
**NEUTRALISATION OF ACIDIC
EFFLUENTS WITH LIMESTONE**

by

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EXECUTIVE SUMMARY

Background and motivation

Acid mine waters contain high concentrations of dissolved heavy metals and sulphate, and can have pH values as low as 2,5. These conditions may prohibit discharge of untreated acid mine waters into public streams, as they have a detrimental effect on aquatic plant and fish life. Acid mine water drainage also causes ground water pollution. Currently, chemicals such as lime, sodium hydroxide and sodium carbonate are used for the neutralisation of acid water. Limestone can also be used which has the following advantages: low raw material cost, non-hazardous nature of material, low potential of accidental overtreatment, and production of a low-volume, high-density sludge. Disadvantages associated with limestone are the long retention time required for complete reaction and the fact that it is not completely utilised. Should these disadvantages be overcome, it will be the preferred alkali to use due to its low cost. The price (1993) of limestone is only R100/t compared to R280/t for lime.

The aim of this study was to develop a method whereby acid waters would be in contact with limestone to ensure effective neutralisation and efficient use of the limestone. A fluidised bed was proposed for this purpose. The bed is packed with small chips of limestone. The acid water together with the recycle stream enters the bottom of the column; their combined upward velocity fluidises the limestone particles ensuring good contact with the acid water. The neutralised stream passes out of the top of the column. In practise, fresh limestone is added to the top of the bed as it is consumed through dissolution in the acid water.

The main advantage of this process is that the neutralising medium, limestone, can be kept in the reactor as opposed to a rotating drum where the limestone is partially washed out with the treated stream. The fluidised bed ensures a much more efficient usage of the limestone - by controlling the feed and wastage rates of CaCO_3 to and from the bed, the exact time (and hence degree of utilization) of the neutralising medium in the bed can be controlled. The degree to which the acid stream is neutralised is controlled by its retention time in the bed, i.e. the bed height. A second advantage of the fluidised bed operation is the attrition that occurs between the closely associated particles which keeps the CaCO_3 surfaces clean of any CaSO_4 or iron hydroxide that might inhibit the neutralisation rate.

Objectives

The following specific aims were set for the project:

- * Literature survey
- * Determination of the market size for the neutralisation of acid water.
- * Laboratory studies to determine the kinetics of limestone neutralisation.
- * Pilot plant studies on acid water (synthetically made-up acid water and acid mine drainage) to determine the technical feasibility of limestone neutralisation in a fluidised-bed reactor.

- * Determination of the economic feasibility of the fluidised-bed limestone neutralisation process.

All the aims set for the project were met.

Results and conclusions

The findings from the study can be summarised as follows:

- * Kinetics. The kinetics of acid neutralisation using CaCO_3 may be represented by the rate equation:

$$-\frac{d[\text{H}_2\text{SO}_4]_b}{dt} = K S [\text{H}_2\text{SO}_4]_b$$

where K is the rate constant based on surface area, S is the total CaCO_3 surface area available and $[\text{H}_2\text{SO}_4]_b$ is the concentration of acid in the bulk liquid (as $\text{mg CaCO}_3/\text{l}$). For effluents with little or no heavy metals, the value of K is $2,45 \times 10^{-3} \text{ min}^{-1} \cdot \text{cm}^{-2}$; for effluents that contain significant quantities of iron, a layer of $\text{Fe}(\text{OH})_3$ forms on the CaCO_3 surfaces that causes K to decrease from the abovementioned value, depending on the thickness of the $\text{Fe}(\text{OH})_3$ layer.

- * Rate. It was determined that the rate of neutralisation is directly related to the dosage of CaCO_3 , influenced by the particle size of limestone (the finer the particle, the higher the rate of neutralisation) and the type of metal in solution. The presence of iron(II) retards the rate dramatically while iron(III) has no influence. Aeration marginally accelerated the rate of limestone neutralisation as a result of CO_2 -stripping.

It was determined under continuous conditions that a contact time of 4 min is sufficient for the neutralisation of acid water containing 4 g/l free acid and 580 mg/l iron(III), while a contact time of at least 40 min is required for the same water, but which contains iron(II) instead of iron(III).

- * Water quality. The limestone neutralisation process improves the quality of the water by removing free acid and acid associated with Fe(III) completely. Sulphate is removed up to the point where the water is saturated with calcium sulphate. The level to which the pH of acid water is increased depends on the metals that will remain in solution during neutralisation. If magnesium is present in the water, it coprecipitates partially with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Iron(III) and aluminium(III) are effectively removed during limestone neutralisation as metal hydroxides.
- * Reactor type. A fluidised-bed reactor with multiple stages of increasing diameters is preferred for the limestone neutralisation process as it allows fluidisation of the bigger particles but also prevents washout of the smaller particles in the case where ungraded particle size limestone is used. The cone-shaped and pipe-shaped fluidised-bed reactors perform equally well in the limestone neutralisation process.

- * Limestone utilisation. In the case of iron(III)-rich water, the limestone is completely utilised while the ferric hydroxide sludge which is produced is washed out together with the effluent. No bleed-off stream is therefore necessary to get rid of impurities in the limestone or produced sludge. In the case of iron(II)-rich water, gypsum and ferric hydroxide sludge and coated limestone particles accumulate in the fluidised-bed reactor. About 70% of the limestone is utilised in the case of water containing 600 mg/l iron(II). It is expected that a fraction of the trapped limestone could be recovered from the waste sludge through a backwash operation.
- * By-products. Gypsum and CO₂ are produced which could be recovered as by-products.

Contribution and benefits from project

The main contribution from this study is that it was demonstrated that acid water can be neutralised effectively in a fluidised-bed reactor. By using the fluidised-bed reactor for limestone neutralisation, the main weaknesses of limestone (its low reactivity and its scaling with gypsum and iron hydroxide precipitates in other systems) which prevented it from being used on a wide basis in the past, were 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 is prevented due to the attrition between the particles under fluidised conditions.

The comparative advantages associated with the use of limestone under practical conditions, compared to other alkalis such as lime and sodium hydroxide, are the following:

- * More cost-effective. At prices of R100, R240, R280 and R1 500 per ton for limestone, unhydrated lime, hydrated lime and sodium hydroxide respectively (1993), the alkali cost for the neutralisation of acid water with an acid content of 2 g/l amounts to 20 c/kℓ in the case of limestone, 27 c/kℓ in the case of unhydrated lime, 41 c/kℓ in the case of hydrated lime, and 240 c/kℓ in the case of sodium hydroxide.
- * No accurate control of dosage is required, as limestone does not dissolve at pH-values greater than 7.
- * Sludge of a higher density is produced in the case of iron(III)-rich .
- * It is safe to handle.
- * It is easy to store.

Should this process be implemented on a large scale, it will lead to a significant growth in the limestone market due to the following reasons:

- * The use of limestone is more cost-effective than other alkalis.

-
- * Industry would be willing to neutralise acid water which was previously not feasible from a cost and control point of view (e.g. seepage water from old coal mines).

Patent protection has been received in South Africa, Canada, Australia and the USA while patent protection is pending in Germany.

Recommendations

It is recommended that:

- * Design criteria be established for the pre-oxidation of iron(II) in the case of iron(II)-rich water in order to make the fluidised-bed limestone neutralisation process suitable for the treatment of any type of acid water.
- * The benefits of the process be demonstrated to industry by the construction and operation of a demonstration plant in order to assist with the transfer of the new technology to potential users.

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GLOSSARY

Acid mine drainage	:	Acid water, rich in iron, produced when pyrites (FeS_2) is oxidised due to the presence of water, air and iron oxidising bacteria.
Contact time	:	Volume of limestone divided by the flowrate of the feed stream.
Dolomite	:	$\text{CaMg}(\text{CO}_3)_2$
Fluidised-bed reactor	:	A column type reactor, packed with solid material, e.g. limestone, through which a fluid or gas is blown, at a rate, high enough, to expand the volume in the reactor occupied by the solid particles.
Hydraulic retention time	:	Empty volume of the reactor divided by the flowrate of the feed stream.
Limestone	:	An ore containing predominantly calcium carbonate.
Slaked lime	:	$\text{Ca}(\text{OH})_2$
Unslaked lime	:	CaO

CHAPTER 1 : BACKGROUND

INTRODUCTION

Acid mine waters contain high concentrations of dissolved heavy metals and sulphate, and can have pH values as low as 2,5. These conditions may prohibit discharge of untreated acid mine waters into public streams, as they have a detrimental effect on aquatic plant and fish life. Acid mine water drainage also causes ground water pollution. Currently, chemicals such as lime, sodium hydroxide and sodium carbonate are used for the neutralisation of acid water. Limestone can also be used which has the following advantages: low raw material cost, non-hazardous nature of material, low potential of accidental overtreatment, and production of a low-volume, high-density sludge. Disadvantages associated with limestone are the long retention time required for complete reaction and the fact that it is not completely utilised. Should these disadvantages be overcome, it will be the preferred alkaline to use due to its low cost. The price of limestone is only R100/t, compared to R280/t for unslaked lime (1993).

It is the aim of this study to develop an alternative method for treating acid waters with limestone ensuring effective neutralisation and efficient use of the limestone. A fluidised bed is proposed for this purpose.

A schematic drawing of the proposed process appears in Figure 1.1. The bed is packed with small chips of limestone. The acid water together with the recycled stream enters at the bottom of the column; their combined upward velocity fluidises the limestone particles ensuring good contact with the acid water. The neutralised stream passes out of the top of the column. In practise, fresh limestone is added to the top of the bed as it is consumed through dissolution in the acid water.

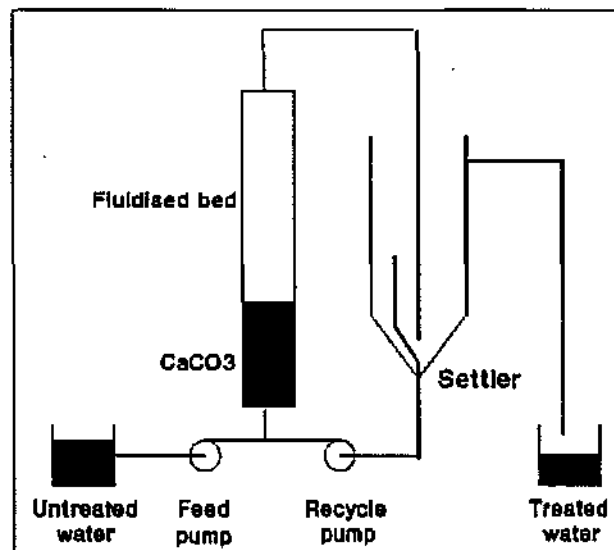


Figure 1.1 Fluidised bed system for acid water neutralisation

The main advantage of this process is that the neutralising medium, limestone, can be kept in the reactor as opposed to a rotating drum where the limestone is partially washed out with the treated stream. The fluidised bed ensures a much more efficient use of the limestone - by controlling the feed and wastage rates of CaCO_3 to and from the bed, the exact time (and hence degree of utilisation) of the neutralising medium in the bed can be controlled. The degree to which the acid stream is neutralised is controlled by its retention time in the bed, i.e. the bed height.

A second advantage of the fluidised bed operation is the attrition that occurs between the closely associated particles: it is hoped that this attrition will keep the CaCO_3 surfaces clean of any CaSO_4 or iron hydroxide that might inhibit the neutralisation rate.

OCCURRENCE OF ACID WATER

Neutralisation of acid water is widely applied by industry to meet legislative requirements before discharging into receiving waters. Lime is widely used to neutralise acidic effluents such as the following:

- Acid mine water, which is produced 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.
- Effluent from metallurgical plants at mines for example uranium and acid plants.
- Effluent from the chemical industry.

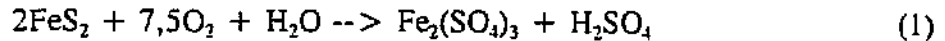
Table 1.1 shows the industries that are neutralising acidic effluents.

Table 1.1 : Industries that neutralise acidic effluents or streams.

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 the most from the limestone neutralisation process. Acid mine drainage (AMD) is formed through bacterial oxidation of pyrites when exposed to oxygen, carbon dioxide and water. The oxidation reaction can be represented as follows (Barnes, 1968):



The reaction occurs underground during or after mining activities and on surface in old mine dumps containing pyrites.

Seepage from these sources ends up in public streams from time to time. The acidic water is detrimental to plant and fish life as a result of its low pH and high concentrations of iron.

When underground water interferes with mining operations, it is pumped to the surface and discharged into public streams. In the case of acid water, it is partially neutralised underground and completely neutralised at surface. To date only lime, sodium hydroxide and sodium carbonate have been used to date for this purpose. These chemicals have the disadvantage that it requires accurate dosing in order to prevent under or over dosages. Accurate dosing of it underground is impossible. 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 of gypsum as a result of the high calcium concentration. In case of the fluidised limestone process, this dosing problem could be overcome as limestone will only dissolve as long as the water is undersaturated with respect to CaCO_3 . This usually occurs at a pH of between 6 and 7.

Table 1.2 shows the volume of acid water that needs to be, or is, neutralised by the mining industry. It shows that 196 000 tons of limestone is required per year for the neutralisation of only AMD, while 222 000 tons is required for the neutralisation of all mining industry's acid waters.

Edible oil.

In the edible oil industry, sulphuric acid is used to separate the oil from the soap. The acid water is treated with lime/caustic soda in order to remove oil and suspended solids from the water and to neutralise it. It is estimated that 73 000 tons of limestone could be used by the edible oil industry for partial neutralisation of their effluent. Due to the high buffering capacity of the water, it might be necessary to also dose lime as a final treatment for neutralisation.

Table 1.2 : Estimated volume of acid water produced by the mining industry.

Source	Area	Volume (M ³ /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
Sub-total		114		456	196 000
Met. plants	Zinc processing	3	20	60	26 000
TOTAL		117		516	222 000

AMD - Acid mine drainage

Carbonate content of limestone was taken at 85% (as CaCO₃)

Metal Finishing.

Phosphoric acid is employed in the chemical brightening step. This anodising step provides the finished article with a high decorative sheen. The pH drops from 10 - 12 to 3 as a result of the scrubbing of extracted acid fumes with insufficient quantities of alkaline rinse flows. Rinse waters from chemical surface treatment processes usually only require pH correction.

Explosive.

Strong sulphuric acid solutions are used in the explosive industry in their manufacturing process. As lime is currently used for neutralisation of the effluent, it could be replaced with limestone. As the effluent contains only organic material as impurities (no metals), the recovery of gypsum as a by-product is possible.

Pigment.

In the manufacturing of titanium dioxide, fairly concentrated solutions of H₂SO₄ are used. The effluent is neutralised with lime or powdered limestone.

EFFECT OF ACID WATER

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

- * Mineralisation of surface water. Lime or limestone treatment can contribute to solving this problem as sulphate can be removed from containing high sulphate acid water ($\text{SO}_4 > 2\,500 \text{ mg/l}$) to the solubility level of gypsum ($\text{SO}_4 = 1\,500$ to $2\,500 \text{ mg/l}$), depending on the ion-strength and temperature of the water).

Mineralisation is one of the most important water quality problems in South Africa (Heynike, 1981; Water Research Commission, 1982). The average total dissolved solids (TDS) content of the water in the Vaal Barrage, one of the major water supply sources in the RSA, has increased from 100 mg/l in the early sixties to more than 400 mg/l at the end of the seventies, and is expected to increase to more than 800 mg/l by the year 2000. Heynike (1981) estimated that consumers in the PWV area would face additional costs of approximately R139 million/a, should the TDS concentration in Vaal Barrage water increase from 300 to 800 mg/l . Sulphate would be an important contributing factor to these increased TDS concentrations.

Sulphate significantly affects the utilisation of water (Toerien and Maree, 1987). It is directly responsible for the mineralisation of receiving waters when discharged in excessive amounts but often constitutes an even greater indirect problem through salinity-associated corrosion, transferring of tastes to drinking water, scaling of pipes, boilers and heat exchangers, and giving rise to bio-corrosion. Therefore, the treatment of sulphate polluted water will contribute considerably to the prevention of salination of South Africa's surface water.

- * Corrosion. Soft water, which is slightly acid, leads to corrosion of pipelines e.g. Cape water.
- * Plant and fish 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.

LEGAL REQUIREMENTS

Current approach

Table 1.3 gives the criteria set for the discharge of acidic and sulphate-rich effluents into public water courses (Water Act 54 of 1956 and Water Amendment Act 96 of 1984).

Table 1.3 Criteria set for the discharge of acidic and sulphate-rich effluents into public water courses.

Parameter	General Standard	Specific Standard
pH	5,5 - 9,5	5,5 - 7,5
Sulphate	none	none
Conductivity (mS/m)	250 or 75% above intake	250 or 15% above intake

According to the Water Act, local authorities have the right to adjust these criteria as required for their specific areas (see Table 1.4).

Table 1.4 Criteria set by local authorities for discharge of acidic and sulphate-rich effluents into sewerage systems

Local Authority	pH	Sulphate mg/l SO ₄	Conductivity mS/m
Johannesburg Mun.	> 6	1 800	500
Germiston Mun.	6-10	1 800	500
Alberton Mun.	6-10	1 800	500
Krugersdorp Mun.	6-10	1 800	500
East Rand Regional Services Council	6-10	-	500
Cape Town Mun.	5,5-12	500	-
Western Cape Regional Services Council	5,5-12	500	300
Durban Mun.	6	200	-

Future approach

At present, the Department of Water Affairs uses the uniform effluent standard approach to control pollution from point sources in South Africa. In future, a new approach, which combines the receiving water quality objectives (RWQO) (to control non-hazardous pollutants) and pollution prevention (to control hazardous pollutants) approaches, will be used to control pollution from both point and non-point sources (Van der Merwe and Grobler, 1990). The concept of waste load allocation (WLA) is central to the RWQO approach to water pollution control. In principle, WLA is the assignment of allowable discharges to a water body in such a way that the water quality objectives for designated water uses are being met. Principles of benefit-cost analysis are used in these assignments. It involves determining water quality objectives for desirable water uses, understanding the relationships between pollutant loads and water quality and using these to predict impacts on water quality. 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.

CONVENTIONAL TREATMENT WITH LIME

The most suitable technology to date for the treatment of acid water is lime treatment. Neutralisation with lime can be applied through the following processes:

Conventional process.

The flow diagram of the conventional process is shown in Figure 1.2. The main disadvantage of this process is that sludge with a low density is produced.

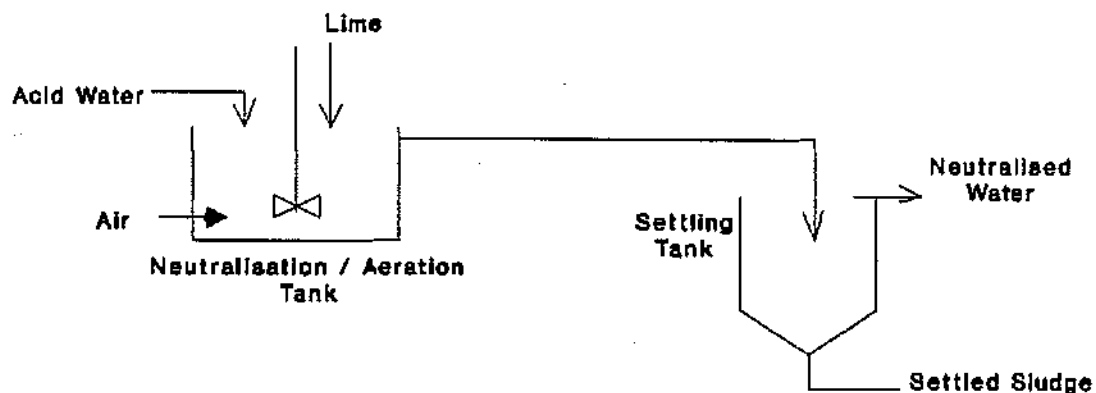


Figure 1.2 The conventional process for acid water neutralisation

High Density Sludge (HDS) process.

The HDS Process (Figure 1.3) has the following benefits above the conventional process (Osuchowski, 1992):

- * A sludge of 10 times higher density is produced. Hereby less sludge drying facilities are required. The capital costs associated with the construction of sludge ponds (including pumping and piping facilities) varies between R1/m³ and R3/m³.
- * The sludge is settled faster, therefore, a smaller clarifier is required. The saving on the clarifier is reduced by approximately 38%.

The HDS process consists of the following stages:

- * pH correction 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 and to mix the conditioned sludge with the acid mine water entering the tank. 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 polyelectrolyte can be dosed to the clarifier to promote flocculation.

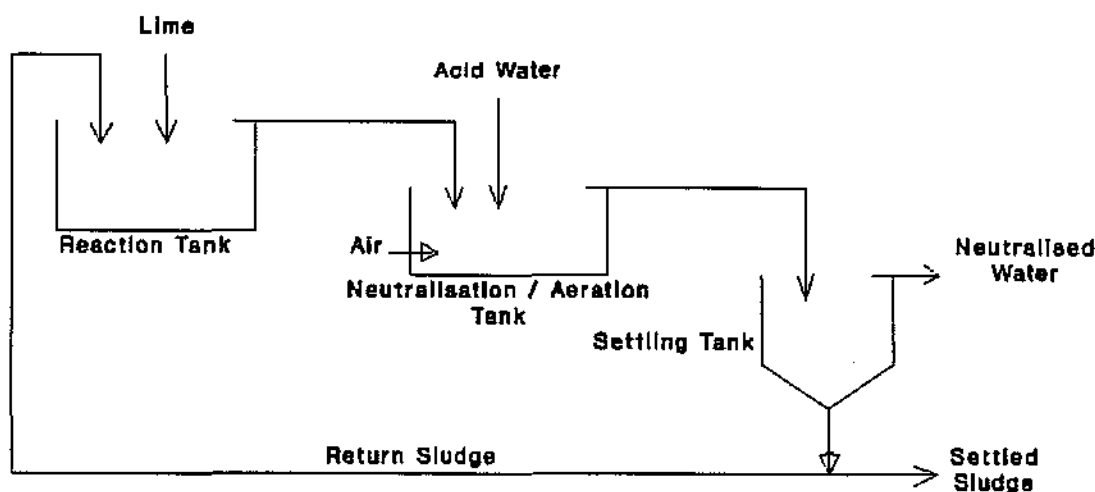


Figure 1.3 The High Density Sludge process for acid water neutralisation

Lime In-Line Aeration and Neutralisation System (ILS).

In the case of lime neutralisation, incomplete dissolution of the lime is often a problem. The US Bureau of Mines overcame this problem by developing the ILS system (Ackman and Erickson, 1986; Ackman and Kleinmann, 1991). The ILS system is the combination of a jet pump aeration device and a static mixer which contains no moving parts. Jet Pumps are nozzles that entrain air by venturi action. Water enters under pressure and is converted by the jet pump into a high-velocity

stream which passes through a suction chamber that is open to the atmosphere. If the system is used for neutralisation as well as aeration, the suction chamber also serves as the injection point for the alkaline material.

The ILS process has the following benefits compared with the conventional method of lime neutralisation:

- * Reduced cost without sacrificing the quality of the treated water.
- * No sludge recirculation is required as the lime is completely utilised.

Limedust

Rich and Hutchinson (1990) used limedust, a waste product in the manufacturing of lime, for the neutralisation of acid mine water. The limedust that was used contained 15-18% CaO and 72-75% CaCO₃. The main advantage associated with the use of limedust is that it is cheaper than lime.

Calcium carbonate provides an alternative means of neutralising acid mine water. Its main advantage over other chemicals are its lower price (delivered at a price of approximately R100/t compared to R280/t for lime) (Van Baalen, 1993) and the production of smaller sludge volumes (Henzen and Pieterse, 1978). It is foreseen that the use of limestone for the neutralisation of acid water will increase in future should the following aspects be proven:

- * Limestone is completely utilised.
- * Limestone particles are not prevented from dissolution through the formation of a protective layer of gypsum or iron hydroxide on its surface.

CHAPTER 2. LITERATURE OVERVIEW ON LIMESTONE NEUTRALISATION

INTRODUCTION

The occurrence of acid mine drainage (AMD) with coal mining is well documented (Appalachian Regional Commission, 1969), as well as a review on the different treatment methods that have been developed (Hill and Wilmoth, 1971). Lime neutralisation, in conjunction with aeration, is normally used for the treatment of acid mine water. The high cost of lime as compared to limestone and the poor quality sludge (slow settling, large volumes and low solids content) have stimulated work in the utilization of limestone (Henzen and Pieterse, 1978). This chapter deals with the current state-of-the-art of limestone treatment of acid mine drainage. Several researchers have reported the use of CaCO_3 as a neutralising agent for acid waters (Braley, 1954; Barnes and Romberger, 1968; Henzen and Pieterse, 1978; Thompson, 1980).

CHEMICAL REACTIONS DURING NEUTRALISATION

Equilibrium reactions of the carbonic system

Limestone neutralisation has the effect that acidity decreases and alkalinity and pH increase. The various parameters are expressed by the following functions:

$$[\text{Acidity}] = 2[\text{CO}_2] + [\text{HCO}_3^-] + [\text{H}^+] - [\text{OH}^-] \quad (1)$$

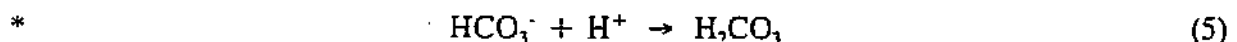
$$[\text{Alkalinity}] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] + \text{H}^+ \quad (2)$$

$$\text{pH} = -\log [\text{H}^+] \quad (3)$$

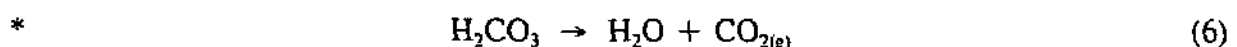
The values of the various parameters are determined by the equilibrium constants of the following equilibrium equations (Barnes, 1968):



$$\log (K_{25^\circ}) = 2.0$$



$$\log(K_{25^\circ}) = 6.4$$



$$\log (K_{25^\circ}) = 1.5$$

Reactions 5 and 6 (secondary reactions) take place only below a pH of about 6.4, but reaction 4 can proceed to pH 8.3, where solid CaCO_3 is in equilibrium with the normal atmosphere (pressure of CO_2 about $10^{-3.5}$ atm).

