occasionally for other heavy metals.

Neutralisation Rate determinations

Crushed and precipitated limestone samples were sieved into various particle size ranges. Their reactivity were determined by monitoring the neutralization rate of acid water during batch studies in beakers at atmospheric pressure. The following steps were followed:

- A 500 mℓ beaker was filled with acid water and dosed with $CaCO_3$ having a specific particle size range.
- Samples were taken at different intervals, filtered and analyzed for pH, acidity and alkalinity.

Determination of coagulant and flocculant dosage rates.

The flocculant solution was prepared according to the recommendations of the suppliers. Various dosages of coagulant and flocculant were added to the reaction vessels, containing the acid water and $CaCO_3$ sludge mixture, after which the contents were mixed in order to determine the optimum coagulant and flocculant dosages. In order to establish these optima, the following steps were followed:

- A series of 1 litre measuring cylinders were lined up beneath a series of stirrers.
- To each cylinder a different dosage of the same coagulant (PAC6) was added.
- Followed by rapid mixing of the coagulant throughout the liquid for 30 seconds.
- Adding of the flocculant, followed by slow and gentle mixing (1 minute) to allow for the contact between small particles and subsequent agglomeration into larger particles.

Determination of settling rates.

Laboratory settling tests were carried out using 1000 ml, graduated measuring cylinders. Treated water from the reactor vessel was added to graduated cylinders. The height of the water-sludge interface over time was recorded until the settling rate approached zero. Description of the settling rate determination:

- A sample of the unsettled neutralised acid water was placed in a 1000 ml graduated cylinder.
- Depth of the sludge blanket (in mm) was determined at recorded time intervals.
- A depth-time plot was used to calculate the sludge settling rate in m/h.

Sludge volume:

Treated water from the reaction vessel was poured into a measuring cylinder. The reading after 24 hours is considered the sludge volume and is expressed as a percentage (%) of the total sample volume (Vogel, 1989).

Sludge solids or mixed-liquor suspended solids:

The mixed-liquor suspended solids (MLSS) or sludge solids content is the mass of solids in the reaction vessel.

- Sample was taken from the reaction vessel.
- The supernatant water was drained off.

- Sludge was dried at 100°C and the percentage of solids was calculated.

Sludge volume index (SVI):

The sludge volume index was measured by filling a one litre graduated cylinder with mixed liquor (treated water and sludge from reaction vessel) and allowed to settle for 30 min. The volume of the sludge (V) was measured in millilitres. The mixed liquor suspended solids concentration (MLSS) was calculated in mg/l according to APHA (1985). The sludge volume index was calculated as:
SVI (ml/mg) = Settle Sludge Volume (ml/l) / MLSS (mg/l) x 1000

Analytical

- The limestone samples were analysed for $CaCO_3$ content.
- Water samples were taken regularly during batch studies and filtered through Whatman No 1 filter paper. Sulphate, iron(II), and pH determinations were carried out manually according to standard procedures described (APHA, 1985). The metal concentrations in the water was determined on an ICPES spectrometer. (APHA, 1985).
- Sludge samples were analysed for sludge solids (MLSS), sludge settling rates and sludge volume.

Experimental

The desirable effect of the following parameters on neutralisation (acid and sulphate removal) as well as on sludge characteristics (sludge settling rate, sludge volume and sludge solids content) were investigated. The following experiments were carried out:

Study 1. *The effect of particle size on limestone neutralisation.*

Study 2. *The effect of the acid concentration in the feedstock on the final sludge characteristics.*
The experimental conditions for Study 2 are listed in Table 3.

Study 3. *Effect of limestone source on the final sludge characteristics.*

The sludge settling rate is influenced by various parameters, such as sludge concentration and acid concentration of the feed water. The purpose of Study 3 was to determine whether the source of the limestone has an effect on the sludge settling rate. In addition to the chemical properties of the limestone, the geological history and its crystal structure play a role in its neutralisation ability. The reaction rate is a function of the size of the particle. The limit of the fineness is an economic one. Cost of grinding increases at an accelerating rate when the particle size decreases. The experimental conditions for Study 3 are listed in Table 4 (first part).

Study 4. *Method of limestone addition on sludge settling rate and sludge volume (Improved crystal growth).*

Due to the increased capital and running costs associated with poor sludge settling it was decided to explore further ways whereby the sludge settling rate and sludge density could be increased or sludge volume reduced. The difference in sludge volume was investigated when the total limestone dosage was applied in a single portion as opposed to application in several small portions. This study was carried out using four different waters. The experimental conditions for Study 4 are listed in Table 5 (first part).

Study 5. *Flocculant addition on sludge characteristics.*

<u>Coaggulant and flocculant:</u> The polymer PAC6 (a poly-aluminium-hydroxy chloride) and 3095 (poly-acrylamide, co-polymer of acrylamide and acrylic acid) were used as coagulant and flocculant, respectively. The coagulant was used as received from the manufacturer, while a stock solution of 2.5 g/l of 3095 was used in the flocculation tests. The experimental conditions for Study 5 are listed in Table 6 (first part).

Study 6. *Combined treatment of limestone and lime.*

Limestone is the preferred product for neutralization of the bulk of the acid concentration due to its low cost and that it can quickly raise the pH of acid water to 6. To raise the pH to higher values, either limestone with a small particle size (e.g. < 75 µm) or lime should be dosed. Should the pH need to be raised to above 7.5 for removal of metals and magnesium or further sulphate removal, lime must be used.

Study 6a. *Effect of sludge from the limestone neutralisation stage on required lime dosage.*

During treatment of mineral separation plant effluents, the clarifier is a large contributor to the capital cost, while lime is a large contributor to the running cost. It was therefore important to determine whether sludge from the limestone neutralization stage has an effect on the required lime dosage during further treatment to raise the pH to 10 or higher. The experimental conditions for Study 6a are listed below (Table 7).

Study 6b. *Effect of sludge solids content on lime dosage and settling rate.*

The experimental conditions for Study 6b are listed in Table 8 (first part).

Study 7. *Effect of lime treatment and gypsum crystallisation on sludge settling rate and sludge volume.*

The experimental conditions for Study 7 are listed in Table 9.

Results and Discussion

Study 1: The effect of particle size on limestone neutralisation.

Particle size is an important parameter in the limestone neutralization process. The smaller the particle size, the larger the surface area and the faster the rate of neutralization. The limestone products supplied by Cape Lime and Saldanha Bay were therefore divided into various particle size fractions to study the relationship between rate of neutralization and particle size. Figure 6 shows the cumulative percentage passing through sieves of increasing sieve size for various limestones. It was noted that Limestone SE (precipitated $CaCO_3$, a by-product from the paper industry) is the finest, followed by CapeLime limestone and Limestone Unimin, while Limestone Saldanha Shell and Limestone Saldanha Calcitic were the coarsest samples.

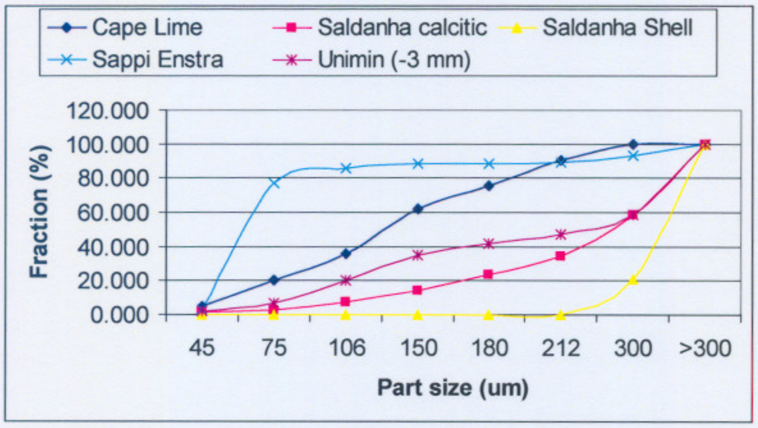
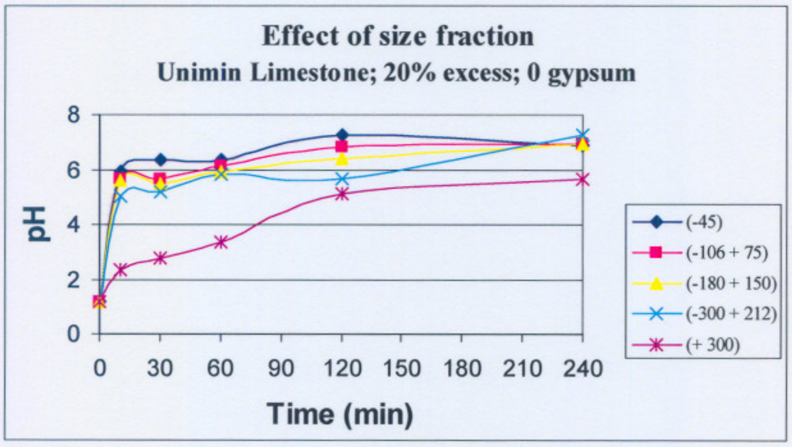


Figure 6. Cumulative passing percentage through sieves of increasing sieve size.

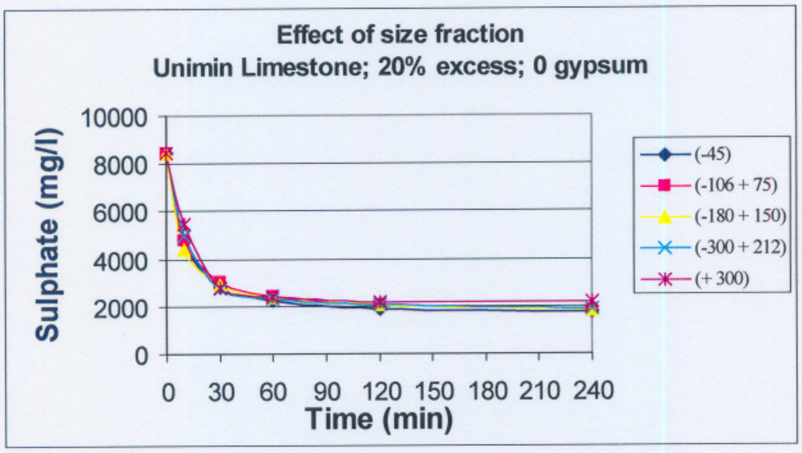
Figure 7 and Figure 8 show the relationship between particle size and performance for limestone from Unimin and limestone Saldanha Calcitic, respectively. It was noted that:

- The finer the limestone, the higher was the pH achieved. The courser fractions of Unimin limestone afforded higher pH values (Figure 7.a) when compared with the coarser fractions of Saldanha calcitic limestone. With limestone, pH values of 6 and higher were achieved with particle sizes of 300 µm and smaller. With limestone from Saldanha Calcitic, a pH of 6 was only achieved with particle size of 75 µm and smaller (Figure 8).
- Sulphate was removed from 8 200 down to 2 000 mg/ℓ with Unimin limestone.
- Iron removal was achieved when the pH was raised above 6. The iron in the water was in the Fe(II)-state. This can be removed after oxidation to iron(III) and precipitated as $Fe(OH)_3$. The iron(II)-concentration in this water was low (280 mg/ℓ) with an acidity equivalent of 501 mg/ℓ (as $CaCO_3$). This represents only 6.2% of the total acidity of the water (8 000 mg/ℓ).

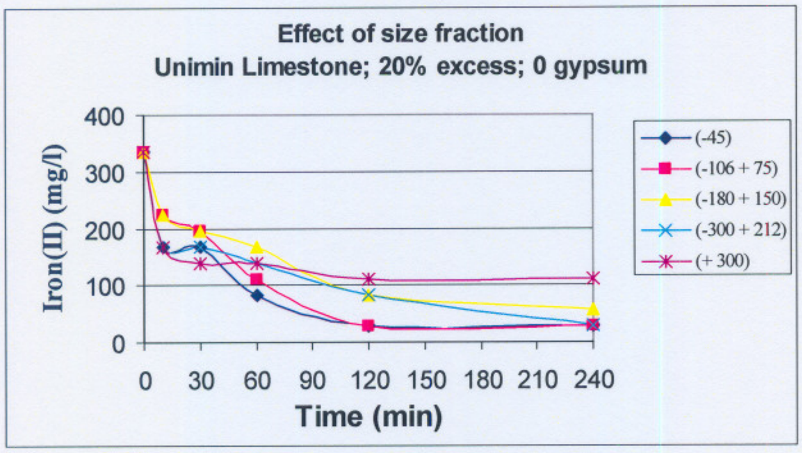
From the above findings it appeared that the process should be designed in such a way that the bulk of the acid (80% of the 8 000 mg/ℓ) should be neutralized with the coarse fraction in the limestone with the aim to raise the pH from 1 to near 4, while the fine fraction should be used for raising the pH to above 6 where iron(II) removal can be achieved as well as sulphate that is associated with iron(II). A two-stage neutralization process would meet this requirement. Coarse limestone should be contacted with the process water in the first stage. The partially neutralized water should then flow to the second stage where the fine limestone fraction is dosed. Separation of coarse and fine limestone can be achieved by passing the limestone slurry through a particle separation system where particles smaller than 100 µm are washed out at the top and the course particles at the bottom.



