CSIR

DIVISION OF WATER, ENVIRONMENT AND
FORESTRY TECHNOLOGY

Report to the

WATER RESEARCH COMMISSION

on

UNDERGROUND NEUTRALISATION OF MINE WATER WITH LIMESTONE

by

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PRETORIA

EXECUTIVE SUMMARY

Background and motivation

Acidic effluents arise in the mining industry mainly from discard overburden, slimes dams, sand dumps, underground workings and metallurgical plants. Limestone can be used to neutralise acid mine drainage (AMD), which results from the oxidation of sulphur containing minerals, such as pyrites. Pyrite oxidation occurs underground during or after mining activities and on surface in old mine dumps containing pyrites.

Acid water is neutralised with a discharge or recycle aim in mind. Acid water contributes to corrosion of pipelines and mineralisation of surface water. Neutralised acid water also contributes to surface water mineralisation. Acid water is generally detrimental to aquatic life and has a negative aesthetic impact on rivers and streams. The result of inadequate dosing control is that water from low to high pH values (3 to 10 respectively) are pumped through the vertical mine water pipelines, resulting in either corrosion as a result of the low pH, or scale formation (gypsum) as a result of high calcium concentrations in typical mine water. Accurate pH control is also important for heavy metal removal from acid water.

Lime neutralisation of acid water is widely applied to meet legislative requirements regarding discharge of effluent into receiving waters. Lime and chemicals like sodium hydroxide and sodium carbonate have the disadvantage that they require accurate dosing to prevent under or over application. This is difficult to achieve underground in mining operations, resulting in water with low or high pH values (3 to 10 respectively) to be pumped through the vertical mine water pipelines. This may result in either corrosion as a result of low pH, or gypsum scale formation when lime is dosed as a result of the high calcium concentration. Since large amounts of lime are required, neutralisation of effluents is a costly operation.

The CSIR, in collaboration with the WRC, has developed a fluidised bed neutralisation process which uses limestone or dolomite as the neutralising agent (Maree and du Plessis, 1993). This effectively overcomes the dosing problem as limestone will only dissolve as long as the water is undersaturated with respect to $CaCO_3$. Dissolution usually stops at a pH between 6 and 7.

The benefits associated with limestone neutralisation include:

- Direct savings on the purchase cost of neutralisation material.
- Simplified pH-control as limestone and dolomite dissolution occurs mainly at pH-values below 7. Since the flow rate of underground mine water may vary by a factor of 10 (Pulles *et al.*, 1994), lime/soda ash systems can only function well if its dosing rates are adjusted accordingly. The fluidised-bed limestone neutralisation process is not affected by changes in flow rate as the acid feed water is bled into the recycle stream which passes through an excessive amount of limestone.
- Minimisation of material wastage which would occur as a result of over-dosage (due to pH-solubility relationship referred to above).
- Elimination of hazardous chemical usage for neutralisation (limestone/dolomite is easy and safe to handle).
- Simple bulk chemical storage facilities (the raw materials are not readily soluble in neutral water).
- Utilisation of equipment at existing lime neutralisation plants.

The development stage of the limestone neutralisation process had been completed prior to this study, but further development was required to make the process suitable for the underground treatment of acid water.

Objectives

The aims of the investigation were to:

- Obtain design criteria for iron(II) oxidation prior to neutralisation to make the process suitable for the neutralisation of iron(II)-containing water, which is typically the case with acid mine drainage and underground mine water.

- Modify the process to make it suitable for the underground neutralisation of acid mine water. The major limitations to any underground process are lack of space and means of transport of raw material. A specific aspect to be investigated was the shape of the reactor required to fit into the space available underground.

- Demonstrate that underground mine water can be neutralised with limestone in the fluidised bed limestone neutralisation process.

- Determine the economic feasibility of the fluidised bed limestone neutralisation process.

Materials and Methods

The following studies were carried out:

* Laboratory-scale batch studies to determine the effect of iron, oxygen and bacterial concentrations and temperature on the rate of oxidation.

* Continuous laboratory-scale studies to evaluate the efficiency of the column-shaped fluidised bed, with water recycled through a clarifier to minimise washout of limestone particles.

* Pilot-plant studies at capacities of up to 7 kℓ/h underground in a gold mine for a continuous period of 30 days to determine the contact time required between the acid water and the limestone, chemical composition of feed

and treated water, and the economic feasibility of the fluidised bed limestone neutralisation process.

Results and conclusions

The findings from the study can be summarised as follows:

- *Iron(II)-oxidation.* A biological process upstream of the neutralisation step was successfully used to oxidise iron(II) to iron(III). Limestone neutralisation is more efficient when iron(II) is oxidised to iron(III) upstream of the neutralisation stage. The reason is that iron(II) passes through the limestone neutralisation reactor unchanged due to its relatively high solublity. The volumetric reaction rate was 5,5 g Fe/(ℓ.d) at an iron concentration of 5 g/ℓ Fe, a dissolved oxygen concentration of 8 mg/ℓ, and a temperature of 25 ^{0}C. The required retention time of 22 h for iron(II) oxidation might be too long for application underground due to limited space. For waters with high iron(II) concentrations (greater than 200 mg/ℓ Fe), it is recommended that iron(II) oxidation be applied at surface level. This is still acceptable from a practical point of view. By neutralising only free acid and acid associated with iron(III) underground, the pH of the water could be raised to above 5.5, where the corrosivity of the water is significantly less. The underground mine water tested in this study contained only 5 to 20 mg/ℓ Fe(II), and no pretreatment for iron(II) oxidation was therefore required.

- *Water quality.* The limestone neutralisation process improves the quality of the water by the complete removal of free acid and acid associated with Fe(III). Sulphate is removed up to the point where the water is saturated with calcium sulphate. The pH of the water can be increased from less than 3 to more than 7, while the initial acidity, iron and uranium are removed by 97 % (400 to 12 mg/ℓ as

$CaCO_3$), 95 % (20 to < 1 mg/ℓ Fe) and 83 % (1 100 to 190 mg/ℓ U) respectively. As the iron(II) content of the underground water was less than 100 mg/ℓ (only 5 to 20 mg/ℓ), iron oxidation pre-treatment was not required. The alkalinity of the treated water is generally greater than 120 mg/ℓ (as $CaCO_3$). In the case of a strong acid solution the pH can be increased from 1,1 to 7,0, the acidity reduced from 18,4 to almost 0 g/ℓ (as $CaCO_3$), and sulphate from 13,5 to 1,3 g/ℓ.

- *Kinetics.* The rate of limestone neutralisation is influenced by the following factors:
    - Surface area of limestone particels. The surface area is a function of the type of limestone (amorphous or crystalline) and particle size.
    - Chemical composition of limestone. The higher the magnesium content, the slower is the rate of neutralisation.
    - Chemical composition of the acid water. The rate of neutralisation is fast for waters containing mainly free acid and iron(III). The neutralisation rate is lower when iron(II), aluminium or magnesium is present.
    - Concentrations of acid and limestone.

- *Contact time.* A requirement for underground neutralisation of acid water with limestone is that equipment should fit into the available space, which is limited at best. A column-shaped fluidised bed reactor, with water recycled through a clarifier to minimise washout of limestone particles was evaluated for this purpose. For the water under investigation, it was found that a contact time of 10 min between mine water and limestone can be used for design purposes. The required contact time, however, is a function of the surface area of the limestone and the chemical composition of the mine water.

- *Limestone utilisation.* With the column-shaped fluidised bed reactor, it was found that all the acid fed is neutralised, and stoichiometrically, the equivalent amount of limestone is consumed.

- *Sludge removal.* Precipitates, such as gypsum and ferric hydroxide, and limestone impurities are washed out from the fluidised-bed reactor and separated from the water in a settler downstream of the neutralisation stage. Should certain impurities, such as sand in the case of limestone deposits near the sea shore, accumulate in the reactor, it can be discharged from the bottom of the reactor on a periodic basis.

- *Economic feasibility.* Chemical savings of 66 % can be achieved when the cost of limestone and lime amounts to R100/t and R400/t respectively. For the neutralisation of 164,25 t/d of acid (as $CaCO_3$), limestone cost amounts to R0,06/kℓ, R0,47/kℓ and R1,47/kℓ when waters with acid contents of 0,45 g/ℓ (gold mine water), 3,60 g/ℓ (coal mine drainage) and 11,25 g/ℓ (Uranium raffinate) (all contributions expressed in g/ℓ $CaCO_3$) is treated, respectively. The corresponding capital and construction cost amounts to R1 400 000/(Mℓ/d), R1 500 000(Mℓ/d) and R2 300 000/(Mℓ/d), respectively, and the corresponding running cost (including chemicals, electricity, labour and capital redemption costs) to R0,23/kℓ, R1,60/kℓ and R3,31/kℓ, respectively.

  Oxidation of iron(II)-rich water is required for iron(II) concentrations greater than 0,2 g/ℓ. The cost figures shown above include the oxidation cost. The capital and construction costs for the iron(II) oxidation stage amounts to R458 000/(Mℓ/d) and R730 000/(Mℓ/d) for coal mine drainage and Uranium Raffinate, respectively.

Contribution and benefits from the project

The study demonstrated that underground mine water can be neutralised effectively in a fluidised bed reactor. Iron(II), which reduces the rate of neutralisation, can be oxidised to iron(III) upstream of the neutralisation reactor.

By using the fluidised bed reactor for limestone neutralisation, the main weaknesses of limestone (low reactivity, scaling of limestone particles in other systems such as limestone weirs or anoxic limestone drains) are overcome. The problem of long reaction time as a result of the low reactivity of limestone is solved in the fluidised bed reactor because an excessive amount of limestone is in contact with the acid water. Scaling of limestone particles with compounds such as gypsum, ferric hydroxide 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.

This study has demonstrated that limestone neutralisation of acid water in a fluidised bed reactor offers advantages over conventional neutralisation processes. It can be implemented on full scale after site-specific tests have been carried out to obtain design criteria for specific waters.

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GLOSSARY

Acid mine drainage	:	Acid water, rich in iron, produced when pyrites (FeS_2) is oxidised in water due to the presence of air and iron oxidising bacteria.
Dolomite	:	An ore containing $CaMg(CO_3)_2$
Fluidised-bed reactor	:	A column type reactor, packed with solid material, e.g. limestone, through which a fluid or gas is moved, at a rate, high enough, to expand the volume in the reactor occupied by the solid particles.
Limestone	:	An ore containing predominantly $CaCO_3$.
Slaked lime	:	$Ca(OH)_2$
Unslaked lime	:	CaO

CHAPTER 1. INTRODUCTION

OCCURRENCE OF ACID WATER

Various industries (Table 1) produce acidic effluents, such as the following:

- The mining industry, which produces acid mine drainage (AMD), both underground and on the surface of gold and coal mines when water, ore containing pyrites and air come into contact with each other. It is estimated that about 200 Mℓ/d of acid water is produced in the PWV area alone (Volman, 1984).
- Effluent from metallurgical plants at mines, for example uranium and acid plants.
- Effluent from the chemical industry.

Table 1. Industries that produce acidic effluents or streams (Maree, 1994).

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

Mining industry

The mining industry will benefit most from the limestone neutralisation process. The oxidation reaction of pyrites, which is responsible for AMD, can be represented as follows (Barnes, 1968):

$$2FeS_2 + 7,5O_2 + H_2O \text{ --> } Fe_2(SO_4)_3 + H_2SO_4 \qquad (1)$$

The reaction occurs underground during or after mining activities and on surface in old mine dumps containing pyrites. In underground workings the pumping of mine water reduces the rate at which leaching occurs from exposed surfaces. When mining operations cease, however, and the pumping stops, the water table returns to its natural level - or to a new level as a result of the mining operations. This flooding of the exposed seams stops the oxidation of iron pyrites, but brings into solution the sulphuric acid and iron sulphates which are the products of the oxidation reactions. The pH of such waters may go as low as 1 and dissolve even more iron.

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

Table 2 shows that 196 000 tons alkali (as $CaCO_3$) is required per year for the neutralisation of AMD only, while 222 000 tons is required for the neutralisation of acid waters from the mining industry.

