Wat. Sci. Tech. Vol. 26, No. 1-2, pp. 345-355, 1992.
Printed in Great Britain. All rights reserved.

0273–1223/92 $15.00

TREATMENT OF ACIDIC EFFLUENTS WITH LIMESTONE INSTEAD OF LIME

J. P. Maree, P. du Plessis and C. J. van der Walt

Division of Water Technology, CSIR, P.O. Box 395, Pretoria, 0001, South Africa

ABSTRACT

Traditionally acid mine water is neutralised with lime ($Ca(OH)_2$). Limestone ($CaCO_3$) can be used as an alternative to lime as it is much cheaper. The aim of this study was to investigate the practicality of using cheaper limestone ($CaCO_3$) as an alternative. Beaker and semi-continuous studies were carried out to determine the quality of the water after lime treatment to various pH-values, the influence of $CaCO_3$ dosage, particle size and aeration time on neutralisation rate and the effect of gypsum, magnesium, iron(II) and iron (III).

The rate of neutralisation is fast when stoichiometric dosages of lime are applied. If sufficient crystallisation is allowed, partial removal of sulphate is achieved, as well as complete removal of heavy metals, depending on the pH of the treated water. With limestone the rate of $CaCO_3$ neutralisation depends on the dosage of $CaCO_3$ and particle size. Aeration marginally accelerated the rate of neutralisation as a result of CO_2 stripping. Partial sulphate removal is achieved as a result of $CaSO_4$ crystallisation while magnesium, if present, co-precipitates with the $CaSO_4$. Iron(III) and aluminium(III) are effectively removed but the rate of neutralisation is dramatically retarded by dissolved iron(II). Iron(III) has no influence on the rate of acid water neutralisation. During semi-continuous fluidised bed studies, $CaCO_3$ in the limestone was completely utilised when the particle size was greater than 0.150 mm. The capital costs for lime and limestone neutralisation in a fluidised-bed reactor are similar, but the chemical cost in case of limestone neutralisation amounts to only 29% of that of lime.

KEYWORDS

Acid water; limestone; lime; neutralisation; sulphate removal; heavy metal removal.

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 make discharge of untreated acid mine waters into public streams impossible, as they have a detrimental effect on aquatic plant and fish life. Acid mine water drainage also causes ground water pollution. Traditionally, acid mine water is neutralised by treatment with lime, which results in concomitant precipitation of metal hydroxides such as iron and aluminium hydroxides. Treatment with lime is a suitable process requiring short reaction period due to its relatively high solubility (0.15%). Substantial expenses are incurred as large volumes of water are normally treated this way.

An alternative means of neutralising acid mine water is through treatment with calcium carbonate (limestone). The main advantage of calcium carbonate over lime is that it is significantly cheaper. The delivered price of limestone is approximately R69/t compared to R240/t for lime (R2.86 (South Africa) = 1.00$ (USA)). Another advantage of neutralisation with calcium carbonate is the production of smaller sludge volumes than those produced from the neutralisation with lime (Henzen and Pieterse, 1978).

Several researchers have reported the use of $CaCO_3$ as a neutralising agent for acid waters (Braley, 1951; Barnes and Romberger, 1968; Henzen and Pieterse, 1978; Thompson, 1980). $CaCO_3$ is less expensive as it occurs naturally in a pure state as limestone and with magnesium as dolomitic limestone. Use of high quality limestone (calcium carbonate) is preferable to the use of dolomitic limestone since the latter is considerably less reactive (Hill, 1969) and produces undesirable quantities of magnesium salts (Barnes and Romberger, 1968). Relative to hydrated lime, even high quality limestone requires a long reaction period to treat acid mine water. Despite the long retention time required for neutralisation with limestone, the low cost of this material has encouraged its use in several large-scale applications. At Falconbridge Nickel Mines Ltd in Ontario, Canada, large and variable flows of acid mine water (pH 3.0) were successfully neutralised for several years by mixing the stream with a limestone slurry in an open weir discharging to a large dam (Rivett, 1973). At the Rochester and Pittsburgh Coal Co.'s Lucerne 3A mine (Coal Age, 1969), iron-containing acid mine water 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.