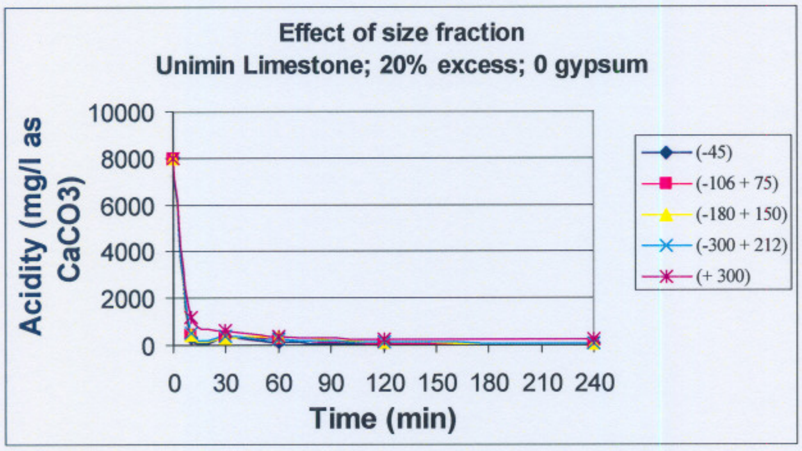
8.a pH



8.b Sulphate



8.c Iron(II)



8.d Acidity

Figure 7. Effect of particle size when acid water was neutralized with Unimin limestone.

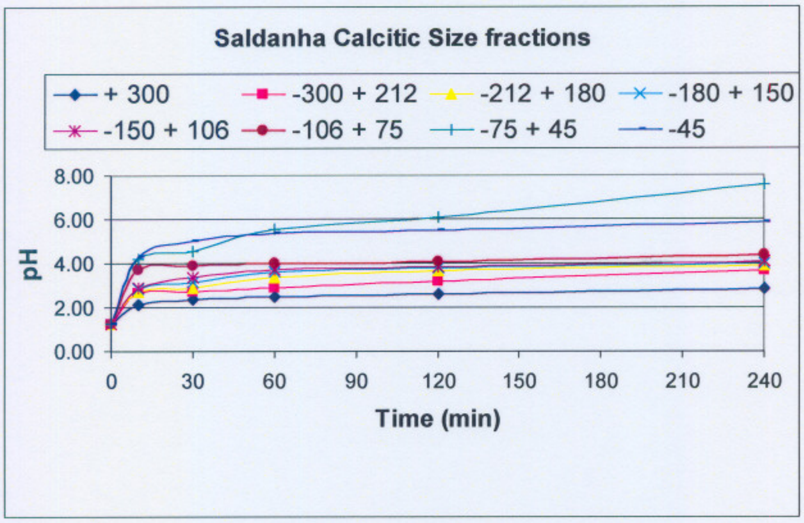


Figure 8. Effect of particle size on pH when acid water was neutralized with calcitic limestone.

Study 2: The effect of the acid concentration in the feedstock on the final sludge characteristics.

The data in Table 3 show that the settling rate was reduced from 0.56 m/h to 0.10 m/h and the sludge volume increased from 7.8 % to 40 % when the acid concentration increased from 6 to 24 g/l.

Table 3. The effect of the sludge concentration on the sludge settling rate

Parameter	**Sludge concentration (g/l)**	
	10	**50**
Water	Ticor	Namakwa S
Acidity (g/l)	6	24
Gypsum (g/l)	40	40
Limestone	Sappi Enstra	Sappi Enstra
Limestone excess dosage (%)	20	20
Limestone dosage (g/l)	8	30.82
pH	6.4	6.4
Settling rate (m/h)	**0.57**	**0.10**
Sludge volume (24 h)	**7.80**	**40.00**

The sludge settling rate and the final sludge volume were significantly influenced by the acid and the sludge concentrations as a result of gypsum and metal precipitation that takes place during neutralisation with limestone.

Study 3: Effect of limestone source on final sludge characteristics.

The data in Table 4 shows that the sludge from water that was neutralized with the Sappi Enstra $CaCO_3$ (+75 to -106μm) settled faster than when precipitated with Cape-lime limestone (+45 to -75 μm). This finding was ascribed to the particle size or the electric charge on the limestone particles.

In addition to the chemical properties of the limestone, the geological history and its crystal structure play a role in its neutralisation ability. The reaction rate is a function of the size of the particle. The fineness of the stone is an economic limitation as cost of grinding increases at an exponential rate as the particle size decreases.

Table 4. Effect of limestone source on sludge settling rate and sludge volume.

Parameter	**Limestone**		
	Cape Lime	Sappi Enstra	Sappi Enstra
$CaCO_3$ screen size (μm)	-75 + 45	-106 + 75	As is
$CaCO_3$ content dry (%)	97.00	88.00	88.00
Experimental conditions:			
Excess $CaCO_3$ (%)	20	20	20
$CaCO_3$-dosage (g/l)	27.96	30.82	30.82
Gypsum (g/l)	0	0	0
Water	N S	N S	N S
Acidity (mg/l)	22600	22600	22600
Aerate	Yes	Yes	Yes
Stir (min)	30	30	30
Results:			
pH			
Time (min)			
0	1.39	1.39	1.39
30	6.24	6.40	5.61
Acidity (mg/l as $CaCO_3$)			
Time (min)			
0	20250	20250	20250
30	100	50	100
Sulphate (mg/ as SO_4)			
Time (min)			
0	21634	21634	21634
30	4043	5523	5664
Settling Rate (m/h)	0.04	0.13	0.10
Sludge volume (%)	47.83	41.33	41.96

Study 4: Method of limestone addition (Improved crystal growth).

The differences in sludge volumes ware investigated when the total limestone dosage was applied in a single portion as opposed to several small portions. This study was carried out using four different acid waters. The results are presented in and it was found that:

- The settling rate increased by a factor of two when limestone was added in several portions to acid water with high acid concentrations (acidity > 15 g/l). The settling rate increased from 0.2 m/h to 0.4 m/h for Namakwa Sands water (20 g/l acidity); from 0.30 m/h to 0.65 m/h for synthetic water (19 g/l acidity) and from 0.07 m/h to 0.13 m/h for Somchem factory water (19 g/l acidity). For Ticor water (4 g/l acidity) the settling rate only increased from 0.7 m/h to 0.8 m/h.
- The sludge volume decreased in the case of Namakwa Sands water (20 g/l acidity) from 42.5 % to 26 %, while it decreased from 43 % to 28.5 % for Somchem factory water (19 g/l acidity).
- With portion wise addition of limestone, the initial sulphate removal rate (at time = 120 min) was slower when the limestone addition was spread over a period of 2 hours. Therefore, the reaction time for gypsum crystallization needs to be increased from 4 to 6 h.

The sludge produced consists mainly of gypsum (Reaction 8). The sludge precipitates upon limestone addition and can be separated from the water in a filter press, from where it can be discarded as a cake.

$$\mathbf{Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4.2H_2O} \qquad \textbf{(Reaction 8)}$$

The improvement in sludge settling rate and sludge density when limestone was dosed in several small portions can be ascribed to the fact that favourable conditions are created for the growth of larger gypsum crystals. By applying a low dosage initially, less gypsum crystals are formed. During further limestone additions, further crystal growth takes place preferentially on the existing crystals at the cost of forming new crystals. On full-scale, this result can be implemented by dividing the gypsum crystallization reactor into 9 or 10 segments and allowing water to pass sequentially through the sections. Limestone addition can be distributed over the sections.

Table 5. Effect of a single limestone addition versus several portions on sludge characteristics.

Parameter	**Water and limestone additions**							
Water	**Synthetic**		**Namakwa Sands**		**Somchem**		**Ticor**	
Limestone additions	Once	Portions	Once	Portions	Once	Portions	Once	Portions
Acidity (g/l)	19	19	20.25	20.25	19	19	4.25	4.25
H_2SO_4 (ml/l)	10.48	10.48						
Excess $CaCO_3$ (%)	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Purity (%)	97	97	97	97	75	75	97	97
Limestone source	CL (+45-75)	CL (+45-75)	CL (+45-75)	CL (+45-75)	SS (as provided)	SS (as provided)	CL (+45-75)	CL (+45-75)
Limestone dosage (g/l)	23.51	23.51	25.05	25.05	34.4	34.4	5.26	5.26
Limestone addition:								
Time (min)	Once	Portions	Once	Portions	Once	Portions	Once	Portions
0	23.51	2.61	25.05	2.78	34.4	3.44	5.26	0.58
15		2.61		2.78		3.44		0.58
30		2.61		2.78		3.44		0.58
45		2.61		2.78		3.44		0.58
60		2.61		2.78		3.44		0.58
75		2.61		2.78		3.44		0.58
90		2.61		2.78		3.44		0.58
105		2.61		2.78		3.44		0.58
120		2.61		2.78		3.44		0.58
135						3.44		0.50
pH								
Time (min)								
0	1.32	1.32	1.53	1.53	0.85	0.85	1.88	1.88
120	1.83	2.27	4.78	4.65			5.21	4.93
240	6.2	6.04	6.43	6.43	5.10	6.2	6.47	6.43
Sulphate (mg/l as SO_4)								
Time (min)								
0	19000	19000	27000	27000	14386	14386	5000	5000
120	3555	4463	4159	4795			2888	3768
240	1868	1935	3768	3959	1074	1130	2529	2715
360	1890	1846	3651	3757			2354	2485
Acidity (mg/l as $CaCO_3$)								
Time (min)								
0	19000	19000	20250	20250	18750	18750	4250	4250
240					50	25		
Settling Rate (m/h)								
Time (min)								
120	0.37	0.83	0.21	0.41	0.07	0.13	0.62	0.74
240	0.28	0.71	0.19	0.41			0.70	0.81
360	0.26	0.66	0.20	0.37			0.79	0.86
Sludge volume (%)	37.9	26.1	42.5	26.0	43	28.5	14.1	11.5

Study 5: Effect of flocculant addition on sludge characteristics

The data in Table 6 show that the settling rate of limestone treated water increased from 0.57 m/h when no flocculant was added to 6.8m/h when a dosage of 0.75 mg/l Montan 3095 flocculant was added. Flocculant addition had a slight negative effect on the sludge volume, which increased with increased flocculant dosages. Although flocculant addition is beneficial for the sludge settling rate, it was investigated for any possible negative effects on the mineral separation process.

Table 6. Effect of flocculant addition on sludge settling rate.

Parameter	**Flocculant Montan 3095 (mg/l)**				
	0.000	**0.025**	**0.125**	**0.250**	**0.750**
Water	Ticor	Ticor	Ticor	Ticor	Ticor
Precipitated $CaCO_3$ (mg/l)	7826	7826	7826	7826	7826
Acidity (mg/l $CaCO_3$)	4500	4500	4500	4500	4500
Fast mixing (4) (sec)	30	30	30	30	30
Slow mixing (2) (sec)	30	30	30	30	30
Slope	9.5	13.71	35.38	70.77	114.06
Settling Rate (m/h)	0.57	0.82	2.12	4.25	6.84
Sludge volume (%)	7.8	8.0	8.4	9.9	12.2
Flocculant cost (R/m^3) (R24/kg)	0.000	0.001	0.003	0.006	0.018

Study 6a: Effect of sludge on the required lime dosage.