Table 2. Estimated volume of acid water produced by the mining industry (Maree, 1994)

Source	**Area**	**Volume ($M\ell/d$)**	**[Acid] g/ℓ $CaCO_3$**	**Load t/d $CaCO_3$**	**Limestone t/a**
AMD	Reef	50	4	200	86 000
	Witbank	44	4	176	76 000
	Natal	20	4	80	34 000
Subtotal		114		456	196 000
Metallurgical plants	Zinc processing	3	20	60	26 000
TOTAL		117		516	222 000

AMD - Acid mine drainage.
Carbonate content of limestone was assumed to be 85% (as $CaCO_3$).

EFFECTS OF ACID WATER

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

- Salinisation of surface water. Impairment of river water quality because of mine water pollution may render it unsuitable for industrial and potable water supply, and often unsuitable for irrigation.

- Corrosion. Acidic effluents and even soft water, which is slightly acid, can lead to corrosion of pipelines.

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

- depletion of numbers of sensitive organisms and reduction in the diversity of the community within the river corridor;
- depletion of numbers and reduction in the diversity of the benthic macro-invertebrate community (organisms living on and in the stream bed);
- loss of spawning gravels for fish reproduction and nursery streams; and
- fish mortalities, particularly of indigenous salmonoid species.

Clear streams can turn into highly ochreous ones of a vivid orange appearance. Such discharges make rivers virtually fishless by coating the river bed with precipitating iron hydroxides. Depletion of the numbers and diversity of benthic (bottom dwelling) species occurs because the precipitate has a smothering effect, reducing oxygen and covering the river bed with iron oxides. This process also reduces the extent of spawning gravels for fish breeding, by occluding the interstices of the gravel with fine sediment, and therefore limits the availability of nursery streams. The low pH can be directly toxic, causing damage to fish gills. Solubilized metals, not only those which emerge from the mine water, but those - such as aluminium, the third most abundant element within the Earth's crust - can become dissolved within streamwater because of the acidic conditions. Such conditions are extremely toxic to fish (NRA, 1994).

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

LEGAL REQUIREMENTS

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

The legislative requirements of industrial effluent is primarily related to section 21 of the Water Act (ACT 54 of 1996). Section 21 requires that any person who uses water for industrial purposes shall purify or otherwise treat such water in accordance with requirements which the minister in consultation with the SABS may prescribe in the Gazette. The applicable standards are the General Standard and the Special standard. The relevant criteria for discharge of acidic and sulphate-rich waters are given in Table 3.

Table 3. Criteria set for the discharge of acidic and sulphate-rich effluents into public water courses.

Parameter	**General Standard**	**Special Standard**
pH	5,5 - 9,5	5,5 - 7,5
Sulphate	no criterion	no criterion
Conductivity (mS/m)	inlet + 75	250 or inlet + 15%

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

According to the Water Act, local authorities which accept industrial effluent have the right to establish criteria as deemed necessary and require such criteria to be met. Table 4 gives the general criteria set by various local authorities in various provinces.

Table 4. Typical criteria set by local authorities for discharge of acidic and sulphate-rich effluents into sewerage systems in various provinces.

Province	**pH**	**Sulphate** **mg/ℓ SO_4**	**Conductivity** **mS/m**
Gauteng	6 - 10	1 800	500
Western Cape	5,5 - 12	500	-
Natal	>6	200	300

Current and future approach

In the past the Department of Water Affairs used only the uniform effluent approach to control pollution from point sources in South Africa, as required by the relevant sections in the Water Act, 1995. This approach did not achieve the desired results. The Act does however also make provision for the more stringent standards to be promulgated or exemptions to be granted.

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

* Motivate that all avenues of pollution prevention through waste minimisation, recycling of effluent and migration prevention has been investigated and applied.

* Perform an impact assessment for the catchment where the discharge is proposed to be made if, after the first step has been done, the effluent does not meet the uniform effluent standards. Such impact assessment must ascertain

what the requirements of all the users of water in the receiving water body will be, as well as the extent to which the receiving water body will be affected.

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

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

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

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

NEUTRALISATION TECHNOLOGY FOR ACID MINE WATER

Introduction

The most suitable technology to date for the treatment of acid water is lime treatment. The conventional and High Density Sludge processes are used. The fluidised-bed neutralisation process which uses limestone or dolomite as the neutralising agent has been developed recently and offers cost benefits above existing processes.

Conventional treatment with lime

The flow diagram of the conventional process is shown in Figure 1. The main disadvantage of this process is that sludge with a low density is produced.

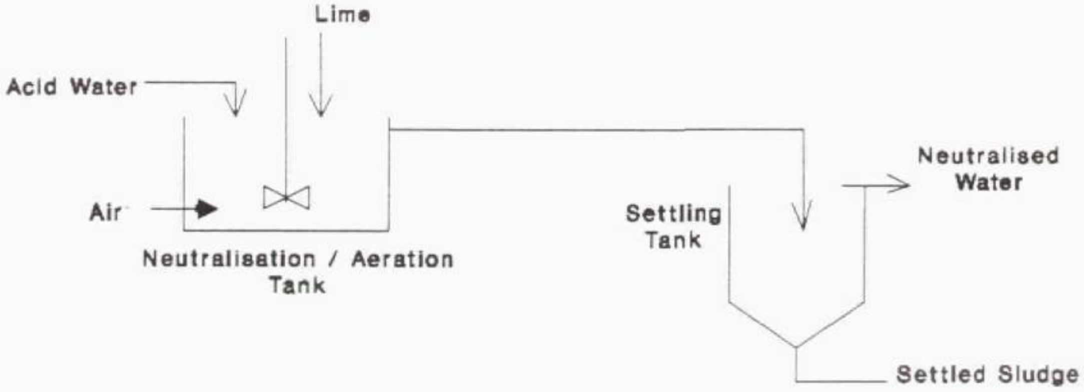

Figure 1. The conventional process for acid water neutralisation.

High Density Sludge (HDS) process

The HDS process (Figure 2) consists of the following stages:

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

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

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

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

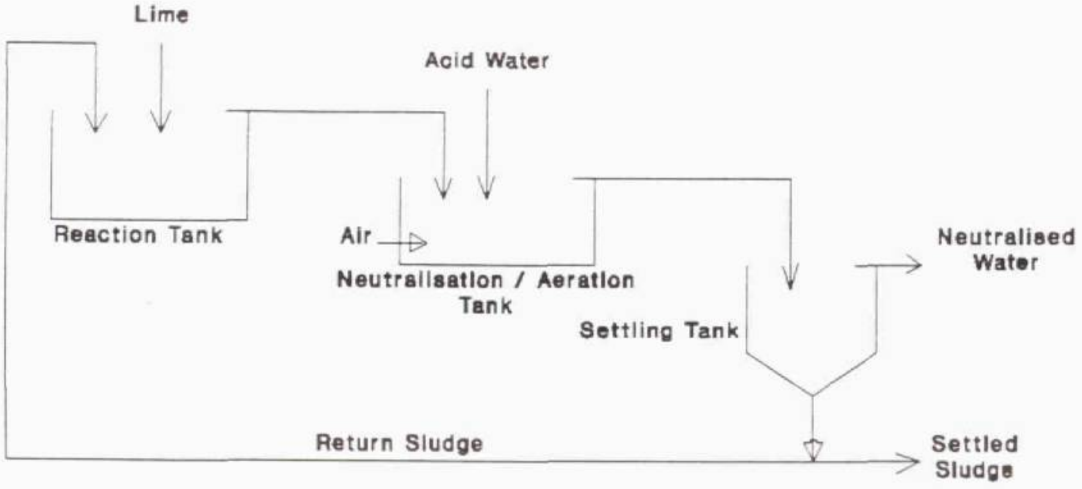

Figure 2. The High Density Sludge process for acid water neutralisation.

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

- A sludge with a density 10 times higher than that of the conventional process is produced. As a result less demanding sludge drying facilities are required. The capital costs associated with the construction of sludge

ponds (including pumping and piping facilities) vary between R1/m^3 and R3/m^3 of sludge handling.
- The sludge settles faster, therefore, a smaller clarifier is required. The saving on the clarifier is approximately 38%.

Limestone neutralisation process

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 the vertical mine water pipelines, resulting in either corrosion as a result of the low pH, or scale formation (gypsum) as a result of the high calcium concentrations. Since large amounts of lime are required, neutralisation of effluents such as the above is a costly operation.

The CSIR has developed, with financial support from the WRC, a fluidised-bed neutralisation process which uses limestone or dolomite as the neutralising agent (Maree and du Plessis, 1993). In case of the fluidised limestone process, this dosing problem is overcome as limestone will only dissolve as long as the water is undersaturated with respect to $CaCO_3$. This usually occurs at a pH below 7.

The benefits associated with neutralisation of acid water with limestone are the following:

- Direct savings on the purchase cost of neutralisation media.
- Simplified process control. No pH-control is required as limestone and dolomite dissolution occurs mainly at pH-values below 7. Since the flow rate of underground mine

water may vary by a factor of 10 (Pulles *et al.*, 1994), lime/soda ash systems can only function well if its dosing rates are adjusted accordingly.

- Minimisation of material wastage which would occur as a result of over-dosage (due to pH-solubility relationship referred to above).
- Elimination of hazardous chemical usage for neutralisation (limestone/dolomite is easy and safe to handle).
- Simple bulk chemical storage facilities (the raw materials are not readily soluble in neutral water).
- Utilisation of equipment at existing lime neutralisation plants is possible.

AIMS OF INVESTIGATION

The development stage of the limestone neutralisation process had been completed, but further development was required to make it suitable for the underground treatment of acid water. The aims of the investigation were to:

1. Obtain design criteria for iron(II) oxidation prior to neutralisation in order to make the process suitable for the neutralisation of iron(II) containing water, such as acid mine drainage and underground mine water.

2. Modify the process in order to make it suitable for the underground neutralisation of acid mine water. The major limitations to any underground process are lack of space and means of transport of raw material. Specific aspects that had to be investigated were the shape of the reactor in order to fit into the space available underground in a mine.

3. Demonstrate that underground mine water can be neutralised with limestone in the fluidised-bed limestone neutralisation process.

4. Determine the economic feasibility of the fluidised-bed limestone neutralisation process for treatment of underground mine water.

The various aims are addressed as follows in the various chapters:

1 - Chapter 2
2 - Chapters 3 and 4
3 - Chapter 4
4 - Chapter 4

CHAPTER 2. LABORATORY STUDIES ON BIOLOGICAL OXIDATION OF IRON(II)

INTRODUCTION

As a result of predominantly reducing conditions underground, mine water often contains more iron(II) than iron(III). In the limestone neutralisation process iron(III) is preferred to iron(II), as the latter may reduce the rate of limestone neutralisation (Maree & du Plessis, 1993). This study included an investigation into the factors that influence the kinetics of iron(II) oxidation.

MATERIALS AND METHODS

Apparatus and experimental

The reactor used for iron(II)-oxidation had a diameter of 440 mm and a height of 620 mm. The feed water was aerated by blowing compressed air through a diffuser. The oxygen concentration in the water was controlled by adjusting the flow rate of the air. A synthetic feedstock was prepared, containing 33,4 g/ℓ $FeSO_4.7H_2O$; 0,31 g/ℓ KH_2PO_4; 0,39 g/ℓ $MgSO_4.7H_2O$ and 0,39 mg/ℓ $(NH_4)_2SO_4$ in tap water. The reactor was inoculated by adding acid mine water rich in iron-oxidising bacteria. The study was conducted in batch mode by following the steps below:

- Each new batch experiment was made-up by mixing 500 mℓ treated water from the previous batch experiment with 500 mℓ iron(II)-rich water, or in the ratio as specified.
- The reactor contents was aerated continuously. Filtered samples were taken regularly and analyzed for iron(II), acidity and pH.
- Aeration was stopped when the iron(II) was completely oxidised to iron(III), whereafter 50% of the iron(III)

solution was replaced with a fresh iron(II) solution.

- Aeration was restarted, followed by the rest of the procedure described above.