An alternative, more efficient means of neutralisation with limestone is by using the fluidised bed process (Clayton _et_ _al_., 1990). The first aim of this study was to further develop the fluidised bed approach by investigating specific aspects of $CaCO_3$ neutralisation, namely rate of neutralisation, influence of aeration, concomitant sulphate and heavy metal removal, behaviour of magnesium present in dolomitic limestone and the acid mine water, influence of iron on the efficiency of the process and influence of particle size on the rate of neutralisation. Second, the capital and running cost of the two processes were compared.

MATERIALS AND METHODS

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

Beaker Tests

Beaker tests were employed to study the kinetics of acid water neutralisation with lime and limestone. The acid waters used during the study were a diluted sulphuric acid solution, and an acid mine water (AMW) from an old coal mine in the Witbank area (Table 2). Analytical grade lime and raw limestone obtained from Pretoria Portland Cement (PPC) (PPC sinterstone) were used in the neutralisation studies. The PPC sinterstone was screened and graded into various size fractions. The specific particle sizes used in the tests were: <0.150 mm; 0.300 - 0.425 mm; 1.000 - 1.400 mm and 1.400 - 1.700 mm. The limestone was analysed 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.

Neutralisation by lime addition. On addition of lime to 500 ml of acid water, rapid stirring was applied for 2 minutes, followed by 8 minutes slow stirring prior to 10 minutes settling. The supernatant was decanted, filtered and analysed for pH, calcium, magnesium, iron(II), acidity and heavy metals. These measurements enabled determination of acid mine water quality after treatment with lime to various pH values and the rate of gypsum crystallisation.

Neutralisation by calcium carbonate addition. After the addition of calcium carbonate to 500 ml of acid water, the contents were stirred at a speed sufficient to keep the calcium carbonate from settling. Samples were taken regularly and analysed for pH, calcium, magnesium, iron(II), iron(III) and acidity (APHA, 1985). These measurements enabled quantification of the influence of $CaCO_3$ concentration, magnesium presence in dolomitic limestone, gypsum concentration, iron(II) concentration, iron(III) concentration, and $CaCO_3$ particle size, on the kinetics of $CaCO_3$ neutralisation.

Semi-continuous Tests

The feasibility of the process on a semi-continuous basis was examined using the laboratory-scale apparatus represented in Figure 1. It consisted of a vertical perspex tube 35 mm in diameter and 900 mm in length, and a peristaltic and centrifugal pump. The acid feedwater was fed via a Gilson peristaltic pump while the recycle pump (a centrifugal pump) controlled the degree of fluidisation.

The reactor was packed with 100 g of PPC sinterstone of one of the size ranges mentioned above. 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 porosity of the fluidised bed was calculated to be 0.6 and the average upflow velocity 33 m/h. The acid stream to the unit was introduced at 165 ml/min. The treated effluent was sampled at regular intervals and analysed for acidity, calcium, magnesium and pH. The dry mass and carbonate content of the residual solids (after treatment) were determined to determine a carbonate balance on the system.

The experimental conditions during the beaker and semi-continuous tests are listed in Table 1.

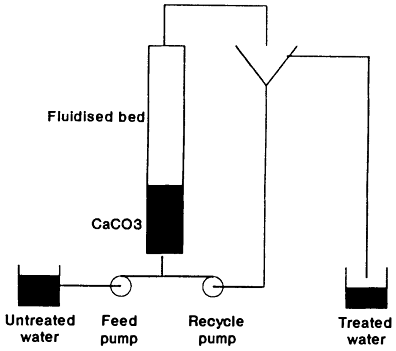


Fig. 1. Experimental apparatus for acid water neutralisation.