During treatment of effluents from mineral separation plants, the clarifier is a large contributor to the capital cost, while lime is a large contributor to the running cost. It was therefore important to determine whether sludge from the limestone neutralization stage has an effect on the required lime dosage during further treatment. Table 7 and Figure 9 show the results when limestone neutralized water with the following solids concentrations were treated with lime:

- 0.0 % – Ticor neutralized water (4.25 g/l acidity, Sappi Enstra, treated water without the sludge)
- 1.1 % – Ticor neutralized water (4.25 g/l acidity, Sappi Enstra, treated water with sludge)
- 6.0 % – Namakwa Sands water (24 g/l acidity, Sappi Enstra, treated water with sludge)

Table 7. Effect of sludge of neutralisation stage on lime dosage.

Parameter	**Sludge**		
	Only water, 10 % lime slurry	Sludge present, 10 % lime slurry	Sludge present, 1 % lime slurry
Limestone treatment			
pH			
Time (min)			
0	1.4	1.4	1.4
30	6.2	6.2	6.2
Acidity (mg/l as $CaCO_3$)			
Time (min)			
0	20250	20250	20250
30	100	100	100
Sulphate (mg/ as SO_4)			
Time (min)			
0	21634	21634	21634
30	4043	4043	4043
Limestone price (R/t)	225	225	225
Limestone cost (R/m^3)	6.29	6.29	6.29
Lime treatment			
Slurry concentration (%)	10	10	1
Lime dosage (g/l)	**0.5**	**4.5**	**4.5**
pH	10.34	10.27	10.44
Lime price (R/t)	900	900	900
Lime cost (R/m^3)	0.45	4.05	4.05

Experimental conditions:	*Water sample:*	*Namakwa Sands (22600mg/l acidity)*
	Limestone:	*Cape Lime (+45 to - 75 um particle size)*
	Excess $CaCO_3$:	*20 % (97% $CaCO_3$ content)*
	Mixing:	*30 min stirring with aeration*

It was noted that:

- Sludge had a major effect on the required lime dosage. The following lime dosages were required to raise the pH from 6.8 to 10.4:
    - for 0 % solids – 0.4 g/l
    - for 1.1 % solids – 1.2 g/l
    - for 6.0 % solids – 4.5 g/l
- It was assumed that lime is adsorbed onto the sludge particles and therefore not completely available for pH adjustment. The high lime consumption cannot be ascribed to the reaction with CO_2, in the form of HCO_3^- , which is produced during limestone neutralisation at a near neutral pH-range (Reaction 9). This was confirmed by the low acidity of less than 100 mg/l after aeration of the limestone treated water.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O \qquad \textbf{(Reaction 9)}$$

- The lime slurry concentration had no effect on the required lime dosage (Table 7). It was argued that if the lime slurry concentration were diluted to ca. 1% where it is soluble, the lime efficiency would be improved. As there was no observed difference when 1% or 10 % lime slurry was dosed, it was concluded that hydroxyl ions are adsorbed onto the sludge particles.

From this finding it was concluded that the following options need to be considered during the design of a full-scale plant:

- Lime dosage should be limited to the minimum with the aim to minimize the running cost.
- Sludge that is produced during limestone treatment should be separated to minimize the lime dosage.

This is particularly of interest where water with a high acid concentration (> 10 g/l) is concerned, and when a high sludge concentration is produced.

- Limestone should be milled to a particle size of less than 50 µm, with the aim of maximising neutralisation. It appears that limestone does not get adsorbed onto the sludge that is produced, as is the case with lime.

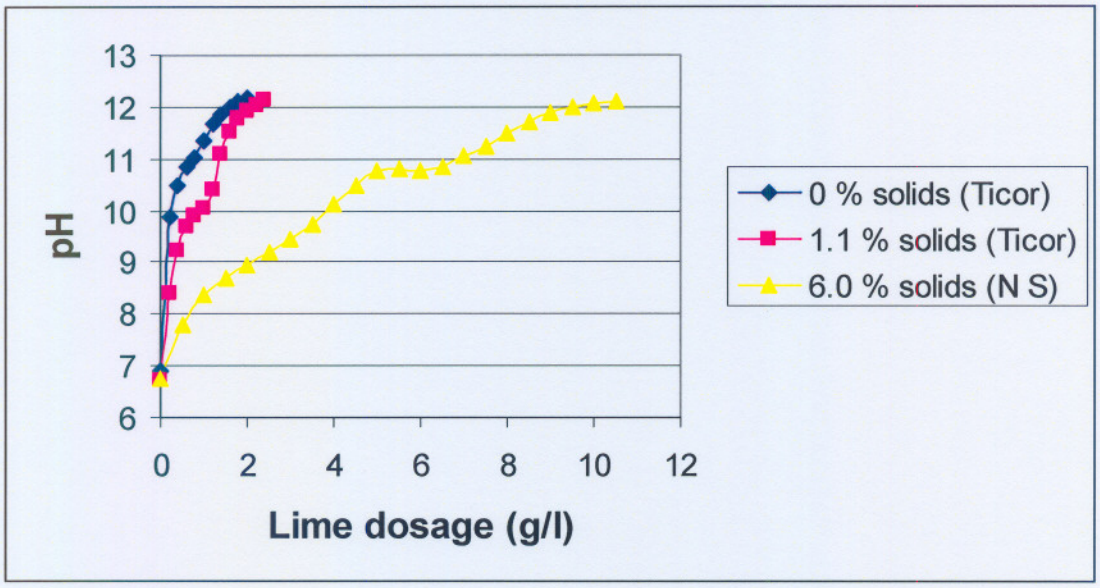


Figure 9. **Effect of solids content on lime dosage.**

Study 6b: Effect of sludge solids content on lime dosage and settling rate.

Table 8 shows the effect of sludge solids content (both precipitated sludge and additional gypsum) on the lime dosage and the sludge settling rate. It was concluded that:

- Lime dosage was influenced by the sludge solids content.
- Sludge from the mineral separation plant adsorbs lime. Water combined with sludge required a 40 to 50 % higher lime dosage to raise the pH from 6.1 to 11.7 than when the pH of decant water was used (Experiments 1 versus 2 and 3 versus 4).
- Gypsum sludge, even a high solids content of 50 g/l, had almost no effect on the required lime dosage (Experiments 1 versus 3, and 2 versus 4).
- Sludge settling rate. The sludge settling rate was in the order of 1 m/h.
- Sludge solids content. The solids content of settled sludge when gypsum was added amounted to 30 to 40 % compared to only 3.5 % where no gypsum was added. The gypsum that was added represented gypsum re-circulation under full-scale conditions.

Table 8. Effect of sludge solids content on lime dosage and sludge settling rate.

Parameter	**Feed**	**Sludge solids content (g/l)**			
Exp No		**1**	**2**	**3**	**4**
Experimental conditions:					
Solids (%)		5.7	5.7	0.7	0.7
Gypsum (g/l)		50	50	0	0
Sludge decant or not		With sludge	Decant water	With sludge	Decant water
Lime dosage (g/l)		3.10	2.25	3.05	2.02
Lime ratio		1.38	1.00	1.51	1.00
Water (ml)		1000	1000	1000	1000
Initial sulphate (mg/l)		5118	5118	5118	5118
Reaction time (h)		4	4	4	4
Results:					
pH	6.08	11.34	11.71	11.56	11.75
Alkalinity (mg/l $CaCO_3$)	110	200	350	270	330
Sulphate (mg/l SO_4)		1638	1628	1857	1762
Settling Rate (m/h)		0.72	1.98	0.89	0.90
Sludge volume (%)		20.00	14.63	18.41	19.57
Sludge solids content (g/l)		28.5	39.0	3.6	3.5

From these findings it was concluded that the required lime dosage is not influenced by solids in general, but by specific compounds, such as ferric hydroxide and other precipitates that originate from the process water from the mineral separation plant.

Study 7: Effect of lime treatment on sludge settling rate and sludge volume.

The effect of lime treatment on sludge settling rate and sludge volume was investigated on Ticor water with an acidity of 4.25 g/l (Table 9). It was found that:

- Sulphate concentration was reduced with limestone from 5118 mg/l to 2429 mg/l. Raising the pH with lime resulted in increased sulphate removal with increased pH values. The sulphate concentration of 1638 mg/l at a pH of 11.3 was however higher than the target value of 1350 mg/l. This can be ascribed to the presence of sodium in the feed water. A concentration of 150 mg/l sodium will keep 300 mg/l sulphate in solution.
- The sludge settling rate was in the order of 1.0 m/h for Ticor water. The solids content of the settled sludge after lime treatment varied between 14 and 20 %.

Table 9. The chemical composition of Ticor feed and treated water at different pH-values.

Parameter		**Target pH**			
	Feed	**7**	**9**	**11**	**12**
Lime (g/l)		0.05	0.65	1.65	3.10
Water (ml)		1000	1000	1000	1000
Gypsum (g/l)		40	40	40	**50**
Reaction time (h)		4	4	4	4
pH	6.78	7.05	8.12	10.24	11.34
Alkalinity (mg/l $CaCO_3$)	110	90	70	80	200
Sulphate (mg/l SO_4)	5118	2429	2116	1713	1638
Magnesium (mg/l Mg)					
Sodium (mg/l Na)					
Settling Rate (m/h)		0.83	0.95	1.08	0.90
Sludge volume (%)		11.58	14.29	19.72	20.00

Ticor feed water acidity = 4.25 g/L

The above experiments were repeated using a synthetic acid water with an acidity of 8 g/l (Table 10). The results of these tests showed that:

- Sulphate concentration was lowered with limestone from 8 427 mg/l to 2 434 mg/l. Lime addition to pH 10 resulted in further sulphate removal to a concentration of 1 932 mg/l. This value was higher than the target of 1 350 mg/l because magnesium was not completely removed at a pH 10, since pH 11 is required for complete magnesium removal. The 120 mg/l of magnesium in solution is equivalent to 480 mg/l sulphate. If complete magnesium removal had been achieved, the sulphate concentration would have been lowered to 1 452 mg/l, while a higher calcium concentration in solution would have lowered the sulphate concentration further down to the target value of 1 350 mg/l.
- The sludge settling rates were in the order of 1.5 m/h for the synthetic water and 0.6 m/h for Ticor water. This finding shows that the sludge from actual process water settles slower than that from synthetic water.
- Sludge with a high solids content of 50.4 % resulted using synthetic feed water. This was significantly higher than the 13.9 % achieved with the Ticor water(Table 10).

Table 10. The chemical composition of feed (acidity = 8 g/l) and treated water at different pH-values.

Parameter	**Feed**		**Lime dosage (g/l)**			
			0	0.16	0.71	
Water	Synthetic	Synthetic	Synthetic	Synthetic	Synthetic	Ticor
Limestone treatment:						
Limestone	Sappi E	Sappi E	Sappi E	Sappi E	Sappi E	Sappi E
CaCO3 content (dry) (%)		88.00	88.00	88.00	88.00	
Particle size		-75 + 45	-75 + 45	-75 + 45	-75 + 45	
Excess dosage (%)		20.00	20.00	20.00	20.00	
Limestone dosage (g/l)		10.91	10.91	10.91	10.91	
Gypsum (g/l)		0	40	40	40	
Lime treatment:						
Lime				Roche	Roche	
Dosage (g/l)			0	0.16	0.71	
Reaction time (h)			4	4	4	
Water quality:						
pH			7.21	8.44	9.97	
Acidity (mg/l $CaCO_3$)	8000					
Iron(II) (mg/l Fe)	200	<28	<28	<28	<28	
Magnesium (mg/l Mg)	200	200	200	200	120	
Sulphate (mg/l SO_4)	8427		2434	2413	1932	2400
Sludge characteristics:						
Settling rate (m/h)		1.48	1.36	1.22	1.18	0.57
Sludge volume (%)		8.48	10.53	10.07	15.67	7.79
Solids content before settling (%)		1.5	5.1	5.1	5.2	1.1
Solids content after settling (%)		17.8	48.2	50.4	32.9	13.9

Conclusions

- Particle size is an important parameter in the limestone neutralization process. It has been shown that the smaller the particle size, the larger is the surface area and the faster is the rate of neutralization.
- The sludge settling rate and the final sludge volume are significantly influenced by the acid concentration and the sludge solids content as a result of gypsum and metal precipitation. The settling rate was reduced from 0.56 m/h to 0.10 m/h and the sludge volume increased from 7.8 % to 40 % when the acid concentration increased from 6 to 24 g/l.
- The limestone source and particle size has an effect on the sludge settling rate and the final sludge volume. A finer limestone particle size resulted in faster settling rates and lower sludge volumes.
- The sludge settling rate is influenced by the method of dosing limestone to the acid water. The settling rate increased when limestone was added incrementally rather than a single dose. The settling rate doubled when limestone was added incrementally to acid water with high acid concentrations (acidity > 15 g/l). The settling rate increased from 0.2 m/h to 0.4 m/h for Namakwa Sands water (20 g/l acidity), from 0.30 to 0.65 for synthetic water (19 g/l acidity) and from 0.07 m/h to 0.13 m/h for the Somchem factory water (19 g/l acidity). For the Ticor water (4 g/l acidity), however the settling rate increased only from 0.7 to 0.8 m/h.
- Flocculant addition is beneficial for the sludge settling rate, but has a slight negative effect on sludge volume. The settling rate of limestone treated water increased from 0.57 m/h, when no flocculant was added, to 4.3 m/h at a dosage of 0.75 mg/l Montan 3095 flocculant.
- The sludge formed had a major effect on the required lime dosage. The following lime dosages were required to raise the pH from 6.8 to 10.4:
    a. for 0 % solids – 0.4 g/l
    b. for 1.1 % solids – 1.2 g/l
    c. for 6.0 % solids – 4.5 g/l

CHAPTER 4 DESALINATION OF NEUTRALISED MINE EFFLUENTS

Introduction

Background

Namakwa Sands is currently replacing their existing neutralization process with the integrated limestone/lime process developed by the CSIR.