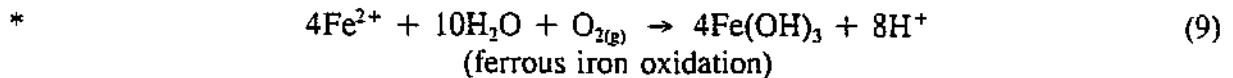
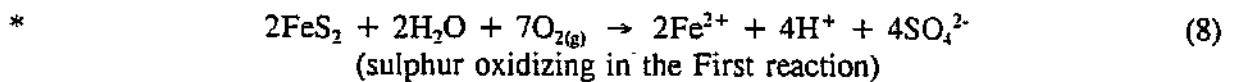
Precipitation of metals

Treatment of mine drainage water is important to eliminate the negative effect of the acid water on the environment. The principal source of acid in mine drainage is the dissolving of the products of oxidation of the iron sulphide or pyrite (FeS_2). The total oxidation process in the presence of water can be represented by the following reaction (Barnes, 1968):



$$\log(K_{25^\circ}) = 829,4$$

The iron of pyrite generally forms Fe^{2+} but is not usually oxidised to the extent of forming $\text{Fe}(\text{OH})_3$ at the same location where the sulphide is oxidized to form acid. The total reaction normally proceeds by at least two steps:



During neutralisation with lime or limestone, heavy metals precipitate as metal hydroxides. The level to which metals are removed during neutralisation can be predicted by Eh-pH diagrams. Figure 2.1 shows Eh-pH diagram for the distribution of the predominant stable aqueous species and solid phases of iron, carbon and sulphur, as these are the most important in reactions involving the generation and neutralization of acid waters.

The principal problem after neutralisation, and generally the most expensive part of drainage treatment, is the removal of precipitated, amorphous ferric oxyhydroxide hydrates from the treated water.

Oxidation of iron(II)

The presence of iron(II) in acid water is causing a problem during neutralisation as ferrous hydroxide is relatively soluble up to pH values of pH 7.5. In order to remove iron(II), aeration is applied to oxidise iron(II) to iron(III), which is relatively insoluble for pH values greater than 3.0. The rate of iron(II) oxidation increases with pH as indicated in Figure 2.2 (Singer and Stumm, 1969).

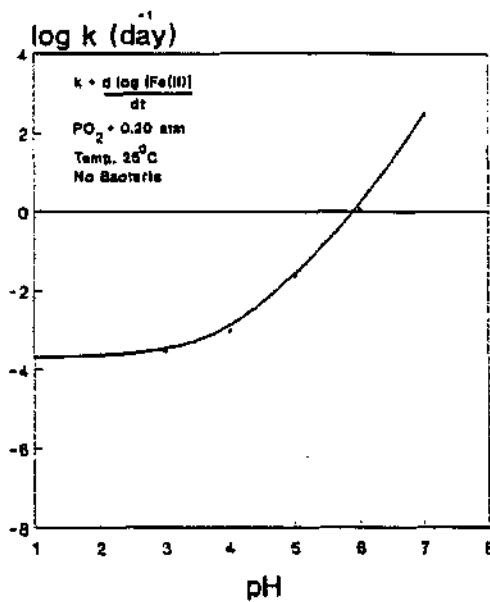


Figure 2.2 Oxygenation rate of iron(II) as a function of pH.

KINETIC MODEL

Introduction

The kinetics of calcium carbonate dissolution from packed beds of crushed limestone will be described in this section (Letterman, *et al.*, 1991).

It is assumed that the rate of CaCO_3 dissolution depends on the transport of hydrogen ions from the bulk solution to the limestone surface. The kinetics of the dissolution process were described by a film-transport type model, based on the difference between the hydrogen-ion concentration at the surface and the concentration in the bulk solution (Letterman, *et al.*, 1991).

Recent work on the kinetics of CaCO_3 dissolution has shown that the CaCO_3 dissolution rate in slightly acid to alkaline solutions is controlled by an interface calcium-ion mass transfer resistance and a first order surface reaction acting in series (Diaz, *et al.*, 1985). The equations presented in this model assumed that the rate of CaCO_3 dissolution within a limestone contactor can be modelled using three resistances acting in series

- * Liquid film transport resistance.
- * Surface reaction resistance.
- * Residue layer resistance. It is assumed that the porous layer is formed by insoluble alumina-silicate (clay) impurities that remain on the particle surface as the CaCO_3 dissolves from the limestone matrix.

The mathematical model described here is used for contactor design under a steady

state operating condition and for relative high-purity, high-calcium limestone. With a reasonable constant influent water flow rate, chemical composition and temperature, it can be assumed that steady state conditions exists.

Dissolution-rate Model

The reaction rate expression (dissolution rate) is given by the film transfer relationship (Letterman, *et al.*, 1991).

$$r = K_0 \cdot a \cdot (C_{eq} - C) \quad (10)$$

where r = reaction rate (dissolution rate)

K_0 = overall dissolution rate constant

a = area of limestone particles per unit volume of fluid

C_{eq} = calcium concentration in the fluid when the calcium carbonate in the limestone is in equilibrium with the influent flow

C = bulk fluid calcium-ion concentration

The different parameters in equation (10) will now be discussed in detail.

(a) K_0 - overall dissolution-rate constant

This constant is related to the three resistances in the mathematical model described before:

- 1) K_L - liquid-film mass-transfer coefficient
- 2) K_F - residue layer mass-transfer coefficient
- 3) K_C - surface reaction rate constant for calcium dissolution

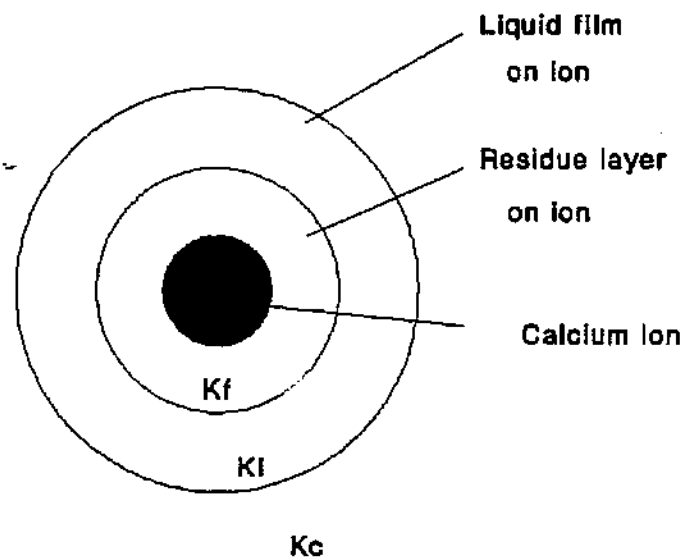


Figure 2.3 : Various zones that influence the dissolution rate of CaCO_3 .

The overall dissolution rate constant is given by a combination of these resistances

$$K_o = \left(\frac{1}{K_F} + \frac{1}{K_L} + \frac{1}{K_C} \right)^{-1} \quad (11)$$

The expressions for each resistance will now be given (Garside and Al-Diborni, 1977).

1) K_L - liquid film mass transfer coefficient

$$K_L = (5.7)U_s \cdot MR_c^{-0.87} \cdot S_c^{-2/3} \quad (12)$$

$1 \leq MR_c \leq 30$ (low Reynolds numbers)

$$K_L = (1.8)U_s \cdot MR_c^{-0.44} \cdot S_c^{-2/3} \quad (13)$$

$30 \leq MR_c \leq 10\,000$ (high Reynolds numbers)

$$\text{The modified Reynolds number } MR_c = \frac{(d \cdot U_s)}{v(1 - \epsilon)} \quad (14)$$

- d - volume mean limestone particle diameter
- U_s - Superficial velocity (empty column fluid velocity)
- v - Kinematic viscosity
- ϵ - bed porosity
- D - calcium ion diffusivity

and the Schmidt number by

$$S_c = \frac{v}{D} \quad (15)$$

2) K_F - residue layer mass-transfer coefficient

$$K_F = \frac{(D \cdot \epsilon_r)}{\delta \cdot \tau_r} \quad (16)$$

- D - calcium ion diffusivity
- ϵ_r - porosity of the layer
- δ - thickness of the layer
- τ_r - pore length factor (tortuosity)

The magnitude of K_F decreases as calcium carbonate dissolves and the thickness of the residue layer increases.

3) K_C - surface reaction rate constant

The dissolution of low-solubility minerals is often controlled by reactions at the interface between the solid phase and water. Where surface protonation is a controlling surface reaction, the pH of the solution in the interface region is an important rate determining parameter. Data was obtained from experiments to derive an empirical relationship between the equilibrium interfacial pH (pH_{eq}) and the magnitude of K_C .

An experiment with an initial bulk solution calcium concentration C_b equal to zero and with the initial rate of increase of the calcium-ion concentration J_o , is given by

$$J_o = K_o (C_{\text{eq}} - C_b) = K_o C_{\text{eq}} \quad (17)$$

K_o is at present represented by two resistances K_L and K_C .

$$J_o = \frac{K_L K_C}{K_L + K_C} \times (C_{\text{eq}} - C_b) \quad (18)$$

J_o is a function of the solution pH.

Given the assumption that at low pH K_C is large and significantly greater than K_L then

$$J_o = K_L C_{\text{eq}} \quad (19)$$

$$\text{since } \left(\frac{K_L K_C}{K_L + K_C} = \frac{K_L K_C}{K_C} = K_L \right)$$

from equation (18)

The constant K_L can now be obtained from equation (19)

$$K_L = \frac{J_o}{C_{\text{eq}}} \quad (20)$$

at a low pH (Figure 2.4).

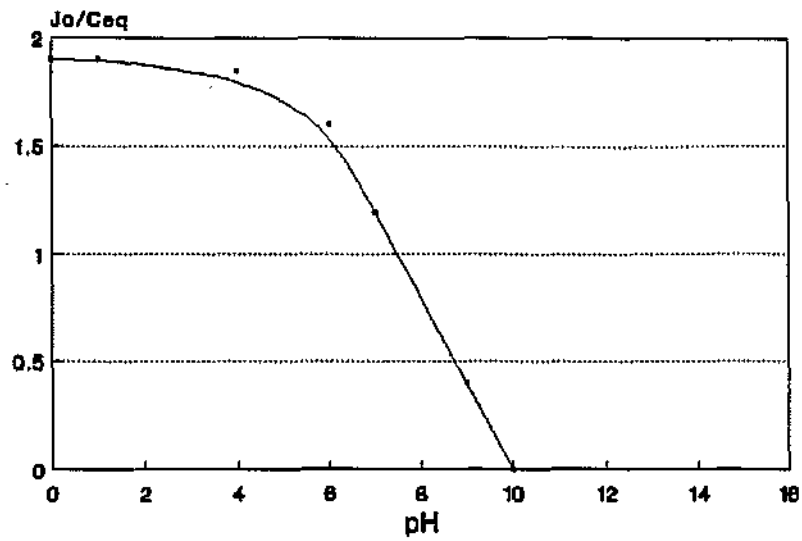


Figure 2.4 Relationship between the liquid film transfer coefficient, K_L , and pH.

Thus from equation (18) the constant K_C can be obtained using the value for K_L .

From equation (18):

$$J_o = \frac{K_L K_C C_{eq}}{K_L + K_C}$$

$$K_L K_C = \frac{J_o}{C_{eq}} (K_L + K_C)$$

$$= \frac{J_o}{C_{eq}} K_L + \frac{J_o}{C_{eq}} K_C$$

$$K_C (K_L - \frac{J_o}{C_{eq}}) = (\frac{J_o}{C_{eq}}) K_L$$

$$K_C = \frac{(\frac{J_o}{C_{eq}}) K_L}{K_L - (\frac{J_o}{C_{eq}})}$$

$$= K_L \left(\frac{(\frac{J_o}{C_{eq}})}{(K_L - (\frac{J_o}{C_{eq}}))} \right)$$

$$= K_L \left(\frac{K_L}{J_o/C_{eq}} - \frac{J_o/C_{eq}}{J_o/C_{eq}} \right)^{-1}$$

$$K_C = K_L \left(\frac{K_L C_{eq} - 1}{J_o} \right)^{-1} \quad (21)$$

(b) a - area of limestone particles per unit volume of fluid

$$a = \frac{6(1 - \epsilon)}{d \Phi} \quad (22)$$

ϵ = bed porosity

d = volume mean limestone-particle diameter

Φ = sphericity

(c) C_{eq} - equilibrium calcium iron concentration

In the dissolution-rate model, the rate of calcium-ion transport from the surface to the bulk solution, is assumed to depend on the equilibrium calcium-iron concentration called C_{eq} . Experiments were done to determine the magnitude of C_{eq} and the corresponding equilibrium pH called pH_{eq} . These volumes were determined using the effluent calcium-ion concentration as an independent variable.

The dispersed-plug show model for steady flow in a packed-bed reactor is given by the following differential equation

$$N_D \frac{d^2C}{dZ^2} - \epsilon \frac{dC}{dZ} + \tau E = 0 \quad (23)$$

$$\text{with } N_D = \frac{F\epsilon}{U_s L} \quad (24)$$

F - dispersion coefficient

ϵ - bed porosity

U_s - superficial fluid velocity

L - overall depth of limestone in the column

E - mean fluid residence time

$$E = \frac{LE}{U_s} \quad (25)$$

Z - dimensionless axial distance

$$Z = \frac{z}{L} \quad (26)$$

The reactant concentration of calcium-ions in the packed bed can be modelled by using equation (14) above and all the equations related to the reaction rate (r) (equation (1)).

LIMESTONE PROPERTIES AND ITS SELECTION

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

Most limestones are rated by the producer with regard to their calcium carbonate or calcium carbonate equivalent content. The higher the CaCO₃ content, the greater the alkalinity available and the fewer the impurities. In comparing pure lime and limestone, it should be noted that when both are compared on the same basis, such as CaCO₃ equivalent, 1 kg of lime has 1.35 times the alkalinity of 1 kg of limestone.

Several investigators have reported that limestone that contains magnesium carbonate in appreciable quantities reacts very slowly (Jacobs, 1947; Hoak *et al.*, 1945; Ford, 1970). Hoak *et al.* (1945) reported that dolomitic limestone's rate of reaction was approximately inversely proportional to the quantity of magnesium carbonate it contained (above about 2%). Ford (1970) conducted studies with 14 limestones of various compositions by treating both artificial and actual mine drainage and found that in general the neutralising efficiency of a stone increased with higher percentages of CaO and lower percentages of MgO, thus, the calcites, CaCO₃, were more effective than dolomites or magnesites. Empirically he established that the efficiency of a limestone can be predicted by the following equation:

$$\text{Efficiency (\%)} = \text{CaO} + (\text{SA} \times \text{D})$$

where: CaO - CaO (as CaCO₃) (%)
SA - Surface area (m²/g)
D - Density (g/ml)

The following factors should be considered in the selection of a limestone:

- * high calcium carbonate content,
- * low magnesium content,
- * low amount of impurities and
- * large surface size, i.e. smallest particle size.

After a preliminary screening of the proposed stones by their chemical analysis, a simple laboratory test is recommended. Twice the stoichiometric amount of limestone of the size to be used is added to a sample of AMD. The sample is mixed by introducing air. The pH is recorded for 5 h. A pH-time plot is used to evaluate the limestone.

In addition to the reaction rate, the characteristics of the sludge should also be considered. Three characteristics of the sludge are important, i.e., settling rate, sludge volume and sludge solids content. To perform these tests, a sample of the unsettled neutralised AMD is placed in a 1000-ml graduated cylinder and the depth of the sludge blanket determined periodically for 2 to 12 h. This data is then plotted. The final reading is considered the sludge volume, usually expressed as a percent of the total sample. The supernatant water should then be drained off. The sludge is then dried and the percentage of solids is calculated.

A good limestone should have a high neutralising rate, fast settling sludge, small volume of sludge, and a sludge with a high solids content.

In addition to the chemical properties of the limestone, the geological history of the stone and its crystal structure play some role in its neutralisation ability. Crystal structure has some bearing on the surface area of the stone particle. Several investigators have shown that the reaction rate is a function of the size of the particle (Jacobs, 1947; Hoak *et al.*, 1945; Ford, 1970). The limit on the fineness of the stone is an economic one. Cost of grinding increases at an accelerating rate as the particle size decreases. The cheapest small particle size material in mining areas is 'rock dust' of which 60 to 70% passes a 200 mesh. To obtain a smaller size may not be economical viable.

CLASSIFICATION OF ACID WATER

The efficiency of limestone treatment depends on the amount and ionic state of iron in acid water. For this purpose, acid water can be divided into three groups:

- * Low iron water. Low iron water is the easiest to treat. This type of AMD usually has a low acidity and therefore, coating of the stone with calcium sulphate is not a problem.
- * Ferric iron water. Acid water containing ferric iron produces ferric hydroxide during neutralisation. Braley (1954) reported that ferric iron rich water is responsible for coating of the limestone bed in the case of packed-bed reactors.
- * Ferrous iron water. Acid water containing ferrous iron is the most difficult to treat with limestone. Several people have reported that the mineral acidity and ferric iron in AMD can be easily removed; however, the ferrous iron and the acid released upon its oxidation and/or hydrolysis are difficult to remove (Hoak, 1945; Glover, *et al.*, 1965, Holland, *et al.*, 1970). When limestone reacts with ferrous-iron AMD, the mineral acidity is neutralised, the pH increased (normally not greater than 6.5), and the ferric iron precipitates as ferric hydroxide. However, the oxidation of ferrous iron at low pH-values is slow and it can not be precipitated at low pH-values, thus, little ferrous iron is removed. If the neutralisation step is followed by aeration to oxidise and hydrolyse

the ferrous iron, a decrease in pH occurs due to the hydrogen liberated. Thus an excess of limestone must be added to the AMD. Holland *et al.* (1970) reported that the greater the excess the faster the ferrous iron oxidation. This is probably due to the higher pH attained with greater amounts of limestone. Hill and Wilmoth (1971) concluded that direct feed of pulverized dry or slurred limestone appears to be the only appropriate system to deal with ferrous iron rich water. Mihok *et al.* (1968) demonstrated that a tumbler could be used to produce a limestone slurry with very small particle size (90% less than 40 mesh) which in turn was effectively used for the neutralisation of ferrous rich AMD.

LIMESTONE TREATMENT SYSTEMS

Various limestone treatment systems have been investigated (Hill and Wilmoth,, 1971).

Aerated limestone powder reactor.

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

Limestone powder was found to react rapidly with free acid, ferric and aluminium salts in AMD, but not in the ferrous containing AMD (Glover, 1967). Ferrous containing AMD can only be treated if aeration is also applied as it has the effect that iron(II) is slowly oxidised (Figure 3.5). Automatic dosage of limestone powder in stoichiometric quantities is required in this approach to prevent any losses which are difficult to control.

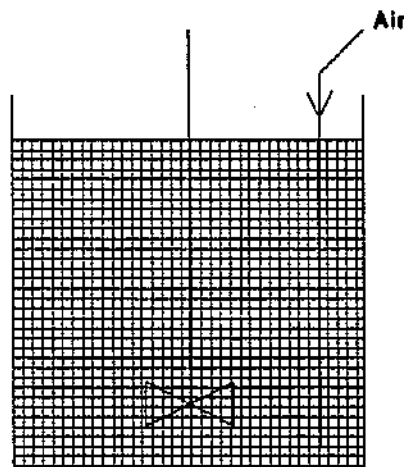


Figure 2.5 : Aerated powder limestone reactor.

Stationary limestone grit reactor.

Stationary limestone beds can be operated by vertical fluid flow (Figure 2.6) or horizontal fluid flow (Figure 2.7). These approaches have the advantage that an excessive amount of limestone is in contact with the acid water. Losses of limestone particles can still be recovered by a screening or sedimentation device downstream of the limestone bed. A disadvantage of this approach is that the vertical reactor and the channel blocks due to the formation of reaction products such as gypsum or ferric hydroxide on the limestone particles.

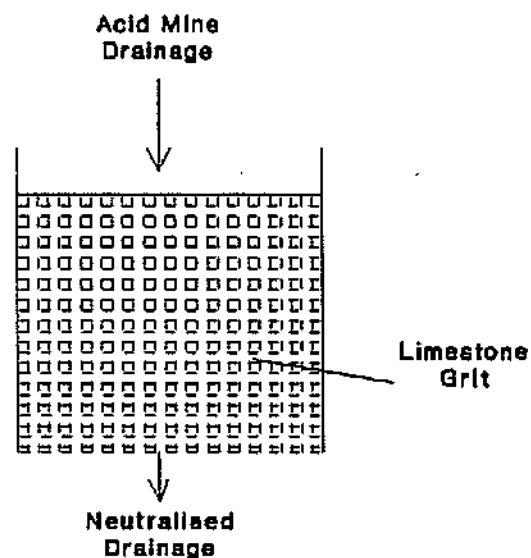


Figure 2.6 : Stationary limestone grit reactor with vertical fluid flow.



Figure 2.7 : Stationary limestone grit reactor with horizontal fluid flow.

Stationary aerated limestone grit reactor.

The purpose of stationary aerated grit reactors (Figure 2.8) is to treat ferrous containing acid water. The reactivity of the limestone bed in these aerated stationary beds fell appreciably after one or two per cent of the limestone has been consumed under continuous flow conditions, but it was possible to restore the activity by upflow fluid expansion of the beds (Figure 2.9). However, after seven per cent of the limestone had been consumed, a hard, dark-coloured scale formed on the limestone particles and the activity could no longer be restored by upflow expansion.

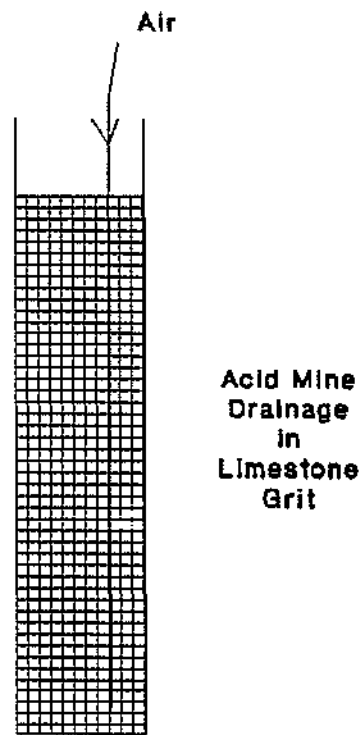


Figure 2.8 : Stationary aerated limestone grit reactor.

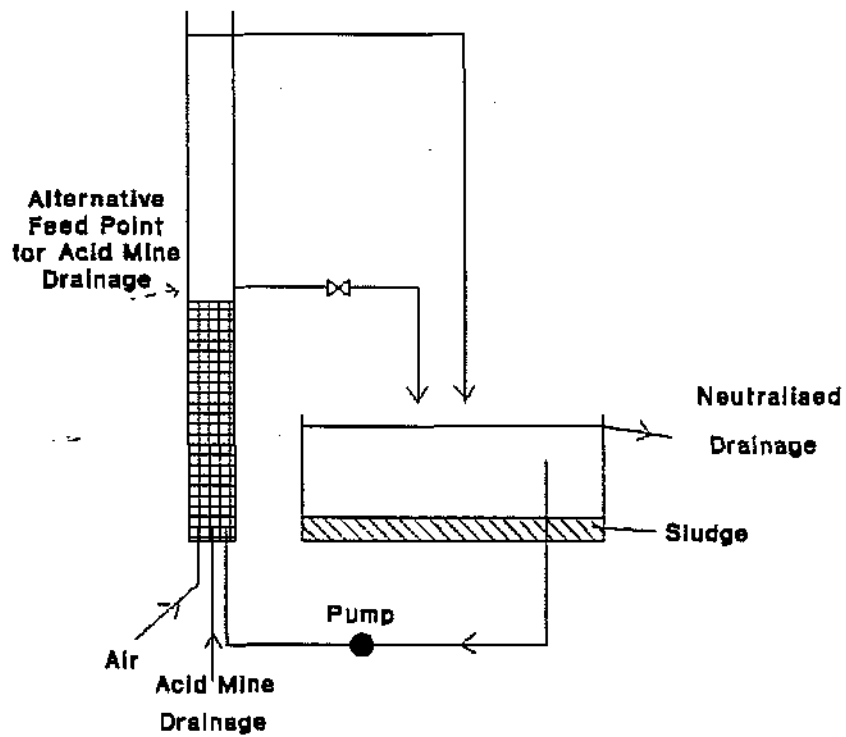


Figure 2.9 : Stationary aerated limestone grit reactor with intermittent wash by upflow expansion.

Rotating drum

The U S Bureau of Mines investigated the use of the tube mill for limestone neutralisation (Deul and Mihok, 1967; Mihok, *et al.*, 1968; Mihok, 1970). In this process, 3 inch pieces of limestone were fed, together with acid mine water, to a rotating tube mill. The drum had a diameter of 1 m, a length of 8 m, and was rotated at a speed of 25 rpm. The rotation has the effect that the limestone is milled to a powder of less than 400 mesh. Acid water was fed to the drum at a rate of 2,3 Ml/d. The retention time of the water in the tube is calculated to be 0,25 min ($2300 \text{ kl/d} \div (24 \text{ h/d} \times 60 \text{ min/h} \times \pi \times (0,5 \text{ m})^2 \times 8 \text{ m})$). The chemical composition of the water that was treated is shown in Table 2.1. A schematic diagram of a rotating drum reactor is shown in Figure 2.10.