All the experiments were carried out under the following conditions, unless indicated differently:

- a temperature of 25 ^{0}C.
- a dissolved oxygen concentration of 8 mg/ℓ.
- reactor depth of 620 mm. Aeration was applied using compressed air.

Analytical

Manual determinations of sulphate, sulphide, alkalinity, calcium and pH were carried out according to analytical procedures as described in Standard Methods (APHA, 1985). With the exception of sulphide, all the analyses were carried out on filtered samples. Acidity was measured by titrating 5mℓ of the feed and treated solutions with 0,1 N NaOH to a pH of 8,3.

RESULTS AND DISCUSSION

Kinetics of biological iron(II) oxidation

The iron(II) is oxidised to iron(III) in the presence of acidophilic iron-oxidising bacteria, such as *Ferrobacillus ferrooxidans*, and precipitated as $Fe(OH)_3$ at pH values greater than 3:

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

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

The rate of iron(II) oxidation is influenced by factors such as iron(II) concentration (Figure 3), oxygen concentration (Figure 4), reactor depth (Figure 5), bacterial concentration

(Figure 6), and temperature (Figure 7).

Iron(II) concentration. Figure 3 shows that oxidation rate increases as the iron(II) concentration increases from 3,1 to 15,5 g/ℓ. The volumetric rate of iron(II) oxidation rate was 5,5 g Fe/(ℓ.d) at an iron concentration of 5 g/ℓ Fe.

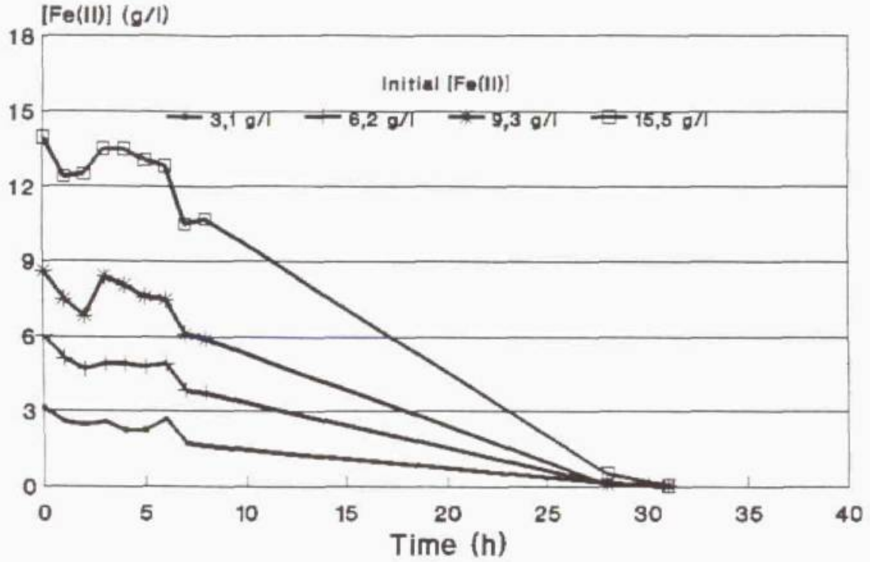

Figure 3. Oxidation rate of iron(II) as a function of iron(II) concentration.

Oxygen concentration. Figure 4 shows that 0,3 mg/ℓ of oxygen is required for optimum iron(II) oxidation. The oxidation rate does not increase significantly with higher oxygen concentrations. This finding is probably due to a low bacterial concentration which limits the rate of oxidation. Figure 5 shows the rate of iron(II) oxidation without aeration at different water depths in the reactor. The oxidation rate decreased with increased depth, which is expected as the only possible oxygen ingress was that introduced through diffusion at the surface of the water.

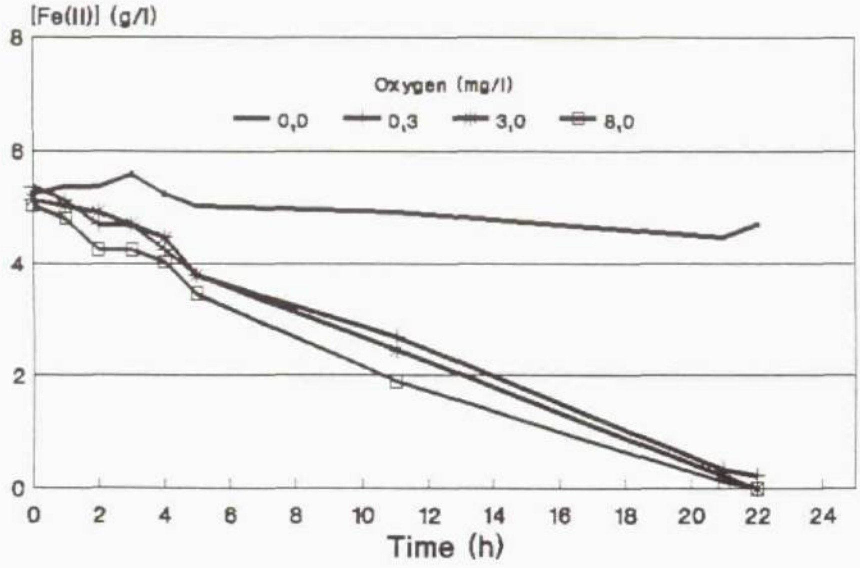

Figure 4. Effect of oxygen concentration on the rate of iron(II) oxidation.

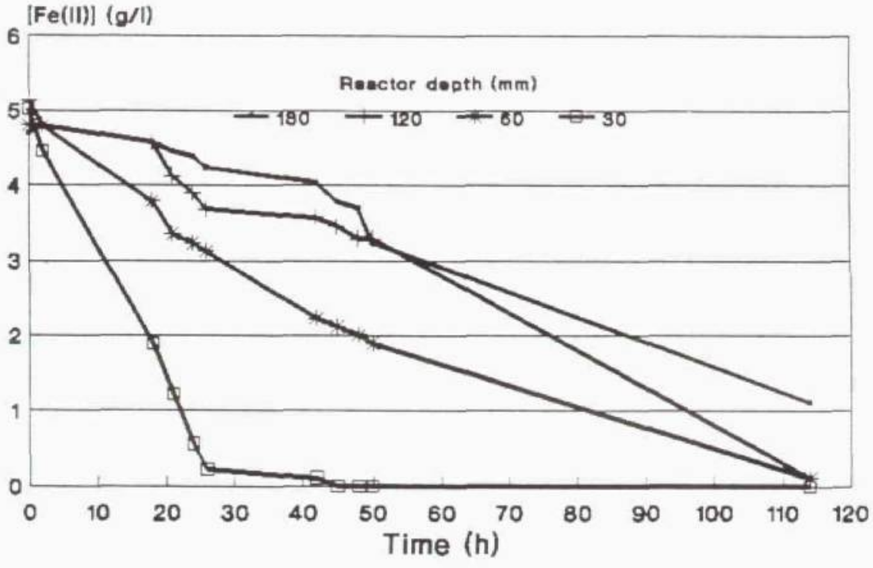

Figure 5. Effect of reactor depth on the rate of iron(II) oxidation.

Bacterial concentration. Oxidation of iron(II) with air under acidic conditions is approximately 1000 times faster when catalised by iron oxidation bacteria. Figure 6 shows that the iron(II) oxidation rate is related to the bacterial concentration. As oxygen was not limiting in the system (Figure 4), it is assumed that the bacterial concentration limits the oxidation rate. Emphasis should therefore be placed on increasing the bacterial concentration. Umita *et al.* (1988) showed that it is possible to increase the rate to 30 g Fe/(ℓ.d), by using granular activated carbon in a fluidised-bed reactor as a support medium for the iron oxidising bacteria.

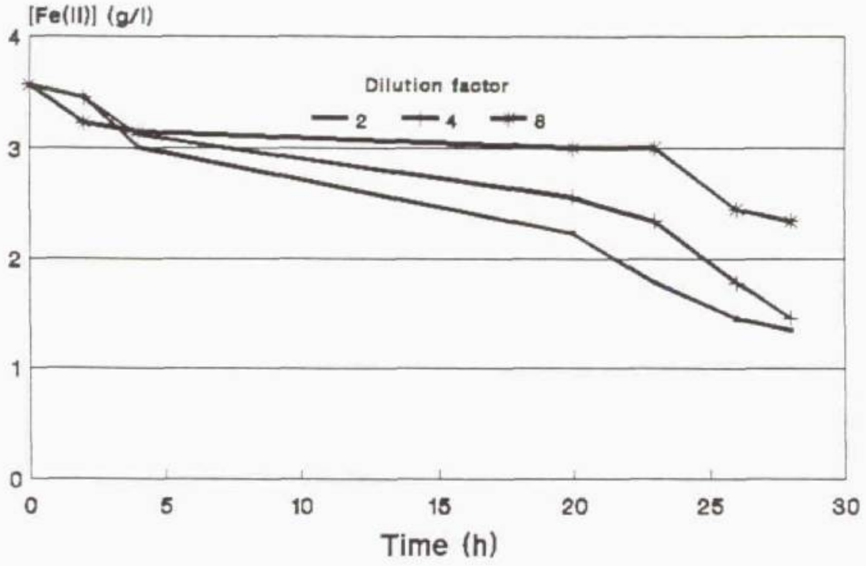

Figure 6. Effect of bacterial concentration on the rate of iron(II) oxidation.

Temperature. Figure 7 shows the effect of temperature on the rate of iron(II) oxidation. The activation energy (E) for biological iron(II)-oxidation is calculated from Figure 8 and the Arrhenius equation as 10,5 kcal/mole.

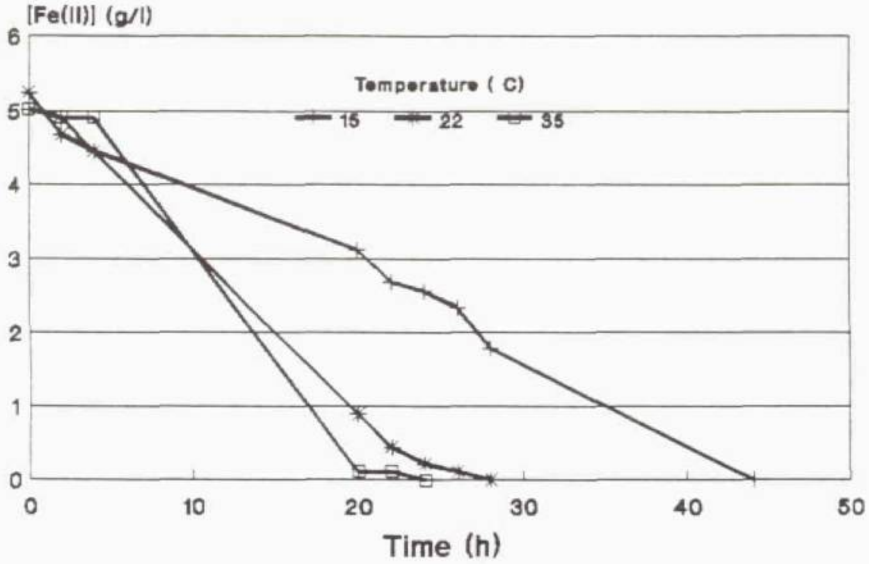

Figure 7. Effect of temperature on the rate of iron(II) oxidation.