Effluent from Namakwa Sands HAL circuit is fed to the neutralisation plant. The water has a low pH and high sulphate content. The acidity consists of free acid (H_2SO_4) and metals associated with sulphate e.g. iron. This acid water will be neutralised with limestone ($CaCO_3$) followed by addition of lime ($Ca(OH)_2$) to raise the pH to 12 where magnesium sulphate is removed as $Mg(OH)_2$. In the neutralisation process, gypsum will be removed to below its saturation level at neutral pH.

Limestone neutralised water (shown in italics in Table 11), has been treated with the DesEl process. The purpose of the study was to establish the suitability of the DesEl process for desalination of the neutralised Namakwa Sands process water.

Table 11. Chemical composition of Namakwa Sands feed and treated water at different pH-values

	Feedwater			**Treated water**			
Treatment process	Feed	Feed	Feed	*$CaCO_3$*	**$Ca(OH)_2$**	**$Ca(OH)_2$**	**$Ca(OH)_2$**
	16-Dec-03	18-Dec-03	19-Dec-03				
pH	1.2			*5.4*	7.0	8.5	10.0
Free acidity (mg/l CaCO3)		18870					
Acidity (mg/l CaCO3)	27000						
Alkalinity (mg/l CaCO3)	0	0	0	*0*			56
Chloride (mg/l Cl)	94	76	58	*115*			0
Sulphate (mg/l SO_4)	30000			*4328*	3854	2146	1937
Calcium (mg/l Ca)	376	484	608	*515*	478	45.5	1.25
Magnesium (mg/l Mg)	182	178	246	*205*	205	205	9
Iron(II) (mg/l Fe)	279			*168*	28	0	0
Total iron (mg/l Fe)	1364	1146	1390	*0.45*	0.137	0.048	0.013
Iron(III) (mg/l Fe)	1085						
Aluminium (mg/l Al)	772	680	784	*0.9*	4.12	0.04	0
Manganese (mg/l Mn)	17.4	15.4	19.6	*16.5*	10.7	0.01	0
Zinc (mg/l Zn)	2	1.5	3.4	*0*	0	0	0
Arsenic - (inorg)	0.092	0.086	0.092	*0*			0
Cadmium (mg/l Cd)	0.16	0.144	0.162	*0*	0.019	0.01	0.005
Chromium (mg/l Cr)	24	22	24	*0*	0.16	0.108	0
Lead (mg/l Pb)	2.2	2.2	2.4	*0.25*	0.449	0.144	0
Mercury - (mg/l Hg)	0.026	0.026	0.032	*0*			0
Nickel (mg/l Ni)	1.48	1.46	1.58	*0.15*	0.158	0.085	0.042
Titanium (mg/l Ti)	102	86	118	*0*	0.028	0.03	0.026
Uranium (mg/l U)	1	<0.1	0.6	*0.2*			<0.2
Thorium (mg/l Th)	14.2	0.8	11.4	*0.5*			<0.2
Zirconium (mg/l Zr)	1.2	<0.1	0.6	*<0.1*			<0.2

The DesEl system automatically cycles through a purification, regeneration and purge cycle. The process uses a Programmable Logic Controller (PLC) to control all cycle times, and using a conductivity set point to initiate the opening and closing of solenoid valves.

During the purification cycle, the conductivity controller monitors the conductivity of the solution at the outlet of the capacitive cell and controls the position of a solenoid valve. If the conductivity of the treated solution is less than the desired set point, treated water will be discharge as the purified stream. If the conductivity rises above the set point, the water will be circulated through the cell till the discharge set point is reached. The removal of ions from the aqueous solution is thus monitored via conductivity measurements. Figure 10 shows a schematic of the DesEl unit in purification configuration.

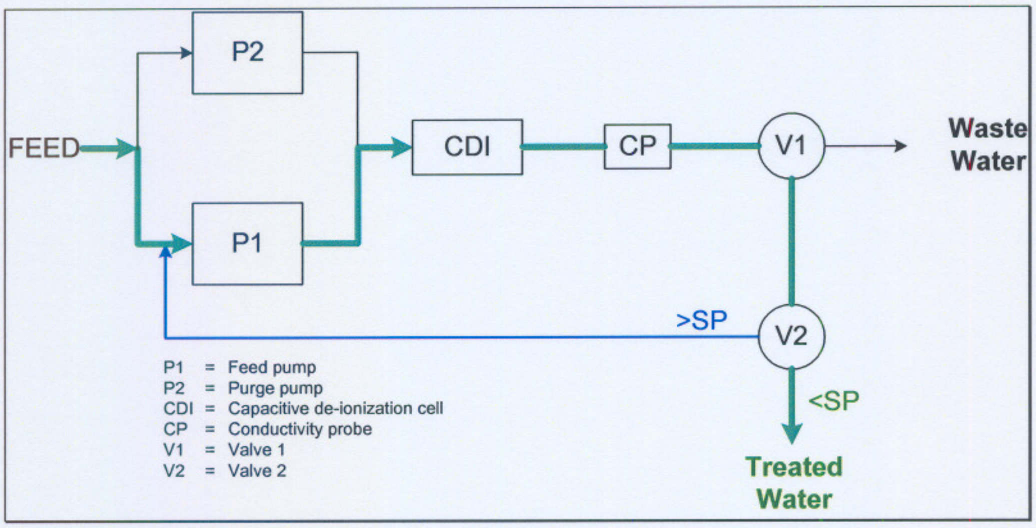


Figure 10. Schematic diagram of purification cycle

During the regeneration cycle, when sufficient dissolved salts are deposited on the electrodes and the conductivity has increased beyond the desired set point, the electrodes are regenerated by shorting the electrodes to earth. The polarity of the cell is then reversed to remove the contaminants. A purge step is used to flush the ions from the cell. After treatment, the adsorbed ions are released into the waste stream. This solution, with a high concentration of dissolved salts, is discharged (flushed) through a valve as a brine stream. By simply controlling the applied voltage, the ions are released, thereby regenerating the cell.

The optimum process conditions are dependant on the combination of the following parameters:

- Purification cycle which includes the
    - Purification time, and
    - Purification flow rate
- Regeneration cycle which includes the
    - Regeneration time, and
    - Regeneration flow rate
- Purge cycle which includes the
    - Purge time, and
    - Purge flow rate
- Conductivity set point

The DesEl unit employs the "Charge Barrier" innovation consisting of ion-selective layers. This enables greater than 90% water recoveries for brine.

The overall purpose of the study was to determine the suitability of the DesEl process for desalination of the neutralised Namakwa Sands process water.

The specific aims of the experimental process evaluation study were to determine the following:

- Water quality of feed and treated water
- Feed rate and processing rate of purified water (Rate at which pure water is produced)
- Water recovery (Pure to waste water ratio)
- Sulphate rejection
- Treatment (power) cost. (Power parameters were logged on a data logger to determine the energy requirements. Power (W) = Amps (A) x volt (V)).

Materials and Methods

Feedwater

Acid water for test purposes was obtained from Namakwa Sands. The acid water was neutralised with limestone and used for the desalination tests.

Equipment

A laboratory, bench-scale unit was used for the removal of sulphate as well as the other salts (Figure 11).

Figure 11. Bench scale DesEl test unit

Experimental

One-stage and two-stage DesEl treatment processes to remove sulphate and other dissolved solids, were evaluated. The following parameters were recorded:

- water recovery
- processing rate
- salt rejection and
- power cost

Table 12 shows the experimental conditions for the one-stage and two-stage treatment processes.

Table 12. Experimental conditions for the one-stage and two-stage DesEl treatment processes.

		One-stage Treatment	Two-stage treatment	
			Stage 1	Stage 2
Conductivity Controller				
Range	(mS/cm)	10	10	10
Set Point	(mS/cm)	2	4	0.7
Hyst	(mS/cm)	0.02	0.02	0.02
PLC Settings				
Purify time	(sec)	120	120	120
Regen time	(sec)	120	180	120
Purge time	(sec)	45	45	45
Pump Settings:				
Purify flow rate	(ml/min)	110	110	290
Purge flow rate	(ml/min)	60	64	60
Treatment Cycle				
Total cycle time	(sec)	240	300	240
Total run time	(min)	20	35	16
Treatment	(cycles)	5	7	4
Discharge/cycle	(sec)	85.1	102.1	116.6
Discharge/Purify time	(%)	70.9	85.1	97.2

Analytical

Water samples of the treated and waste streams were analysed for sulphate, calcium, magnesium, manganese, and chloride.

Results and Discussion

Water Quality

Table 13 shows the quality of the feed and treated water when the limestone neutralised process water was treated with the DesEl unit in a one-stage treatment process. The conductivity set point for the one-stage treatment process was set at 2 mS/cm.

It was noted that:

- Electrical conductivity decreased from 6.29 mS/cm to 0.77 mS/cm with the one-stage treatment process.
- Total dissolved solids concentration decreased from 4 767 mg/l to 466 mg/l.
- Sulphate concentration was decreased from 3 668 mg/l to 351 mg/l.

Table 13. Water quality of feed and treated water for the one-stage DesEl process (Run14).

		One-stage treatment process		
		Feed	**Treated**	**Waste**
Parameter	**Unit**		**Stage 1**	**Stage 1**
Volume	mL	1030	780	250
EC (mS/cm)	mS/cm	6.29	0.768	19.77
TDS	mg/l	4767	466	22242
Salt Load	%	100	7.41	92.59
Sulphate	mg/l	3668	351	17643
Magnesium	mg/l	447	43	2102
Calcium	mg/l	312	31	1436
Manganese	mg/l	44.89	4.60	196.49
Chloride	mg/l	66	8	195

Based on the influent water quality, the operating parameters of the DesEl unit can be adjusted to produce a preferred product water quality. During this study, the main objective was to determine the suitability of the DesEl process for desalination of neutralised Namakwa Sands process water.

Table 14 shows the quality of the feed and treated water when the limestone neutralised process water was treated with the DesEl unit in a two-stage desalination process. The conductivity for the first stage was set at 4.0 mS/cm and at 0.7 mS/cm for the second stage. During the two-stage process, the treated water of stage 1 was used as feed water for Stage 2.

It was observed that:

- Electrical conductivity decreased from 7.3 mS/cm to 1.47 mS/cm after Stage 1and to 0.22 mS/cm after Stage 2.
- Total dissolved solids decreased from 5 743 mg/l to 924 mg/l in Stage 1 and to 130 mg/l in Stage 2.
- Sulphate concentration decreased from 4 434 mg/l to 695 mg/l in Stage 1 and to 98 mg/l in Stage 2.

Table 14. Water quality of feed and treated water for the two-stage DesEl process.