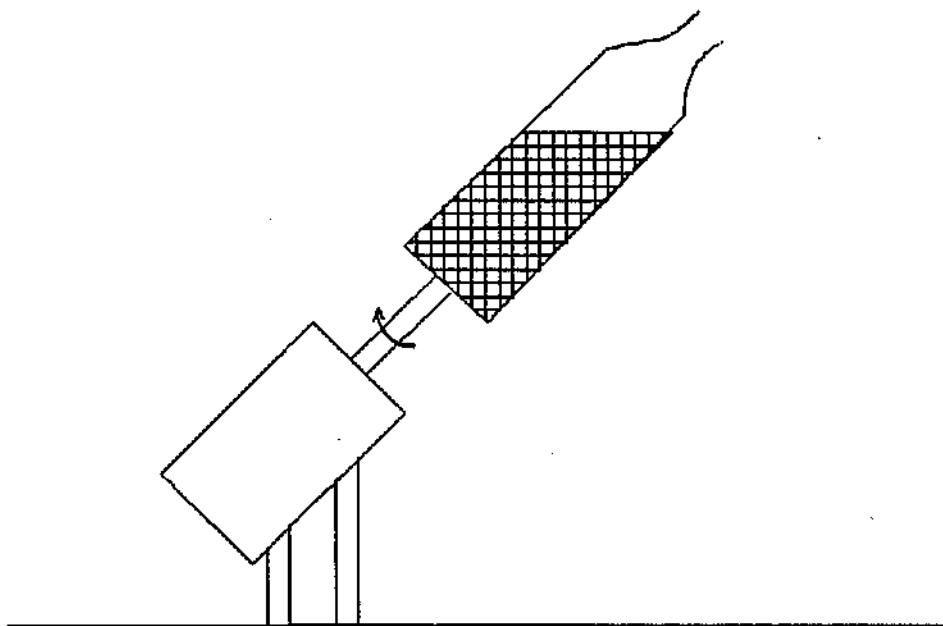


Figure 2.10: Schematic diagram of a rotating drum reactor.

The pH of the water after treatment was 7,4. The process is not yet implemented. One disadvantage of the process is high losses of limestone (about 40%).

At the Rochester and Pittsburgh Coal Co.'s Lucerne 3A mine (Coal Age, 1969), acid mine water containing iron was continuously treated in a revolving drum charged with limestone chips. The treated water was fully neutralised and all iron was removed. A drawback of the above systems is that CaCO_3 is used inefficiently - a large portion being washed out with the treated effluent stream.

Table 2.1 : Chemical quality of acid water fed to the rotating drum.

Parameter	Concentration (mg/l)
Acidity	1700
Iron(II)	36
Iron(III)	324
pH	2,8

Limestone-Lime treatment

Wilmoth (1974) compared in parallel studies the cost advantage associated with the use of limestone-lime treatment versus lime in a completely mixed reactor. As limestone is not effective for the treatment of iron(II)-rich effluents, he proposed a two-stage process where limestone is used in the first stage and lime in the second stage. First, the AMD is treated with limestone to a pH of 4,0 to 4,5 to take advantage of the pH range when limestone is most effective. The water then passes through a second reactor where lime is applied to raise the pH range to the desired level. Benefits associated with this approach are the following:

- * Iron(II) can be removed.
- * Sludge of high density is produced which is characteristic of the limestone process.
- * Cost is reduced by 25%.

Although this two-stage process is more cost effective than the conventional lime neutralisation process, it was not adopted in general by the mining industry because it is more complex (two stages instead of one).

CONCLUSIONS

1. A limestone with a high CaCO_3 content and a low magnesium and other impurities content is best suited for treating AMD. Its selection for full-scale application should be based on the chemical composition, cost and laboratory test using the actual limestone and acid water.
2. For pulverized limestone systems, the smaller the limestone particle size, the faster is the reaction and the greater is the utilization of the limestone. An excess of 1,4 to 3 times the stoichiometric amount of limestone is required.
3. All the limestone processes described are applicable to the low-iron acid mine drainage situation.

-
4. Rotating drums and pulverized limestone systems are applicable to ferric-iron rich acid mine drainage water and for ferrous-iron concentrations up to 100 mg/l.
 5. The limestone-lime treatment system is able to deal with iron free, ferric-rich as well as ferrous-rich acid water..

CHAPTER 3. KINETIC STUDIES

INTRODUCTION

In Chapter 2 (Literature overview), it is shown that acid water can be treated with limestone when it is in the pulverised form. To pulverise limestone, however, adds cost to the process. Therefore, the objective of this study was to develop a process where ungraded commercially available limestone can be used for the neutralisation of acid water. A fluidised-bed process was selected for this purpose. It was the aim of this study to investigate the following specific aspects of CaCO_3 neutralisation:

- * Examining the kinetics of CaCO_3 neutralisation
- * Influence of aeration.
- * Concomitant sulphate and heavy metal removal.
- * Behaviour of magnesium present in dolomitic limestone and the acid mine water.
- * Effect of contact time on the efficiency of neutralisation.
- * Influence of various metals on the efficiency of limestone neutralisation.
- * By-product recovery.
- * Reactor design.
- * Quality of water before and after neutralisation.

MATERIALS AND METHODS

Investigation of the above parameters was carried out using beaker, batch and semi-continuous fluidised bed tests. The following acid waters were used during the study:

- * Synthetic laboratory prepared acid water. The acid solutions were prepared from sulphuric acid, ferrous sulphate, ferric sulphate and aluminium sulphate, hydrogen peroxide and tap water.
- * Witbank water obtained from sampling point no 4 (see Table 3.1 for analysis and Figure 3.1 for location on a map). This sample represents a mixture of acid mine water and possible seepage from an industrial plant.
- * Witbank water obtained from sampling point no 12 (see Table 3.1 for analysis and Figure 3.1 for location on a map). This sample represents mainly acid mine water.

Raw limestone obtained from PPC Lime (Lime Acres near Postmasburg) was used in the neutralisation studies. Table 3.2 shows the chemical composition of the limestone. The limestone was screened and graded into various size fractions; the specific particle sizes used in the tests were: <0,150 mm; 0,150 - 0,300 mm; 0,300 - 0,425 mm; 0,425 - 0,600 mm; 0,600 - 1,400 mm; 1,400 - 1,700 mm and > 1,700 mm.

The feasibility of the process was examined using the laboratory-scale equipment illustrated in Figures 3.2 and 3.3 The former was used for particle size studies and the latter for all the other studies.

The plant illustrated in Figure 3.2 consisted of a vertical perspex tube 35 mm in diameter

and 900 mm in length. The reactor was packed with 100 g of PPC limestone. The bed was expanded from its static height of 110 mm to a height of 140 mm at which point the bed was fluidised. The nominal upflow velocity at fluidisation was 33 m/h. The acid stream was introduced at 165 ml/min.

The plant illustrated in Figure 3.3 consisted of a two-stage vertical perspex reactor to fluidise the calcium carbonate particles and a settler to separate the produced iron hydroxide and calcium sulphate sludges from the water. The tube has a bottom section with a diameter of 32 mm and a length of 135 mm and a top section with a diameter of 69 mm and a length of 392 mm. The empty volume of the fluidised bed reactor and settler were, respectively, 1,58 and 10,02 l. The water in the system was recycled with a pneumatic pump at a rate of 2,75 l/min to fluidise the calcium carbonate particles. The upflow velocities of the water through the bottom and top part of the tube were 213 and 46 m/h, respectively. The bed was expanded from its static height of 100 mm to a height of 120 mm at which point the bed was fluidised. For the continuous studies, acid water was fed to the system at a rate of 100 ml/min. The hydraulic retention time of the water in the fluidised-bed reactor was 16,27 min. and in the settler 104 min. In most experiments 600 g of limestone was put in the fluidised-bed reactor. In its fluidised state the limestone particles filled a volume of 0,45 l. From the volume filled by the limestone particles and the total volume of water in the system, it is calculated that the limestone was in contact with the acid water for 4,5 min.

Table 3.1 Chemical composition of acid mine water samples.

Parameter	Water sample 4 (mine/industrial)	Water sample 12 (mine)
Acidity (as CaCO ₃)	1 813	2 700
Sulphate (as SO ₄)	7 250	2 639
Calcium (as CaCO ₃)	677	198
Magnesium (as CaCO ₃)	1 021	278
Sodium (as Na)	1 592	115
Potassium (as K)	16	3
Iron(II) (as Fe)	408	56
Iron(III) (as Fe)	23	179
Aluminium (as Al)	127	238
Manganese (as Mn)	17	15
Copper (as Cu)	0,07	0,10
Lead (as Pb)	0,10	0,00
Zinc (as Zn)	1,60	0,90
Nickel (as Ni)	1,00	0,70
Chromium (as Cr)	0,06	0,07
Arsenic (as As)	0,03	0,00
Vanadium (as V)	2,12	0,22
Boron (as B)	3,00	0,60
pH	3,1	2,8

Table 3.2 : Chemical composition of limestone.

Compound	Content (%)
CaCO ₃	96,0
MgCO ₃	1,5
SiO ₂	1,0
R ₂ O ₃	1,5
Moisture	0,7

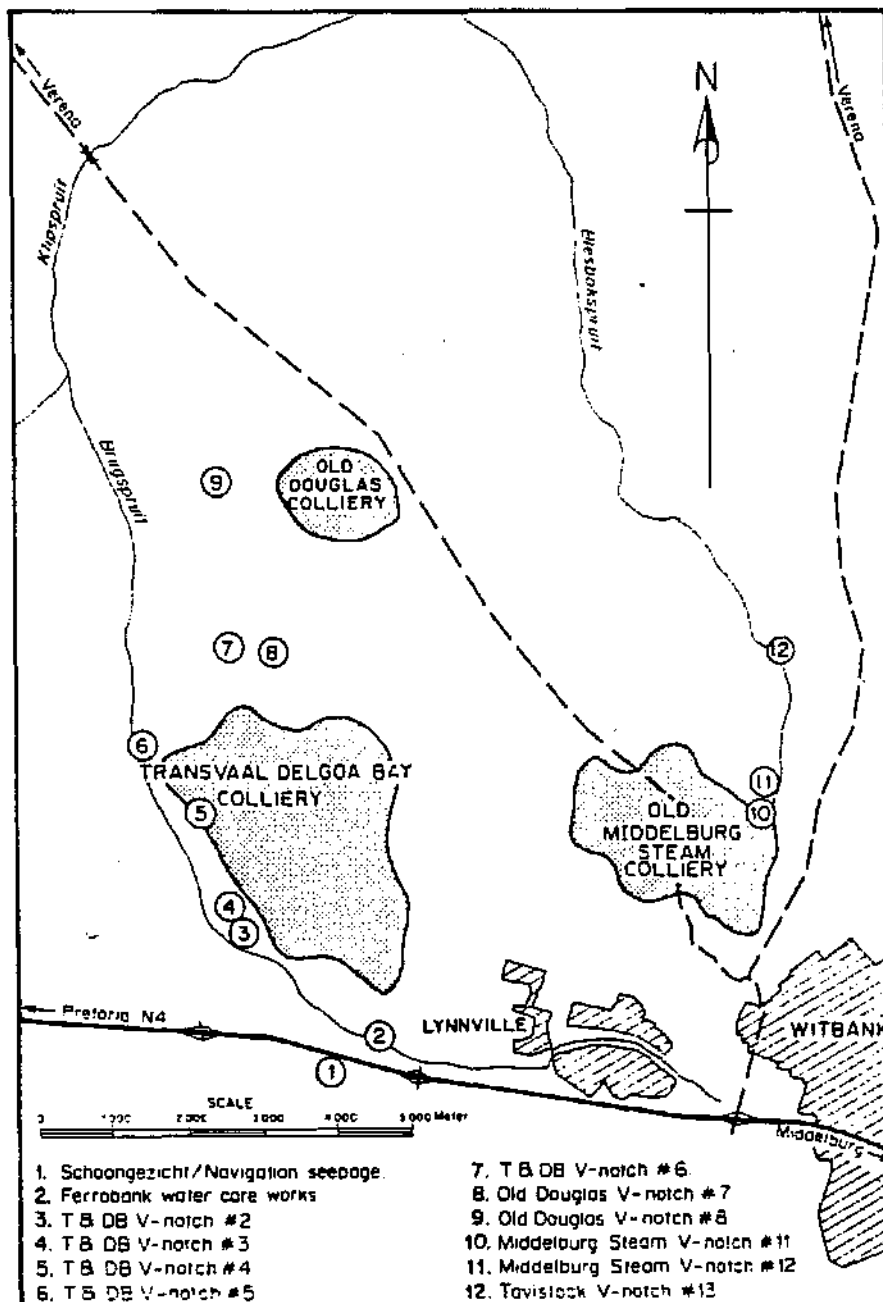


Figure 3.1 : Location of sampling points of AMD in the Klipspruit valey near Witbank.

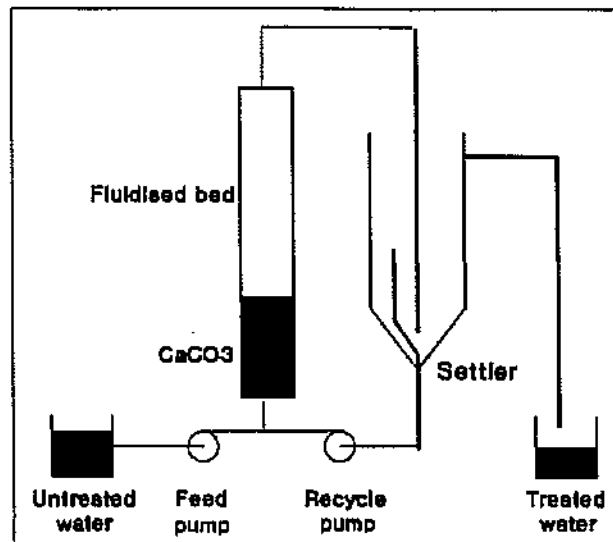


Figure 3.2 : Flow diagram of uniform fluidised-bed reactor and settler.

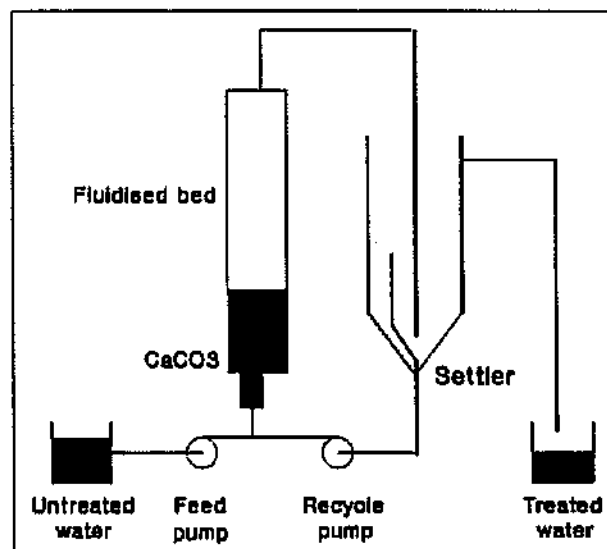


Figure 3.3 : Flow-diagram of two-stage fluidised-bed reactor and settler.

Beaker Tests

Beaker tests were employed to study the influence of particle size on the kinetics of acid water neutralisation with limestone. The following procedure was followed:

- * 500 ml of acid solution was put in glass beakers.
- * The contents of the beakers were stirred at a speed sufficient to keep solid particles in suspension.

* Limestone samples were added to the beakers.

Samples were taken regularly and analyzed for pH, calcium, magnesium, iron(II), iron(III) and acidity (APHA, 1985).

Batch Tests

Batch tests were employed to study the effect of contact time, type of cation, and effect of iron(II) oxidation on the neutralisation of acid water with limestone. The behaviour of the various parameters, namely pH, sulphate, calcium, acidity and the metals (iron(II), iron(III) or aluminium(III)) were also studied. After the addition of the acid solution to the fluidised bed reactor and settler, limestone of specific particle size range was added to the fluidised bed reactor. Samples were taken regularly and analyzed for pH, calcium, magnesium, iron(II), iron(III) and acidity (APHA, 1985).

Semi-continuous Tests

Semi-continuous tests were carried out to determine the effects of particle size and contact time on the efficiency of limestone neutralisation. The feasibility of the process on a semi-continuous basis was examined by feeding acid water to the system. The treated effluent was sampled at regular intervals and analyzed for acidity, calcium, magnesium and Ph. The dry mass and carbonate content of the residual solids (after treatment) were determined to execute a carbonate balance on the system.

Analytical

The limestone was analyzed for its calcium, magnesium and alkalinity content by dissolving it in a stoichiometrically excessive amount of hydrochloric acid. Calcium and magnesium were determined with EDTA, while the alkalinity content was determined by titrating the excess of hydrochloric acid with sodium hydroxide.

RESULTS AND DISCUSSION

The various aspects that influence the kinetics of calcium carbonate neutralisation will be discussed in the following paragraphs.

Neutralisation kinetics

Both calcium concentration and particle size have a major influence on rate of dissolution.

CaCO₃ concentration

Figures 3.4a and 3.4b show the rate at which waters 12 and 4 from the Witbank area were neutralised for various CaCO₃ contact concentrations with a particle size of <0,150 mm. These results indicate that the higher the CaCO₃ contact concentration, the more efficient the neutralisation process. This observation, and the fact that CaCO₃ is almost insoluble for pH values greater than 7,5, makes the fluidised-bed reactor ideal for CaCO₃ neutralisation. A higher CaCO₃ concentration in contact with the acid solution will result in a high reaction rate, but excessive CaCO₃ will not dissolve due to its low solubility at high pH values.

This section proves that the rate of neutralisation is influenced by the calcium carbonate concentration. However, it also leads to the following question:

- * Is the rate of limestone neutralisation a function of its concentration, or rather a function of its surface area? This issue will be discussed under 'Particle size'.
- * Is the rate of limestone neutralisation influenced by metals present in mine water, e.g. iron? This question arises from the fact that Figure 3.4 shows that the rate of neutralisation of mine water takes place in two stages, a fast first phase and a slow second phase. The first phase is possibly associated with the neutralisation of pure H₂SO₄ solutions, while the slow second phase can possibly be explained by the iron content of the water (see under "Kinetic equation"). Both waters 4 and 12 contain iron. Water 4 contains 511 mg/l iron (of which 408 mg/l is in the Fe(II) form), while water 12 contains 235 mg/l iron (of which 179 mg/l is in the Fe(II) form). As Fe(II) and Fe(III) may have different influences on the neutralisation rate of CaCO₃, it is necessary to investigate the influence of each of the iron species (see 'Influence of iron').

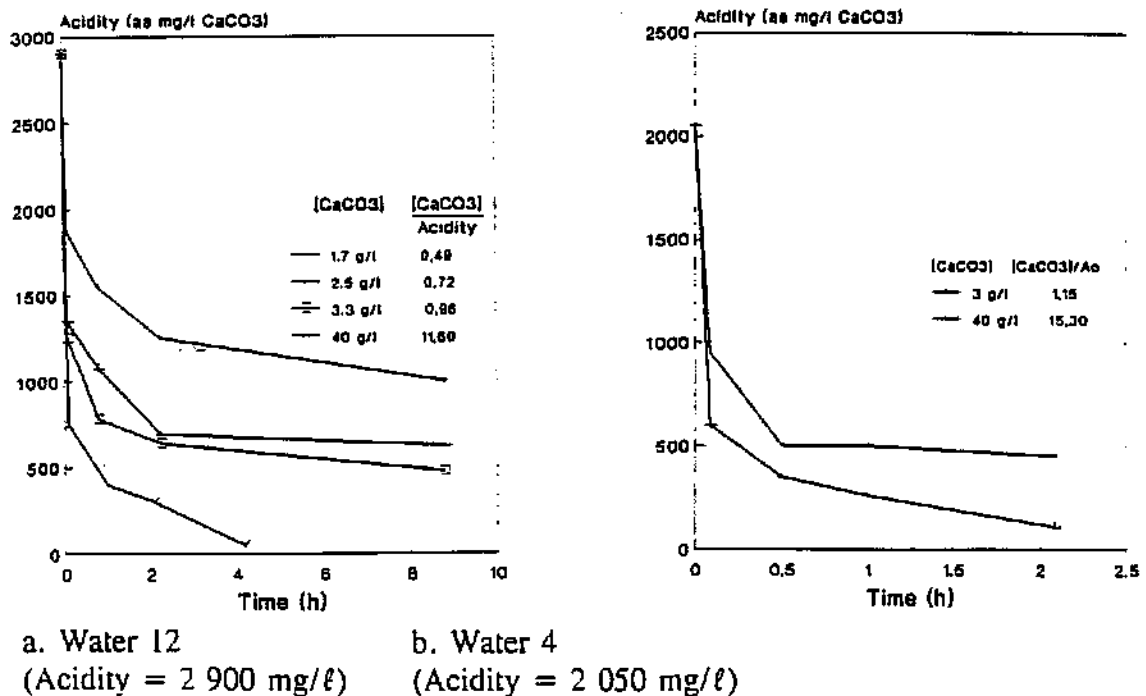


Figure 3.4 : Rate at which acid mine water is neutralised in the presence of various CaCO₃ concentrations (Particle size < 0,015 mm).

Particle size.

Figure 3.5 shows from beaker studies that the neutralisation rate decreases with increasing particle size (<0,150 mm; 0,300-0,425 mm; 1,000-1,400 mm; 1,400-1,700 mm), i.e. the reaction rate is mass transfer controlled for a pure H₂SO₄ solution. The acidity of the untreated water was 7 550 mg/l (as CaCO₃) while a limestone dosage of 6 g/l was applied.

Fluidised-bed reactor studies were also carried out using limestone with the same particle size as that used during batch studies. At the specified acid water feed rate, the nominal retention time of the water in the bed was 0,51 minutes. Although this is apparently a short retention time, the high concentration of CaCO₃ particles in the bed (approximately 190 times in excess of the acid concentration) provides sufficiently high surface area for a faster neutralisation rate. The results of the semi-continuous fluidised bed neutralisation tests appear in Figures 3.6 to 3.8. Lower pH values resulted for greater particle sizes (<0,150 mm, pH 5,9; 0,300 mm - 0,425 mm, pH 5,3; 1,000 mm - 1,400 mm, pH 4,1; 1,400 mm - 1,700 mm, pH 2,1) (Figure 3.6). Similarly, the greater the particle size, the greater was the residual acidity value (<0,150 mm, 390 mg/l (as CaCO₃); 0,300 mm - 0,425 mm, 400 mg/l (as CaCO₃), 1,000 mm - 1,400 mm 500 mg/l (as CaCO₃); 1,400 mm - 1,700 mm, 1700 mg/l (as CaCO₃)) (Figure 3.7). This confirms that the rate of neutralisation is influenced by the surface area. The short period which the water was in contact with the fluidised bed limited this mass transfer. Maximum acidity removal was achieved during the initial phase of the semi-continuous studies. During that period, the [CaCO₃]/Acidity ratio was at its maximum (about 190). The [CaCO₃]/Acidity ratio decreased with H₂SO₄ feed, and the residual acidity values of the treated water increased. In full-scale applications, the [CaCO₃]/Acidity ratio would be kept constant by feeding limestone continuously to the bed of the reactor. A constant low acidity value would be maintained in the effluent.

An important economic consideration is the degree of utilisation of the calcium carbonate in the limestone. Figure 3.8 shows that the CaCO₃ content of the limestone in the fluidised bed was almost completely utilised for particle sizes greater than 0,300 mm. For the particle size 0,300 mm - 0,425 mm, 85,9g of acid (as CaCO₃) was removed by 100g of limestone, while 83,3% acid was removed with a particle size of 1,000 mm - 1,400 mm and 80,3% with a particle size of 1,400 mm - 1,700 mm. The average of these figures (83,1%) compares well with the average total amount of alkalinity in the limestone (88%) as shown in Table 3.3. It can be argued that the total carbonate content in the limestone will be completely utilised in full-scale applications, as a much longer contact time will be possible (15 min.) than in the laboratory studies.

For a particle size of <0,150 mm, only 67 g CaCO₃ of the available 85 g CaCO₃ in the limestone was utilised (79% efficiency). This is due to partial wash out of very small particles prior to complete reaction. Therefore powder limestone should not be dosed to acid water when using a fluidised bed reactor. If powder dosing is required, a completely mixed reactor should be employed. As a result of the large surface area of a powder, the reaction time compared to the CaCO₃ with larger particle sizes, would be short.

Figure 3.8 also illustrates that larger limestone particle sizes required more acid to be passed through the bed to exhaust it. This observation is to be expected as the residual pH and acidity values as described above indicate that completion of the neutralisation reaction is influenced by the surface area of the limestone and the contact time between the limestone and the acid solution.