RESULTS AND DISCUSSION

Lime Treatment

Neutralisation and heavy metal removal. Table 2 shows the relationship between the lime dosage and the water quality when acid mine water is treated. At a pH value of 11, manganese, nickel, zinc, aluminium and magnesium were completely removed as a result of the low solubility product values of most metal hydroxides. These metals were only partially removed at pH 6.5. Iron removal was effective because it contained mainly iron(III), which precipitates at pH 3. Iron(II) is more difficult to remove than iron(III) as it is still partially soluble at pH 7.

TABLE 1 List of Experimental Parameters for Beaker and Semi-continuous Experiments

Exp No	Water	[Acidity] (mg/l)	Lime dosage (g/l)	Lime-stone dosage (g/l)	Limestone particle size (mm)	Gypsum dosage (g/l)	Table/ Figure
1	AMW	2700	0	0	-	0	T.2
2	AMW	2700	0.3	0	-	0	T.2
3	AMW	2700	1.0	0	-	0	T.2
4	AMW	2700	3.0	0	-	0	T.2
5	AMW	2700	10.0	0	-	0	T.2
6	AMW	2700	2.76	0	-	0	T.3
7	AMW	2700	2.00	0	-	0	T.3
8	AMW	2900		1.7	<0.150	0	F.2
9	AMW	2900		2.5	<0.150	0	F.2
10	AMW	2900		3.3	<0.150	0	F.2
11	AMW	2900		40.0	<0.150	0	F.2
12	AMW	2900		3.3	<0.150	0	Described
13	AMW	2900		3.3	<0.150	0	Described
14	AMW	2900		3.3	<0.150	0	Described
15	AMW	2900		3.3	<0.150	0	F.3a & 3b
16	AMW	2900		3.3	<0.150	1	F.3a & 3b
17	AMW	2900		3.3	<0.150	10	F.3a & 3b
18	H^+	4650		6.0	<0.150	0	F.4
19	Fe(II)	4300		6.0	<0.150	0	F.4
20	Fe(III)	4030		6.0	<0.150	0	F.4
21	H^+	7550		6.0	<0.150	0	F.5
21	H^+	7550		6.0	0.300-0.425	0	F.5
22	H^+	7550		6.0	1.000-1.400	0	F.5
23	H^+	7550		6.0	1.400-1.700	0	F.5
24	H^+	6200		100.0	<0.150	0	F.6
25	H^+	6320		100.0	0.300-0.425	0	F.6
26	H^+	6250		100.0	1.000-1.400	0	F.6
27	H^+	6100		100.0	1.400-1.700	0	F.6

Sulphate removal. During lime treatment, neutralisation occurs with the soluble calcium hydroxide resulting in a decrease in acidity and an increase in pH and calcium concentration in the bulk water. The resulting increase in dissolved calcium concentration can result in supersaturation with respect to calcium sulphate and concomitant precipitation with sufficient reaction time. Table 3 shows the sulphate concentration upon completion of crystallisation after various lime dosages were applied to acid mine water. The different lime dosages applied were calculated to achieve neutralisation in one case, and maximum sulphate removal in the other case. Sulphate was removed from 3770 to 1700 mg/l (54% removal) in the case of a high lime dosage (2760 mg/l), and to 2100 mg/l (44% removal) when a low lime dosage was applied (1998 mg/l). The level to which the sulphate was removed was determined by the solubility product of calcium sulphate which is a function of the calcium and sulphate concentrations as well as the ionic strength of the solution.

$CaCO_3$ Neutralisation

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

$CaCO_3$ neutralisation rate. Both concentration and particle size have a major influence on rate of dissolution of limestone. Figure 2 shows the rate at which acid mine water was neutralised for various $CaCO_3$ concentrations with a particle size of <0.150 mm. These results indicate that the higher the $CaCO_3$ concentration, the more efficient the neutralisation process. This observation, and the fact that $CaCO_3$ is almost insoluble for pH-values greater than 7.5, makes the fluidised-bed reactor ideal for $CaCO_3$ neutralisation. A high $CaCO_3$ concentration in contact with the acid solution will result in a high reaction rate, but no excessive $CaCO_3$ will dissolve due to its low solubility at higher pH values.