		Two-stage treatment process				
			Stage 1	Stage 1	Stage 2	Stage 2
Parameter	**Unit**	**Feed**	**Treated**	**Waste**	**Treated**	**Waste**
Volume	mL	1660	1310	350	2255	187
EC (mS/cm)	mS/cm	7.31	1.47	19.3	0.22	12.71
TDS	mg/l	5743	921	21466	130	11855
Salt Load	%	100	12.66	87.34	13.36	86.64
Sulphate	mg/l	4434	695	17015	98	9284
Magnesium	mg/l	539	86	2029	12	1117
Calcium	mg/l	375	61	1386	9	770
Manganese	mg/l	53.71	9.02	189.93	1.29	107.66
Sodium	mg/l	0	0	0	0	0
Chloride	mg/l	77	16	191	2	130

These results showed that a two-stage DesEl treatment system was capable of removing 98% of the sulphate from the limestone neutralised water.

Process parameters

Table 15 shows the process parameters when the limestone neutralised water was treated with the DesEl unit in one-stage and two-stage treatment processes, respectively. The conductivity for the one-stage process was set at 2.0 mS/cm. The conductivity for first stage of the two-stage process was set at 4.0 mS/cm and at 0.7 mS/cm for the second stage.

The following observations were noted:

- The water recovery for the one-stage treatment process was 76% and 79 % for Stage 1 and 92% for Stage 2 of the two-stage process. Higher water recoveries were achieved with the two-stage process.
- High salt removal was achieved with both the one- and two-stage processes. 91% salt removal was achieved with the one-stage process, 84 % in the first stage of the two-stage process, and 86 % in the second stage.
- The processing rate (rate at which pure water is produced) for treatment with the one-stage process was 2.34 l/h, while the feed rate was 3.09 l/h. The processing rate for treatment with the two-stage process was 2.25 l/h for the first stage and 8.46 l/h for the second stage, and the feed rate 2.85 l/h and 9.16 l/h, respectively. Higher processing rates were achieved with the two-stage process.
- The energy needed for the one-stage treatment process where the water with a sulphate concentration of 3 834 mg/l was treated to less that 400 mg/l is 7.14 kWh/m^3. At an energy cost of 18 c/kWh, the treatment cost was 1.29 R/m^3 feed treated and 1.70 R/m^3 pure water produced.
- The energy needed for the first stage of the two-stage process where neutralised water with a sulphate concentration of 4 474 mg/l was treated down to 700 mg/l SO_4 (Stage 1) is 6.72 kWh/m^3. At an electricity cost of 18 c/kWh, the treatment cost is 1.21 R/m^3 feed treated and 1.53 R/m^3 pure water produced.
- The energy needed for the second stage of the two-stage process where water with a sulphate concentration of 745 mg/l is treated down to 109 mg/l SO_4 (stage 2) is 1.65 kWh/m^3. At an electricity cost of 18 c/kWh, the treatment cost is 0.30 R/m^3 feed treated and 0.32 R/m^3 pure water produced. The results showed that less energy was needed for the two-stage process as oppose to the one-stage treatment process.

Table 15. Process parameters and results for the one-stage and two-stage DesEl treatment processes.

		One Stage Treatment	Two Stage Treatment	
Parameter	**Unit**	**Stage 1**	**Stage 1**	**Stage 2**
Sulphate In	mg/l	3834	4474	745
Sulphate Out	mg/l	387	695	109
Sulphate Rejection	%	90.8%	84.1%	85.9%
Feed Rate	L/h	3.09	2.85	9.16
Processing Rate	L/h	2.34	2.25	8.46
Flux Rate	mL/min/m^2	57	55	207
Water Recovery	%	76%	79%	92%
Treatment cost - feed	R/m^3	1.70	1.53	0.32
Treatment cost - pure	R/m^3	1.29	1.21	0.30

Based on the influent water quality, the operating parameters of the DesEl unit can be adjusted to produce a preferred product water quality. The main objective was to reduce the sulphate concentration of the water from 4000 mg/l to less than 200 mg/l, was achieved with a two-stage process. The same result could also be achieved with a one-stage process, but the energy cost would be much higher.

All the experimental results obtained with different DesEl settings are reported in *Appendix A:* .

Brine Treatment

Gypsum will crystallise out from the brine solution to its saturation level. Water recovery could be increased significantly and brine treatment/handling could be reduced through implementation of the following steps for the two-stage treatment process:

- Allow the over-saturated gypsum in the brine of Stage 1 to crystallize to its solubility level.
- Recycle the water after crystallisation to the feed of Stage 2.
- Recycle the brine of Stage 2 back to the feed of Stage 1.

The only waste would be the thickened gypsum/$Mg(OH)_2$-rich sludge.

Figure 12 shows the integrated process flow diagram for a two-stage treatment process for optimum water recovery. This approach offers the benefit that no or very little brine treatment is required. The electricity cost for treatment will, however, be higher than the reported values in Table 15, due to the higher sulphate load of the feed water.

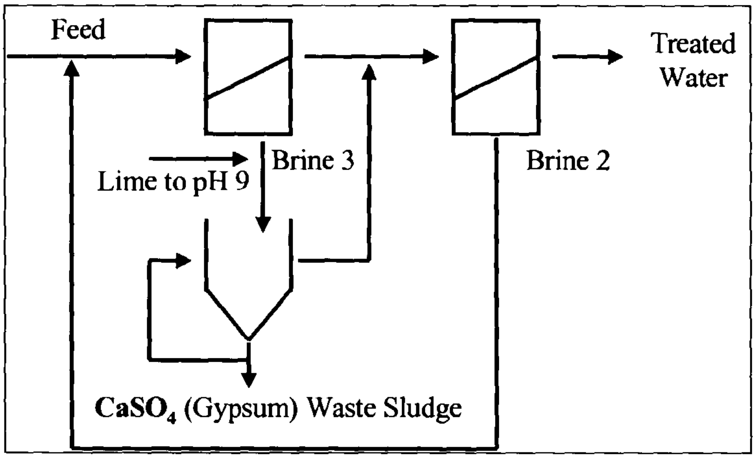


Figure 12. Integrated process flow diagram for a two-stage DesEl treatment process.

This approach offers the benefit that a high water recovery (> 90%) can be achieved. Only gypsum sludge disposal is necessary.

Conclusions

- The DesEl test unit can be used effectively to treat the sulphate and metal rich effluent of the Namakwa Sands neutralisation plant.

- One-stage DesEl treatment process
  - Sulphate was removed from 3668 mg/l to 351 mg/l, magnesium from 447 mg/l to 43 mg/l, calcium from 312 mg/l to 31 mg/l, manganese from 44.9 mg/l to 4.6 mg/l and chloride from 66 mg/l to 8 mg/l.
  - The electricity cost amounted to 1.29 R/m^3 feed treated and 1.70 R/m^3 pure water produced.

- Two-stage DesEl treatment process

- Sulphate was removed from 4434 mg/l to 100 mg/l, magnesium from 539 mg/l to 12 mg/l, calcium from 375 mg/l to 9 mg/l, manganese from 53.7 mg/l to 1.3 mg/l and chloride from 77 mg/l to 2 mg/l.
- The electricity cost amounts to 1.21 R/m^3 feed treated and 1.53 R/m^3 pure water produced during the first stage. For the second stage, the cost amounts to 0.30 R/m^3 feed treated and 0.32 R/m^3 pure water produced.

Both the one-stage and two-stage treatment processes can be used to reduce the sulphate concentration. This study showed that for treatment of high sulphate concentrations (4 000 mg/l) with the DesEl system, the two-stage process is the better option due to:

- Higher overall water recovery
- Higher overall processing rate
- Lower energy need.

CHAPTER 5 CASE STUDY ON LIMESTONE NEUTRALISATION OF ARSENIC RICH EFFLUENT FROM A GOLD MINE.

Introduction

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

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

Treatment of Fe(II)-rich water with limestone conventionally requires a multiple-stage neutralisation system. The expected capital cost of such a system is unacceptably high due to the long residence time required for iron oxidation (Maree *et.al.,* 1998). An integrated iron oxidation and limestone neutralisation process was developed to overcome this disadvantage. The process consists of a neutralisation reactor and a clarifier. Discard leachate is treated in an aerated sludge reactor into which limestone powder (100% < 200 µm) is dosed to a level slightly in excess of stoichiometric requirements. Iron oxidation is achieved within 2 h when the plant is operated in sequential batch mode and within 5 h under continuous conditions. Gypsum crystallises to an over-saturation index less than 1.1. A clarifier is required to return sludge to the neutralisation reactor to maintain a minimum concentration of suspended solids.

The following conclusions were reached:

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

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

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

This chapter discusses the options for treating acid water, rich in iron, arsenic and sulphate with the integrated limestone neutralization process.

It is suggested that limestone can be used for neutralization instead of lime to offer the following benefits:

- Cost saving.
- Less pH control is required.

The objectives of this investigation were the following:

- To identify the most suitable limestone type and source for neutralization of arsenic rich acid water.
- To compare lime and limestone sludge for meeting Toxicity Characteristic Leaching Procedure (TCLP) specifications.

Materials and Methods

Feedstock

Samples of acidic water for test purposes were collected from a gold mine. The feed water had a pH of 1.5, and contained a high concentration of arsenic. It furthermore contained high concentrations of sodium, chloride, magnesium, calcium, manganese and iron (II). The acidity of the raw water was 33 500 mg/L, and the sulphate concentration is 40 000 mg/L. Table 16 shows the chemical composition of the feed water.

Table 16. Chemical composition of the arsenic rich acid water.

Parameter	Units	Quality
pH		1.5
Acidity	mg/L as $CaCO_3$	33 500
Iron(II)	mg/L as Fe	51
Sulphate	mg/L as SO_4	40 000
Sodium	mg/L as Na	17
Potassium	mg/L as K	19
Calcium	mg/L as Ca	346
Aluminium	mg/L as Al	9
Chromium	mg/L as Cr	6
Manganese	mg/L as Mn	45
Iron	mg/L as Fe	1 366
Cobalt	mg/L as Co	49
Nickel	mg/L as Ni	317
Copper	mg/L as Cu	67
Zinc	mg/L as Zn	48
Arsenic	mg/L as As	4 766
Chloride	mg/L as Cl	136
Fluoride	mg/L as F	606

Different types and qualities of powdered calcium carbonate, required for test purposes were obtained from Aqua-lime (Sappi Enstra, Ngodwana, Syferfontein , TSB and Highveld Limestones).

Equipment

Figure 13 and Table 17 describe the flow-diagram and process parameters of the pilot plant. It consisted of two Turbulators in series, feed pumps (feed water to Turbulator 1, Figure 14) and limestone slurry to Turbulators 1 and 2), clarifier, recycle pump and a feed-water storage tank.

The Turbulator consisted of a motor which directly drives a rotor via a hollow shaft. Due to the high speed (2000 rpm, 66 Hz) a partial vacuum is created by the rotor and air is sucked via the hollow shaft into the slurry. A strong vortex is created at both the upper and lower ends of the rotor. The bottom stream is pulled through the rotor and deflected upwards, forming a wave at the outside, upper end of the mixing vessel, drawing any powders and solids into the upper vortex. The stream is subsequently deflected downwards and sweeps the bottom of the vessel and prevents any solids-settlement. The Turbulator allows proper mixing of the acidic water and the calcium carbonate. The advantage is that it can mix/disperse slurries up to 60% solids contents.