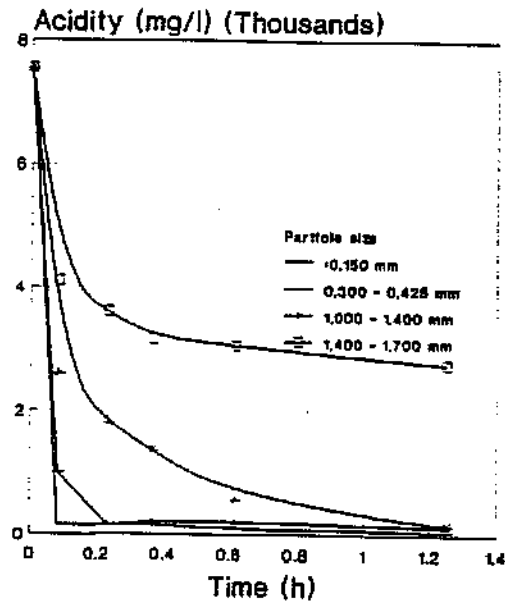


Figure 3.5 : Neutralisation of a $7,55\text{ g/l H}_2\text{SO}_4$ solution with four different sizes of CaCO_3 . $[\text{CaCO}_3] = 6,0\text{ g/l}$

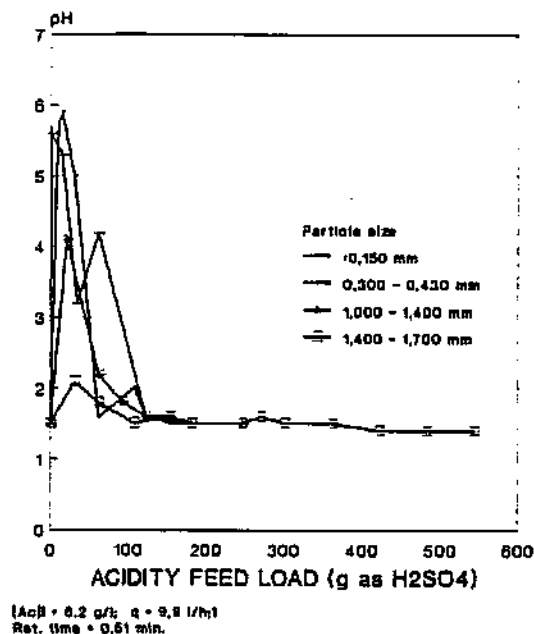


Figure 3.6 : Influence of particle size on the pH of CaCO_3 treated water. $[\text{Acidity}]_0 = 7,55\text{ g/l}$; Ret. time = 0,51 min.; Mass of $\text{CaCO}_3 = 100\text{ g}$.

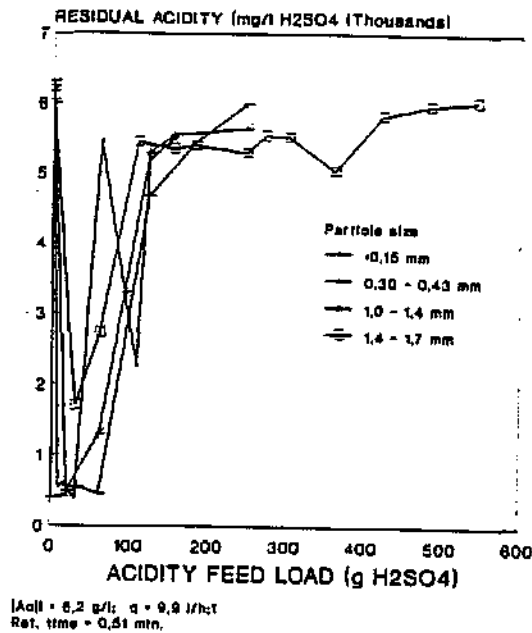


Figure 3.7 : Influence of particle size on the residual acidity of CaCO₃ treated water.
[Acidity]₀ = 7,55 g/l; Ret. time = 0,51 min.

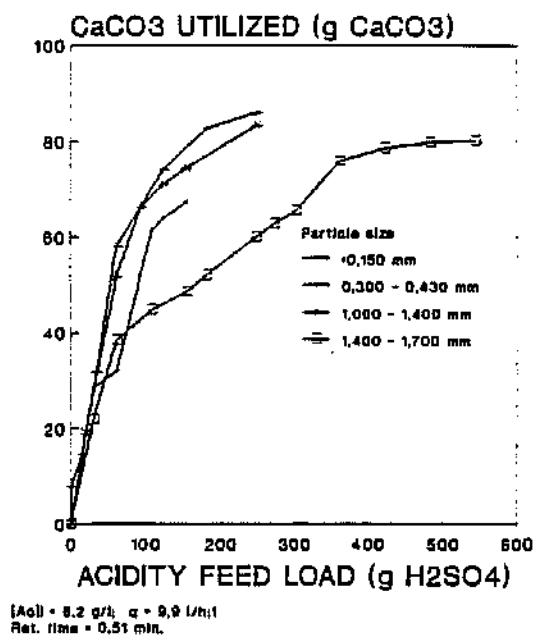


Figure 3.8 : Utilisation of CaCO₃ of various particle size during neutralisation of acid water.

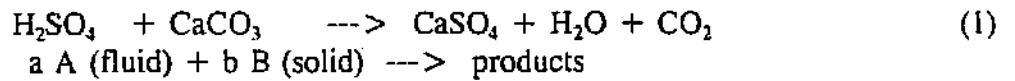
[Acidity]₀ = 6,2 g/l;
Ret. time = 0,51 min.
Mass of CaCO₃ = 100 g

Table 3.3 : Utilisation of carbonate in limestone samples with different particle sizes.

Limestone Particle size (mm)	Carbonate utilised (% CaCO ₃)	Carbonate not utilised (% CaCO ₃)	Total Carbonate (% CaCO ₃)
< 0,150	67,3	3,8	71,1
0,300 - 0,430	85,9*	0,9*	86,8*
1,000 - 1,400	83,3*	6,8*	90,1*
1,400 - 1,700	80,3*	7,3*	97,3*
Average of (*)	83,1	5,0	88,1

Kinetic equation

The reaction between sulphuric acid and CaCO₃ is a solid-fluid reaction of the form:



It is expected that the rate of the reaction is diffusion controlled, i.e. based on surface area

$$-r_A = k_s C_{As} \quad (2)$$

where k_s - reaction rate constant based on surface area and C_{As} - H₂SO₄ concentration at the CaCO₃ surface.

The rate of mass transfer of H₂SO₄ (A) through the fluid film by diffusion to the surface of the CaCO₃ particles is:

$$-r_d = k_m (C_{Ab} - C_{As}) \quad (3)$$

where C_{Ab} - concentration of H₂SO₄ in the bulk liquid and k_m - mass transfer coefficient.

Under steady state $-r_A = -r_d$, i.e.

$$C_{As} = k_m / (k_m + k_s) C_{Ab} \quad (4)$$

From the above three expressions

$$-r_A = -r_d = -\bar{r} = k_s k_m / (k_s + k_m) C_{Ab} \quad (5)$$

If mass transfer is controlling, $k_s \gg k_m$, hence

$$-\bar{r} = k_m C_{Ab}$$

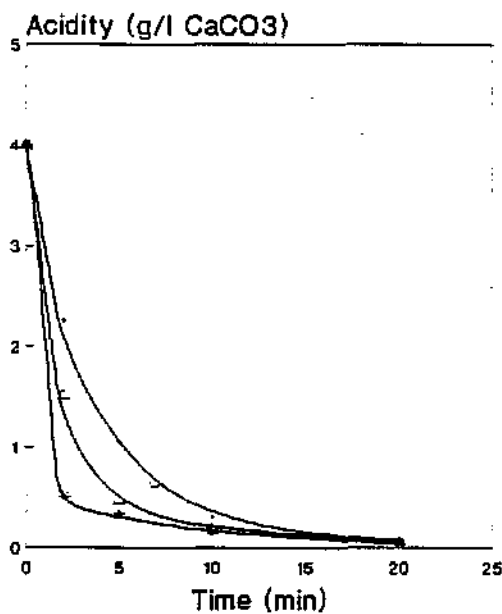
$$\text{or } -\bar{r} = K S C_{Ab} \quad (6)$$

where S - total available surface area of the CaCO_3 and
 K - rate constant per unit surface area.

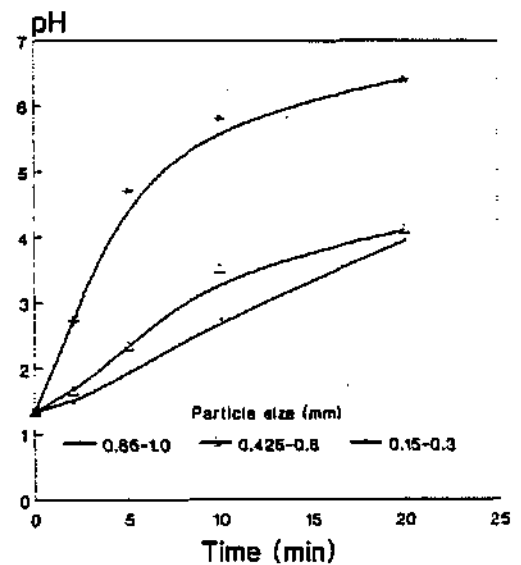
In order to show that the proposed rate equation is correct, it is necessary to prove that the rate equation is a function of the following two parameters:

- * H_2SO_4 concentration, to establish whether the rate is indeed first order and
- * CaCO_3 particle size, to establish whether mass transfer is controlling.

Figures 3.9a and 3.9b show the results of beaker tests when synthetic acid water is neutralised with limestone samples of different particle size. Firstly, by examining the results for any one CaCO_3 particle size, it is apparent that the rate of neutralisation decreases with decreasing acidity, i.e. acid concentration. Manipulation of this data showed that there is in fact a linear relationship between neutralisation rate and acid concentration, i.e. the reaction is first order with respect to the acid concentration.



a. Acidity versus time



b. pH versus time

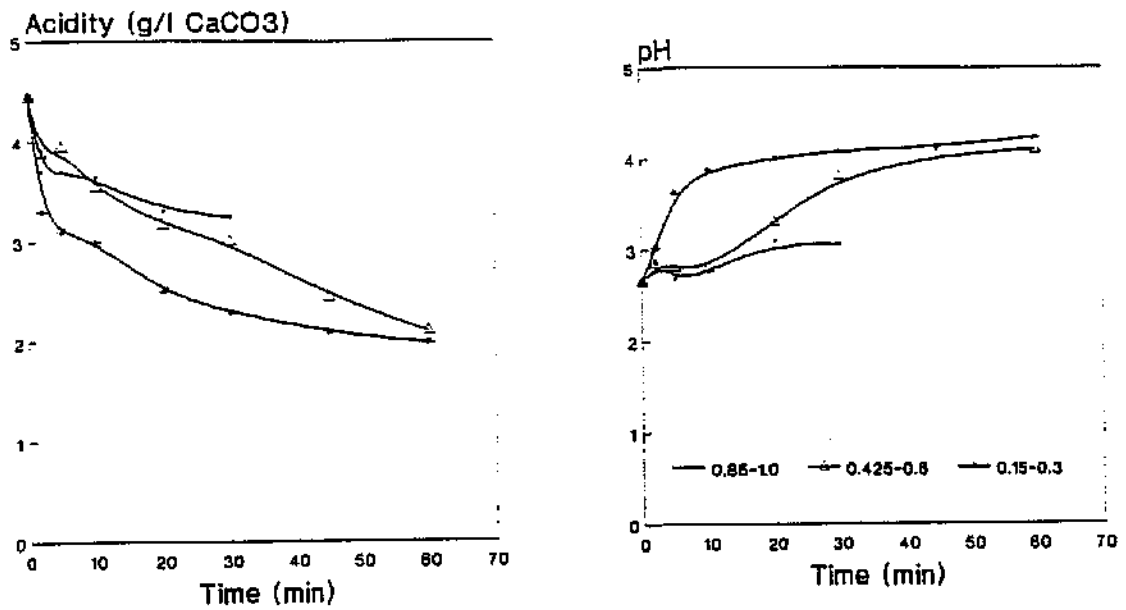
Figure 3.9 : Neutralisation of a 4 g/l H_2SO_4 solution with three different sizes of CaCO_3 . (Note that the rate of neutralisation decreases with decreasing acidity and increasing particle size.)

Secondly, the overall neutralisation rate increases with decreasing particle size, i.e. the reaction is mass transfer controlled. Knowing the mass, density and particle size of the CaCO_3 used in each experiment, the total available surface area could be calculated for each case. From a plot of rate/unit surface area versus acid concentration (see equation (6)), the rate constant K ($\text{min}^{-1} \cdot \text{cm}^{-2}$) was obtained for each particle size. All three particle sizes yielded approximately the same value (see Table 3.4) - an average of $2,45 \times 10^{-3} \text{ min}^{-1} \cdot \text{cm}^{-2}$ - confirming that K is independent of surface area and proving that the form of equation (6) is correct. Equation 6 represents a first order reaction which means that the rate of neutralisation decreases with decreasing acidity, i.e. acid concentration. Hence, the use of a fluidised bed for neutralisation is favoured. The average rate of a first order reaction is faster in a plug flow reactor (the fluidised bed is semi-plug flow) (Levenspiel, 1972) and allows the acid water to come into contact with large excesses (and therefore large surface areas) of CaCO_3 .

Table 3.4 K values for CaCO_3 neutralisation (H_2SO_4 solution)

Particle size	K ($\text{min}^{-1} \cdot \text{cm}^{-2}$)
0,850 - 1,000	$2,29 \times 10^{-3}$
0,425 - 0,600	$2,40 \times 10^{-3}$
0,150 - 0,300	$2,45 \times 10^{-3}$
Average	$2,45 \times 10^{-3}$

Having established the kinetics of CaCO_3 neutralisation of a pure H_2SO_4 solution, attention was turned to the iron-containing acid mine water. The results of these beaker tests appear in Figures 3.10a and 3.10b. Their general form is the same as for the synthetic acid water: the neutralisation rate decreases with decreasing acidity and increasing CaCO_3 particle size. However, the relationship between the rate and acidity is not linear - the rate becomes severely retarded as time progresses. For example, for the CaCO_3 size range 0,85 - 1,00 mm, virtually 100% of the acidity is neutralised within 20 minutes in the case of the synthetic acid water (see Figure 3.9) compared to only 25% for the acid mine water (Figure 3.10). As for the synthetic acid water, an average rate constant K ($\text{min}^{-1} \cdot \text{cm}^{-2}$) was calculated from the three CaCO_3 particle sizes. Unlike K for the H_2SO_4 solution (which remained constant), this K varies with time as shown by Figure 3.11. It starts off close to the value for the pure H_2SO_4 solution and decreases to about 0,5 after 20 minutes. An explanation for this phenomenon is that as time progresses, an increasingly thick layer of $\text{Fe}(\text{OH})_3$ precipitates onto the CaCO_3 particles creating a large diffusional resistance. Such a layer was, in fact, observed to form on the particles in the tests. The rate constant K , which incorporates a mass transfer coefficient, is therefore decreased. It is interesting to note that in the case of the synthetic acid water (no iron present), K did not vary with reaction time which seems to indicate that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) does not form an inhibiting layer on the limestone particles.



a. Acidity versus time

b. pH versus time

Figure 3.10 : Neutralisation of acid mine water (4,44 g/l as CaCO_3) with three different sizes of CaCO_3 .

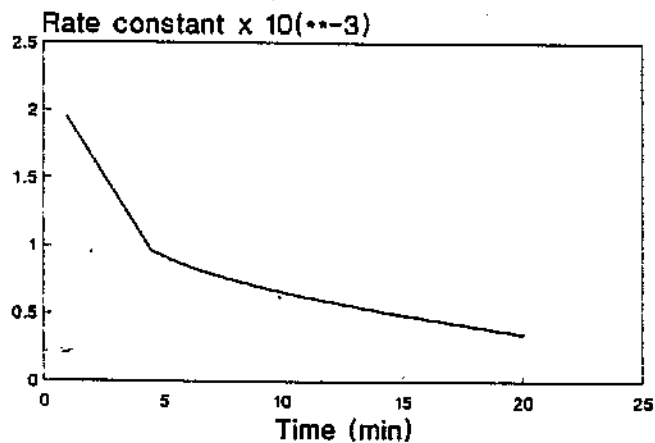
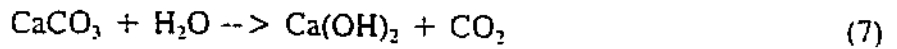


Figure 3.11 : The variation of K with time for mine water.

Aeration

Ford (1972) indicated that neutralisation of acidic effluents with CaCO_3 is more efficient when aeration is applied. The reason for this is that the equilibrium position is shifted in such a way that more CaCO_3 dissolves because of the removal of dissolved CO_2 .



To verify this finding, two neutralisation tests were performed on water 12 with and without aeration respectively. Analysis of results from these tests, as shown in Figure 3.12, indicates that the rate of neutralisation is only marginally increased by aeration.

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystallization.

Figures 3.13a and 3.13b show the rate at which acidity and sulphate are removed by limestone in the presence of various amounts of gypsum (0, 1 and 10 g/l). The gypsum concentration was found to have little influence on the rate at which acidity is removed, but a major influence on the rate of sulphate removal. The higher the gypsum concentration, the faster is the rate of sulphate crystallisation. This agrees with the finding of Maree *et al.* (1992) who showed that rate of crystallisation is influenced by the concentration of gypsum seed crystals as indicated by the following equation:

$$d[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]/dt = k[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}](S)[C - C_0]^2 \quad (8)$$

where $d[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]/dt$ - rate of crystallization; k - reaction rate constant; $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}](S)$ - surface area of seed crystals; C_0 - initial concentration of calcium sulphate in solution, and C - saturated concentration of calcium sulphate in solution.

The fact that the rate of acidity removal was not influenced by the gypsum concentration indicates that the rate of neutralisation during the slow phase (as discussed under 'CaCO₃ neutralisation') is not influenced by the saturation level of CaSO₄·2H₂O, but rather by a factor such as iron in the water.

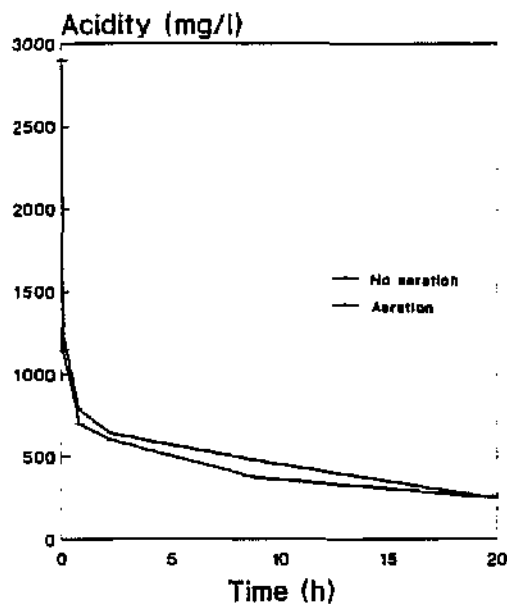
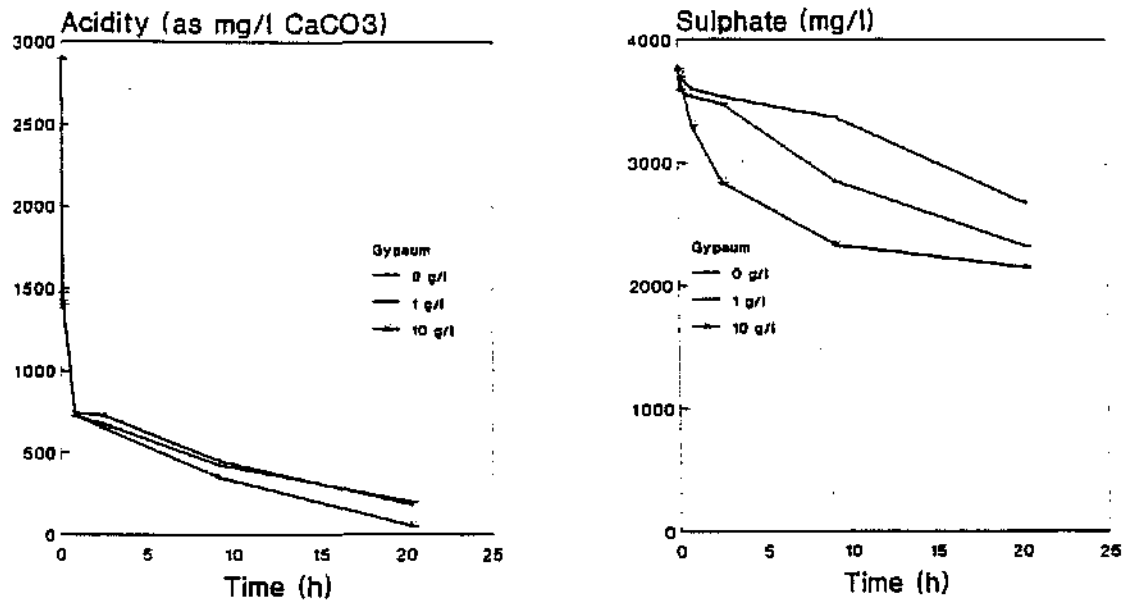


Figure 3.12 : Influence of aeration on the neutralisation rate of an acidic effluent (water 12) with CaCO₃. Acidity = 2 900 mg/l; [CaCO₃] = 3,3 g/l; Particle size < 0,15 mm.



a. Neutralisation

b. Sulphate removal

Figure 3.13 : Neutralisation and sulphate removal during CaCO_3 treatment of water 12 in the presence of gypsum seed crystals.

Acidity = 2 900 mg/l; $[\text{CaCO}_3] = 3,3 \text{ g/l}$; Particle size $< 0,15 \text{ mm}$

Magnesium behaviour

The limestone used contained 85,6% Ca (as CaCO_3), 8,3% Mg (as CaCO_3) and had a particle size of $< 0,150 \text{ mm}$. A question arose about the manner in which the calcium and magnesium carbonate components of limestone dissolves during treatment of acid water. A study was initiated in which acid mine water (no 4) (with an acidity value of 1,9 g/l as CaCO_3) was neutralised with 3 and 40 g/l limestone respectively. Upon completion of neutralisation (3 hours), 45 g/l gypsum was added to enhance gypsum crystallization. The ratio in which Mg and Ca dissolved, differed for different limestone dosages. A limestone dosage of 3 g/l showed a ratio of 17:100 (193:1128) for Mg:Ca dissolved during neutralisation of the acid water. A dosage of 40 g/l showed a ratio of 30:100 (473:1570) (Table 3.5). The ratio of Mg:Ca in the limestone dosed is 9:100, indicating that the MgCO_3 fraction in the limestone dissolves faster in acid water than the CaCO_3 fraction. Obviously, a limestone dosage applied, which is smaller than the acidity of the water, will completely dissolve. The ratio of Mg:Ca dissolved, will be the same ratio as is found in the raw limestone.

Magnesium co-precipitates with calcium as a $\text{Ca}_x\text{Mg}_y\text{SO}_4_{x+y}$ complex if the neutralised water is oversaturated with respect to calcium sulphate. In the case of a 3 g/l limestone dosage, 84 mg/l magnesium precipitated together with 818 mg/l calcium, while in the case of 40 g/l limestone, 381 mg/l magnesium precipitated together with 1263 mg/l

calcium. Calculations show that the ratio of Mg:Ca that precipitated as a $\text{Ca}_x\text{Mg}_y\text{SO}_{4_{x+y}}$ complex amounts to 10:100 and 30:100 for 3 and 40 g/l limestone dosages respectively. A similar observation was made previously for co-precipitation of magnesium with calcium carbonate (Benjamin *et al.*, 1977).

Metal and fluoride removal

Iron(III) and aluminium(III) are removed efficiently during limestone neutralisation. At the pH of the treated water, (6 to 7,5), the solubility of these metals is very low. When water no 12 was treated with 3,3 g/l of <0,150 mm limestone (same reactions as reported in Figure 3.13), iron and aluminium were removed from 263 and 294 mg/l to 0,07 and 0,10 mg/l respectively. The fluoride concentration was decreased from 8 to 0,3 mg/l but no magnesium and manganese removal was obtained due to their high solubility in the above-mentioned pH range.

Effect of contact time

Figures 3.14 and 3.15 show the efficiency of CaCO_3 utilisation when acid water, containing 4 000 mg/l acidity and 582 mg/l Fe(III), is neutralised with limestone in the two-stage fluidised-bed reactor. An amount of 600 g of limestone with a particle size of 0,600 to 1,400 mm was put in contact with the acid water. The Y1-axis indicates the amount of CaCO_3 utilised in the process and the Y2-axis the time that the limestone particles were in contact with the acid water. The X-axis indicates the load of acid that was passed through the reactor. The amounts of CaCO_3 that were fed initially are indicated by the horizontal lines. In the case of Figure 3.14, 540 mg/l (as 100% CaCO_3) was fed, and in case of Figure 3.15, 180 mg/l. The CaCO_3 -content in the limestone was 90%. The contact time decreased with time (therefore also with the load at which acid was fed to the system) because of dissolution of the limestone in the acid water. The lines indicated by: square-signs represent the experimental relationship between limestone utilised and acidity neutralised (experimental lines), plus-signs represent the theoretical case should limestone have been utilised in stoichiometric quantities equal to the amount of acid that was fed to the system (theoretical lines) and triangle-signs show the total amount of CaCO_3 that was available at the beginning of the experiment. By comparing the experimental and theoretical lines of Figure 3.14 (where 600 g CaCO_3 was initially available to provide a contact time of 4,5 min.) with that of Figure 3.15 (where 200 g CaCO_3 was initially available to provide a contact time of 1,5 min.), the following observations were made:

- * It is clear that the longer the contact time, the closer the experimental and theoretical lines are to each other.
- * The closer the two lines are to one another, the bigger is the fraction of the acid content that is neutralised in the water.
- * In the case of Figure 3.14, where 600 g CaCO_3 was available, the experimental and theoretical lines are close to one another up to the point where 300 g acidity (as CaCO_3) was fed to the reactor, and 300 g of limestone still left in the reactor. The corresponding contact time at this point was 3 min. After this point, the experimental

and theoretical lines divert from one another due to the shortened contact period between the limestone particles and the acid water.

Table 3.5 : Magnesium behaviour during CaCO₃ neutralisation and gypsum crystallization.