TABLE 2 Heavy Metal Removal from Acid Mine Water with Lime Treatment

Parameter	Lime dosage (mg/l)				
	0	300	1000	3000	10000
pH	2.7	3.7	4.3	11.6	12.1
Calcium	198	698	1467	1445	2925
Magnesium	257	283	287	9	<5
Silica	67	66	47	<0.03	<0.03
Aluminium	232	218	66	0.4	<0.05
Iron(II)	56				
Iron(III)	179				
Iron	235	14	2.4	0.05	0.04
Manganese	13.5	14.0	12.5	<0.03	<0.03
Zinc	0.9	0.91	0.82	<0.03	<0.03
Nickel	0.85	0.91	0.85	<0.03	0.04
Sulphate	2668	2514	2436	1160	1299
Alkalinity				460	2050
Acidity	2700				
Fluoride	6.90	6.51	5.25	1.16	1.42

Ca, Mg, Acidity & Alkalinity expressed as $CaCO_3$. Lime expressed as $Ca(OH)_2$.
All the other elements/compounds expressed as the element or compound.

TABLE 3 Chemical Composition of Acid Mine Water Before and After Lime Treatment

Parameter	Concentration		
	Untreated	Neutralised to pH 7.1	Neutralised to pH 10.1
Lime dosage		1 998	2 760
Acidity	2 700		
Alkalinity		50	182
Calcium	198	2 292	2 506
pH	2.8	7.1	10.1
Sulphate	3 770	2 100	1 700
Reaction time (h)		1.3	1.3

Units: Lime - as $Ca(OH)_2$; Acidity, Alkalinity and Calcium - as $CaCO_3$;
Sulphate - as SO_4

The rate of neutralisation takes place in two stages, a fast first phase and a slow second phase. The first phase is associated with the neutralisation of pure H_2SO_4 solutions. Clayton et al. (1990) proposed the following equation:

$$-dc/dt = K\ S\ C_{ab} \qquad [1]$$

where $-dc/dt$ = reaction rate; K = rate constant per unit surface area; S = total available surface area of $CaCO_3$ and C_{ab} = concentration of H_2SO_4. The value of K was found to be constant over the total length of the reaction in the case of pure H_2SO_4 solutions. The slow second phase can be explained by the iron content of the water and/or the saturation level with respect to dissolved calcium sulphate. Clayton et al.(1990) determined the value of K for iron-containing water. In this case the value of K starts off close to the value of pure solutions, but decreases thereafter to less than 0.5 of the initial value. They ascribed this to an increasingly thick layer of $Fe(OH)_3$ precipitate forming on $CaCO_3$ particles, thereby creating a large diffusional resistance. This could possibly explain the slow rate of neutralisation of the acid mine water. The acid mine water contains 235 mg/l iron (of which 179 mg/l is in the Fe(II) form). As Fe(II) and Fe(III) may influence the neutralisation rate of $CaCO_3$ individually, it is necessary to investigate the influence of each of the iron species (see 'Influence of iron').

When the water is undersaturated with respect to calcium sulphate, acidity removal is achieved at a high rate. Once the water is saturated with respect to calcium sulphate, further dissolution of calcium carbonate is limited by the rate at which calcium sulphate crystallises out of solution.

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.

$$CaCO_3 + H_2O \longrightarrow Ca(OH)_2 + CO_2 \qquad [2]$$

Two neutralisation tests were performed on acid mine water with and without aeration respectively. The rate of neutralisation was found to increase only marginally by aeration.

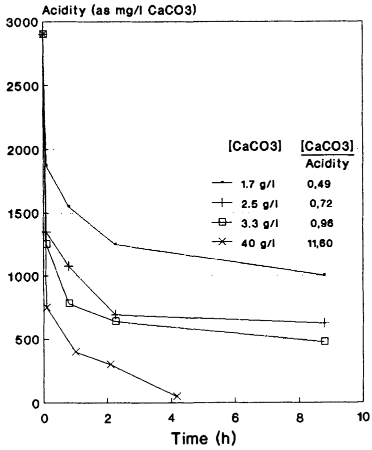


Fig. 2. Rate at which acid mine water is neutralised in the presence of various $CaCO_3$ concentrations.