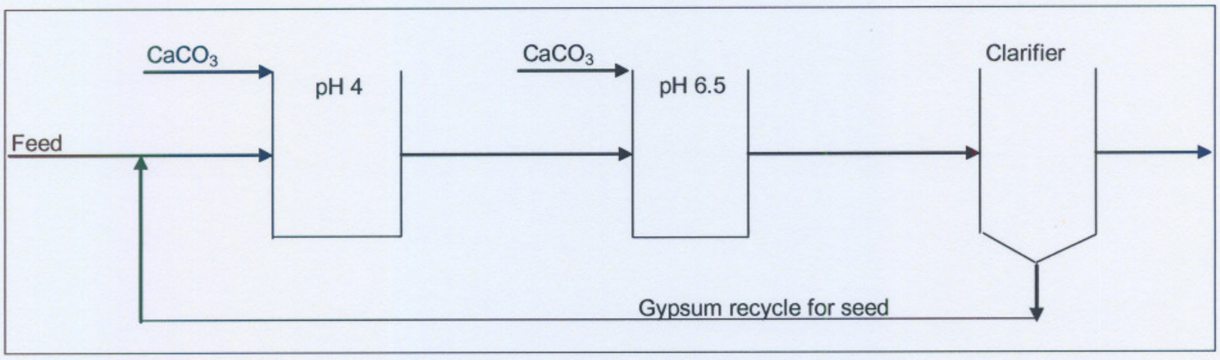


Figure 13. **Process flow diagram of on-site pilot plant for studies on an arsenic rich, acid water.**

Table 17. **Dimensions and flow rate characteristics of the pilot plant.**

Parameter	Feed	Turbulator 1	Turbulator 2	Clarifier
Volume (l)		850	150	400
Feed rate (l/min)	1.5			
Limestone feed rate (l/min)		0.20	0.25	
Recycle rate (l/min)		2.5		
Hydraulic residence time (h)		7.3	1.3	3.4

Figure 14. **Turbulator Unit**

Experimental

Continuous studies were carried out on arsenic rich, acid water using the set-up as described above (Figure 13). Arsenic rich acid water and Ngodwana limestone slurry (20% slurry of 69% $CaCO_3$) were fed to Turbulator 1 and 2. Samples were collected from both the lime and limestone processes and analysed for pH, acidity, sulphate, iron(II) (at 4h intervals) and other heavy metals (daily).

The effects of the following parameters were investigated:

- Limestone source (Sappi Enstra, Ngodwana, Syferfontein, TSB and Highveld)
- $CaCO_3$ slurry dosage (to pH 4.3 in Turbulator 1 and to pH 6.5 in Turbulator 2)
- The leachate potential of arsenic: Four sludge samples (2 from lime process and 2 from limestone process) were subjected to TCLP tests to determine the leachate potential of arsenic.

Analytical

Water Analysis

Samples from the continuous experiments were taken at regular time intervals (4h). The samples were filtered and analyzed for pH, acidity, sulphate, iron(II), on site. Determinations were carried out manually according to standard procedures (APHA, 1985). A composite sample was send to SGS Lakefield Research Laboratories for heavy metal determinations.

Sludge Characteristics

Tests to determine MLSS and the sludge-settling rate were carried out manually according to standard procedures (APHA, 1985).

Sludge samples from both the lime and limestone processes were collected daily and dried at room temperature. Composite samples were sent to SGS Lakefield Research Laboratories for TCLP tests.

TCLP Leach Testing

Leach testing was done using the TCLP test as described by the Department of Water Affairs and Forestry (TCLP test). The leachates were submitted for analysis by ICP-OES and ICP-MS.

The TCLP test (US EPA) is designed to determine the environmental mobility of both organic and inorganic constituents present in multi-phase waste. The extraction fluid used is a function of the alkalinity of the solid phase of the waste material. The extraction fluids consist either of acetic acid or a blend of acetic acid and sodium hydroxide. Acetic acid is the strongest acid present in typical landfills and this test is typically used to characterize a material destined for disposal to landfill as a hazardous or non-hazardous waste. This TCLP test was specifically aimed at ensuring that the arsenic present in the sludge would remain immobile when the sludge was disposed of to landfill.

The TCLP test was carried out as follows:

Acid solution (2L) was added to the dried solid sample (100g). The sample was agitated end over end for 20 h and the suspension filtered prior to analysis of the filtrate.

Results and Discussion

Limestone selection

Figure 15 and Figure 16 depict a comparison of the performances of limestones from various sources for the treatment of arsenic rich process water. It was noted that:

- Sappi Enstra performed better than Syferfontein, TSB and Highveld limestones. A product from Sappi Ngodwana was also tested. It afforded similar results to the Sappi Enstra product. With the Sappi Enstra product the pH could be raised from 3 to 6.2 in 15 minutes and to 7 after 60 minutes.
- Acidity decreased from 50 000 mg/L in the raw water to 50 mg/L in less than 4 hours (Figure 16).
- Sludge settling rate was found to be 0.2 m/h.

It was found that Sappi Ngodwana calcium carbonate was the most suitable neutralising agent for the present effluent.

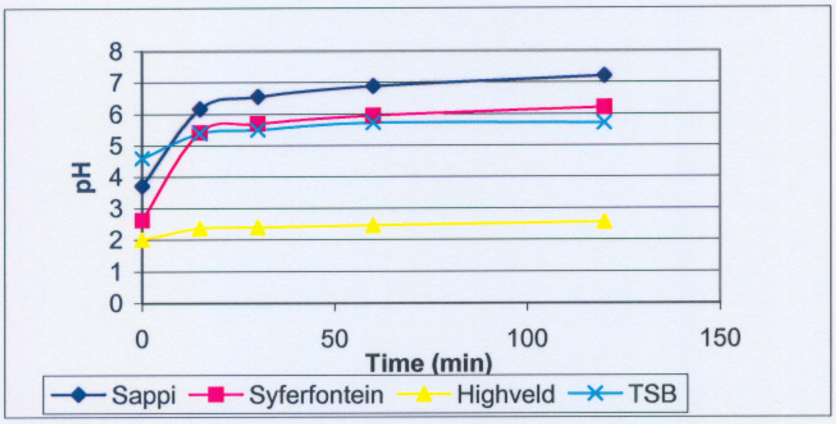


Figure 15. **Effect of different limestones on pH**

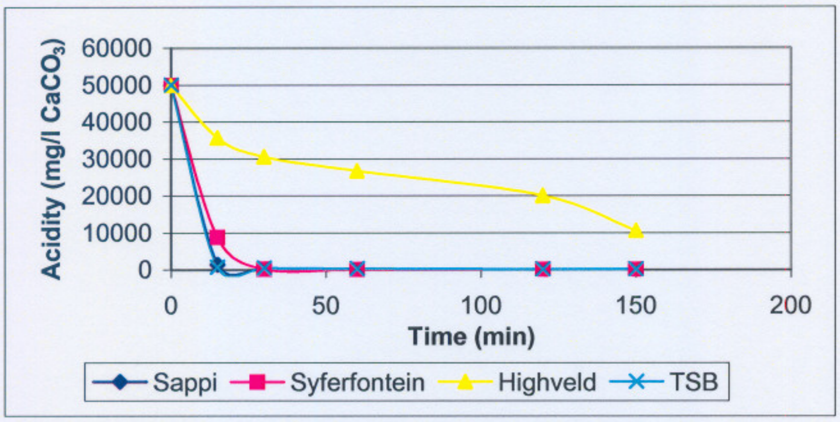


Figure 16. **Effect of different limestones on acidity**

Limestone versus lime treatment

Table 18 compares the chemical compositions after arsenic rich, acid water had been treated with lime and limestone (Sappi Ngodwana), respectively. It was noted that:

- The chemical composition of limestone treated water was similar to that of lime treated water. In both cases the pH was raised from 1.6 to above 6.4. Acidity was reduced from 33 g/l (as $CaCO_3$) to less than 0.06 g/l (as $CaCO_3$), sulphate was reduced from 40 g/l to less than 7 g/l, arsenic reduced from 4 g/l to less than 0.4 g/l, after sludge separation.

- The sludge-settling rates for the lime and limestone processes were the same in both cases (0.2 m/h).

Table 18. Comparison between chemical compositions of lime and limestone treated water.

Parameter	Minimum detectable limit	Feed	Lime pH4 (R1)	Lime pH6.5 (R2)	Limestone pH4 (R1)	Limestone pH6.5 (R2)
pH		1.5			4.2	6.4
Acidity (mg/L as $CaCO_3$)		33 294			438	61
Sulphate (mg/L as SO_4)		40 000			7 873	6 840
Iron(II) (mg/L as Fe)		51			7	6
Sodium (mg/L Na)	0.05	80	69	64	440	350
Potassium (mg/L K)	0.11	52	60	59	54	32
Calcium (mg/L Ca)	0.05	590	460	450	490	250
Magnesium (mg/L Mg)	0.02	1 200	1 200	1 100	1 100	560
Aluminium (mg/L Al)	0.08	90	23	<0.08	12	<0.08
Chromium (mg/L Cr)	0.04	3.2	0.08	<0.04	0.08	<0.04
Manganese (mg/L Mn)	0.01	68	120	44	180	43
Iron (mg/L Fe)	0.02	17 000	4.1	0.59	16	0.53
Cobalt (mg/L Co)	0.12	33	27	7.3	28	4.2
Nickel (mg/L Ni)	0.05	230	170	41	190	26
Copper (mg/L Cu)	0.12	53	25	<0.02	17	0.03
Zinc (mg/L Zn)	0.17	44	34	1.9	38	1.2
Arsenic (mg/L As)	0.34	4 100	0.93	0.44	0.59	< 0.34
Chloride (mg/L Cl)	5.0	<5	33	34	46	52
Fluoride (mg/L F)	0.1	<0.1	0.19	<0.1	0.31	0.19

Water quality following limestone treatment

Figure 17, 20 and 21 show the behaviour of various parameters during continuous treatment of the arsenic rich acid, water with limestone. At a $CaCO_3$ dosage to acid concentration ratio of 1.67 (Figure 17) and higher, the

- pH was consistently raised from 1.5 to 6.4
- Acidity was reduced from 33.5 g/l to less than 0.06 g/l (as $CaCO_3$).

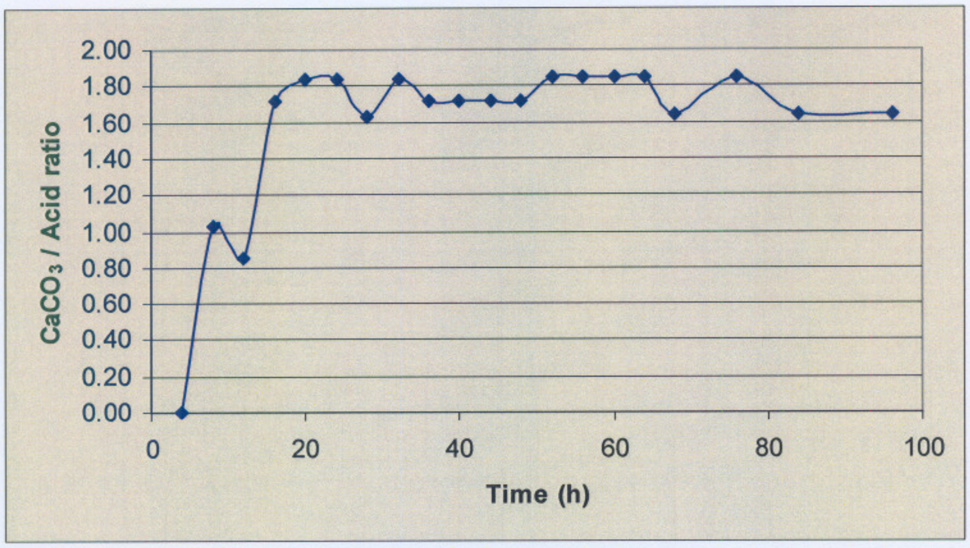


Figure 17. CaCO$_3$-dosage : acid concentration ratio of arsenic rich feed water as a function of time.

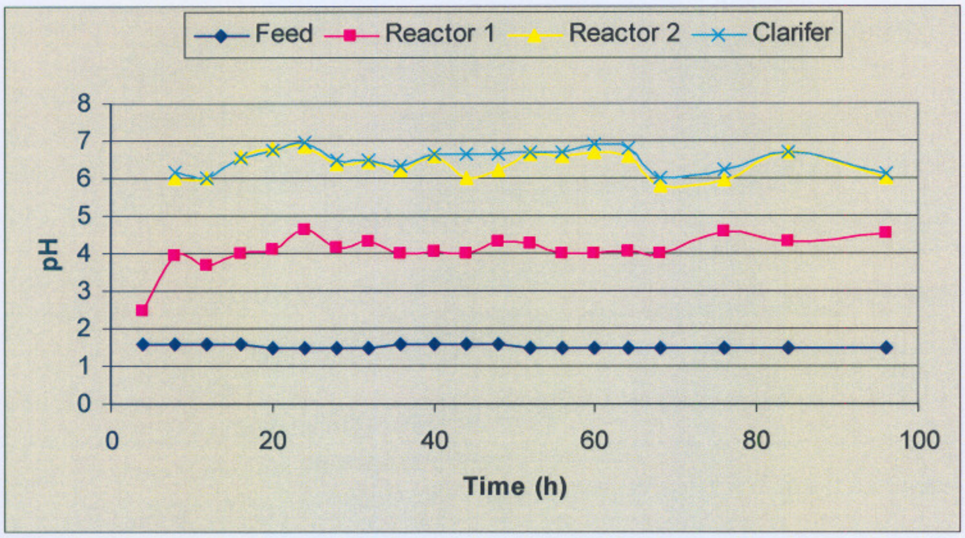


Figure 18. Behaviour of pH when arsenic rich, acid water was treated with limestone.