	Raw	Low Limestone Dosage		High Limestone Dosage	
		Neutr.	Cryst.	Neutr.	Cryst.
Chemical added		Lime-stone	Gypsum	Lime-stone	Gypsum
Dosage		3 g/l	45 g/l	40 g/l	45 g/l
Sulphate	7 182	7 074	5 508	6 210	4 590
SO ₄ _{Neutr.} - SO ₄ _{Cryst.}			+1 566		+1 620
Calcium	790	1 918	1 100	2 359	1 096
Ca _{Raw} - Ca _{Neutr.}		-1 128		-1 570	
Ca _{Neutr.} - Ca _{Cryst.}			+ 818		+1 263
Magnesium	892	1 084	1 000	1 365	984
Mg _{Raw} - Mg _{Neutr.}		- 193		- 473	
Mg _{Neutr.} - Mg _{Cryst.}			84		381
Acidity	1 900	620	150	170	50
Ac _{Raw} - Ac _{Neutr.}		+1 280		+1 730	
Ac _{Raw} - Ac _{Cryst.}			+1 750		+1 850
pH	2,8	6,1	7,6	6,1	8,0
K _{SP}			631		524

$K_{SP} = [Ca^{2+}]/100x[SO_4^{2-}]/96$ where
 $[Ca^{2+}]$ - measured as mg/l CaCO₃ and $[SO_4^{2-}]$ - measured as mg/l SO₄.
 Acidity = 1 900 mg/l; [Gypsum] = 45 g/l; Particle size < 0,15 mm

In the case of Figure 3.15, where only 200 g of limestone was in contact with the acid water, the corresponding contact time was only 1,5 min and the experimental and theoretical lines divert from the beginning due to the short contact period of less than 3 min.

* One of the benefits of the fluidised-bed process is that limestone is completely utilised.

* One of the benefits of the fluidised-bed process is that limestone is completely utilised. This is shown by the results summarised in Table 3.6.

Table 3.6 : Efficiency of CaCO_3 -utilisation in the fluidised-bed reactor.

Parameter	Value
Contact time (min.)	4,5
CaCO_3 feed (g)	540
Acidity neutralised (g)	543
Utilisation (%)	101

A test, similar to the one that is reported in Figure 3.14 on Fe(III)-rich water, was carried out on a Fe(II)-rich water. The contact time between the limestone particles and the acid water was also 4,5 min (Figure 3.16). The acidity of the feed water was again 4 000 mg/l , while 600 g of limestone with a particle size of 0,600 to 1,400 mm, was used. It is noticed that the experimental and theoretical lines divert from the beginning of the experiment. This is because iron(II) remains in solution during neutralisation, and contributes to acidity and is also responsible for the relatively low pH of 4. The residual acidity content in Figure 3.16 varied around 2000 mg/l. This is much higher than observed with iron(III)-rich water, where the residual acidity value was less than 200 g/l. Acidity associated with iron(II)-rich water can be removed by oxidising iron(II) to iron(III) prior to neutralisation.

The above-mentioned results demonstrate the relationship between the contact period (between limestone particles and the acid water) required for complete utilisation of the limestone and the quality of the water. It indicates that in the case of Fe(III)-rich water, the required contact period is in the order of 3 minutes.

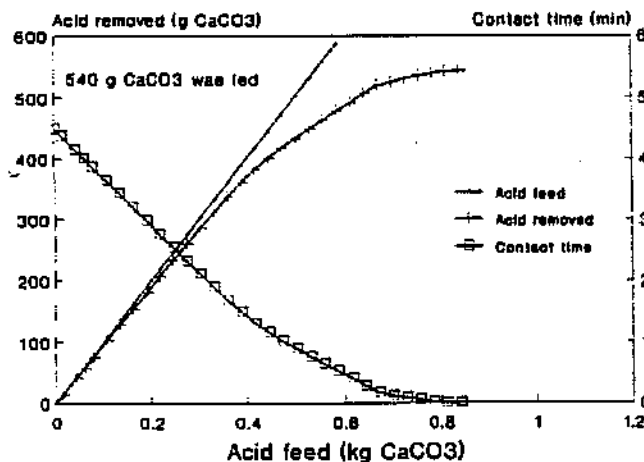


Figure 3.14 : Neutralisation of Fe(III)-rich water in a fluidised-bed reactor under batch conditions with a contact period of 4,5 min. Acidity = 4 g/l; Limestone = 600 g; Particle size = 0,6 -1,4 mm

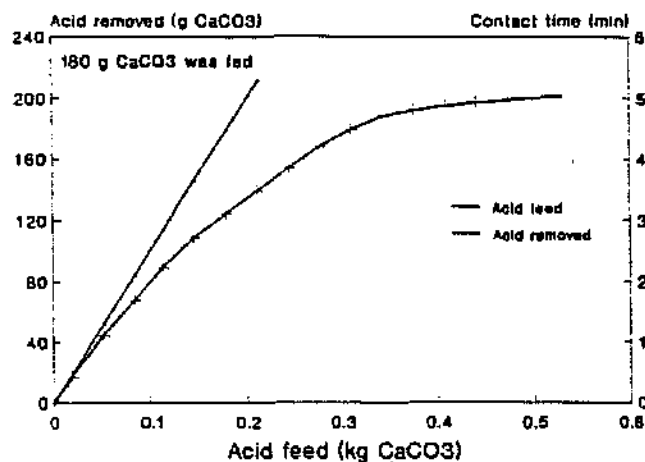


Figure 3.15 : Neutralisation of Fe(III)-rich water in a fluidised-bed reactor under batch conditions with a contact period of 1,5 min.
 Acidity = 4 g/l; Limestone = 200 g;
 Particle size = 0,6 -1,4 mm

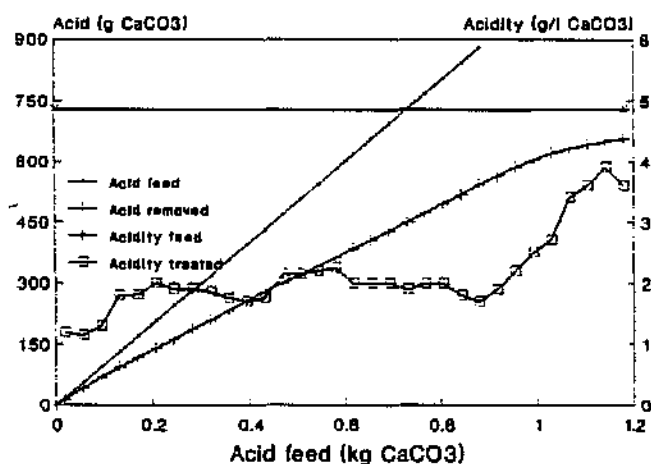


Figure 3.16 : Neutralisation of Fe(II)-rich water in a fluidised-bed reactor under batch conditions with a contact period of 4,5 min.
 Acidity = 4 g/l; Limestone = 600 g;
 Particle size = 0,6 - 1,4 mm

Effect of metals

Influence of iron

The efficiency of the CaCO_3 neutralisation process is strongly influenced by the acid water's iron content. Figure 3.17 shows the influence of both iron(II) and iron(III) on the rate of acidity removal from synthetic solutions during neutralisation with 6 g/l of limestone. The three solutions that were used in the experiment each contained 4 g/l sulphate and varying amounts of iron, namely 0 g/l Fe, 1,75 g/l Fe(II) (equivalent to 3 g/l sulphate) and 1,17 g/l Fe(III) (equivalent to 3 g/l sulphate) respectively. It is evident that Fe(III) has no influence on the rate of acidity removal as indicated by the similarity in the lines representing 0 mg/l Fe and 1000 mg/l Fe(III). The presence of Fe(II), however, significantly retards the rate of neutralisation. This can be caused by the fact that iron(II) precipitates as Fe(OH)_2 on the limestone particles, and mask them to prevent further dissolution in the acid water.

Because acid mine water contains iron(II) (e.g. 408 mg/l in the case of water 4 and 56 mg/l in the case of water 12), it was expected that complete neutralisation would take place at a reduced rate. This was confirmed by the results shown in Figures 3.4, 3.12 and 3.13 which show that more than 1 h is required for complete neutralisation of waters 4 and 12 respectively. Water which contained H_2SO_4 or $\text{Fe}_2(\text{SO})_4$, was neutralised within 15 minutes (Figure 3.17).

Most mine waters contain iron(II), implying that the calcium carbonate neutralisation process needs to be modified by oxidising iron(II) to iron(III). One of the possible cost effective ways will be biological oxidation, using iron-oxidising bacteria.

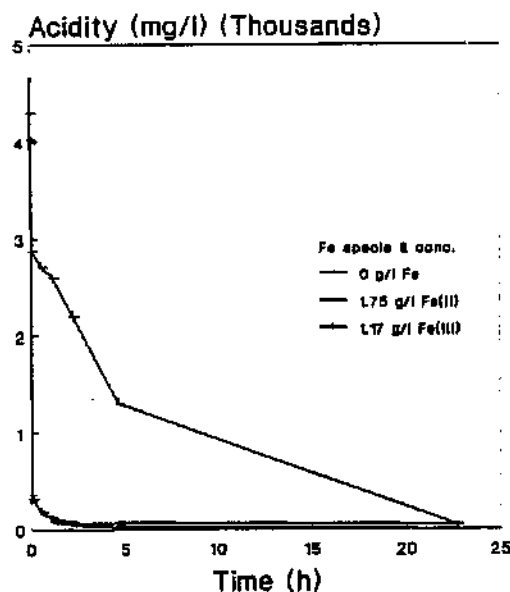


Figure 3.17 : Influence of iron(II) and iron(III) on the rate of neutralisation. [Acidity] = 4 g/l; [Limestone] = 6 g/l; Particle size < 0,15 mm

Comparative rate of neutralisation.

Under 'Influence of iron' it was shown that waters containing H_2SO_4 , H_2SO_4 and Fe(III) and H_2SO_4 and Fe(II) behaved differently when neutralised with limestone. This behaviour was re-investigated in this section under batch conditions for waters containing 4 000 mg/l acidity, 582 mg/l metal (Fe(II), Fe(III) or Al(III) (all as Fe)). The waters were neutralised with 600 g of limestone with a particle size of 0,600 to 1,400 mm. Figure 3.18 shows how differently the ions Fe(III), Fe(II) and Al(III) behave during limestone neutralisation in a fluidised-bed reactor. The contact time required for complete neutralisation was 2 min. in the case of Fe(III), 8 min. in the case of Fe(II) and 30 min. in the case of Al(III). Although the neutralisation of Fe(II) and Al(III) solutions are slower than that of Fe(III), it is encouraging to learn that the dissolution of limestone still takes place in the fluidised-bed reactor, and that it is not masked, which would have prevented the completion of the reaction. The formation of solid intermediate products, such as gypsum and ferric hydroxide, are possibly responsible for the difference in the neutralisation rate.

Explanation for different rates of neutralisation in the case of various cations.

In order to explain the difference in the behaviour between solutions containing various cations (Al(III), Fe(II) and Fe(III)), it is necessary to evaluate the behaviour of all the ions (calcium,

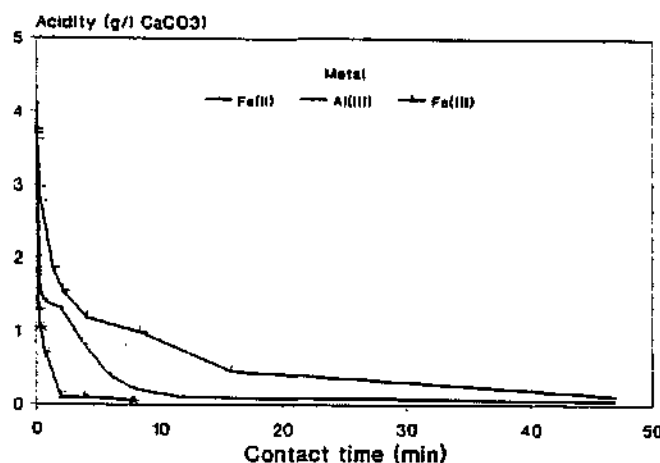


Figure 3.18 : Neutralisation of acid water, containing different metals, in a fluidised-bed reactor under batch conditions.

[Acidity] = 4 g/l; mass limestone = 600 g;

[Fe(II)] (as Fe) = 582 mg/l

hydrogen (acidity), sulphate, iron(II), iron(III) and aluminium(III)) present in solution during the neutralisation reaction. The results are shown in Figures 3.19, 3.20 and 3.21 for Al(III), Fe(II) and Fe(III) respectively.

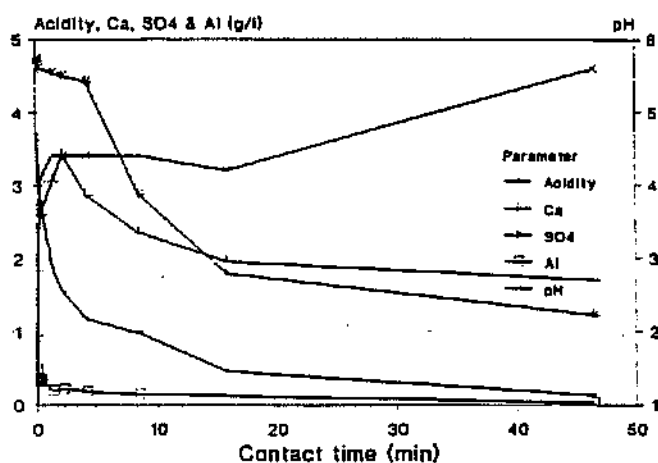


Figure 3.19 : Behaviour of various parameters during neutralisation of Al(III)-rich water. [Acidity] = 4 g/l; mass limestone = 600 g; [Al(III)] (as Fe) = 582 mg/l

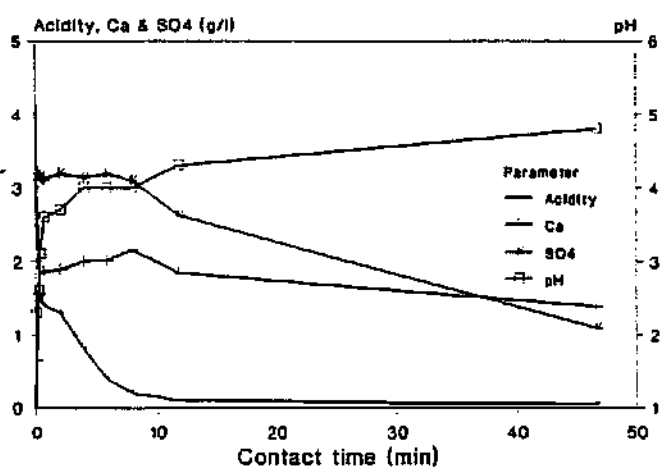


Figure 3.20 : Behaviour of various parameters during neutralisation of Fe(II)-rich water. [Acidity] = 4 g/l; mass limestone = 600 g; [Fe(II)] (as Fe) = 582 mg/l

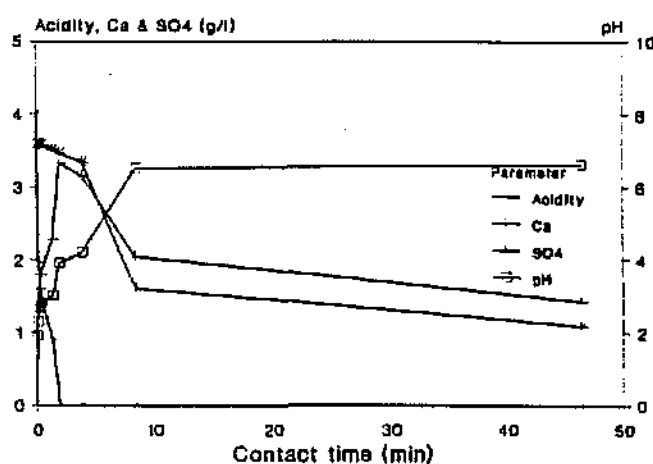
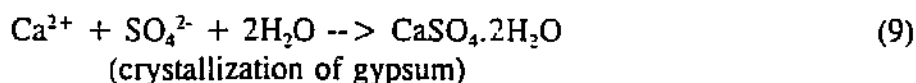


Figure 3.21 : Behaviour of various parameters during neutralisation of Fe(III)-rich water. [Acidity] = 4 g/l; mass limestone = 600 g; [Fe(III)] (as Fe) = 582 mg/l

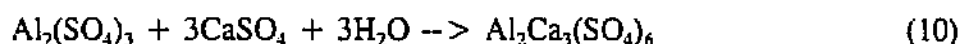
The rate of neutralisation with limestone is influenced by the type of metal ion in solution, as is shown by the following observations from Figures 3.19, 3.20 and 3.21:

- * In the case of Fe(III) and Al(III), the calcium concentration increases to its maximum after a short contact time of only 1,29 min (2 280 mg/l CaCO₃ for Fe(III) and 3 060 mg/l CaCO₃ for Al(III)), while in the case of Fe(II), the maximum concentration was achieved after only 5,8 min. It can therefore be concluded that the Fe(II)-specie has an inhibiting effect on the rate of limestone dissolution. A possible explanation for this inhibiting effect could be the formation of solid intermediate complexes which retard the rate of limestone dissolution.
- * The rate of acidity removal is restricted by the rate at which the metal is removed from solution. In the case of Fe(III), acidity is removed very fast as Fe(III) precipitates completely at pH 3 as Fe(OH)₃, and does not form complexes which remain temporarily in solution. Only gypsum (CaSO₄·2H₂O) crystallised out upon completion of neutralisation (equation 9). The individual ion species in gypsum does not influence the acidity of the water.



In the case of Fe(II) and Al(III), soluble metal-sulphate complexes form which precipitate slowly from solution. It is also noticed that shortly after CaCO₃ has been dosed, the increase in the calcium concentration is stoichiometrically higher than the decrease in the acidity value for Al(III) (Figure 3.19) and Fe(II)-rich waters (Figure 3.11). This is due to the formation of complexes which keep the carbonate ion in solution instead of losing it as CO₂-gas. It is noticed in Figures 3.19 and 3.20 that complete acidity removal was achieved only after Al(III) and Fe(II) were removed completely.

Aluminium-calcium-sulphate is possibly formed in the case of Al(III). Figure 3.19 shows that the pH-value remains low at pH 4,4 due to the buffer effect caused by the aluminium complex in solution. Over the contact period, 2,1 to 15,8 min, in which the pH increased to 5,6, it is calculated that 3155 mg/l SO₄ (as CaCO₃), 1454 mg/l Al (as CaCO₃) and 1470 mg/l Ca (as CaCO₃) were removed from solution due to crystallisation of an inorganic complex. From the above-mentioned figures, it is calculated that the formula of the complex is Al₂Ca₃(SO₄)₆. The crystallisation reaction can be represented by the following equation:



The sulphate value of 1216 mg/l (as SO₄) in the neutralised water is influenced by the solubility of the complex, Al₂Ca₃(SO₄)₆. This sulphate value is less than the 2000 mg/l of SO₄ in solution which is normally achieved from calcium sulphate crystallisation. Christoe (1976) also described that sulphate can be removed from industrial effluents through precipitation by means of inorganic complexes.

In the case of Fe(II) (Figure 3.20), 2400 mg/l SO₄ (as CaCO₃), 780 mg/l Ca (as CaCO₃) and 788 mg/l Fe (as CaCO₃) were removed during phase 2 (contact period 7,91 to 46,7 min). As from a stoichiometric point of view, more sulphate than calcium was removed, it is assumed that, similar to the case of Al(III), a calcium-iron-sulphate complex crystallised out. It still needs to be determined whether the iron in the complex is in the II or III state.

Effect of chemical pre-treatment.

The effect of Fe(III) on the rate of neutralisation was investigated in a series of experiments when it was produced in different ways. Figures 3.22 to 3.23 show the rate of neutralisation for the following solutions:

- * 582 mg/l Fe(III) diluted from commercially available ferric sulphate (Figure 3.22).
- * 582 mg/l Fe(II) oxidised with the equivalent amount of hydrogen peroxide (Figure 3.23).
- * 582 mg/l Fe(II) oxidised with three times the equivalent amount of hydrogen peroxide (Figure 3.24).

Figure 3.22 shows that there is no difference in the rate of neutralisation. As long as the iron remains in the III state, the neutralisation rate remains fast. For practical application, the most economical way of oxidising iron(II) must be determined. A third

possibility would be to have a longer contact time in the fluidised-bed reactor in order to cope with the slower neutralisation rate of Fe(II)-solutions.

The possibility of accelerating the rate of neutralisation of Fe(II)-rich solutions by aerating the fluidised-bed reactor (in order to oxidise Fe(II) to Fe(III)) was also investigated. Figure 3.23 shows that aeration has no effect on the neutralisation rate of Fe(II)-rich solutions. This is at least the case for the short contact time that was used in the fluidised-bed reactor in this particular experiment. From theoretical considerations it was expected that aeration would not have had any effect as Fe(II) can not be oxidised chemically to Fe(III) at pH values lower than 7.

As the rate of neutralisation of Fe(II)-rich effluents is accelerated by treating it with hydrogen peroxide, it was decided to investigate the effect of peroxide treatment also on the rate of solutions rich in Al(III). Figure 3.24 shows that peroxide treatment had no effect on the rate of neutralisation of Al(III)-rich solutions. It is noticed in the graph that aluminium is removed at a similar rate than acidity.

By-product recovery.

It was assumed initially that pure gypsum could be recovered as a by-product from the limestone neutralisation process. This would not be possible in case of Al(III) and Fe(II)-rich waters as inorganic complexes are formed as described in the previous section. In the case of Fe(III)-rich water, however, it would be possible to recover gypsum as a by-product, provided that the fast precipitating Fe(OH)₃ can be separated from the slow crystallising gypsum.

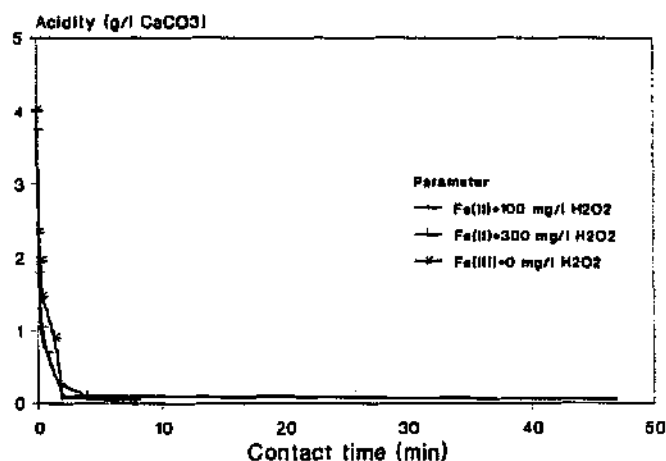


Figure 3.22 : Neutralisation of Fe(III)-rich water in a fluidised-bed reactor under batch conditions for Fe(III) produced in different ways.

[Acidity] = 4 g/l; mass limestone = 600 g; [Fe(III)] (as Fe) = 582 mg/l

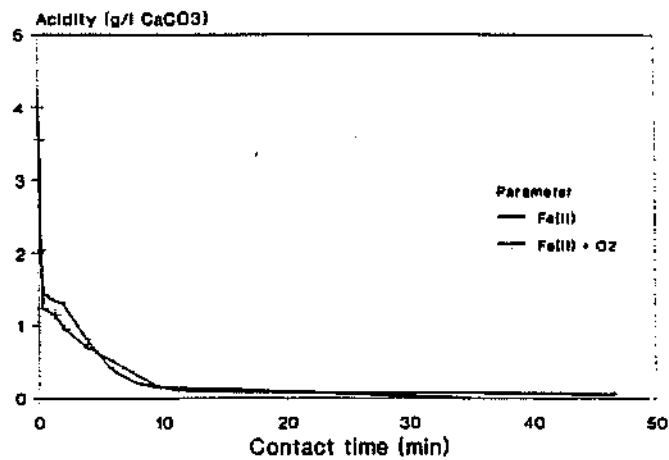


Figure 3.23 : Neutralisation of Fe(II)-rich water in a fluidised-bed reactor under batch conditions in the absence and presence of aeration.
 [Acidity] = 4 g/l; mass limestone = 600 g; [Fe(II)] (as Fe) = 582 mg/l

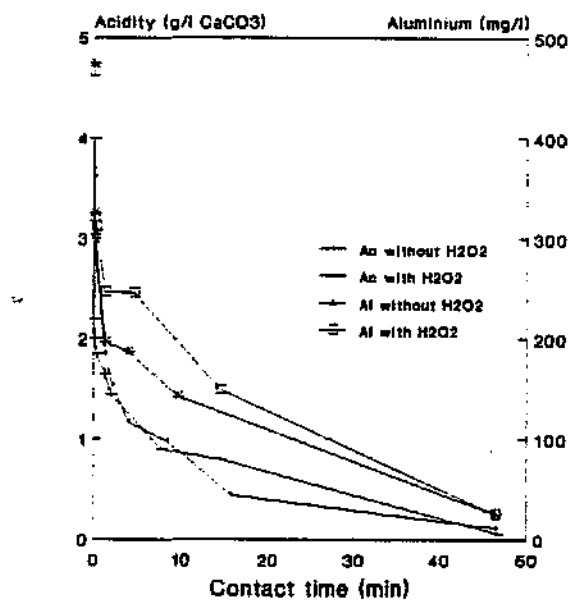


Figure 3.24 : Neutralisation of Al(III)-rich water in a fluidised-bed reactor under batch conditions with and without treatment with hydrogen peroxide.
 [Acidity] = 4 g/l; mass limestone = 600 g; [Al(III)] (as Fe) = 582 mg/l

CO₂-gas can also be recovered as a by-product. The amount of CO₂-gas that can be recovered from a certain acid water can be calculated by determining the amount of alkali that is required to increase the pH of the water to 4,3. Although the pH of water can be increased to 7, it is expected that the last bit of CO₂-gas will remain in solution for the period that the water is in the fluidised-bed reactor. It was determined that the purity of the produced CO₂-gas was higher than 95%.

Reactor design.