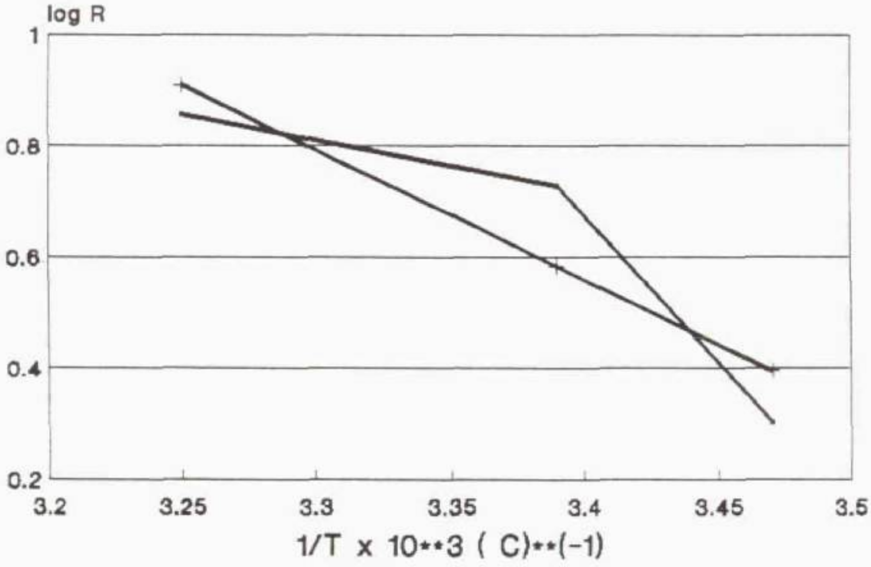

Figure 8. Calculation of activation energy for biological iron(II)-oxidation.

General

The required retention time of 22 h for iron(II) oxidation (Figure 4) might be too long for application underground due to limited available space. For waters with high iron(II) concentrations (greater than 200 mg/ℓ Fe), it is recommended that iron(II) oxidation not be applied underground, but on surface. This is still acceptable from a practical point of view. By neutralising only the free acid and acid associated with iron(III) underground with limestone under anoxic conditions, and not the iron(II), the pH of the water could be raised to above 5,5, where the corrosivity of the water is significantly less. The underground mine water that was tested and discussed in Chapter 4 contains only 5 to 20 mg/ℓ Fe(II), and no pretreatment for iron(II) oxidation is required in that case.

CONCLUSIONS

1. Iron(II) can be oxidised to iron(III) biologically. The volumetric reaction rate is 5,5 g Fe/(ℓ.d) at an iron concentration of 5 g/ℓ Fe, a dissolved oxygen concentration of 8 mg/ℓ, and a temperature of 25 ^{0}C.

2. A retention time of 22 h is required for oxidation of water containing 5 g/ℓ iron(II).

CHAPTER 3. LABORATORY STUDIES TO DETERMINE REACTOR CONFIGURATION

INTRODUCTION

A requirement for underground neutralisation of acid water with limestone is that equipment should fit into the available space, which is limited at best. A compact reactor and high reaction rates are therefore required. The cone-shaped fluidised bed reactor has been used in the past (Maree & du Plessis, 1993). The following problem associated with this design was, however, identified. Good fluidisation of limestone occurs in the middle of the reactor but not along the side. With high concentrations of acid (20 g/ℓ), scaling of limestone particles was observed after some time of continuous operation.

The purpose of this investigation was to overcome that problem by using a column-shaped fluidised bed reactor, with water recycled through a clarifier to minimise washout of limestone particles. Waste sludge accumulates to an equilibrium level in the clarifier and is then washed out together with the neutralised water.

The efficiency of acid water neutralisation and limestone utilised were used as the success criteria of the evaluation.

MATERIALS AND METHODS

Feed water

Artificial acid water, prepared from sulphuric and nitric acid, was used as feed to the limestone plant. The feed water contained, among other compounds/elements, 13 500 mg/ℓ sulphate (as SO_4) and 4 650 mg/ℓ nitrate (as N), with a total acidity value of 18 370 mg/ℓ (as $CaCO_3$).

Limestone

The following limestones were used in the investigation: Tvl and

Cape. Cape limestone had a particle size less than 1,5 mm, while that of Tvl less than 4 mm.

Pilot-plant

The pilot-plant consisted of a fluidised bed reactor and a recycle pump (Figure 9). Table 5 shows the values of various design parameters for the system for a feed rate of 0,8 ℓ/min, a recirculation rate of 45 ℓ/min and 20 kg of limestone in the reactor. The recirculation rate was set to fluidise the limestone. A diaphragm pump was used to feed acid water from a 10 kl stainless steel tank to the fluidised bed reactor.

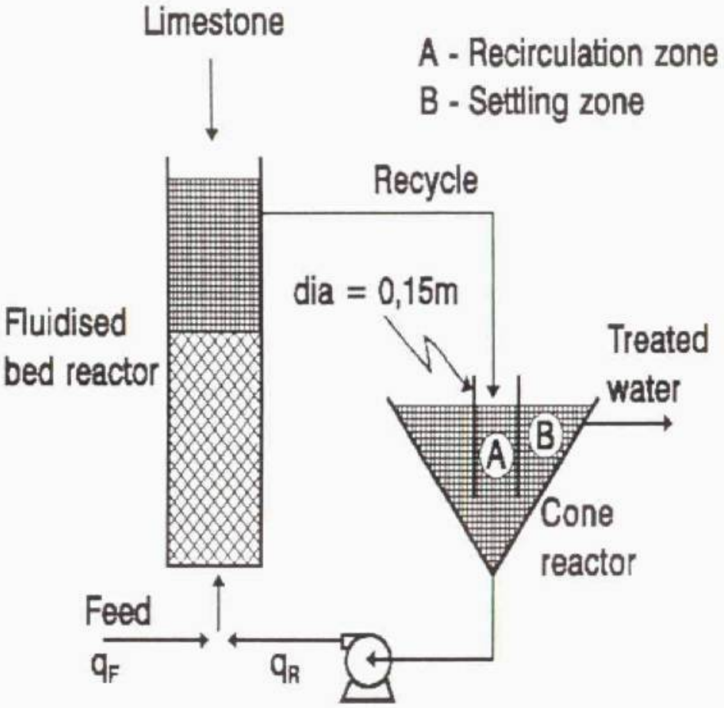

Figure 9. Schematic diagram of limestone neutralisation plant.

Residual limestone

In the design of a limestone neutralisation plant, it is necessary to track the behaviour of impurities. Impurities washed out with the effluent can be separated by means of sedimentation downstream of the fluidised bed reactor. Impurities accumulating in the reactor need to be drawn off at certain time intervals to make space for fresh limestone. The $CaCO_3$-content of the limestone in the fluidised bed was determined by drawing limestone samples daily at the bottom of the fluidised bed reactor, 500 mm above the bottom, and from the recycle stream (withdrawal point 1 540 mm above the bottom).

Limestone feed system

Limestone was fed either manually or by means of screw feeder/hopper. A load cell was used to activate and stop the feeder at the set minimum and maximum mass levels in the load cell. A mass of 20 to 22 kg of limestone was kept in the fluidised bed reactor. The amount of limestone present in the fluidised bed reactor at any time was given by the following equation (derived in Chapter 4 under Limestone feed system):

Mass of limestone in reactor (kg) = $(W_t - W_w)/0,65$

where: W_t = mass of (water + limestone)

W_w = mass of water.

Table 5. Design and typical operational parameters for the pilot-plant.

Parameter	**Cone reactor**			**Fluidised bed reactor**
Height from bottom (H) (m)	0,16	0,25	0,50	1,41
Position in cone	bottom	middle	top	
Feed rate (q_F) (ℓ/min)	0,80	0,80	0,80	0,80
Recycle rate (q_R) (ℓ/min)	56	56	56	56
Diameter (D) (m)	0,16	0,25	0,50	0,19
Empty volume (V) (ℓ)	1,07*1	4,09*1	32,72*1	40,01*2
$Area_{Total}$ (m^2)	0,02	0,05	0,20	0,03
$Area_{Sett\ zone}$ (m^2)	0,002	0,03	0,18	0,00
$Area_{Rec\ zone}$ (m^2)	0,02	0,02	0,02	0,03
Hydraulic ret. time (HRT) (min)	1,10	5,11	40,91	50,01
Upflow velocity ($v_{up,\ Sett\ zone} = q_F/A_{Sett\ zone}$) (m/h)	19,71	1,53	0,27	
Upflow velocity ($v_{up,\ Rec\ zone} = q_F/A_{Rec\ zone}$) (m/h)	192,9	192,9	192,9	120,2
Limestone (W_s) (kg)	0			20
Contact time*3 (CT) (min)	0			25

Notes:

*1 Volume of cone (ℓ) = $\frac{1}{3} \times \pi \times (D/2)^2 \times H \times 1000$

*2 Volume of Fluidised bed reactor (ℓ) = $\pi \times (D/2)^2 \times H \times 1000$

*3 At an assumed limestone concentration of 1 kg/ℓ in the fluidised bed reactor, the contact time between acid water and limestone is calculated as follows:

Contact time (min)
= Volume of limestone (ℓ) ÷ feed rate (ℓ/min)
= (Mass of limestone (kg) / Limestone concentration (kg/ℓ)) ÷ feed rate (ℓ/min)
= (Mass of limestone (kg) / 1 (kg/ℓ)) ÷ feed rate (ℓ/min)

Analytical

Samples were collected and filtered (Whatman No 1) automatically during continuous and batch studies. In the case of batch studies, samples were taken regularly and analyzed for pH, calcium, magnesium, and acidity (APHA, 1985). Alkalinity was determined by titration with sodium hydroxide to pH 7,0. CO_2-gas was allowed to escape from solution prior to pH, acidity and alkalinity analyses were carried out.

The $CaCO_3$ content of the fresh and residual limestone was determined by dissolving 2,5 g of dried material in 100 mℓ of 1 N HCl and titrating 5 mℓ of the filtered solution to pH 7,0 with 0,1 N NaOH.

RESULTS

Chemical composition

Table 6 shows results on the neutralisation of synthetic acid water. The following observations can be made from these results:

- The water was successfully neutralised as indicated by the increase in pH from 1,1 to 7,0
- The sulphate content was reduced by 91 % due to gypsum crystallisation. The figures in Table 6, which are expressed in mg/ℓ $CaCO_3$, suggest that 22 g/ℓ gypsum (as $CaSO_4.2H_2O$) crystallised from solution.
- Calcium and magnesium content increased due to the presence of these compounds in the limestone used.

Table 6. Chemical composition of untreated and treated synthetic solutions.

Determinand	**Concentration**	
	Untreated	Treated
pH	1,1	7,0
Acidity (mg/ℓ $CaCO_3$)	18 370	30
Sulphate (mg/ℓ SO_4)	13 500	1 200
Nitrate (mg/ℓ N)	4 650	4 645
Calcium (mg/ℓ $CaCO_3$)	30	4 910
Magnesium (mg/ℓ $CaCO_3$)	22	702

Figure 10.a to 10.e shows the behaviour of various parameters during continuous treatment of synthetic solutions. During the 220 h of continuous operation, the amount of limestone and impurities was kept constant at 20 kg. At a feed rate of 0,75 ℓ/min, the contact time between the acid water and the limestone is calculated to be 27 min. This calculation was based on the assumption that 1 kg of limestone occupies 1 ℓ during fluidisation. No residual limestone (impurities) was removed in order to determine its effect on the efficiency of neutralisation. The following observations can be made from Figures 10.a to 10.e:

- Figure 10.a shows that the pH of the acid water was raised from 1,1 to more than 5,0 during the first 54 h of the experiment, to above 6,5 from 54 h to 178 h, and to below 3,0 between 178 h and 222 h. Cape limestone was used during the first 54 h, and Tvl limestone during the rest of the time. The higher pH achieved with Tvl limestone can be ascribed to its higher surface area. A longer contact time is therefore required with Cape limestone to produce the same pH. The drop in the pH after 178 h is due the bed filling up completely with impurities from the limestone.

- Figure 10.b shows that acidity was removed from 18,4 to almost 0 g/ℓ (as $CaCO_3$), except for the period after 178 h when the limestone was completely exhausted.

- Figure 10.c shows that sulphate was reduced from 13,3 g/ℓ to approximately 1,3 g/ℓ (as SO_4). This is due to gypsum crystallisation according to the reaction:

  $$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4.2H_2O. \qquad (4)$$

  It is calculated that 21,5 g/ℓ of gypsum was produced. The produced gypsum was discharged together with the effluent as it remained in suspension. Under full-scale conditions the gypsum will be separated from the water in a settler downstream of the fluidised bed reactor.

- Figure 10.d shows that the calcium content increased from 0,1 to 4,5 g/ℓ (as $CaCO_3$).

- Figure 10.e shows that all the acid fed with time was neutralised, and that, stoichiometrically, an equivalent amount of limestone was consumed.