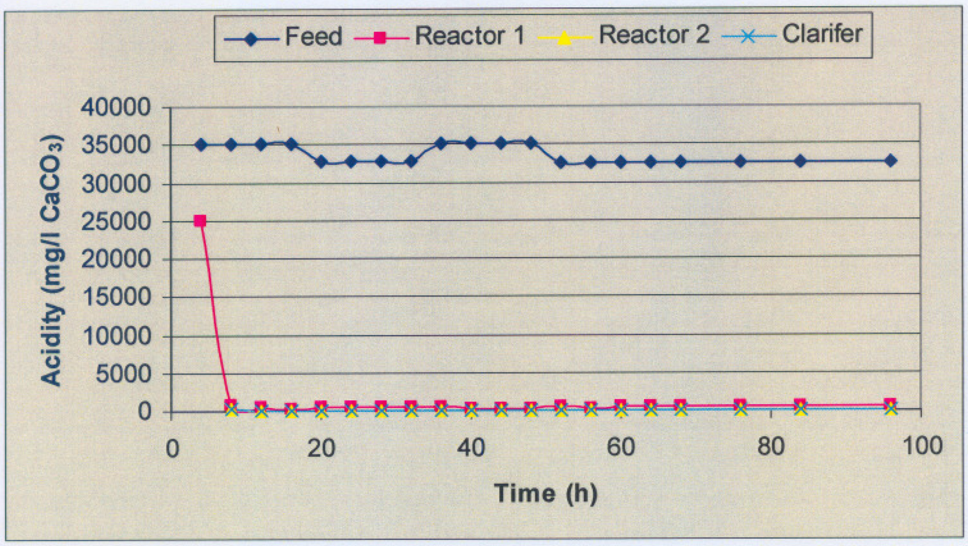


Figure 19. Behaviour of acidity when arsenic rich, acid water was treated with limestone

TCLP results for lime and limestone sludge

The purpose of the TCLP leachate tests was to determine whether limestone had any negative effect on the concentration of leachable arsenic in the limestone sludge compared to the lime sludge.

Table 19 showed that there were no significant differences in the TCLP values of the sludges when the water was treated with lime or with limestone. This was expected, as acid water neutralized with limestone is identical to that neutralized with lime. In the case of limestone neutralization, CO_2 is evolved. CaO remains in solution as $Ca(OH)_2$.

Table 19. TCLP values of the sludges from the lime and limestone treatment processes.

Parameter	Minimum detectable limit	Lime Sludge pH 4 (R1)	Lime Sludge pH 6.5 (R2)	Limestone Sludge pH 4 (R1)	Limestone Sludge pH 6.5 (R2)
Antimony (mg/L Sb)	0.31	< 0.31	< 0.31	< 0.31	< 0.31
Arsenic - (inorg) (mg/L As)	0.34	< 0.34	< 0.34	< 0.34	< 0.34
Barium (mg/L Ba)	0.02	0.02	0.03	0.07	0.11
Cadmium (mg/L Cd)	0.03	< 0.03	< 0.03	< 0.03	< 0.03
Cobalt (mg/L Co)	0.12	2.2	5.0	1.2	4.2
Copper (mg/L Cu)	0.02	1.2	0.7	1.5	0.32
Iron (mg/L Fe)	0.02	0.86	0.29	2.1	0.08
Lead (mg/L Pb)	0.31	4.2	2.0	4.1	3.3
Magnesium (mg/L Mg)	0.02	78	99	44	74
Manganese (mg/L Mn)	0.01	14	22	8.1	30
Mercury - (tot) (mg/L Hg)	0.003	< 3	< 3	< 3	< 3
Nickel (mg/L Ni)	0.05	15	32	6.3	25
Selenium - (inorg) (mg/L Se)	0.02	< 20	< 20	< 20	< 20
Silver (mg/L Ag)	0.003	< 5	< 5	< 5	< 5
Titanium (mg/L Ti)	0.02	< 0.02	< 0.02	< 0.02	< 0.02
Vanadium (mg/L V)	0.07	< 0.07	< 0.07	< 0.07	< 0.07
Zinc (mg/L Zn)	0.17	2.5	5.1	1.8	3.5
Zirconium (mg/L Zr)	0.05	< 0.05	0.08	0.05	0.06

TCLP values for arsenic of less than 5 mg/L indicated that the sludge can be disposed of to landfill as a non-hazardous waste.

Alkali cost comparison

Table 20 compares the costs of lime and limestone treatment.

Table 20. Comparison between the costs of lime and limestone

Parameter	Unit	Lime	Limestone
Acidity	g/l	55	55
Flow	m^3/h	17	17
Purity	%	85	70
Utilization efficiency	%	90	90
Mol mass	Daltons	56	100
Acid load	t/day $CaCO_3$	682	682
Alkali usage	t/d	499	1083
Price	R/t	800	200
Cost	R/month	399 497	216 564
Saving	%	0	45.8

The use of limestone will result in a cost saving of 45.8%.

Conclusions

The present studies showed that:

- Limestone (Sappi Ngodwana) can be used effectively to replace lime for the neutralization of arsenic rich acid water.
- The cost of limestone treatment is 45.8% less than that of lime.
- With limestone treatment, the acidity can be decreased from 33.5 to 0.06 g/l (as $CaCO_3$).
- There is no significant difference in the TCLP characteristics of the resultant sludge when water is treated with lime or with limestone.
- Sludge from the limestone treatment process can be disposed of to a non-hazardous landfill site.

CHAPTER 6 CONCLUSIONS

The main conclusions of this study were:

- Limestone can be effectively used in preference of lime in the neutralisation of AMD.
- The DesEl system can be used effectively for desalination of neutralised AMD and acidic effluents.

AMD and acidic effluents are typically highly acidic with elevated levels of sulphate and dissolved metals, principally iron. The main steps for treatment are:

- Neutralisation by adding alkaline to raise the pH of the water.
- Desalination to further lower the concentration of metals and sulphate.

Both capital cost and operational costs must be considered in water treatment. While cost and ease of implementation play major roles, the chemistry and volume of the acid water ultimately influence the selection and viability of a particular technology. Limestone is the prime choice for acid water neutralization due to its widespread availability, non-proprietary nature, ease of application and cost-effectiveness.

The study on the chemical aspects of the limestone neutralisation process showed that the limestone particle size is an important parameter. The major characteristic of a suitable limestone is a high neutralising rate. It was shown that the smaller the particle size and hence the larger the surface area, the faster the rate of neutralization. Finer limestone particle size also resulted in faster settling rates and lower sludge volumes. Characteristics of high quality sludge are fast settling rates and low sludge volumes. Due to the high capital and running costs associated with poor sludge settling, ways whereby the settling rate and density could be increased (or sludge volume reduced), were also investigated. The studies showed that:

- The sludge settling rate and the final sludge volume are significantly influenced by the acid concentration of the AMD and the sludge solids content as a result of gypsum and metal precipitation. The settling rate was reduced from 0.56 m/h to 0.10 m/h and the sludge volume increased from 7.8 % to 40 % when the acid concentration increased from 6 to 24 g/l, respectively.
- The limestone source and particle size influences the sludge settling rate and the final sludge volume. A smaller particle size results in faster settling rates and lower sludge volumes.

- The sludge settling rate is also influenced by the method of dosing limestone. The settling rate increased when limestone was added incrementally rather than as a single dose. The settling rate doubled when limestone was added incrementally to acid water with high acid concentrations (acidity > 15 g/l). The settling rate increased from 0.2 m/h to 0.4 m/h for Namakwa Sands water (20 g/l acidity), from 0.30 to 0.65 for synthetic water (19 g/l acidity) and from 0.07 m/h to 0.13 m/h for the Somchem factory water (19 g/l acidity). For the Ticor water (4 g/l acidity), however the settling rate only increased from 0.7 to 0.8 m/h.
- Flocculant addition increases the sludge settling rate, but has a slight negative effect on sludge volume. The settling rate of limestone treated water increased from 0.57 m/h, when no flocculant was added, to 4.3 m/h at a dosage of 0.75 mg/l Montan 3095 flocculant.
- The sludge formed had a major effect on the required lime dosage following limestone treatment. The following lime dosages were required to raise the pH from 6.8 to 10.4:
  - d. for 0 % solids – 0.4 g/l
  - e. for 1.1 % solids – 1.2 g/l
  - f. for 6.0 % solids – 4.5 g/l

With the initial limestone neutralisation process, acidity is removed but only partial sulphate and metal removal are achieved. Further treatment is required to make the limestone neutralised water suitable for re-use or discharge. The purpose of the study in Chapter 4 was to assess the suitability of the DesEl process for final desalination of neutralised process water. Laboratory studies showed that:

- The DesEl test unit can be used effectively in one- or two-stage processes to treat the sulphate and metal rich effluent from the Namakwa Sands neutralisation plant.
- One-stage DesEl treatment resulted in the following:
  - o Sulphate concentration was lowered from 3668 mg/l to 351 mg/l, magnesium from 447 mg/l to 43 mg/l, calcium from 312 mg/l to 31 mg/l, manganese from 44.9 mg/l to 4.6 mg/l and chloride from 66 mg/l to 8 mg/l.
  - o The energy cost amounted to 1.29 R/m^3 feed treated and 1.70 R/m^3 pure water produced.
- Two-stage DesEl treatment process resulted in the following results:
  - o Sulphate concentration was lowered from 4434 mg/l to 100 mg/l, magnesium from 539 mg/l to 12 mg/l, calcium from 375 mg/l to 9 mg/l, manganese from 53.7 mg/l to 1.3 mg/l and chloride from 77 mg/l to 2 mg/l.
  - o The energy cost amounted to 1.21 R/m^3 feed treated and 1.53 R/m^3 pure water produced during the first stage. For the second stage, the cost amounted to 0.30 R/m^3 feed treated and 0.32 R/m^3 pure water produced.

Both the one-stage and two-stage treatment processes can be used to reduce the sulphate concentration. This study showed that for treatment of high sulphate concentrations (4 000 mg/l) with the DesEl system, the two-stage process is the better option owing to:

- Higher overall water recovery
- Higher overall processing rate
- Lower energy requirement.

Generally acid mine water is neutralised with lime. The innovative aspects of this and other studies indicate that limestone is a cheaper alternative for treating acid, iron and sulphate-rich water. Chapter 5 described a case study where results from Chapter 3 were implemented in the limestone neutralisation of arsenic rich, acid process water from a gold mine. It showed that limestone can effectively replace lime for the neutralization and arsenic removal of such water.

Results from the case study showed that:

- The cost of limestone treatment is 40-50% less than that of lime.
- With limestone treatment, the acidity can be decreased from 33.5 to 0.06 g/l (as $CaCO_3$).
- There are no significant differences between the resultant sludge when water is treated with lime or with limestone.
- The sludges can be disposed of to a non-hazardous landfill site as the TCLP characteristics indicated that the arsenic would remain bound and not leach out over time.

AMD and acidic effluents can effectively be treated for re-use or discharge by applying the integrated limestone technology followed by desalination with the DesEl process.