Relationship between $CaCO_3$ neutralisation and $CaSO_4.2H_2O$ crystallisation. Figures 3a and 3b 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. (1982), who showed that rate of crystallisation is influenced by the concentration of gypsum seed crystals as in the following equation:

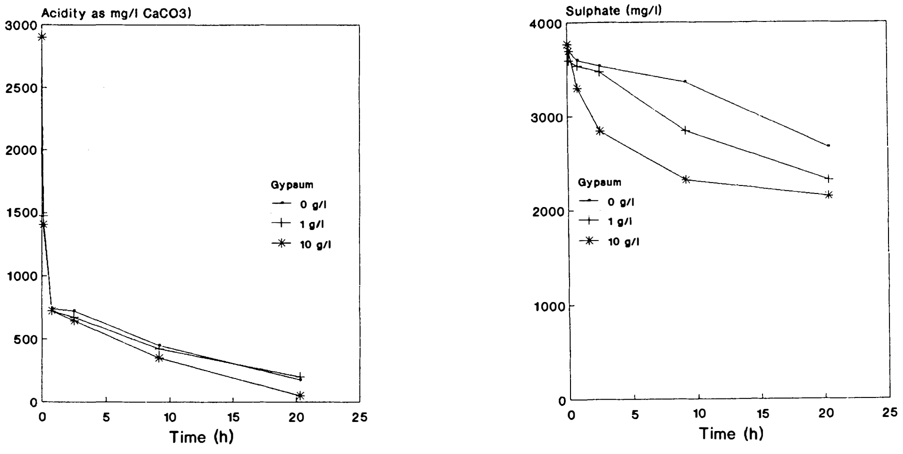
$$d[CaSO_4.2H_2O]/dt = k[CaSO_4.2H_2O](S)[C-C_0]^2 \qquad [3]$$

where $d[CaSO_4.2H_2O]/dt$ = rate of crystallisation; k = reaction rate constant; $[CaSO_4.2H_2O](S)$ = surface area of seed crystals; C = initial concentration of calcium sulphate in solution, and C_0 = 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 '$CaCO_3$ neutralisation') is not influenced by the saturation level of $CaSO_4.2H_2O$, but rather by a factor such as iron in the water.

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 mm. A question arose about the manner in which the calcium and magnesium carbonate components of limestone dissolve during treatment of acid water. A study was initiated in which acid mine water (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 crystallisation. 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 for Mg:Ca dissolved during neutralisation of the acid water. A dosage of 40 g/l showed a ratio of 30:100. 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, when a limestone dosage is applied which is smaller than the acidity of the water, it will dissolve completely. 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 $Ca_xMg_ySO4_{x+y}$ 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 $Ca_xMg_ySO4_{x+y}$ 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).



a. Neutralisation b. Sulphate removal

Fig. 3. Neutralisation and sulphate removal during $CaCO_3$ treatment of acid mine water in the presence of gypsum seed crystals.

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 acid mine water was treated with 3.3 g/l of <0.150 mm limestone, iron and aluminium were removed from 263 and 294 mg/l to 0.07 and 0.10 mg/l respectively. The fluoride concentration 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.

Influence of iron. The efficiency of the $CaCO_3$ neutralisation process is strongly influenced by the acid water's iron content. Figure 4 shows the influence of both iron(II) and iron(III) on the neutralisation rate of acidity in synthetic solutions treated with limestone (6 g/l). The three solutions 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 g/l Fe and 1.17 g/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 masking them from further dissolution in the acid water.

Because acid mine water often contains iron(II), it was expected that complete neutralisation would take place at a reduced rate. This was confirmed by the results shown in Figures 2 and 3. More than 1 h was required for complete neutralisation. Water which contained H_2SO_4 or $Fe_2(SO)_4$, was neutralised within 15 minutes (Figure 4).