Two different shapes of fluidised-bed reactors were evaluated during this study. The one reactor had a uniform diameter (Figure 3.2) while the other had two stages, a bottom section with a small diameter and a top section with a larger diameter (Figure 3.3). The latter shape was the preferred one for the following reasons:

- * High upflow velocity of 212 m/h ensure complete fluidisation of biggest limestone particles in the reactor.
- * By increasing the diameter of the top section of the fluidised-bed reactor, the upflow velocity could be decreased to the value where limestone losses of fine particles can be minimised.

Water quality.

The quality of untreated and treated water under continuous conditions is shown in Table 3.7. Acidity is removed from 7,4 to 0,15 g/l due to the dissolution of limestone, and sulphate from 8,00 to 1,95 g/l due to crystallisation of gypsum. The calcium content in the treated water was 1,00 g/l (as CaCO₃) after dissolution of calcium carbonate and crystallisation of gypsum. The pH increases from 1,9 to 5,5.

Table 3.7 : Chemical composition of untreated and treated water during continuous treatment.

Parameter	Untreated	Treated
Acidity (g/l CaCO ₃)	7,40	0,15
Sulphate (g/l SO ₄)	8,00	1,95
Calcium (g/l CaCO ₃)	0,00	1,00
pH	1,90	5,50

CONCLUSIONS

Technical

1. The kinetics of acid neutralisation using CaCO_3 may be represented by the rate equation:

$$\frac{d[\text{H}_2\text{SO}_4]_b}{dt} = K S [\text{H}_2\text{SO}_4]_b \quad (11)$$

where K is the rate constant based on surface area, S is the total CaCO_3 surface area available and $[\text{H}_2\text{SO}_4]_b$ is the concentration of acid in the bulk liquid (as mg CaCO_3/ℓ). For effluents with little or no heavy metals, the value of K is $2,45 \times 10^{-3} \text{ min}^{-1} \cdot \text{cm}^{-2}$; for effluents that contain significant quantities of iron, a layer of $\text{Fe}(\text{OH})_3$ forms on the CaCO_3 surfaces that causes K to decrease from the abovementioned value, depending on the thickness of the $\text{Fe}(\text{OH})_3$ layer.

2. In batch tests the rate of CaCO_3 neutralisation is directly related to the dosage of CaCO_3 .
3. Aeration accelerated the rate of CaCO_3 neutralisation slightly due to the stripping of CO_2 .
4. Partial sulphate removal is achieved during CaCO_3 neutralisation as a result of CaSO_4 crystallisation. If magnesium is present in the water, it co-precipitates with the CaSO_4 .
5. Iron(III) and aluminium(III) are removed from solution during CaCO_3 neutralisation.
6. The rate of CaCO_3 neutralisation is dramatically retarded by the presence of iron(II) in solution. Iron(III) has no influence on the neutralisation rate.
7. A direct relationship exists between the neutralisation rate and the size of the limestone particles.
8. During semi-continuous and continuous studies in the laboratory, using a fluidised bed reactor, the CaCO_3 in the limestone is completely utilised if a particle size greater than 0,15 mm is used. For particle sizes smaller than 0,150 mm, only 79% of the available calcium carbonate was utilised. This is ascribed to the fact that the powdered CaCO_3 was flushed out by the liquid prior to complete reaction with the acid.
9. The rate of neutralisation decreases in the sequence: $\text{Fe}(\text{III}) > \text{Fe}(\text{II}) > \text{Al}(\text{III})$.

The contact time required to achieve complete neutralisation is as follows for different metal ions:

Fe(III)	-	2 min
Fe(II)	-	8 min
Al(III)	-	30 min

10. The formation of inorganic complexes is responsible for slower neutralisation rates in the case of Al(III) and Fe(II)-containing waters.
11. The rate of neutralisation of Fe(II)-rich water can be accelerated by oxidising the Fe(II), with hydrogen peroxide, to Fe(III).
12. Aeration of Fe(II)-rich water has no effect on the rate of neutralisation.
13. Gypsum can be recovered as a by-product in case of Fe(III)-rich effluents.
14. A fluidised-bed reactor with multiple stages of increasing diameters is preferred for the limestone neutralisation process as it allows fluidisation of the bigger particles but also prevents washout of the smaller particles in the case where ungraded limestone is used.
15. The limestone neutralisation process improves the quality of the water by removing free acid and acid associated with Fe(III), completely. Sulphate is removed to the point where the water is saturated with calcium sulphate. The level to which the pH of acid water is increased depends on the metals that will remain in solution during neutralisation.

General

The study showed that acid water can be neutralised effectively with limestone in a fluidised-bed reactor. The comparative advantages associated with the use of limestone under practical conditions, compared to other alkalis such as sodium hydroxide or sodium carbonate, are the following:

1. more cost-effective,
2. no accurate control of dosage is required, as limestone does not dissolve at pH-values greater than 7,
3. sludge of a higher density is produced in the case of iron(III)-rich waters,
4. it is safe to handle, and
5. it is easy to store.

CHAPTER 4. PILOT SCALE EVALUATION OF THE FLUIDISED-BED LIMESTONE NEUTRALISATION PROCESS

INTRODUCTION

Laboratory studies in Chapter 3 showed that acid water of a variety of compositions can be neutralised effectively with limestone.

The specific aims of pilot plant studies, as described in this chapter, are to:

- * Determine the contact time required between the limestone bed and acid waters rich in iron(III), iron(II) and real industrial acid water.
- * Determine whether a side bleed-off stream from the limestone-bed is required in order to get rid of the impurities in the limestone.
- * Compare the efficiency of the cone-shaped fluidised-bed reactor with the pipe-shaped fluidised-bed reactor.

MATERIALS AND METHODS

Investigation of the above parameters was carried out using batch and semi-continuous fluidised bed tests.

Feed water

The acid solutions used during the study were prepared from sulphuric acid, ferrous sulphate and ferric sulphate and water from Witbank (sample point No 4) representing a mixture of acid mine water and sulphate-rich industrial effluent.

Limestone

Raw limestone obtained from PPC Lime was used in the neutralisation studies. The PPC limestone was screened and graded into various size fractions using sieves with the following opening sizes: 4,000 mm, 2,000 mm, 1,400 mm, 0,600 mm, 0,425 mm, 0,300 mm and 0,150 mm.

The upflow velocity of water at which each of the above-mentioned particle size ranges fluidised was determined by allowing tap water to flow through a 4 cm diameter 'Perspex' tube at different upflow velocities. An amount of 100 g of limestone of a particular particle size was put in the water prior to the water flowing upwards through the pipe at increasing upflow velocities. When the volume of the limestone-bed was increased by 20%, the flow rate was measured and the upflow-velocity at which limestone of specific particle-size fluidised, was calculated.

Pilot plants

The feasibility of the process was examined using a cone shaped fluidised-bed reactor (Figure 4.1) and a pipe fluidised-bed reactor (Figure 4.2). The water in the cone was recycled through a crystallisation reactor in order to decrease the oversaturation level of gypsum in the treated water. Table 4.1 shows the values of various parameters for the two systems for feed rates of 1 l/min and 0.1 l/min, recirculation rates of 35 l/min and 10 l/min were kept and 20 kg and 5 kg of limestone were present in the two reactors, respectively. The recirculation rate was set to increase the bed volume of the limestone by 20 to 50%. Aldoss diaphragm pumps were used to feed acid water from a 10 kl stainless steel tank to the fluidised-bed reactors. A Femco centrifugal pump was used for recirculation of water in the cone reactor, in order to fluidise the limestone and for recirculation of water in the crystallisation reactor. An air pump was used for fluidisation of the limestone in the pipe reactor through water recirculation.

Limestone feed system.

Limestone was fed either manually or with a hopper (20 l) equipped with a screw feeder, to the cone reactor, and manually to the pipe reactor. In the case where the limestone was fed automatically, the amount of limestone was kept between 12 and 14 kg. As sensor, a load cell was used to activate and stop the feeder at the set minimum and maximum mass levels in the load cell. It was determined that 1 kg of limestone replaces 0,372 kg of water in the fluidised-bed reactor. From this relationship it was possible to calculate the amount of limestone present in the fluidised-bed reactor at any time by using the following equation:

$$\text{mass of limestone in reactor (kg)} = (W - W_0)/(1,0 - 0,372)$$

where: W - mass of (cone + water + limestone)

W₀ - mass of (cone + water).

Batch Tests

Batch studies were carried out to determine the rate of neutralisation in the cone reactor and the rate of gypsum crystallisation in the crystallisation reactor. The behaviour of the various parameters, namely pH, sulphate, calcium, acidity and iron(II) were also studied. After the addition of the acid solution to the cone fluidised-bed reactor, ungraded limestone was added. Samples were taken regularly and analyzed for pH, calcium, magnesium, iron(II), iron(III) and acidity (APHA, 1985). After monitoring the fast neutralisation reaction, the procedure was continued in order to monitor the rate of gypsum crystallisation.

Table 4.1 Typical values of design parameters for the two types of pilot plants.

Parameter	Cone reactor height (mm)			Crystallisation reactor	Pipe reactor Stage		
	10 bottom	500 middle	1000 top		1 st	2 nd	3 rd
Feed rate (ℓ/min)	0,5	0,5	0,5	0,5	0,1	0,1	0,1
Recycle rate (ℓ/min)	35	35	35	40	7,2	7,2	0,0
Diameter (mm)	50	250	500	500	60	123	123
Empty volume (ℓ)	0,1	8,2	65,5	196	5,7	8,9	8,9
Hydraulic ret. time (min)	0,1	16,4	131	393	57	89	89
Upflow velocity (m/h)	1079	43	11	12	153	36	0,5
Limestone (kg)	20				5		
Contact time* (min)	40				50		

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

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 in reactor (kg) ÷ feed rate (ℓ/min).

Analytical

Sampling was carried out automatically during continuous and batch studies. A four row pneumatic driven sampler which can take 24 samples per row, was activated at pre-set intervals by an electric timer to advance to the next sample. Composite samples were collected in each sample bottle by pumping water with a multi-channel Gilson peristaltic pump continuously from the reactor(s). Funnels with Whatman No 1 filterpaper were put on each sample bottle in order to collect filtered samples. Calcium and magnesium were determined with EDTA, the alkalinity content was determined by titration with hydrochloric acid to pH 4,3 and the acidity by titration with sodium hydroxide to pH 8,3. In the case of iron(II)-rich samples, precipitation of iron hydroxide on the electrode

was prevented during acidity determinations by first precipitating the iron with an excess amount of sodium hydroxide. The excess sodium hydroxide was then determined through back titration with hydrochloric acid to pH 8.3.

The limestone was analyzed for its calcium, magnesium and alkalinity content by dissolving it in a stoichiometrically excessive amount of hydrochloric acid.

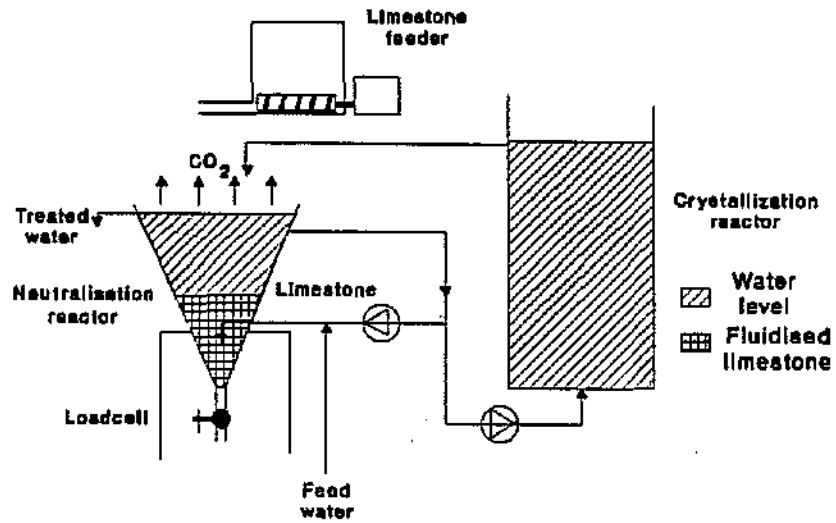


Figure 4.1 Flow diagram of cone shaped fluidised-bed and crystallisation reactors.

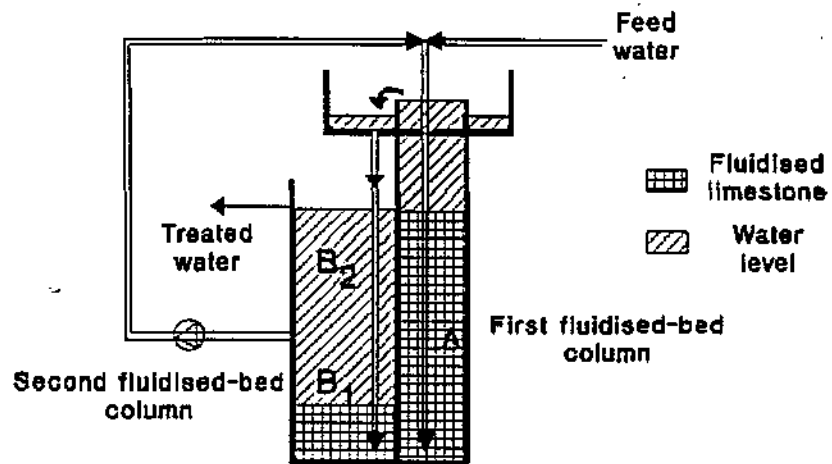


Figure 4.2 Flow diagram of pipe shaped fluidised-bed reactor.

RESULTS AND DISCUSSION

Particle size distribution and fluidisation velocity of limestone

One of the requirements of the fluidised-bed limestone neutralisation process was to develop the process so that commercially available limestone, ungraded with respect to particle size, can be used as feed material. It is therefore necessary to know the particle size distribution of the limestone (Figure 4.3) as well as the velocity at which it fluidises (Figure 4.4). Least square fit analyses on the curve in Figure 4.4 shows that the following function predicts the fluidisation velocity (v) for a specific particle size (ps).

$$v = -3,7 + 66,4 \times ps - 8,3 \times (ps)^2$$

where v is measured in m/h and ps in mm.

Neutralisation of iron(III)-rich water

Figure 4.5 shows the results when artificial mine water containing 4 g/l H_2SO_4 (as $CaCO_3$) and 582 mg/l Fe(III) was neutralised with ungraded limestone in the cone shaped fluidised-bed reactor. The conditions during the studies were as follows:

- * Feed rate of acid water = 1 l/min
- * Limestone addition = 10 kg/addition
- * Assumed limestone concentration during fluidisation = 1 kg/l
- * Contact time = $(10 \text{ kg} \div 1 \text{ kg/l}) \div 1 \text{ l/min}$
= 10 min

The following are concluded from Figure 4.5:

- * The contact time varied between 10 and 22 min as limestone was fed and consumed due to the neutralisation reaction (Figure 4.5a).
- * The pH was increased from 2,2 to 7,5 during the course of the experiment (Figure 4.5b). The drop in the pH for short periods was when the limestone in the reactor was almost finished. The process was purposely run to the stage where limestone was almost exhausted in order to determine the minimum contact time required for complete neutralisation (Contact time is shown in Figure 4.5a). By comparing the pH in Figure 4.5b, after 62 kg of acid (as $CaCO_3$) was fed, with the corresponding contact time in Figure 4.5a, it is noticed that a minimum contact time of 4 min is required to maintain the pH at 7,5 for the specific Fe(III)-rich water. It was possible to determine the minimum contact time required during that stage of the experiment as the contact time between the acid water and the limestone was allowed to decrease gradually by not replacing the consumed limestone with fresh limestone.
- * Acidity decreased from 4200 mg/l to 200 mg/l with the exception of the first 16 kg of acid that was fed and at the end (Figure 4.5c). The acid water was not completely neutralised in the beginning due to too little fluidisation of the bed, while at the end neutralisation was stopped due to the fact that feeding of limestone was terminated.

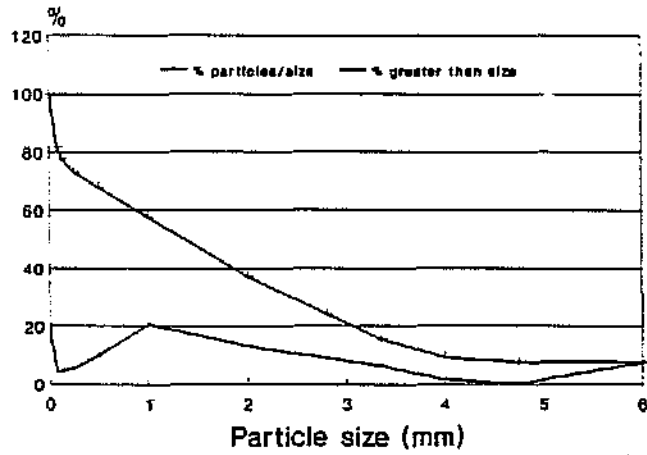


Figure 4.3 : Particle size distribution of limestone.

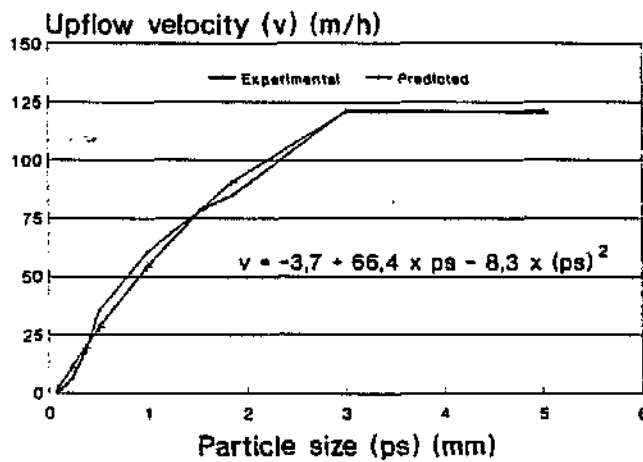


Figure 4.4 : Fluidisation velocity of limestone as a function of particle size.

- * Calcium increased to 1900 mg/ℓ (as CaCO₃) due to the dissolution of limestone according to the following reaction (Figure 4.5d):



- * Sulphate was removed from 4200 to 2000 mg/ℓ as a result of gypsum crystallisation as shown in equation 1 (Figure 4.5e). The level to which sulphate is removed is influenced by parameters such as temperature, ion strength and the solubility of metal-calcium-sulphate complexes.
- * Figure 4.5f shows that the amount of acid that was fed to the reactor was almost equal to the amount of acid that was removed in the reactor due to limestone neutralisation. This shows that acid water is neutralised completely. It also showed that with the 70 kg of limestone that was fed, 60 kg of acid was removed, which represents an 86% utilisation of limestone. This represents almost a 100% efficiency as limestone contains only 86% to 90% CaCO₃.

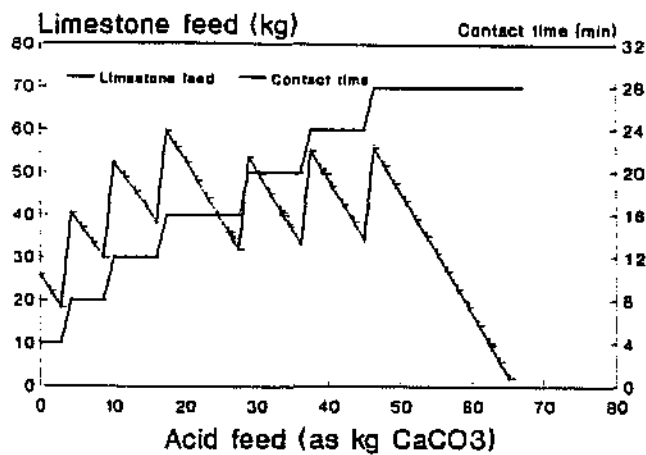
Figure 4.6 shows results similar to those of Figure 4.5 as the same raw materials (Fe(III)-rich water and ungraded limestone) were used. The only difference is that limestone was supplemented well before the stage where it was exhausted. The effects in this change in operation are the following.

- * The contact time between the limestone and the acid water has increased from 10 min (in the case of Figure 4.5) to up to 25 min.
- * The longer contact time and the elimination of short periods of low levels of limestone have to its advantage that no low pH-values came through as well as no high acidity values.

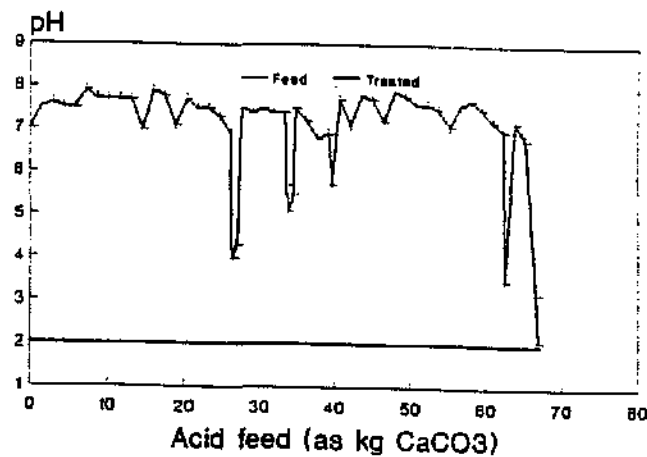
Waste sludge

In the case of iron(III)-rich water, the limestone is completely utilised while the ferric hydroxide sludge which is produced is washed out together with the effluent. No bleed-off stream is therefore necessary to get rid of impurities in the limestone or produced sludges.

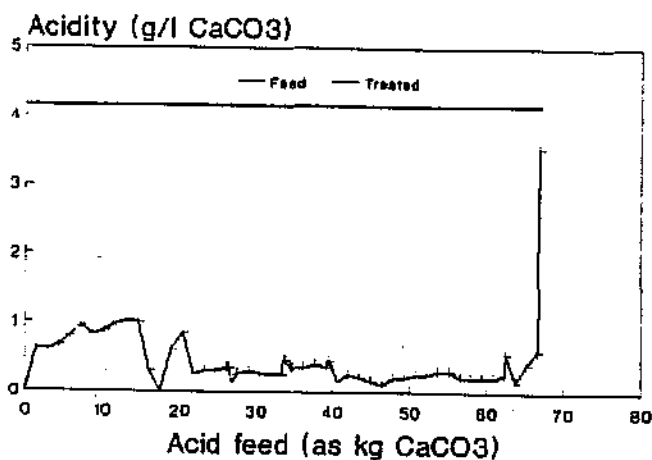
Figure 4.7 shows the rate at which gypsum crystallises from the neutralised water if sufficient time is provided. About 160 min are required to reduce sulphate from 4000 to 1700 mg/ℓ, the solubility level of gypsum under the specific conditions.



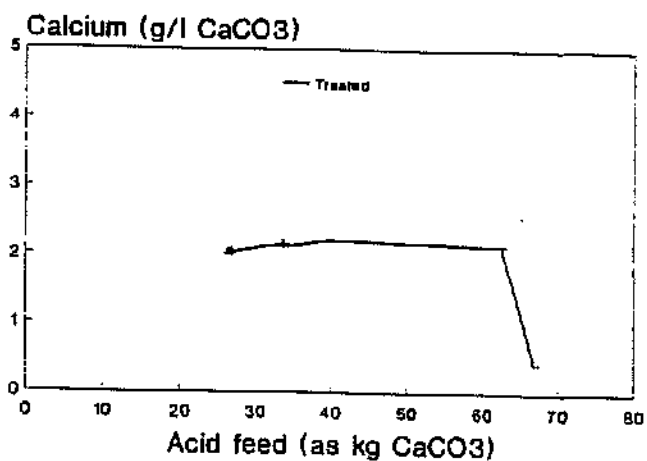
a. Limestone feed and contact time



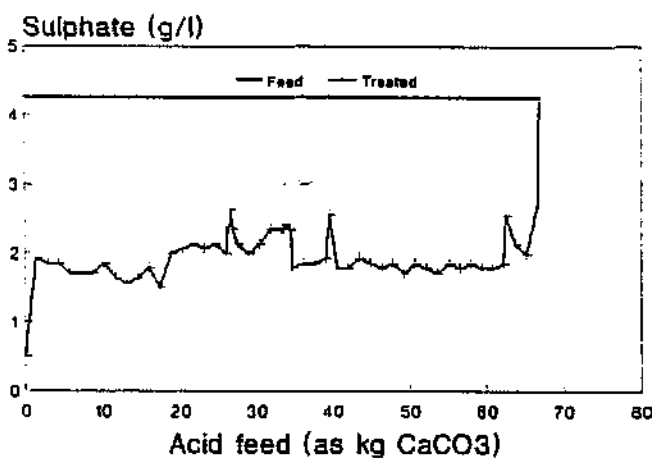
b. pH



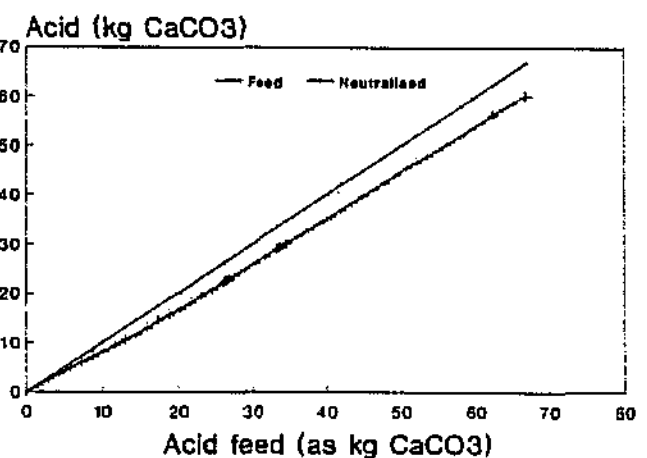
c. Acidity



d. Calcium

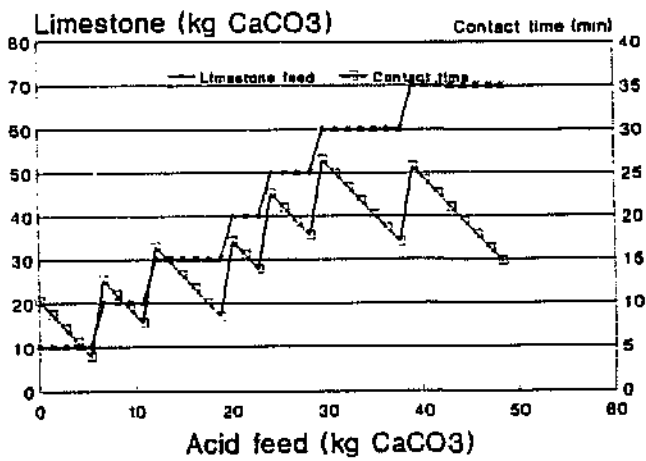


e. Sulphate

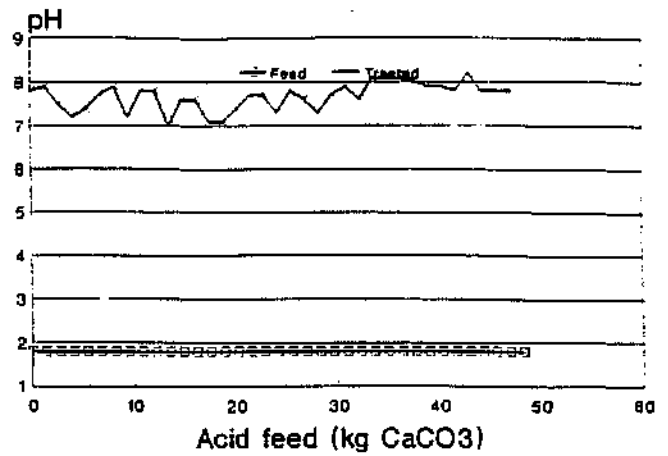


f. Acid load

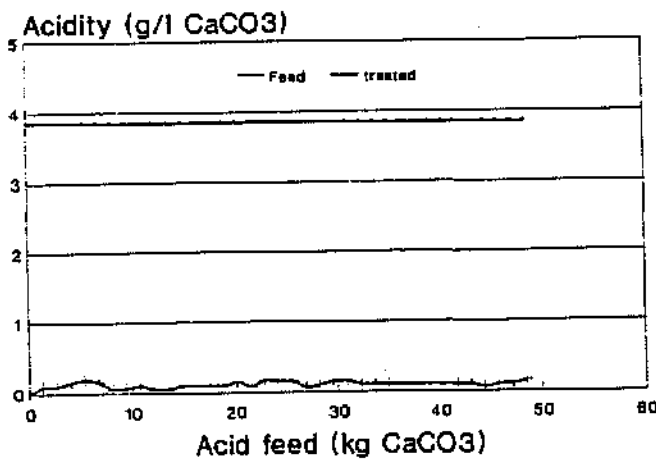
Figure 4.5 : Effect of contact time on the efficiency of limestone neutralisation of iron(III)-rich water.