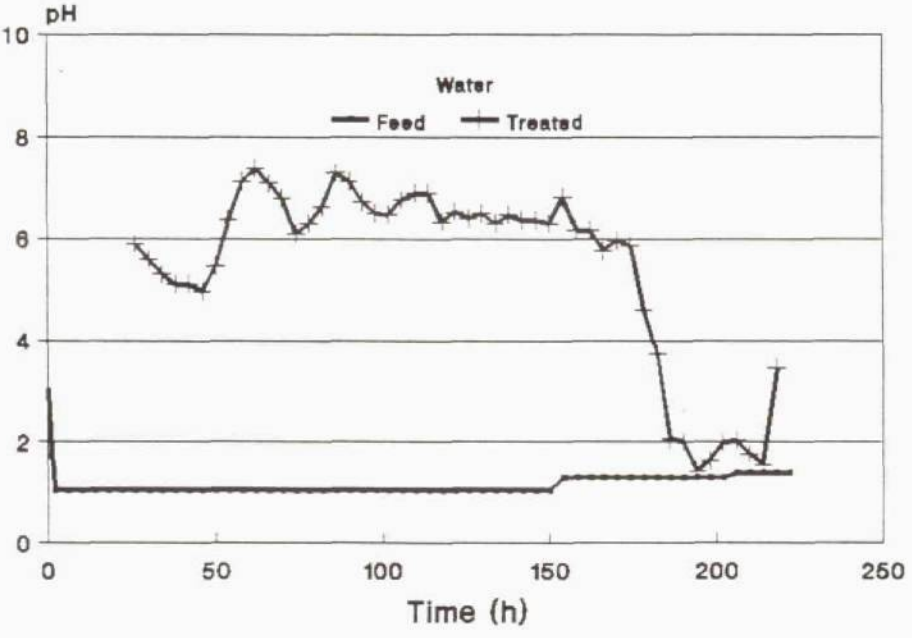

Figure 10.a Variation of pH during limestone neutralisation.

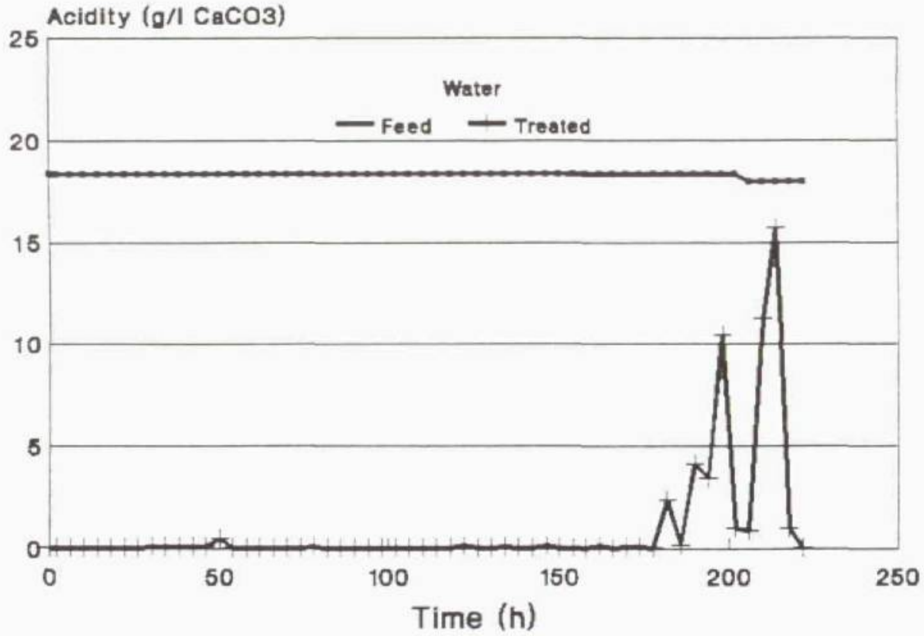

Figure 10.b   Acidity levels during limestone neutralisation.

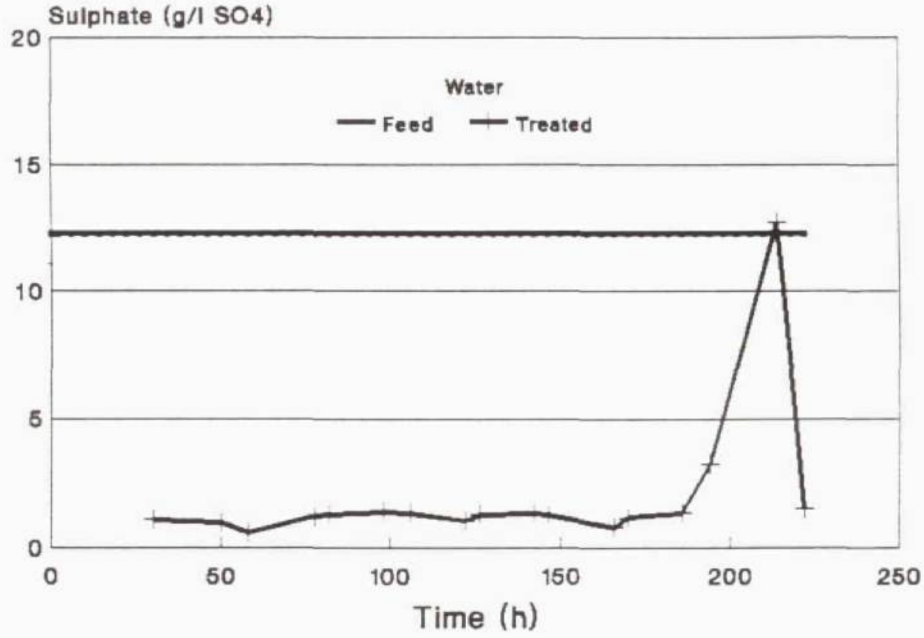

Figure 10.c   Variation of sulphate during limestone neutralisation.

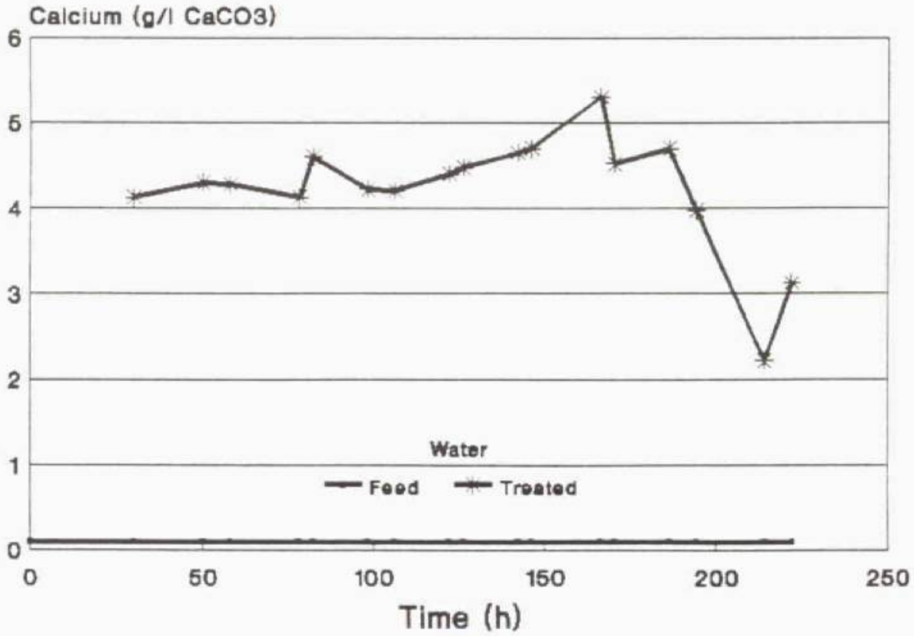

Figure 10.d Variation of calcium during limestone neutralisation.

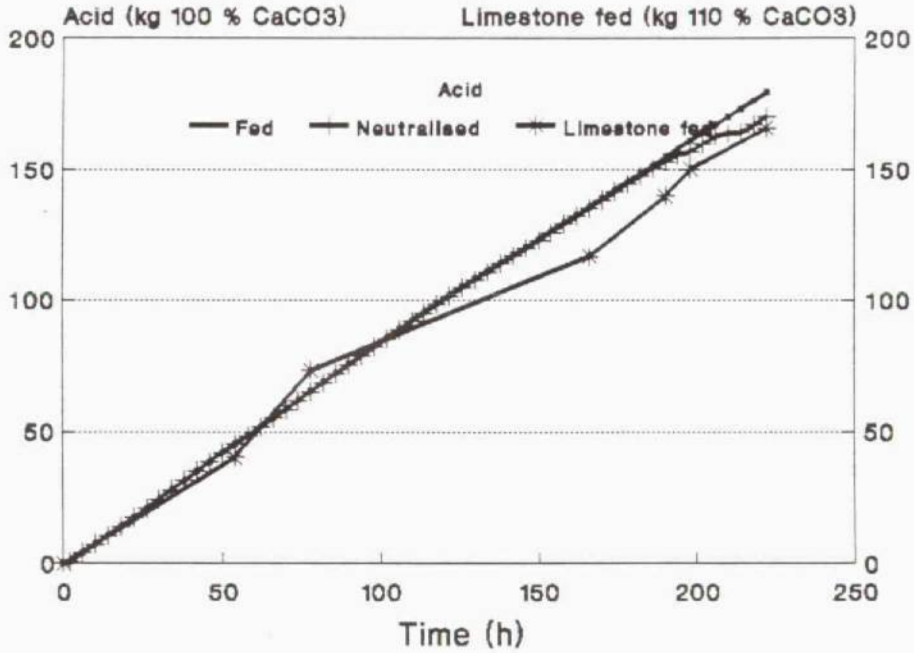

Figure 10.e Efficiency of acid removal and limestone utilisation.

Impurities in limestone

Both limestones types used in this experiment (Cape and Tvl) contain about 20 % non-carbonate materials. The effect of the impurities in the limestone on the performance of the fluidised bed reactor was studied by determining the $CaCO_3$ content of the limestone and in the residual limestone on a daily basis at different heights in the reactor. Figure 11 shows the change in the $CaCO_3$ content in the residual limestone at different heights with time. It is noticed that $CaCO_3$-content is first exhausted in the top of the reactor where the finer particles are, followed by the middle and the bottom. The $CaCO_3$-fraction in the sample collected from the top was less than 2 % after only 50 h of operation, compared to 70 h in the case of samples collected from the middle of the reactor. At the bottom of the reactor, the $CaCO_3$ was exhausted only after 200 h, at the time when neutralisation had stopped. The reason for limestone being exhausted first at the top of the reactor can be explained as follows:

* Limestone particles change from coarse to fine along the height of the bed. Fine particles have a greater surface area than course particles and reacts faster with acid water. The coarse limestone left is less efficient due to its lower reaction rate and accumulate in the bottom part of the reactor.

* Sludge (gypsum) and impurities in the limestone are finely divided and accumulate from top to bottom in the reactor, leaving less space for limestone. In order to maintain the efficiency of the process at a certain level, it is necessary to withdraw impurities on a regular basis.

This exercise showed that continuous neutralisation can be ensured by withdrawing a portion of the residual limestone in the upper part of the reactor at regular intervals. The withdrawal can be activated by monitoring the $CaCO_3$-content in the bed at different heights on a daily basis.