Most mine waters contain iron(II), implying that the calcium carbonate neutralisation process needs to be modified by oxidising iron(II) to iron(III). The most cost effective way to do this is probably by means of biological oxidation with iron-oxidising bacteria.

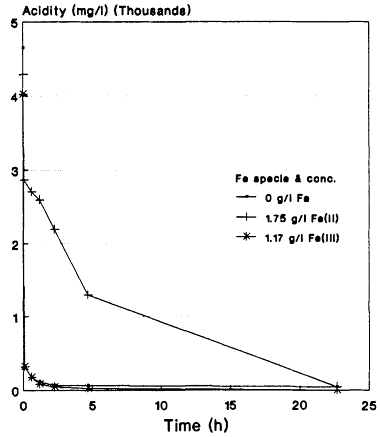


Fig. 4. Influence of iron(II) and iron(III) on the rate of neutralisation.

Particle size. Figure 5 shows 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 H_2SO_4 solution. Clayton et al. (1990) determined the value of the rate constant, K ($min.^{-1}cm^{-2}$), in equation 1 as being 2.45×10^{-3} $min.^{-1}cm^{-2}$ for different particle sizes. Equation 1 represents a first order reaction which means that the rate of neutralisation decreases with increasing acidity.

The fact that the rate equation is first order and that the reaction rate depends on the available surface area of $CaCO_3$, favours the use of a fluidised bed for neutralisation. It is an established fact that the average rate of a first order reaction is faster in a plug flow reactor (the fluidised bed is semi-plug flow) (Levenspiel, 1972). The fluidised bed allows the acid water to come into contact with large excesses (and therefore large surface areas) of $CaCO_3$. Fluidised bed reactor studies were also carried out using limestone with the same particle size as that used during the 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, it was hoped that the high concentration of $CaCO_3$ particles in the bed (approximately 190 times in excess of the acid concentration) would provide a sufficiently high surface area for a faster neutralisation rate. The results of the semi-continuous fluidised bed neutralisation tests appear in Figure 6. Lower pH values were achieved 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). Similarly, the greater the particle size, the greater was the residual acidity value (<0.150 mm, 390 mg/l (as $CaCO_3$); 0.300 mm - 0.425 mm, 400 mg/l (as $CaCO_3$), 1.000 mm - 1.400 mm 500 mg/l (as $CaCO_3$); 1.400 mm - 1.700 mm, 1700 mg/l (as $CaCO_3$)). This confirms that the rate of neutralisation is influenced by the surface area. The short contact period of water 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 [$CaCO_3$]/Acidity ratio was at its maximum (about 190). The [$CaCO_3$]/Acidity ratio decreased with H_2SO_4 feed, and the residual acidity values of the treated water increased. In full-scale applications, the [$CaCO_3$]/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.

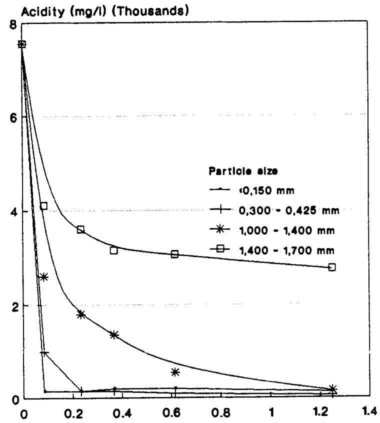
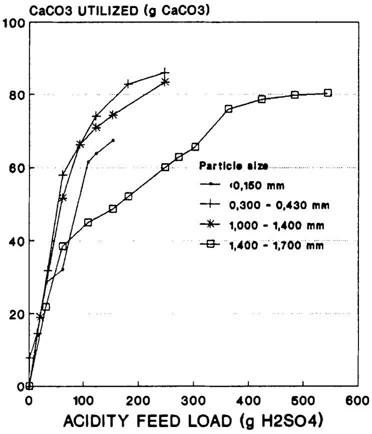


Fig. 5. Neutralisation of a 7.55 g/l H_2SO_4 solution with four different sizes of $CaCO_3$.