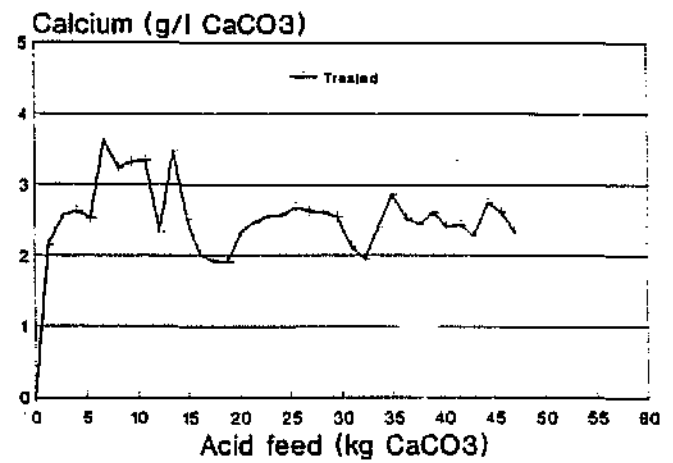
a. Limestone feed and contact time



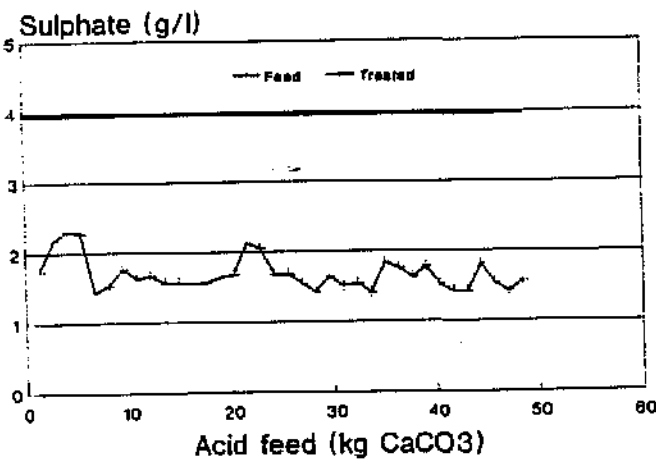
b. pH



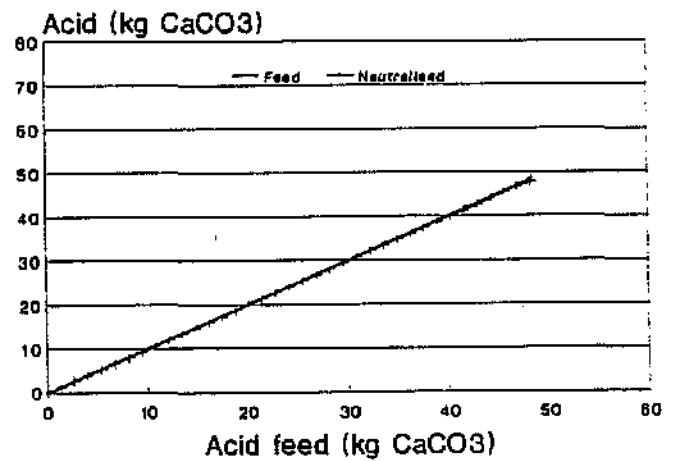
c. Acidity



d. Calcium



e. Sulphate



f. Acid load

Figure 4.6 : Effect of contact time on the efficiency of limestone neutralisation of iron(III)-rich water.

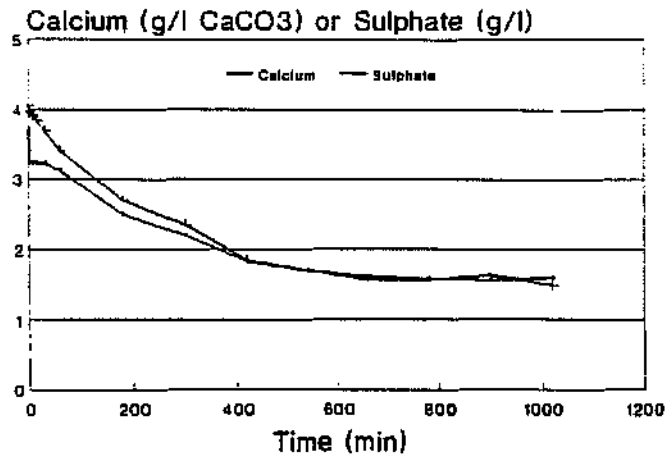


Figure 4.7 : Crystallisation rate of calcium sulphate under batch conditions.

Neutralisation of iron(II)-rich water

Maree *et al.* (1992) showed that the rate at which iron(II)-rich water is neutralised is much slower than in the case of iron-free or iron(III)-rich water. The purpose of this section was to determine the effect of contact time between limestone and acid water and the effect of hydraulic retention time on the efficiency of the neutralisation of iron(II)-rich water.

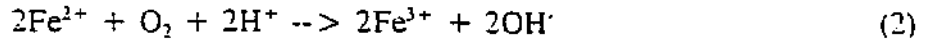
Contact time.

Figure 4.8a shows the contact time between limestone and acid water. The contact time was increased stepwise by decreasing the feed rate. The limestone was supplemented by adding between 5 and 20 kg of limestone at a time to the cone, 65 kg in total.

By increasing the contact time from 10 to 50 min, Figure 4.8 shows that:

- * The pH of the treated water was increased from 4,0 to 7,8 (Figure 4.8b).
- * The acidity decreased from 750 to 300 mg/l (as CaCO₃) (Figure 4.8c).
- * The iron(II) content decreased from 225 to 75 mg/l (Figure 4.8d).

The reduction in the iron(II) concentration is due to its oxidation with air. The reaction is catalysed by iron oxidising bacteria, such as *Ferrobacillus ferrooxidans*. In the absence of iron oxidising bacteria, the rate of iron(II)-oxidation is slow for pH values less than 7 (Garrels and Thompson, 1960). The pH of the feed water was only 2,4. The oxidation reaction is represented by the following equation:



As iron(II) is fairly soluble at neutral pH values, it contributes to acidity of the treated water and also a reduced pH. Its removal is therefore required to ensure effective neutralisation. Thus, by allowing sufficient contact time in the fluidised-bed reactor, iron can be removed effectively as shown in Figure 4.8.

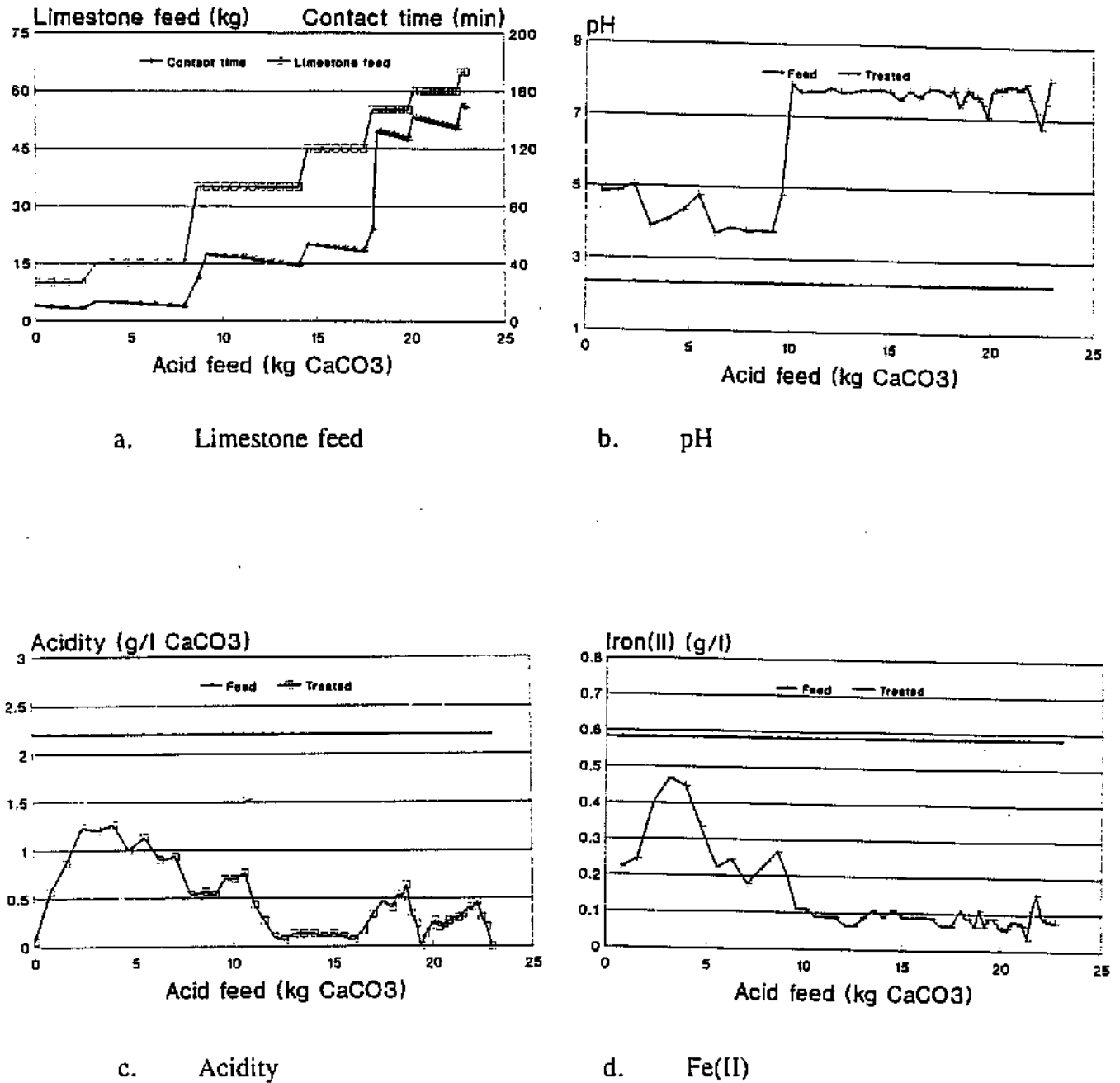


Figure 4.8 : Effect of contact time on the efficiency of limestone neutralisation of iron(II)-rich water.

Hydraulic reaction time.

A question that needs to be answered is whether the limestone plays any role in iron(II) oxidation or whether iron(II) oxidation mainly takes place in the water phase of the system. In order to investigate this, neutralisation of iron(II)-rich water was investigated in two systems, namely the cone fluidised-bed reactor (Figure 4.1) and the pipe reactor (Figure 4.2), where the contact time between the limestone and the acid water was of the same order, but with different hydraulic retention times. The contact time varied between 40 and 140 for both systems, while the hydraulic retention time varied from 549 to 900 min for the cone reactor and from 115 to 190 min for the pipe reactor.

Table 4.2 shows the effect of hydraulic retention time on the efficiency of the neutralisation of iron(II)-rich water. It is noted that similar results were obtained for the two systems with equal contact times, although the hydraulic retention time in the two systems varied.

Table 4.2 Effect of contact time and hydraulic retention time on neutralisation of iron(II)-rich water.

Parameter	Untreated	Cone System			Pipe System	
Hydraulic retention time (min)		900	756	549	190	115
Contact time (min)		140	110	20	120	30
pH	2,4	8,0	7,2	5,1	8,2	6,0
Acidity (mg/l CaCO ₃)	3 723	75	155	508	150	500
Iron(II)	560	20	25	256	40	200
Alkalinity (mg/l CaCO ₃)	-	-	150	52	-	50
Calcium (mg/l CaCO ₃)	10	1 821	1 756	1 304	1 600	1 300
Sulphate	3 723	1 911	1 906		1 400	1 600
Exp No		12	14	14	4P	4P

It was also noted that by keeping the contact time constant for a period of time, the presence of iron(II) has the effect that the pH value of the treated water decreases and the acidity increases gradually for both the cone and the pipe reactors (Figures 4.9 and 4.10 respectively). Figure 4.9 shows the effect in the case of the cone reactor when the

contact time was kept to between 40 and 46 min. It is assumed that partial coating of the limestone particles occurred when iron(II) is oxidised to iron(III), resulting in the precipitation of ferric hydroxide, which led to the decrease in pH and increase in acidity of the treated water. Conditions are favourable for ferric hydroxide precipitation under the mentioned conditions as the pH of the treated water varied between 4,5 and 8,0, while the solubility of ferric hydroxide becomes almost zero for pH-values greater than 3,0.

Similar observations were made in the case of the pipe reactor. However, there were more coated particles in the pipe reactor than in the case of the cone reactor, and the pH of the treated water (Figure 4.10c) was lower than that of the cone (Figure 4.10c). The difference in pH behaviour could be ascribed to the longer retention time that was available in the cone system relative to the contact time in the pipe reactor. Therefore, a smaller fraction of the iron(II) was in the immediate vicinity of the limestone particles during its oxidation stage, which is presumably responsible for the coating of the particles.

Limestone utilisation

The maximum value of the ratio of acid removed (as CaCO_3) / limestone fed (as CaCO_3) was determined for both the cone and the pipe systems with iron(II)-rich water. A maximum number was obtained by allowing the limestone to be consumed to the minimum level required to keep the pH of the treated water at 7 (just before more limestone was added). The maximum value for the cone system was found to be 0,71 and for the pipe system 0,70. This ratio is low compared to the 0,96 in the case of iron(III)-rich water (as discussed under 'Neutralisation of iron(III)-rich water'). It is therefore concluded that limestone utilisation is influenced rather by the iron(II) content of the water, than by the type of reactor. The 29 to 30% unused limestone in the case of iron(II)-rich water can be ascribed to gypsum and ferric hydroxide sludges and coated limestone particles which accumulated in the fluidised-bed reactor. Trials afterwards on the partially coated limestone particles showed that it would be possible to recover a fraction of it through a backwash operation.

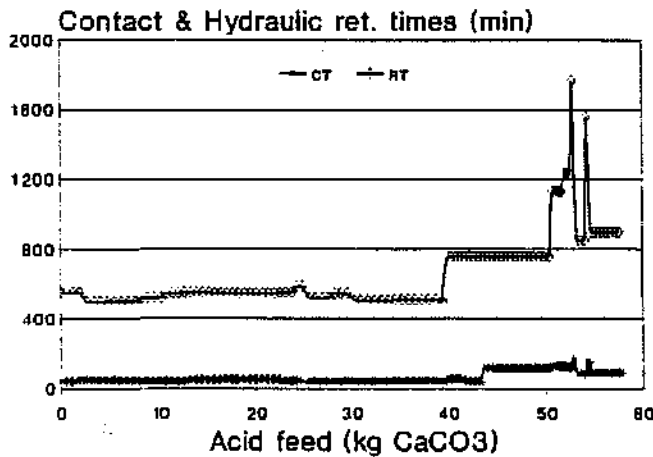
Neutralisation of Witbank coal mine water

The purpose of this section was to demonstrate the feasibility of the limestone neutralisation process on an industrial water. The water that was selected for this purpose is from the Witbank area and is a mixture of acid mine water from an old coal mine and an industry which has high concentrations of sulphate, sodium and chloride in its effluent. Figure 4.11 shows the results when this water was neutralised with limestone in the cone reactor. The following conditions existed during the experiment:

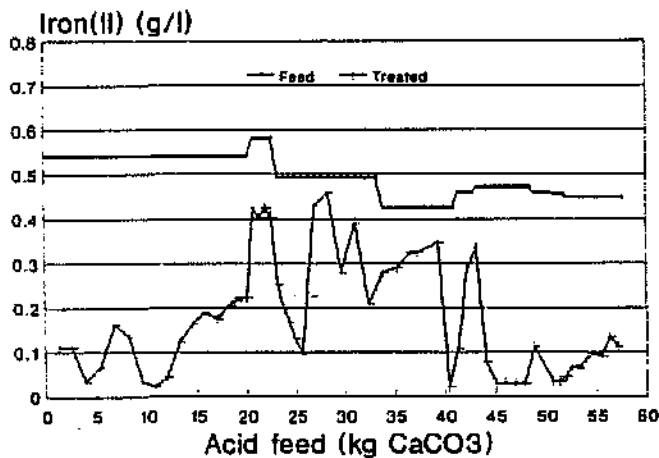
Feed rate	= 350 ml/min
Contact time	= Decrease gradually from 57 to 43 min
Hydraulic retention time	= 800 min
Temperature	= 40,0 °C
Limestone addition	= 20,0 kg

The following are concluded from Figure 4.11:

- * The contact time varied between 57 and 43 min as limestone was fed and consumed due to the neutralisation reaction (Figure 4.11a).
- * The pH was increased from 3,0 to 8,0 during the course of the experiment (Figure 4.11b).

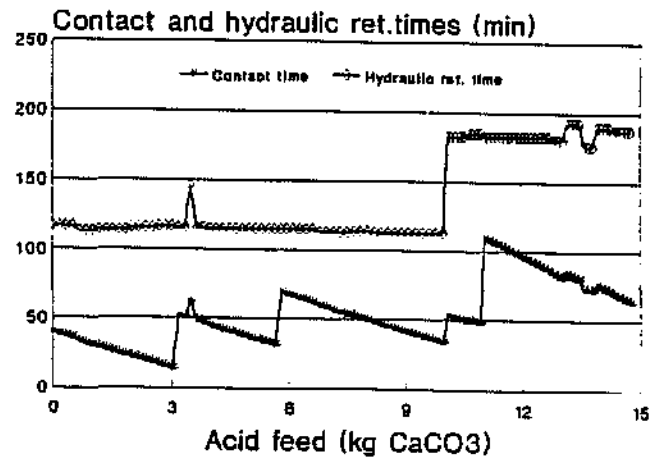


a. Contact time

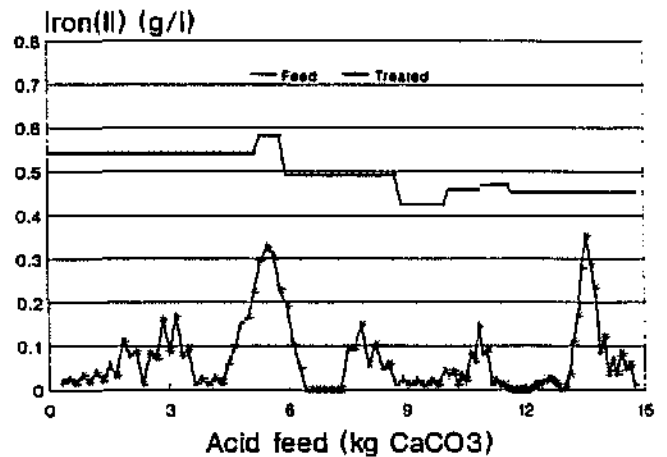


b. Iron(II)

Fig. 4.9 : Effect of iron(II)-rich water during limestone neutralisation on the behaviour of iron(II) acidity and pH in the case of the cone reactor. Contact time = 40 min.



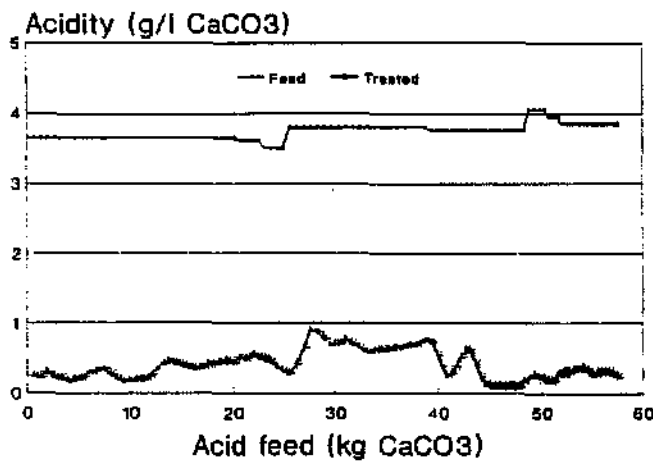
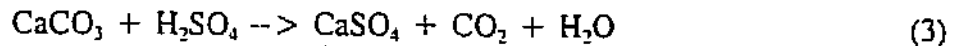
a. Contact time



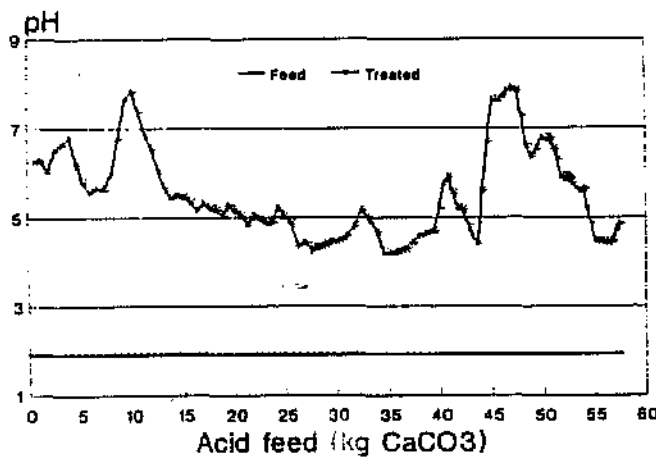
b. Iron(II)

Fig. 4.10 : Effect of iron(II)-rich water during limestone neutralisation on the behaviour of iron(II), acidity and pH in the case of the pipe reactor. Contact time = 40 min

- * Acidity decreased from 2 400 mg/l to 600 mg/l (Figure 4.11c). The high acidity value of 600 mg/l, together with a high pH value of 8,0 in the treated water, can be explained by the fact that stoichiometrically less sulphate precipitated than calcium dissolved. The result is that a fraction of the CO_3^{2-} from the calcium carbonate that dissolved during neutralisation, remained in solution as sodium bicarbonate, which contributed to the acidity value.
- * The calcium content remained constant at 1350 mg/l (as CaCO_3) as stoichiometrical equal amounts dissolved (reaction 3) and crystallised as gypsum. (Figure 4.11d).

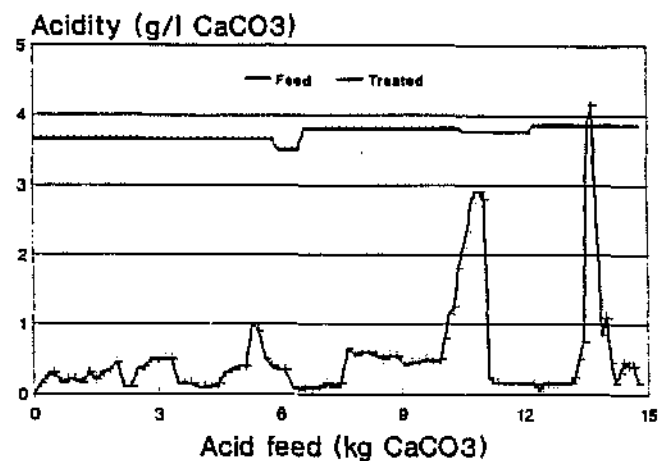


c. Acidity

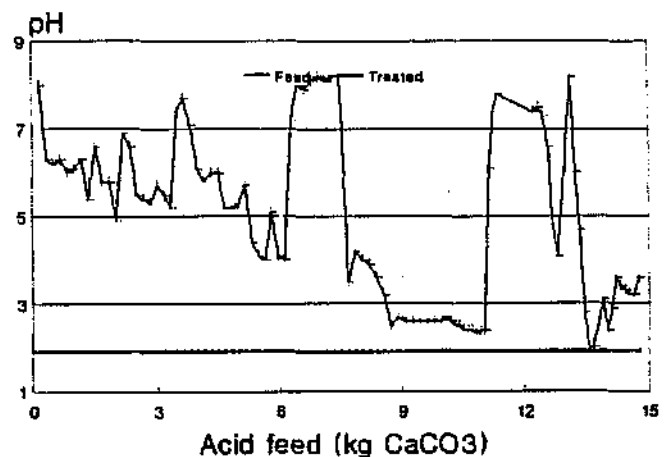


d. pH

Fig. 4.9 : Effect of iron(II)-rich water during limestone neutralisation on the behaviour of iron(II), acidity and pH in the case of the cone reactor. Contact time = 40 min.