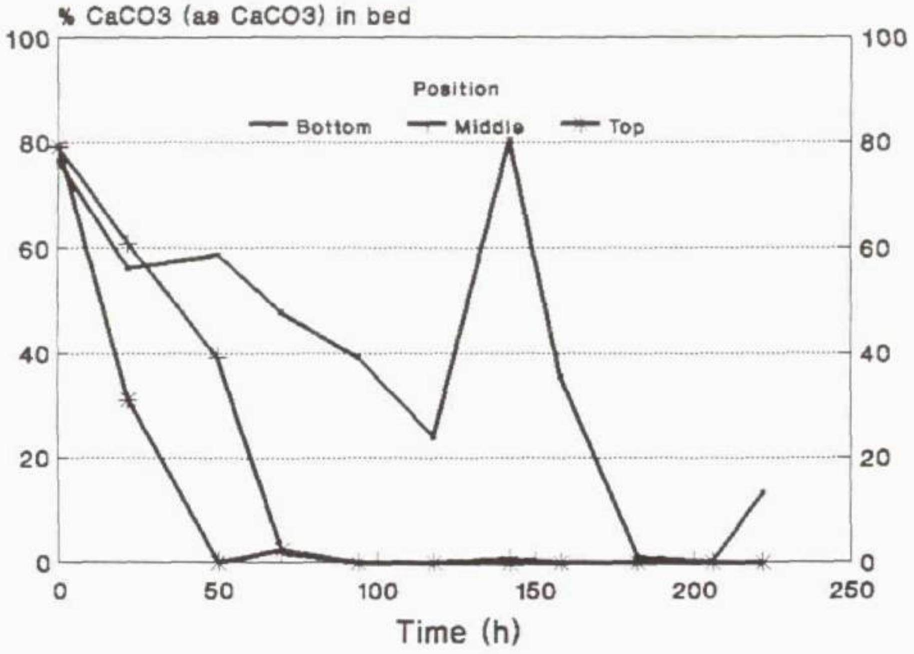

Figure 11. $CaCO_3$-content of limestone in the fluidised bed reactor.

CONCLUSIONS

1. The chemical composition of the synthetic feedstock can be changed as follows by treating it with the limestone neutralisation process:

- The pH can be increased from 1,1 to 7,0.
- The acidity can be reduced from 18,4 to almost 0 g/ℓ (as $CaCO_3$).
- Sulphate can be reduced from 13,5 to 1,2 g/ℓ.
- The calcium content in the water will increase until the water is saturated with gypsum.

2. All the acid fed is neutralised, and stoichiometrically, the equivalent amount of limestone is consumed.

3. The $CaCO_3$-content in the fluidised bed reactor is first consumed at the top, where the finer particles are, followed by the middle, and lastly at the bottom, where the coarser particles are. Impurities accumulate from top to bottom in the reactor, resulting in less available space for limestone, and consequently less effective neutralisation of acid water. Continuous neutralisation can be ensured by withdrawing a portion of the residual limestone (mainly impurities) in the upper part of the reactor at regular intervals.

CHAPTER 4. PILOT SCALE NEUTRALISATION OF UNDERGROUND MINE WATER

INTRODUCTION

The purpose of the pilot scale investigation was to demonstrate that underground mine water can be neutralised with limestone in the fluidised bed limestone neutralisation process. Specific aspects to be studied were to determine:

- The contact time required between the limestone and the acid water.
- Chemical composition of water before and after treatment.
- Economic feasibility of the fluidised bed neutralisation process.

MATERIALS AND METHODS

Feed water and limestone

The pilot-plants were positioned at level 50 (1,3 km below the surface) North Shaft of the Western Areas Gold Mining Company. Acid water from the gold mining operations was treated. The mine discharges 70 Mℓ/d to the surface to keep it away from the mining operations. The underground water originates from rain which seeps into dolomite compartments in the first 200 to 300 m below the soil surface, and also from dust suppression activities at the mining face. The study was carried out underground to demonstrate that the fluidised bed process can be operated under typical operating conditions in areas where limited space is available, and that no sophisticated dosing equipment is required. Limestone obtained from various sources was used in the investigation (Table 7).

Table 7. Characteristics of limestone used during the pilot-plant study

Limestone	**Purity (% as $CaCO_3$)**	**Particle size range (mm)**	**Bulk density kg/ℓ**	**Void %**
Tvl A	83	2-5	1,24	57,5
Tvl B	90	2-5	1,40	51,0
Tvl C	85	2-5	1,21	57,5
Cape A	97	0,1-4	1,43	49,8

Void (%) = (Density - Bulk density)/Density x 100

Pilot-plants

Mine water was treated underground in a laboratory-scale plant (capacity of 0,09 to 0,6 kℓ/h) from 13 to 27 May 1994 and in a pilot-plant (capacity of 1 to 10 kℓ/h) from 10 January to 18 February 1995. The pilot-plant (Figure 12) consisted of a fluidised bed reactor, a recirculation clarifier, a limestone silo and a recycle pump (Envirotech pump). The purpose of the recirculation clarifier was to allow fine limestone particles washed out from the fluidised bed reactor to settle and return to the fluidised bed reactor via the recycle pump. A settler for removal of solids from the neutralised water is downstream of the system shown in Figure 12. Table 8 shows the values of various parameters for the system. After startup, the feed rate was gradually increased from 1,0 to 7,2 kℓ/h. The recycle flow rate was 35 kℓ/h. Between 100 and 180 kg of limestone was present in the reactor at any time. The recirculation rate was set to fluidise the limestone. A compressed air pump was used to feed acid water to the plant.

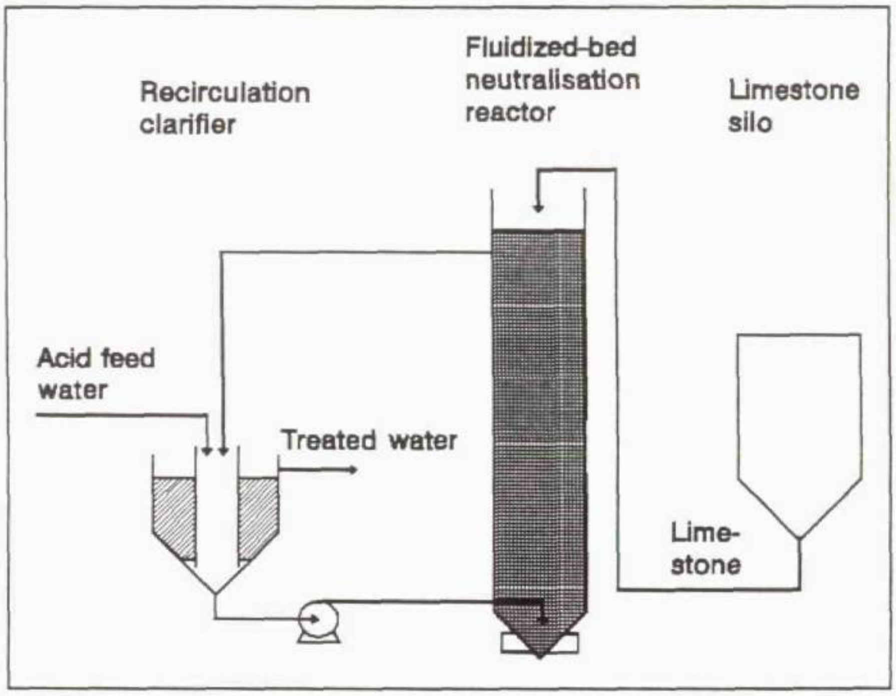

Figure 12. Schematic diagram of the limestone neutralisation plant.

Table 8. Design and typical operational parameters for the pilot-plant

Parameter	Fluidised bed reactor	Recirculation clarifier
Feed rate (kℓ/h)	3	3
Recycle rate (kℓ/h)	35	35
Diameter (mm)	355	-
Area (m^2)	0,099	0,98
Height (m)	4,0	0,8
Empty volume (kℓ)	0,396	0,864
Upflow velocity (m/h)	354	3
Limestone (kg)	140	-
Contact time (min)	2,8	-
Actual contact time (min)	1,8	-

The hydraulic retention time, contact time and actual contact time was calculated as follows:

$$\begin{aligned}
\mathrm{CT} &= \text{Bed volume}/Q \\
&= A.h_B/Q \\
\mathrm{ACT} &= \text{Bed interstitial volume}/Q \\
&= (A.h_B - V_s)/Q \\
&= (A.h_B - m_s/\rho_s)/Q \\
&= (A.h_B/Q).(1 - m_s/(\rho_s.A.h_B)) \\
&= \mathrm{CT}.(1 - m_s/(\rho_s.A.h_B)) \\
\mathrm{HRT} &= A.h_T/Q
\end{aligned}$$

where:

ρ_s = solid density (2,85 kg/ℓ)
ρ_b = bulk density
CT = contact time between limestone and water
ACT = actual contact time between limestone and water
C_s = limestone concentration in the bed of the reactor
A = bed cross-sectional area
h_B = height of limestone bed in fluidised bed reactor during fluidisation
V_s = volume of solids
Q = flowrate
m_s = mass of solids
ρ_s = density of solids
HRT = hydraulic retention time
h_T = height of fluidised bed reactor.

For a limestone concentration of 1 g/ℓ in the bed of the reactor,

$$\begin{aligned}
C_s &= m_s/(A.h_B) \\
&= 1\ \text{kg}/\ell\text{, during fluidisation,} \\
\mathrm{ACT} &= 0{,}65 \times \mathrm{CT}
\end{aligned}$$

Limestone feed system

Limestone was stored in a 75 ℓ silo with a cone shaped bottom. The feedrate of the limestone was controlled with a commercial vibrator. A load cell was used to activate and stop the feeder. The mass of limestone in the fluidised bed reactor was allowed to fluctuate over a range of 20 kg. The amount of limestone present in the fluidised bed reactor at any time was calculated by the following equations:

$$\text{Mass of limestone in reactor (kg)} = (M_t - M_{ow})/0{,}65 \qquad (2)$$

The equation was derived as follows for the situation when X ℓ of water (w) is replaced by X ℓ limestone (s):

$$\begin{aligned}
M_t &= M_w + M_s \\
&= (V-X).\rho_w + X.\rho_s \\
&= V.\rho_w - X.\rho_w + X.\rho_s \\
X &= (M_t - V.\rho_w)/(\rho_s - \rho_w) \\
M_s &= \rho_s.X \\
&= \rho_s.(M_t - V.\rho_w)/(\rho_s - \rho_w) \\
&= (M_t - V.\rho_w)/(1 - \rho_w/\rho_s) \\
&= (M_t - M_{ow})/(1 - \rho_w/\rho_s)
\end{aligned}$$

where: M_t = mass of water and limestone

M_w = mass of water in reactor when limestone is present

M_{ow} = mass of water in reactor when no limestone is present

M_s = mass of limestone

V = empty volume of reactor

X = volume of water replaced by limestone

ρ_s = density of limestone

ρ_w = density of water

If $\rho_s = 2{,}85\ g/\ell$ and $\rho_w = 1{,}0\ g/\ell$

then $M_s = (M_t - M_{ow})/0{,}65$

Continuous studies

Acid water was pumped through the fluidised bed reactor continuously to investigate the following aspects:

- Chemical composition of feed and treated water.
- Effect of contact time on the efficiency of neutralisation.

Batch studies

Batch studies were carried out in beakers to determine:

- The effect of limestone concentration.
- Rate of neutralization with different limestones.

The variation in pH was monitored after a specific amount of limestone was added to 1 ℓ of stirred mine water.

Analytical

The same procedure was followed as described in Chapter 3.

RESULTS

Table 9 shows the composition of the water before and after limestone neutralisation in the pilot-plant, while Figures 13 to 17 show the temporal behaviour of various parameters during continuous treatment. Figure 18 shows the effect of different limestones on the rate of neutralisation.