[Ac]I = 6,2 g/l; q = 9,9 l/h;1
Ret. time = 0,51 min.

Fig. 6. Utilisation of $CaCO_3$ of various particle sizes during neutralisation of acid water. $[\text{Acidity}]_0$ = 7.55 g/l; Ret. time = 0.51 min.; Mass of $CaCO_3$ = 100 g.

An important economic consideration is the complete utilisation of the calcium carbonate content of the limestone. Figure 6 shows that the $CaCO_3$ 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 $CaCO_3$) 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 (88.1%) as shown in Table 4. 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 maintained (15 min.) than in the laboratory studies.

TABLE 4 Utilisation of Carbonate in Limestone Samples with different Particle Sizes

Limestone particle size (mm)	Carbonate utilised (% $CaCO_3$)	Carbonate unutilised (% $CaCO_3$)	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*	87.3*
Average of (*)	83.1	5.0	88.1

For a particle size of <0.150 mm, only 67 g $CaCO_3$ of the available 85 g $CaCO_3$ in the limestone was utilised (79% efficiency). This inefficient utilisation is due to partial wash out of very small particles prior to complete reaction. It is therefore recommended that powder limestone should not be dosed to acid water by means of a fluidised bed reactor. If powder dosing is required, it is recommended that the powder be added to a completely mixed reactor. As a result of the large surface area of a powder, the reaction time compared to the $CaCO_3$ with larger particle sizes, would be short.

Figure 6 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.

Economical Feasibility

The chemical and equipment costs are compared in this section for lime and limestone. The cost is based on water with an H_2SO_4 concentration of 4 g/l and a flow of 2.5 Ml/d. Based on an upflow velocity of 1 cm/s and a retention time of 3 min., it was calculated that the diameter of the fluidised bed reactor needs to be 1.92 m and its height 1.8 m. An additional 0.8 m was allowed to prevent $CaCO_3$ escaping from the reactor.

The flow sheets of the two processes are shown in Figures 7 and 8 respectively. The equipment cost of the various items indicated in Figures 7 and 8 are calculated in Table 5, and the chemical cost in Table 6. From Table 5 it is concluded that the equipment cost of the limestone neutralisation process is only 13% more expensive than that of the lime process. The chemical cost of the limestone neutralisation process is, however, much cheaper than that of the lime process. It amounts to only 29% of the lime costs (Table 6).

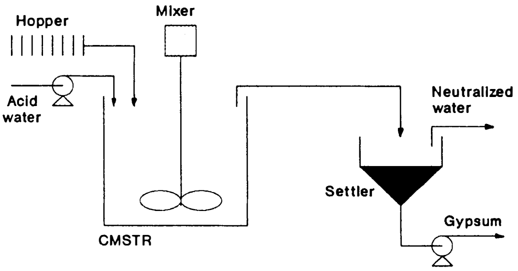


Fig. 7. Flow diagram of the lime treatment process.

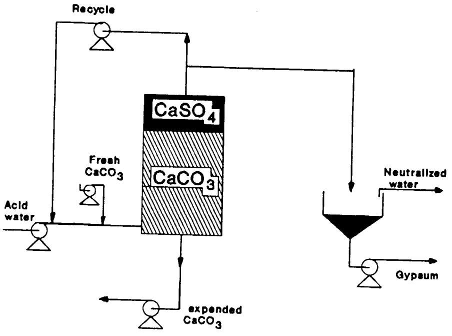


Fig. 8. Flow diagram of the limestone treatment process.

CONCLUSIONS

In case of lime treatment, it was determined that the rate of neutralisation is fast when stoichiometric dosages of lime are applied. Partial removal of sulphate is achieved (if sufficient crystallisation time is provided) and complete removal of heavy metals, depending on the pH of the treated water.