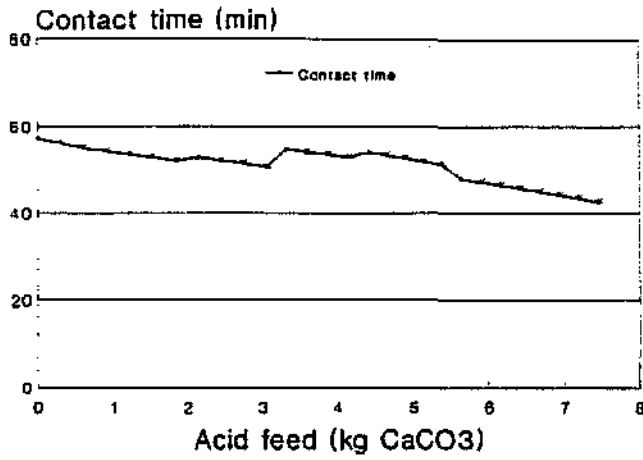


c. Acidity

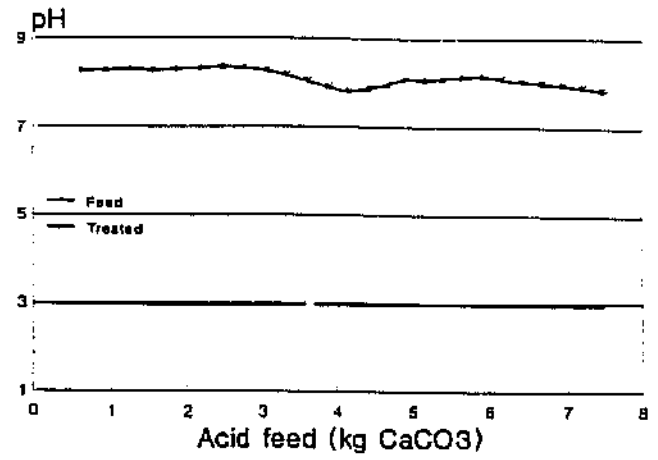


d. pH

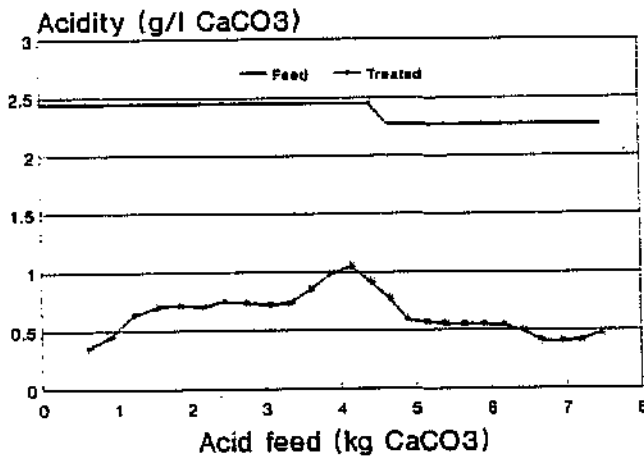
Figure 4.10 : Effect of iron(II)-rich water during limestone neutralisation on the behaviour of iron(II), acidity and pH in the case of the pipe reactor. Contact time = 40 min.



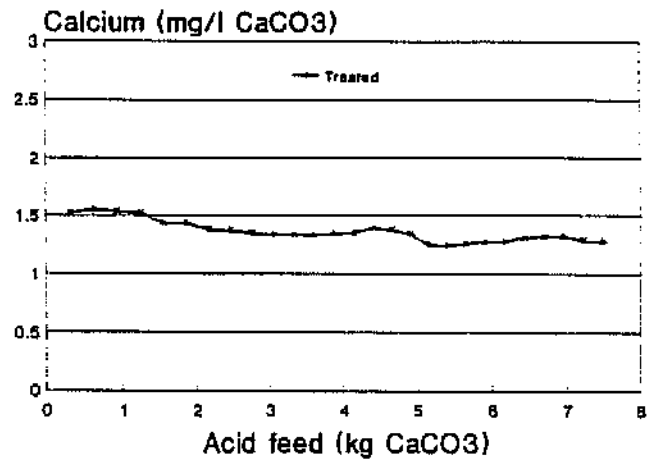
a. Limestone feed and contact time



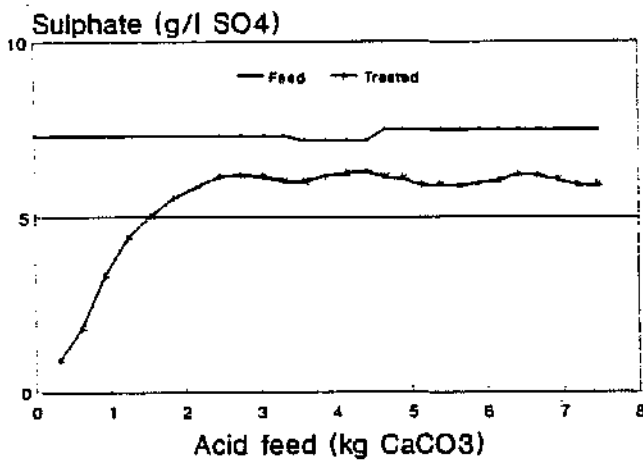
b. pH



c. Acidity



d. Calcium



e. Sulphate

Figure 4.11 Limestone neutralisation of Witbank water.

- * Sulphate was reduced from 7 400 to 6 000 mg/l as a result of gypsum crystallisation as shown in equation 1 (Figure 4.11e). The high sulphate level in the treated water compared to the previous studies can be ascribed to the sodium content of the untreated water. Sulphate associated with sodium in the untreated water will remain so during the neutralisation process. Only sulphate associated with free acid or metals that will precipitate during neutralisation can be removed as calcium sulphate.

The chemical analyses of the water before and after neutralisation is shown in Table 4.3.

Table 4.3 : Chemical composition of Witbank water before and after limestone neutralisation.

Parameter	Untreated	Treated
pH	3,0	8,0
Acidity (mg/l CaCO ₃)	2 400	600
Alkalinity (mg/l CaCO ₃)	-	150
Sulphate (mg/l SO ₄ ²⁻)	7 250	6 000
Chloride (as Cl)	502	498
Ammonia (as N)	186	196
Calcium (as CaCO ₃)	1300	1 350
Magnesium (as CaCO ₃)	1 043	1 083
Iron(II) (as Fe)	540	0 - 100
Iron(III) (as Fe)	560	0 - 100
Manganese (as Mn)	17	17
Zinc (as Zn)	3,0	0,6
Sodium (as Na)	1 577	1 567
Potassium (mg/l K)	484	481
Nickel (mg/l Ni)	1,0	0,7

CONCLUSIONS

It was determined that a contact time of 4 min is sufficient for the neutralisation of acid water containing 4 g/l free acid and 580 mg/l iron(III), while a contact time of at least 40 min is required for the same water, but which contains iron(II) instead of iron(III).

In the case of iron(III)-rich water, the limestone is completely utilised while the ferric hydroxide sludge which is produced is washed out together with the effluent. No bleed-off stream is therefore necessary to get rid of impurities in the limestone or produced sludges. In the case of iron(II)-rich water, gypsum and ferric hydroxide sludges and coated limestone particles accumulate in the fluidised-bed reactor. About 25% of the limestone is trapped this way, but it can be partially recovered from the waste sludge through a backwash operation. Coal mine water from the Witbank area was effectively neutralised from pH 3,0 to 8,0.

The cone-shaped and pipe-shaped fluidised-bed reactors perform equally well in the limestone neutralisation process.

CHAPTER 5. DESIGN CRITERIA AND ECONOMIC FEASIBILITY

INTRODUCTION

In Chapters 3 and 4 it is revealed that:

- CaCO_3 in limestone is completely utilised in the fluidised-bed reactor when the particle size is greater than 0,150 mm.
- A fluidised-bed reactor with multiple stages of increasing diameters is preferred for the limestone neutralisation process as it allows fluidisation of the larger particles but also prevents washout of the smaller particles in the case where ungraded limestone is used.
- The rate of neutralisation is a function of the iron(II) content in the acid water. In order to make the fluidised-bed neutralisation process economically feasible in the case of iron(II)-rich water, it is necessary to make provision for iron(II) oxidation. As iron(II)-oxidation does not form part of the study, the contents of this chapter are only aimed at the treatment of iron(II)-free water.
- Partial sulphate removal is achieved during acid water neutralisation with limestone as a result of CaSO_4 crystallisation.

The expected advantages to industry upon adopting the limestone process are as follows:

- The limestone process is cost-effective in comparison with lime (Table 5.1).
- Process control is simplified: (No pH-control is required as limestone dissolution occurs only at pH-values below 7).
- Material wastage through over-dosage is minimised for the same reason.
- Limestone is easy and safe to handle.
- Simple storage facilities are required as the raw materials are not readily soluble in neutral water.
- The existing lime plants can be converted to a limestone plant with relative ease.

Table 5.1 : Cost comparison of lime and limestone as neutralisation agents.

	Slaked lime	Limestone
Chemical formula	Ca(OH)_2	CaCO_3
Price** (R/t)	280	100
Mol mass	74	100
Price (R/t as Ca(OH)_2)	280	135

**Delivered prices in PWV-area (1993).

Selection of reactor type is also important. Neutralisation in a fluidised-bed reactor rather than in other systems such as rotating drums and the packed bed reactors have the following advantages:

- Limestone particles are utilised more completely.
- Contact time between acid water and limestone particles is minimized as a relatively low concentration of acid is in contact with a high concentration of alkali (in solid form).
- Commercially available limestone can be used and it is not necessary to grade it into a range of defined particle sizes.
- Effects of scaling are eliminated due to continuous attrition between moving particles.

The major benefit to industry in using the limestone neutralisation process is an expected 37% reduction in alkali cost (Table 5.1). The main purposes of this section are to assess the availability of limestone and to determine the capital cost required for the conversion of 5 M ℓ /d lime treatment plant to a limestone treatment plant.

AVAILABILITY OF LIMESTONE

The process whereby limestone is mined, crushed and converted to lime is shown in Figure 5.1.

Limestone is supplied by major companies, such as PPC Lime and Anglo Alpha. The largest deposit of limestone is at Lime Acres near Kimberley. The purity of that deposit is higher than 90%. It is estimated that South Africa mines five million tons of limestone per year. From this limestone, 1,8 million tons of lime (as CaO) is produced per year.

Limestone is mainly converted to calcium oxide (CaO) which is used by the various industries as shown in Table 5.2. Only 5% of the calcium oxide is hydrated and sells as hydrated lime (Ca(OH)₂). The benefit of calcium oxide is that it has a molecular weight of only 56 compared to the 74 of hydrated lime. Its transport cost is therefore less.

Table 5.2 : Uses for calcium oxide in South Africa.

Application	Percentage (%)
Steel and Ferro Alloys	50
Mining	25
Calcium carbide (Ca ₂ C)	16
Paper	5
Other	4

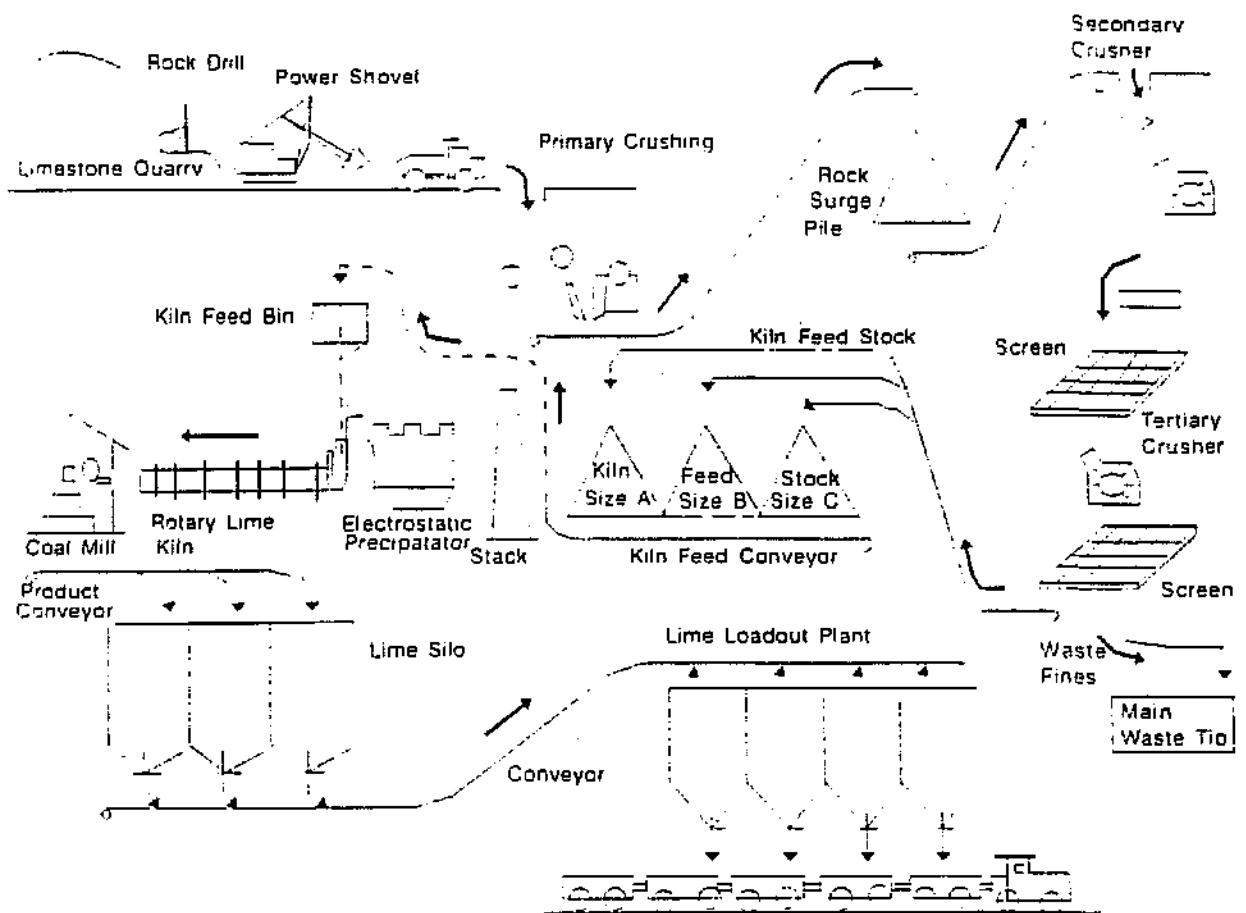


Figure 5.1 : Process whereby limestone is mined, crushed and converted to lime (obtained from PPC brochure).

It is estimated that up to 418 000 t/a of limestone could potentially be used in water treatment. This amount would be available as five million tons of limestone is mined per year.

PROCESS DESIGN CRITERIA

Reactor type: Pipe reactors in series with increasing diameter.
Cone shape

In the case of a pipe reactor, the following criteria need to be applied:

Upflow velocity: 7 - 100 m/h
A slow upflow velocity of 7 m/h is required in the last pipe reactor (or at the top of the cone) in order to prevent washout of the small limestone particles, but high enough to wash out the produced sludge.

A high upflow velocity of 100 m/h is required in the first pipe reactor (or at the bottom of the cone) in order to ensure complete fluidisation of the coarse limestone particles. The upflow velocity is controlled through recirculation of water at a rate q_r .

Contact time: 2 - 10 min for waters with an iron(II) concentration of less than 100 mg/l. Typically, the limestone will occupy 50% of the empty space of the reactor. The residency time of the water in an empty reactor will be referred to as the nominal retention time (RT). The corresponding retention time for a 2 - 10 min contact time therefore amounts to 4 - 20 min.

Volume: The volume (V) is calculated from the feed flowrate (q_f) and the retention time (RT).

$$V = q_f \times RT \quad (1)$$

Cross surface area: The cross surface area (A) of the reactor is determined from the flowrate (feed + recycle) ($q_f + q_r$) and the upflow velocity (v):

$$v = (q_f + q_r)/A \quad (2)$$

Diameter: The diameter (D) in the case of a pipe reactor is calculated from the cross surface area:

$$A = \pi \cdot D^2/4 \quad (3)$$

Height: The height (H) is calculated from the volume of the reactor (V) and the cross surface area (A).

$$V = A \times H \quad (4)$$

The height of the reactor is therefore influenced by the recycle flowrate, as the higher the recycle flow rate is, the smaller is the cross sectional area (equation 2), and accordingly, the greater must be the height (equation 3).

Temperature: The process has been tested over the range 15 to 50°C with no negative effects in any range. The process could therefore possibly be used over a wider range.

Pretreatment: In the case of iron(II)-rich water, pre-treatment is required in order to oxidize iron(II) to iron (III). This can be done biologically (aerobic reactor or in wetlands) or chemically (chlorine, ozone, etc.). No results are available at this stage as it was not within the scope of this project to investigate.

In the case of the cone shaped reactor, the same criteria can be followed as in the case of the pipe reactor, except for the calculation of the dimensions of the reactor. The volume of a cone is a function of its height and diameter:

$$V = 1/3 \times \pi \times (D/2)^2 \times H \quad (5)$$

ECONOMIC FEASIBILITY

The economic feasibility for the conversion of a hydrated lime neutralisation plant (Figure 5.2) to a limestone neutralisation plant (Figure 5.3) is calculated in this section. The calculations are based on a plant with a capacity of 5 Mℓ/d and water with an acid content of 4 g/ℓ (as CaCO₃). The design parameters for a 5 Mℓ/d fluidised-bed limestone neutralisation plant are shown in Table 5.3.

The following assumptions were made in the study:

- * The capital costs involved in the lime neutralisation plant and the limestone neutralisation plant is the same.
- * The running cost of the two processes are the same. It is assumed that labour, supervision, electricity, transport cost, etc are the same.

Table 5.3 : Design parameters for the limestone fluidised-bed neutralisation process.

Parameter	Reactor		
	A	B ₁ Bottom	B ₂ Top
Retention time (min)	4	10	10
Contact time (min)	2	5	0
Upflow velocity (m/h)	120	7,5	1,9
Diameter (m)	3	12	12
Height (m)	2	0,3	0,3
Volume (kl)	14	35	35
Feed flowrate (m ³ /h)	208	208	208
Recycle flowrate (m ³ /h)	625	625	0
Limestone consumption (t/d)	23,5		

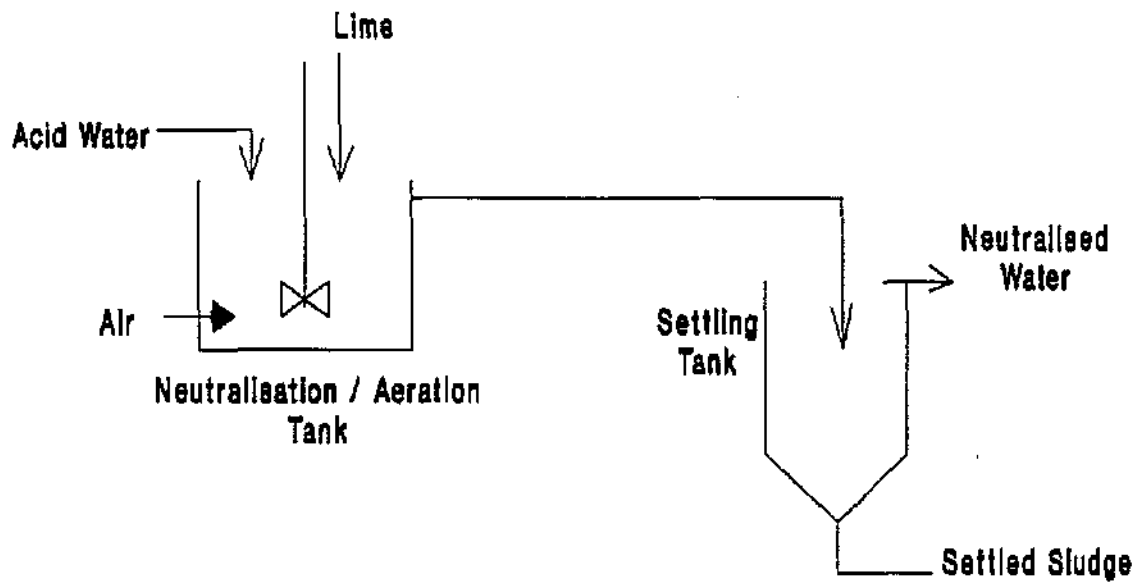


Figure 5.2 : Flow diagram of the lime treatment process.

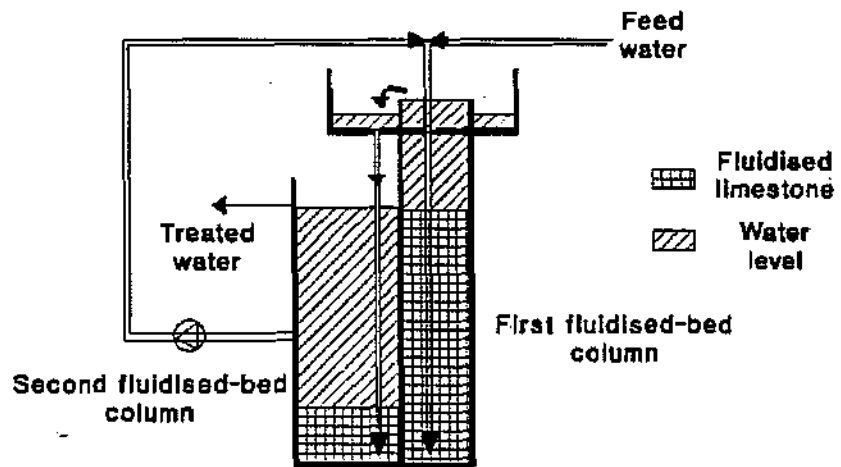


Figure 5.3 : Flow diagram of the limestone treatment process.

The purchase cost of lime (6 355 t/a) for a 5 Mℓ/d plant to treat water with an acid content of 4 g/ℓ (as CaCO₃) is R1 779 482/a. The purity of both lime and limestone were taken at 85%. Neutralisation with limestone (R100/ton versus R280/ton), reduces the alkali cost by 51% (from R1 779 482/year to R858 824/year). This was arrived at as follows:

1,00 t of lime is equivalent to 1,35 t of limestone ($100/74 \times 1$)

The cost of 1,00 t of lime is R280.

The cost of 1,35 t of limestone is R135 ($100 \times 1,35$).

Thus, the saving in chemicals by using limestone is 51,8% or R920 659/a.

The economic implications of converting the full-scale lime plant to a limestone neutralisation plant is calculated in Tables 5.4, 5.5, 5.6 and 5.7.

Table 5.4 : Cost of main items required for fluidised-bed process.

Item	Cost (R) (1993)
Fluidised-bed reactor	25 887
Limestone feed sensor	14 133
Feed pump (208 kℓ/h)	9 686
Recirculation pump (417 kℓ/h)	26 415
Flow meter (417 kℓ/h)	26 415
Limestone feeder	35 334
Limestone silo	40 198
TOTAL EQUIPMENT COST (E)	178 068

Table 5.5 : Equipment and construction cost of fluidised-bed process (1993).

Item	Amount (R)	Amount (R)
Equipment (E)		178 068
Additional equipment (m)		110 758
Piping (0,32E)	56 982	
Concrete (0,089E)	15 848	
Steel (), 017E)	3 027	
Instrumentation (0,073E)	12 999	
Electricity (0,083E)	14 789	
Insulation (0,034E)	6 054	
Paint (0,006E)	1 068	
Direct costs (E + m = M)		288 826
Labour (L = 0,36M)		103 977
Direct costs and labour (M+L)		392 803
Indirect costs: Engineering + Construction (0,34(M+L))		133 553
Direct, Labour and Indirect Costs (A)		526 356
Contingency and Contractor's Fee (0,18) CAPEX		94 744
Technology fee		60 000
TOTAL CAPEX (R)		755 844

Table 5.6 : Calculation of running cost.

Item	Amount (R)
Limestone (8 588 t/a; R100/t)	858 824
Interest on loan (15 years, 17%)	170 686
TOTAL RUNNING COST	1 029 509

Table 5.7 : Calculation of savings.

Item	Amount (R)
Cost of lime (6 355t/a; R280/t)	1 779 482
Minus total running cost	1 029 509
Savings	749 973

PAYBACK PERIOD = Construction cost ÷ Savings
= 12 months

It is shown in the above that the payback period for the conversion of a lime neutralisation plant to a limestone neutralisation plant is 12 months. Should available equipment be used, or luxury items such as the feedpump, flowmeter, limestone silo and the limestone feeder, not be installed, the expected payback period can be reduced to 4 to 5 months.

STATUS OF DEVELOPMENT

The fluidised-bed limestone neutralisation process has been shown to be technically and economically feasible in laboratory, pilot and paper studies. A continuous laboratory plant is in operation to demonstrate this. The process has been patented in South Africa, Canada, Australia and the USA while patent protection is pending in Germany.

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