Table 9. Chemical composition of feed and treated water during pilot-plant study

Parameter	**Chemical composition**		**Removal (%)**
	Feed	**Treated**	
pH	2,8	7,8	
Acidity (mg/ℓ $CaCO_3$)	300 - 400	12	97
Alkalinity (mg/ℓ $CaCO_3$)	negative	120	
Sulphate (mg/ℓ SO_4)	500 - 800	500 - 800	0
Calcium (mg/ℓ Ca)	100	175	
Iron (mg/ℓ Fe)	5 - 20	< 1	95
Uranium (μg/ℓ U)	1 100	190	83

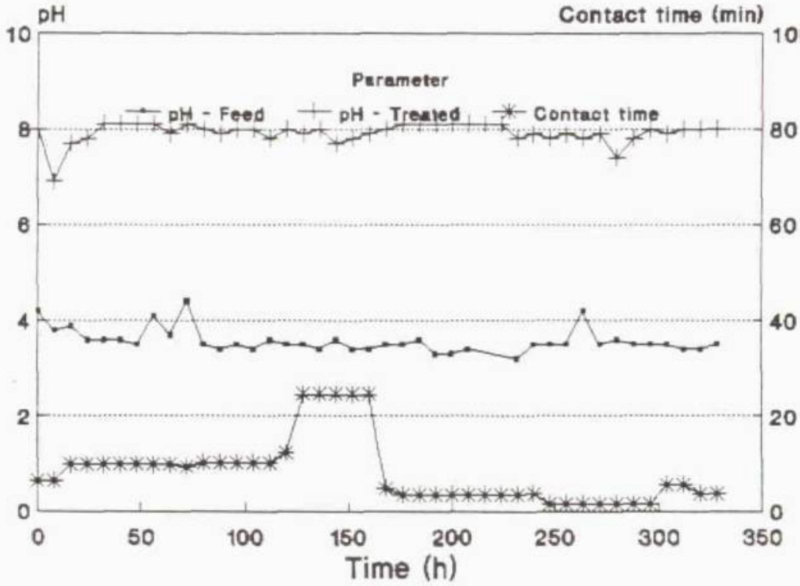

Figure 13.a pH-levels when acid water is neutralised with limestone during laboratory-scale studies.

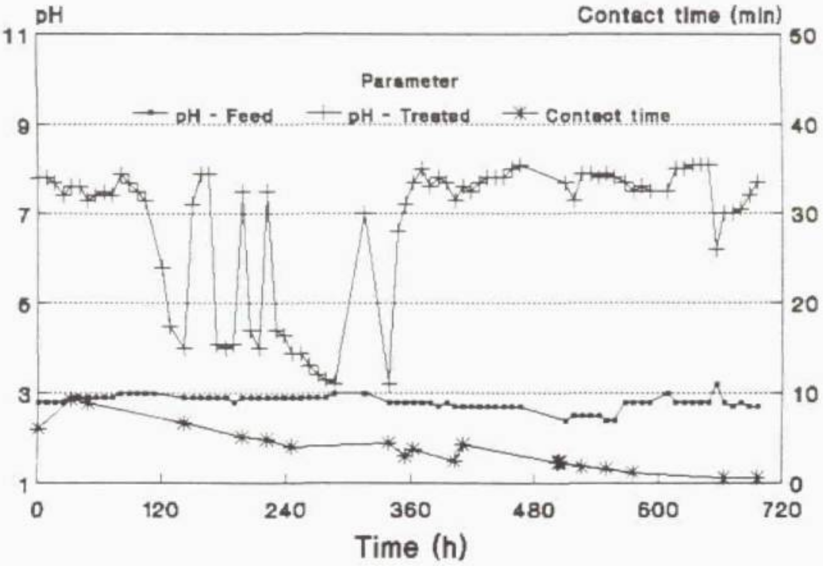

Figure 13.b pH-levels when acid water is neutralised with limestone during pilot plant studies.

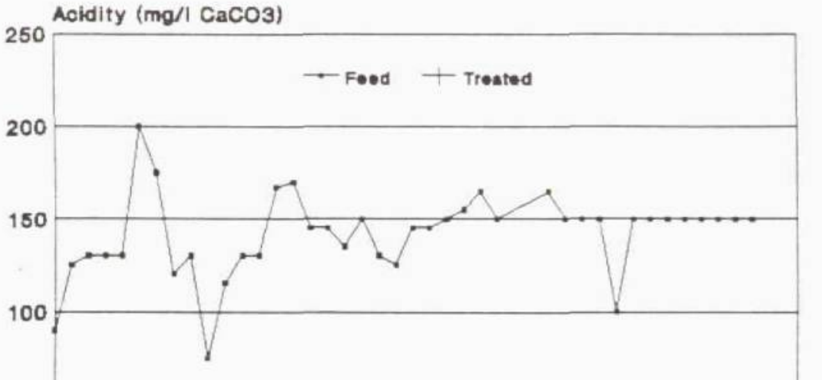

Figure 14.a Acidity removal when acid water is neutralised with limestone during laboratory-scale studies.

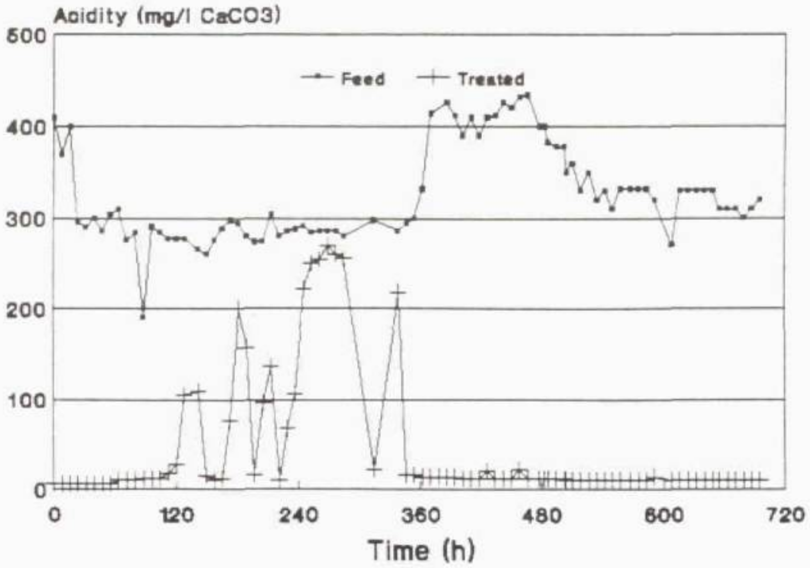

Figure 14.b Acidity removal when acid water is neutralised with limestone during pilot-plant studies.

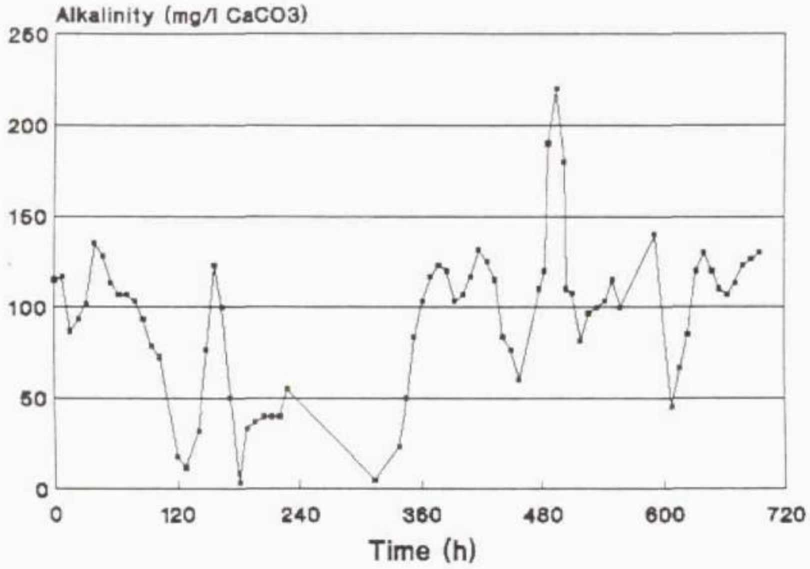

Figure 15. Alkalinity production when acid water is neutralised with limestone in the pilot-plant.

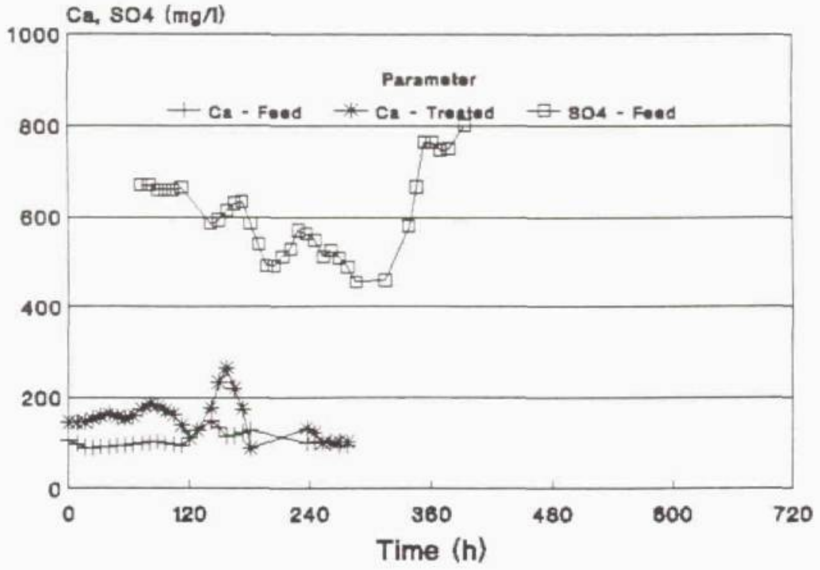

Figure 16. Calcium and sulphate concentrations when acid water is neutralised with limestone in the pilot-plant.

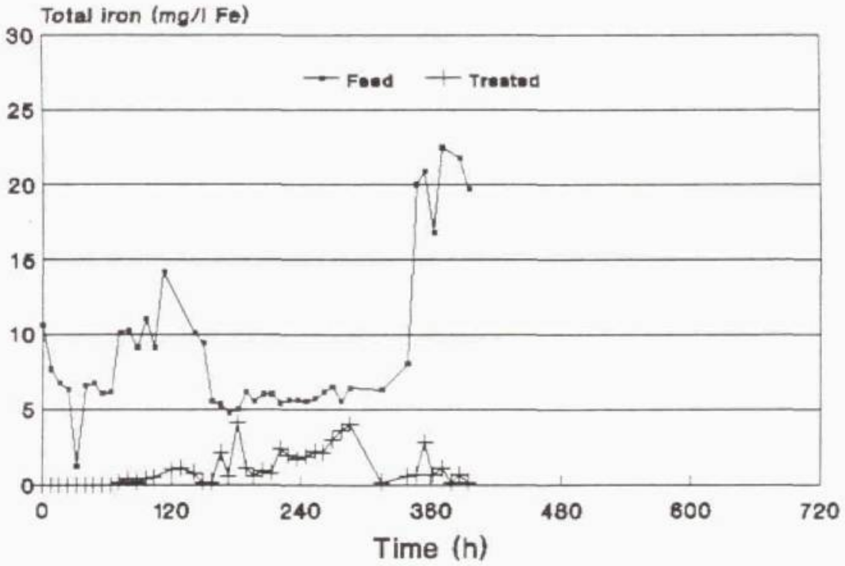

Figure 17. Iron concentrations when acid water is neutralised with limestone in the pilot-plant.

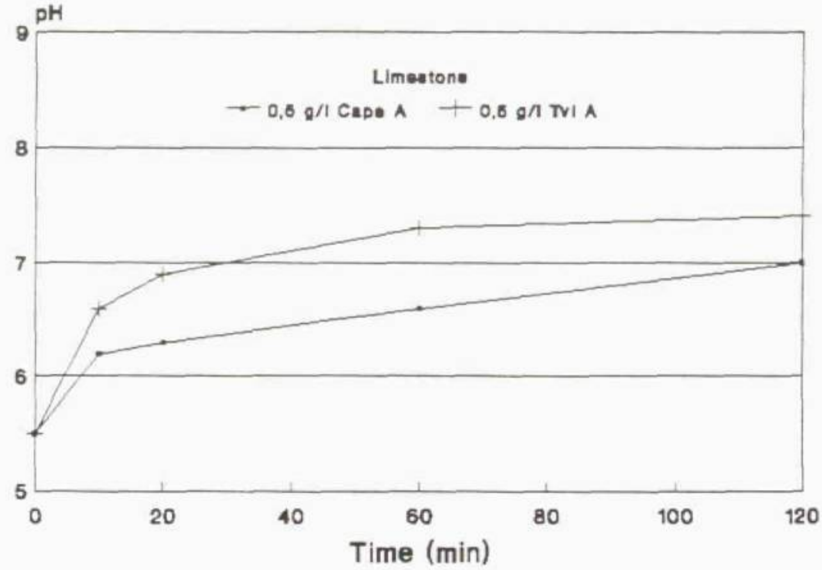

Figure 18. Effect of different limestone types on the rate of neutralisation.