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APPENDIX A: EXPERIMENTAL RESULTS ON DESALINATION WITH THE DESEL PROCESS

		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10	Run 11	Run 12	Run 13	Run 14	Run 14	Run 15	Run 16	Run 17	Run 18	Run 19	Run 20
Exp Number		Exp 1.1	Exp 1.2	Exp 1.3	Exp 2.1	Exp 2.2	Exp 2.3	Exp 3.1	Exp 3.2	Exp 3.3	Exp 4.1	Exp 4.2	Exp 4.3	Exp 5.1	Exp 5.2	Exp 5.2.1	Exp 5.3	Exp 6.1	Exp 6.2	Exp 6.3	Exp 7.1	Exp 7.2
Water Source		NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Conductivity Controller																						
Range (mS/cm)	P3	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Set Point 1 (mS/cm)	P1	4	4	4	4	4	4	4	4	4	4	4	4	2	2	2	2	2	2	2	0.7	0.7
Hyst (mS/cm)	P1.3	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
PLC Settings																						
Purify Time (s)		120	120	120	120	120	120	120	120	120	60	120	180	60	120	120	180	60	120	180	120	150
Regen Time (s)		60	120	180	60	120	180	60	120	180	120	120	120	120	120	120	120	180	180	180	120	120
Purge Time (s)		45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45	45
Pumps																						
Purify Flow (mL/min)		294	294	294	178	178	178	110	110	110	110	110	110	110	110	110	110	110	110	110	290	290
Purge Flow (mL/min)		64	64	64	64	64	64	64	64	64	60	60	60	60	60	60	60	60	60	60	60	60
Run Time (hh:mm)		00:36	00:40	00:50	00:45	00:45	00:50	00:39	00:36	00:35	00:39	00:33	00:35	00:24	00:24	00:20	00:25	00:24	00:25	00:30	00:16	00:18
Run Time (min)		36	40	50	45.25	44	50	39	36	35	39	32	35	24	24	20	25	24	25	30	16	18
Run time (sec/cycle)		180	240	300	180	240	300	180	240	300	180	240	300	180	240	240	300	240	300	360	240	270
Cycle Time (min)		3.0	4.0	5.0	3.0	4.0	5.0	3.0	4.0	5.0	3.0	4.0	5.0	3.0	4.0	4.0	5.0	4.0	5.0	6.0	4.0	4.5
Run (cycles)		12	10	10	15	11	10	13	9	7	13	8	7	8	6	5	5	6	5	5	4	4
Discharge (s/cycle)		13.9	25.7	28.4	28.8	37.7	43.8	66.3	83.0	102.1	56.2	94.8	91.2	40.9	84.5	85.1	87.3	45.5	85.1	76.4	116.6	137.6
Discharge/Purify time (%)		11.6	21.4	23.6	24.0	31.4	36.5	55.2	69.2	85.1	93.7	79.0	50.6	68.2	70.5	70.9	48.5	75.8	70.9	42.4	97.2	91.7
Volume (mL)	**Feed**	1445	1800	1920	2065	1790	1815	2245	1820	1660	1960	1780	1520	1000	1230	1030	1050	800	1030	950	2442	2848
Conductivity (mS/cm)		7.15	7.15	7.15	7.31	7.31	7.31	7.31	7.31	7.31	6.29	6.29	6.29	6.29	6.29	6.29	6.29	6.29	6.29	6.29	1.44	1.44
SO_4		4441	4441	4441	4474	4474	4474	4474	4474	4474	4211	4211	4211	3834	3834	3834	3834	3834	3834	3834	745	745
Volume (mL)	**Pure**	820	1260	1390	1290	1230	1300	1580	1370	1310	1340	1390	1170	600	930	780	800	500	780	700	2255	2660
Treated Conductivity (mS/cm)		3.14	2.63	2.41	2.23	1.47	1.37	1.61	1.49	1.47	1.59	1.48	1.48	0.965	0.793	0.768	0.774	0.836	0.765	0.836	0.22	0.29
SO_4		1274	1175	961	1009	711	645	766	705	695	821	694	700	490	400	387	391	423	386	423	109	144
Salt rejection (%)		75.1%	74.3%	75.6%	80.9%	86.2%	86.6%	84.5%	84.7%	84.1%	82.7%	81.6%	81.9%	90.8%	90.5%	90.8%	90.6%	91.7%	90.8%	90.2%	85.9%	81.2%
Volume (mL)	**Brine**	625	540	530	775	560	515	665	450	350	620	390	350	400	300	250	250	300	250	250	187	188
Conductivity (mS/cm)		12.77	15.96	17.66	14.35	17.02	18.49	17.74	19.3	19.12	13.32	20.8	20.6	12.6	20.3	19.77	21.3	12.78	19.52	19.56	12.71	14.9
SO_4		9273	11554	7928	5823	14556	14531	15005	17015	16778	10206	17463	18776	9193	17784	17121	19066	9368	16811	16861	9300	11523
Feed Rate (ml/min)		40.14	45.00	38.40	45.64	40.68	36.30	57.56	50.56	47.43	50.26	55.63	43.43	41.67	51.25	51.50	42.00	33.33	41.20	31.67	152.63	158.22
Feed Rate (L/h)		2.41	2.70	2.30	2.74	2.44	2.18	3.45	3.03	2.85	3.02	3.34	2.61	2.50	3.08	3.09	2.52	2.00	2.47	1.90	9.16	9.49

Processing Rate (mL/min)	22.78	31.50	27.80	28.51	27.95	26.00	40.51	38.06	37.43	34.36	43.44	33.43	25.00	38.75	39.00	32.00	20.83	31.20	23.33	140.94	147.78
Processing Rate (L/h)	1.37	1.89	1.67	1.71	1.68	1.56	2.43	2.28	2.25	2.06	2.61	2.01	1.50	2.33	2.34	1.92	1.25	1.87	1.40	8.46	8.87
Processing Rate (L/d)	32.80	45.36	40.03	41.05	40.25	37.44	58.34	54.80	53.90	49.48	62.55	48.14	36.00	55.80	56.16	46.08	30.00	44.93	33.60	202.95	212.80
Flux Rate (mL/min/m2)	33	46	41	42	41	38	60	56	55	51	64	49	37	57	57	47	31	46	34	207	217
Water Recovery (%)	57%	70%	72%	62%	69%	72%	70%	75%	79%	68%	78%	77%	60%	76%	76%	76%	63%	76%	74%	92%	93%
Running Cost																					
Power (Watts)	20.10	18.97	19.46	20.28	18.93	18.89	24.25	20.65	19.09	19.05	23.50	20.66	17.59	_____	22.02	20.34	14.15	29.05	19.71	15.03	15.44
Time (sec)	2170	2415	3008	2715	2646	3008	2351	2166	2104	2352	1923	2103	1445	_____	1203	1503	1444	1502	1785	963	1082
Rate (c/kW.hr)	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18	18
	10	*15*	*8*	*0*	*6*	*8*	*11*	*6*	*4*	*12*	*3*	*3*	*5*		*3*	*3*	*4*	*2*	*-15*	*3*	*2*
Energy (Joules)	43609	45809	58535	55048	50079	56831	57002	44736	40168	44796	45185	43450	25424		26493	30573	20426	43627	35188	14471	16711
Energy (Watts.hr)	12.11	12.72	16.26	15.29	13.91	15.79	15.83	12.43	11.16	12.44	12.55	12.07	7.06		7.36	8.49	5.67	12.12	9.77	4.02	4.64
Energy (kW.hr)	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01		0.01	0.01	0.01	0.01	0.01	0.00	0.00
Cost (c)	0.22	0.23	0.29	0.28	0.25	0.28	0.29	0.22	0.20	0.22	0.23	0.22	0.13		0.13	0.15	0.10	0.22	0.18	0.07	0.08
Cost (R)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pure volume (L)	0.82	1.26	1.39	1.29	1.23	1.30	1.58	1.37	1.31	1.34	1.39	1.17	0.60	0.93	0.78	0.80	0.50	0.78	0.70	2.26	2.66
Energy - pure (kW.h/m^3)	14.77	10.10	11.70	11.85	11.31	12.14	10.02	9.07	8.52	9.29	9.03	10.32	11.77		9.43	10.62	11.35	15.54	13.96	1.78	1.75
Energy - feed (kW.h/m^3)	8.38	7.07	8.47	7.40	7.77	8.70	7.05	6.83	6.72	6.35	7.05	7.94	7.06		7.14	8.09	7.09	11.77	10.29	1.65	1.63
Treatment cost - pure (R/m^3)	2.66	1.82	2.11	2.13	2.04	2.19	1.80	1.63	1.53	1.67	1.63	1.86	2.12		1.70	1.91	2.04	2.80	2.51	0.32	0.31
Treatment cost - feed (R/m^3)	1.51	1.27	1.52	1.33	1.40	1.57	1.27	1.23	1.21	1.14	1.27	1.43	1.27		1.29	1.46	1.28	2.12	1.85	0.30	0.29

APPENDIX B: CHEMICAL COMPOSITION OF LIMESTONE TREATED ARSENIC RICH ACID WATER DURING CONTINUOUS OPERATION

Type of operation	Continuous																			
Date	26-Apr	26-Apr	26-Apr	26-Apr	26-Apr	26-Apr	27-Apr	27-Apr	27-Apr	27-Apr	28-Apr	28-Apr	28-Apr	28-Apr	28-Apr	28-Apr	29-Apr	29-Apr	29-Apr	30-Apr
Time	12:00	16:00	20:00	24:00	04:00	08:00	12:00	16:00	20:00	24:00	04:00	08:00	12:00	16:00	20:00	24:00	04:00	12:00	20:00	08:00
Operational time (h)	4	8	12	16	20	24	28	32	36	40	44	48	52	56	60	64	68	76	84	96
Flow rate (l/min)																				
Feed	2.5	2.5	3	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Limestone Turb 1	0.2	0.2	0.2	0.2	0.2	0.2	0.15	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Limestone Turb 2		0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.2	0.25	0.2	0.2
Hydraulic retention time (h)																				
Turbulator 1	5.2	4.8	4.1	7.3	7.3	7.3	7.5	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.5	7.3	7.5	7.5
Turbulator 2	0.9	0.8	0.7	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Clarifier	2.5	2.3	1.9	3.4	3.4	3.4	3.5	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.5	3.4	3.5	3.5
pH																				
Feed	1.6	1.6	1.6	1.6	1.5	1.5	1.5	1.5	1.6	1.6	1.6	1.6	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Turbulator 1	2.45	3.95	3.7	4.01	4.1	4.62	4.16	4.32	4.02	4.07	4.0	4.34	4.27	4.0	4.02	4.03	4.02	4.57	4.32	4.52
Turbulator 2		6.02	6.0	6.6	6.8	6.86	6.38	6.44	6.2	6.6	6.0	6.22	6.62	6.56	6.7	6.6	5.8	5.95	6.66	6.02
Clarifier		6.16	6.0	6.54	6.75	6.94	6.5	6.5	6.3	6.62	6.62	6.61	6.7	6.66	6.9	6.8	6.0	6.2	6.67	6.09
Acidity (mg/l $CaCO_3$)																				
Feed	35000	35000	35000	35000	32750	32750	32750	32750	35000	35000	35000	35000	32500	32500	32500	32500	32500	32500	32500	32500
Turbulator 1	25000	800	400	350	400	400	400	500	400	350	350	350	400	350	500	550	600	550	500	500
Turbulator 2		250	50	50	50	50	50	100	100	50	50	100	50	50	50	50	100	50	50	50
Clarifier		200	50	50	50	50	50	100	50	50	50	50	50	50	50	50	50	50	50	50
Iron(II) (mg/l Fe)																				
Feed																				
Turbulator 1		55.9	67.0	55.9	61.4	44.7	50.3	50.3	55.9	50.3	50.3	44.7	44.7	44.7	44.7	44.7	67.0	39.1	44.7	67.0
Turbulator 2		11.2	5.6	5.6	5.6	5.6	11.2	11.2	11.2	5.6	5.6	7.8	5.6	5.6	5.6	5.6	11.2	5.6	5.6	5.6
Clarifier		11.2	5.6	5.6	5.6	5.6	5.6	11.2	5.6	5.6	5.6	6.7	5.6	5.6	5.6	5.6	5.6	5.6	5.6	5.6
$CaCO_3$-slurry (g/l $CaCO_3$)	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200	200
Acid load (g/h $CaCO_3$)		5250	6300	3150	2948	2948	2948	2948	3150	3150	3150	3150	2925	2925	2925	2925	2925	2925	2925	2925
Alkali load (g/h $CaCO_3$)		5400	5400	5400	5400	5400	4800	5400	5400	5400	5400	5400	5400	5400	5400	5400	4800	5400	4800	4800
Alkali / Acid ratio		1.03	0.86	1.71	1.83	1.83	1.63	1.83	1.71	1.71	1.71	1.71	1.85	1.85	1.85	1.85	1.64	1.85	1.64	1.64