With the limestone process, the rate of $CaCO_3$ neutralisation is directly related to the dosage of $CaCO_3$ and particle size. Aeration marginally accelerated the rate of $CaCO_3$ neutralisation as a result of CO_2 stripping. 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 $CaSO_4$. Iron(III) and aluminium(III) are effectively removed during $CaCO_3$ neutralisation. The rate of $CaCO_3$ neutralisation is retarded by the presence of iron(II) in solution. Iron(III) has no influence on the rate of acid water neutralisation. During semi-continuous fluidised bed studies, $CaCO_3$ in the limestone is completely utilised when the particle size is greater than 0.150 mm.

The capital costs for lime and limestone neutralisation in a fluidised-bed reactor are similar while the chemical cost in case of limestone neutralisation amounts to only 29% of that of lime.

TABLE 5 Equipment Costs of the Lime and Limestone Processes

Equipment	Cost (R)* Lime	Limestone
1 Reactor	30 000	
2 Pumps	21 500	
1 Settler	94 600	
1 Hopper	8 000	
1 Mixer	2 000	
1 Reactor		41 000
5 Pumps		40 500
1 Settler		94 600
Equipment cost	156 000	176 100

TABLE 6 Chemical Cost of the Lime and Limestone Processes

	Cost (R)* Lime	Limestone
H_2SO_4 conc. in water	4.00	4.00
Chemical equivalent (g/l) (85% pure)	3.63	4.90
Flow rate (Ml/d)	2.50	2.50
Chemical cost (R/t)	280	60
Chemical cost (R/a)	927 465	268 275
Chemical cost (R/m^3)	1.01	0.29

* R2.86 (South Africa) = 1.00$ (USA)

ACKNOWLEDGEMENTS

The authors express their sincere thanks to the Water Research Commission for their financial support and to Wates & Wagner Consulting Engineers and the Department of Water Affairs for partial financial support and for the provision of acid mine water from the Witbank area.

REFERENCES

APHA, (1985). Standard methods for the Examination of Water and Wastewater treatment. Twelfth Edition. American Public Health Association, New York.

Barnes, H.L.; Romberger, S.B. (1968). Chemical Aspects of Acid Mine Drainage. J. Water Pollut. Control Fed., 40(3), 371-384.

Benjamin, L., Loewenthal, R.E. and Marais, G.v.R. (1977). Calcium Carbonate Precipitation Kinetics, Part 2. Effects of Magnesium., Water SA, 3(3), 155- 165.

Braley, S.A. (1951). A Pilot Plant Study of the Neutralisation of Acid Drainage from Bituminous Coal Mines. Commonwealth of Pennsylvania, Dept. of Health.

Clayton, J.A., de Villiers, M.G., Maree, J.P. and Pienaar, G. (1990). Calcium carbonate neutralization of acidic effluents in a fluidised bed. Proceedings of The Southern Africa Industrial Water Symposium, Indaba Hotel, Witkoppen, Johannesburg, 27-28 September.

Coal Age, 75(2) (1969) 112-114.

Ford, C.T. (1972). Development of a limestone treatment process for acid mine drainage. Proceedings of the fourth symposium on Coal Mine Drainage Research, Mellon Institute, Pittsburg, Pennsylvania, USA, 26-27 April.

Henzen, M.R. and Pieterse, M.J. (1978). Acidic Mine Drainage in the Republic of South Africa. Progress in Water Technology 9(4),981-992.

Hill, D.W. (1969). Neutralisation of Acid Mine Drainage. Water Poll. Control Fed., 41, 1702-1715.

Levenspiel, O. (1972). Chemical Reaction Engineering. 2nd Edition, Wiley and Sons, New York.

Maree, J.P. Strydom, W.F. van Vuuren, L.R.J. (1982). Kinetics of calcium sulphate crystallisation. Proc. of Symposium on Water Research, Selected in-depth studies, CSIR Conference Centre, Pretoria, South Afrrica, 18 November.

Rivett, Y.L.S. (1973). Acid Neutralisation. Water and Wastes Eng., 10(3), 12-16.

Thompson, J.G. (1980). Acid Mine Waters in South Africa and their Amelioration. Water SA, 6(3), 130-134.