DISCUSSION

General performance

From the pH and acidity values (Figures 13.a, 13.b 14.a and 14.b) it is noted that, with the exception of 5 occasions during the first 360 h of operation of the pilot-plant, an effluent with consistently acceptable pH and low acidity was produced. The exceptions were due to failure of the recycle pump. The speed of the recycle pump was controlled by an electronic speed control. During power fluctuations, however, the speed control cut out and had to be started manually. This problem was subsequently corrected by overriding the electronic speed control unit.

Chemical composition of feed water

During the study, the sulphate content in feed water varied between 500 and 800 mg/ℓ, acidity between 300 and 400 mg/ℓ (as

$CaCO_3$), iron between 5 and 20 mg/ℓ, and pH between 2,7 and 3,0. The acid water is formed largely through bacterial oxidation of pyrites when exposed to oxygen and water. The oxidation reaction can be represented as follows (Barnes, 1968):

$$2FeS_2 + 7{,}5O_2 + H_2O \rightarrow Fe_2(SO_4)_3 + H_2SO_4 \qquad (5)$$

Chemical composition of treated water

Table 9 and Figures 13 to 17 show the composition of the water before and after limestone neutralisation. The pH increased on average from 2,8 to 7,8 and acidity decreased by 97 % due to the following reaction:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \qquad (6)$$

The pH value of 7,8 was measured after CO_2 was allowed to escape from solution. The pH of the water prior to the escape of CO_2 was 5,5. In a full-scale plant, dissolved CO_2 will escape from solution in the settler.

The production of 120 mg/ℓ alkalinity (as $CaCO_3$) is a benefit as it contributes to stabilise the pH of the water as a result of improved buffer capacity (Figure 15). This can assist with the protection of pipelines against chemical corrosion.

Sulphate in the water passed through the process unchanged. The sulphate concentration can only be reduced when the solubility product of gypsum is exceeded. This will occur for waters with a low ionic strength at sulphate concentrations of 2 200 mg/ℓ. As the sulphate content in the feed water varied only between 500 and 800 mg/ℓ, sulphate removal did not occur (Table 9).

Calcium increased during treatment due to the dissolution of limestone (Figure 16).

The iron concentration in the treated water is determined by its oxidation state and the solubility of the specific iron state at the pH after neutralisation. Iron(II) is readily soluble at pH values up to 7,5, while that of iron(III) decreases sharply at pH 3 and higher. Figure 17 shows that iron in the treated water was less than 1 mg/ℓ most of the time. This is due to the fact that most of the iron in the feed water was in the iron(III) state and the pH of 7,8 was greater than the critical value of 3.

Uranium was removed on average from 1 100 μg/ℓ to 190 μg/ℓ. This performance is similar to that of conventional lime treatment (Duggan, 1995).

Contact time

Figures 13 and 14 show the temporal behaviour of pH and acidity of the feed and treated water for the laboratory and pilot scale plants. During this period the contact time between the limestone and the water was gradually decreased (Figure 13.b) to determine the minimum contact time required. At the end of the experiment, when the contact time was only 0,62 min, complete neutralisation was still achieved. The neutralisation rate was 0,48 kg $CaCO_3$/(kℓ.min). This high rate is ascribed to the high surface area of the limestone used. With the laboratory-scale plant complete neutralisation was still achieved at a contact time of 1,6 min.

Due to limited capacity of the feed pump, it was not possible to determine the minimum contact time required for complete neutralisation under continuous conditions. A batch experiment was therefore carried out to give an indication of the minimum contact time. Figure 18 shows the rate of neutralisation under batch conditions when the feed water was treated with two different types of limestone, namely Cape A and Tvl A. Table 10 shows that the minimum contact time for Cape A and Tvl A are 0,060 and 0,014 min respectively. The difference is ascribed to the difference in particle size of the two products. Equation 7 shows that the rate of neutralisation is directly proportional to the surface area of the limestone (Clayton *et al.*, 1990). It is concluded that the feed rate of 7,2 kℓ/h employed was below the maximum feed rate that could be applied. A contact time of 0,60 min was used in the pilot-plant compared with the 0,014 min of the beaker test obtained with Tvl A limestone.

$$-dC/dt = k.S.C \qquad (7)$$

where: S - surface area of $CaCO_3$
C - acid concentration in solution
k - rate constant per unit surface area.

Table 10. Minimum contact time required for various limestones.

Limestone		**Reaction time (min)**	**Contact time (min)** [*1]
Source	**Concentration (g/ℓ)**		
Cape A	0,5	120	0,060
Tvl	0,5	28	0,014

[*1] Contact time = Reaction time x limestone concentration in beaker/limestone concentration in fluidised bed reactor.

The experimentally determined neutralisation rate of a specific limestone, and the acid content in the feed water, can be used to size the reactor empirically (Table 11). A contact time of 2 min is required when Tvl A or Cape A limestone is used. The surface area of more crystalline limestone products is less and hence the rate of neutralisation would be slower. It is recommended that the fluidised bed reactor be designed for a contact time of 10 min to accommodate the use of such limestone types.

Table 11. Sizing of fluidised bed reactor.

Parameter	**Value**
Acid concentration	450 mg/ℓ (as $CaCO_3$)
Type	Tvl A, Cape A or any other limestone with similar properties
Particle size (mm)	0,5 - 4
Feed rate (kℓ/h) (q)	1 000
q_{Rec}/q	3
Recycle rate (kℓ/h) (q_{Rec})	3 000
$[Acid]_{Feed}$ (mg/ℓ$CaCO_3$) (F)	450
$[Acid]_{Treated}$ (mg/ℓ$CaCO_3$) (T)	20
Design contact time (active part) (min)	10
Hydraulic retention time (min) (HRT)	16,8
Reactor volume (active part) (kℓ) (V = q (kℓ/h) x HRT (min) ÷ 60)	166,7
Upflow velocity (m/h) (v)	120
Area (m^2) (A = (q + q_{Rec})/v)	33
Diameter (m)	6,51
Length (m) (V/A)	5,0

ECONOMIC FEASIBILITY

The economic feasibility of the limestone neutralisation process was calculated for scenario's 1 to 3 and that of lime for scenario 3 below:

1. Water containing 450 mg/ℓ acid (as $CaCO_3$) and 10 mg/ℓ iron (II) - an underground gold mine water.

2. Water containing 3 600 mg/ℓ acid (as $CaCO_3$) and 400 mg/ℓ iron (II) - a typical coal mine water.

3. Water containing 11 250 mg/ℓ acid (as $CaCO_3$) and

3 000 mg/ℓ iron (II) - effluent from a Uranium Raffinate plant.

The acid load in all three cases amounts to 10,8 t/d (as $CaCO_3$).

The procedure for feeding limestone to the fluidised bed reactor was assumed to be as follows:

- Limestone is delivered in bulk by truck and tipped and transported to an underground silo via a vertical pipe from surface to underground. The silo contained a supply for 7 days.
- Limestone is transported with a belt conveyor from the bottom of the silo via vibrating feeder to the top of the fluidised bed reactor. The vibrating feeder is activated by the load-cell.

Table 12 shows that:

* *Chemical cost*. For the neutralisation of 10,8 t/d of acid (as $CaCO_3$), chemical cost associated with limestone neutralisation amounts only to 34 % of that of lime neutralisation.

* *Limestone cost for different applications*. Limestone cost amounts to R0,06/kℓ, R0,47/kℓ and R1,47/kℓ when waters with acid contents of 0,45 (gold mine water), 3,60 (coal mine drainage) and 11,25 g/ℓ (Uranium Raffinate) (as $CaCO_3$) are treated, respectively.

* *Capital and Construction cost*. Capital and construction cost amount to R1 400 000/(Mℓ/d), R1 500 000/(Mℓ/d) and R2 300 000/(Mℓ/d) when waters with acid contents of 0,45 (gold mine water), 3,60 (coal mine drainage) and 11,25 g/ℓ (Uranium raffinate) are treated, (acid content expressed as g/ℓ $CaCO_3$) respectively.

- *Running cost.* Running cost (including chemical, electricity, labour and capital redemption costs) amounts to R0,23/kℓ, R1,60/kℓ and R3,31/kℓ when waters with acid contents of 0,45 (gold mine water), 3,60 (coal mine drainage) and 11,25 g/ℓ (Uranium raffinate) are treated, (acid content expressed as g/ℓ $CaCO_3$) respectively.

Table 12. Calculation of chemical, capital and running cost associated with limestone and lime.

Parameter	**Application**			
	Gold mine	Coal mine drainage	Uranium Raffinate	Uranium Raffinate
Alkali	Limestone	Limestone	Limestone	Lime
Chemical cost:				
Acid conc. (g/ℓ $CaCO_3$)	0,45	3,60	11,25	11,25
Iron(II) conc. (g/ℓ Fe)	0,01	0,40	3,00	3,00
Flow (kℓ/h)	1000	125	41,67	40
Acid load (t/d $CaCO_3$)	10,8	10,8	10,8	10,8
Purity (as % $CaCO_3$ or $Ca(OH)_2$)	85	85	85	85
Efficiency (%)	90	90	90	90
Mol mass	100	100	100	74
Dosage (kg/kℓ)	0,59	4,71	14,71	10,88
Usage (t/a)	5153	5153	5153	3814
Delivered price (R/t)	100	100	100	400
Cost (R/a)	515294	515294	515294	1525406
Cost (R/kℓ)	0,06	0,47	1,47	4,35
Ratio Alkali cost/Lime cost	0,34	0,34	0,34	1,00

Parameter	**Application**			
	Gold mine	Coal mine drainage	Uranium Raffinate	Uranium Raffinate
Alkali	Limestone	Limestone	Limestone	Lime
Capital and Construction cost (R):				
Iron(II) oxidation stage	0	1373082	703396	314596
Limestone/Lime feed system	146452	146452	146452	120452
Neutralisation stage	902582*	676253	241245	190863
Clarification stage	437500	53688	17500	17500
Electrical	197132	123628	70974	70974
Piping and fittings	177132	103628	50974	50974
Design, construction, commisioning and other	1430076	1895481	954618	399356
Total(R)	3290874	4373211	2185159	1164714
Total (R/Ml/d)	137120	1457737	2276207	1213243
Running cost:				
Chemical	515294	515294	515294	1525406
Electricity (R0,10/kWh)	544042	221945	127680	96697
Labour	272021	110973	63840	48348
Sub total (R/a)	1331357	848212	706813	1670451
Sub total (R/kℓ)	0,15	0,77	2,02	4,77
Capital redemption (10 years, 16 %) (R/a)	680885	904822	452112	240981
Total (R/a)	2012243	1753034	1158925	1911432
Total (R/kℓ)	0,23	1,60	3,31	5,45

Note:

* - Based on Table 11.

CONCLUSIONS

The following conclusions can be made:

- Underground mine water can be neutralised effectively with the limestone neutralisation process. The pH of the water can be increased from less than 3 to levels above 7, while the following removal efficiencies were obtained: 97 % acidity, 95 % iron and 83 % uranium. The alkalinity of the treated water is greater than 120 mg/ℓ (as $CaCO_3$).

- The contact time required between mine water and limestone depends on the limestone surface area. A contact time of 10 min can be used for design purposes.

- Chemical savings of 66 % can be achieved when the cost of limestone and lime amounts to R100/t and R400/t respectively. For the neutralisation of 164,25 t/d of acid (as $CaCO_3$), limestone cost amounts to R0,06/kℓ, R0,47/kℓ and R1,47/kℓ when waters with acid contents of 0,45 g/ℓ (gold mine water), 3,60 g/ℓ coal mine drainage) and 11,25 g/ℓ (Uranium Raffinate) (as $CaCO_3$) are treated, respectively. The corresponding Capital and Construction cost amounts to R1 400 000/(Mℓ/d), R1 500 000/(Mℓ/d) and R2 300 000/(Mℓ/d), respectively, and the corresponding Running cost (including chemical, electricity, labour and capital redemption costs) to R0,23/kℓ, R1,60/kℓ and R3,31/kℓ, respectively.

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