NEUTRALIZATION OF ACID COAL MINE WATER WITH DOLOMITE IN A FLUIDISED-BED REACTOR

G J van Tonder, J P Maree and P Millard

Division of Water Technology, CSIR, P O Box 395, Pretoria, 0001, South Africa
(E mail: JMaree@watertek.csir.co.za)

ABSTRACT

Traditionally, lime is used for the neutralization of acidic effluents. Limestone and dolomite should be considered as alternatives because of considerations such as lower cost, low solubility at pH values greater than 7 and simple dosing systems required. The paper describes the technical feasibility of neutralising acid mine water from a coal mine with dolomite using fluidised bed technology. A contact time of 15 min between acid water and dolomite was sufficient to increase the pH from 2,5 to 6,5. The acid content was reduced from 600 to less than 50 mg/ℓ (as $CaCO_3$). Impurities in the dolomite was washed out during the process.

INTRODUCTION

Protection of the environment dictates that acidic streams, such as acid mine water, is neutralised prior to discharge into public streams. Traditionally, lime (calcium hydroxide) has been used for this purpose. Limestone (calcium carbonate) and dolomite (calcium magnesium carbonate) can also be considered. By using a fluidised-bed reactor for limestone or dolomite neutralization, the main disadvantages of limestone and dolomite (low reactivity and scaling with gypsum and iron hydroxide precipitates) can be overcome. The low reactivity of limestone and dolomite is overcome in the fluidised-bed reactor as an excessive amount of limestone or dolomite is in contact with the acid water. Scaling of limestone particles is prevented due to the attrition between particles under fluidised conditions.

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

- Limestone/dolomite is more cost-effective. At prices of 18 USA$, 26 USA$, 66 USA$, 100 USA$ and 540 USA$ per ton for dolomite, limestone, unhydrated lime, hydrated lime and sodium hydroxide respectively, the alkali cost for the neutralization of acid water with an acid content of 2 g/ℓ amounts to 3,5 c/kℓ in the case of dolomite, 5,0 c/kℓ in the case of limestone, 7 c/kℓ in the case of unhydrated lime, 13 c/kℓ in the case of hydrated lime, and 86 c/kℓ in the case of sodium hydroxide.

- No accurate control of dosage is required, as the solubility of limestone and dolomite is low at pH-values greater than 7.

- Sludge of a higher density, compared to lime, is produced in the case of iron(III)-rich, resulting in smaller clarifiers .

- It is safe to handle.

- It is easy to store.

According to earlier findings [1, 2, 3, 4] the kinetics of acid neutralization using limestone may be represented by the rate equation:

$$-\frac{d[H_2SO_4]_b}{dt} = K\ S\ [H_2SO_4]_b \qquad (1)$$

where K is the rate constant based on surface area, S is the total available surface area of limestone/dolomite and $[H_2SO_4]_b$ 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 x 10^{-3} $min^{-1}.cm^{-2}$. For effluents containing significant quantities of iron, the value of K is decreased, as a layer of $Fe(OH)_3$ forms on the $CaCO_3$ surface.

The rate of neutralization was found to be directly related to the dosage of $CaCO_3$, the particle size of limestone and the type of metal in solution. The presence of iron(II) in solution retarded the rate markedly, while iron(III) had no influence. Aeration marginally accelerated the rate of limestone neutralization as a result of CO_2-stripping.

The studies also confirmed that limestone neutralization improves water quality by removing free acid and acid associated with Fe(III). Sulphate is removed to the saturation level of calcium sulphate. The pH of the neutralised acid water depends on the metals that remain in solution after neutralization. If magnesium is present partial co-precipitation with $CaSO_4.2H_2O$ occurs, while iron(III) and aluminium(III) are effectively removed as metal hydroxides.

The question arises whether dolomite can be used as well. In South Africa, dolomite is generally cheaper than limestone. The purpose of the study was to determine the technical feasibility of dolomite neutralization of acid mine water from a coal mine in a fluidised bed reactor.

MATERIALS AND METHODS

Feed water and dolomite

Acid mine water, obtained from Hlobane Collieries in Natal, as well as simulated acid water, prepared from sulphuric acid and ferrous sulphate, was used as feed.

Dolomite, with a particle size less than 1 mm, was used in the neutralisation studies.

Pilot plant

The pilot plant consisted of a fluidised-bed reactor, a cone reactor (top part of Sala pump) and a recycle pump (Sala pump) (Figure 1). The purpose of the cone reactor was to allow fine dolomite particles washed out from the fluidised-bed reactor to settle and return to the fluidised-bed reactor via the recycle pump. Table 1 shows the values of various parameters for the system. A feed rate of 1,25 ℓ/min and a recirculation rate of 50 ℓ/min was employed. Between 20 and 22 kg of dolomite was present in the reactor at any time. The recirculation rate was set to fluidise the dolomite. A diaphragm pump was used to feed acid water from either the acid water.

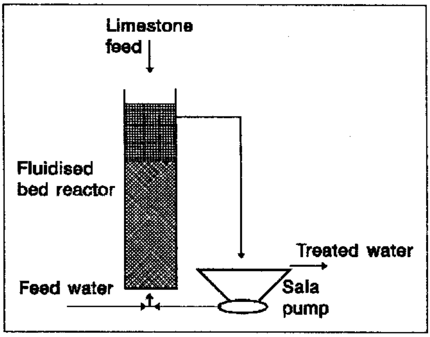

Figure 1. Schematic diagram of limestone/dolomite neutralisation plant.

TABLE 1 DESIGN AND TYPICAL OPERATIONAL PARAMETERS FOR THE PILOT PLANT

Parameter	Cone reactor			Fluidised-bed reactor
Height (mm)	150 bottom	250 middle	500 top	1800
Feed rate (ℓ/min)	1,3	1,3	1,3	1,3
Recycle rate (ℓ/min)	50	0	0	50
Upflow velocity (m/h)	3	1	0,2	105
Diameter (mm)	150	250	500	190
Empty volume (ℓ)	1	4	33	50
Retention time (min)	0,8	3	26	40
Dolomite (kg)	0			20
Contact time (min)**	0			15

** At a dolomite concentration of 1 kg/ℓ in the fluidised-bed reactor, the contact time between acid water and dolomite is calculated as follows:

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

Retention time = Empty volume (ℓ) ÷ feed rate (ℓ/min)

Dolomite feed system.

Dolomite was fed either manually or by means of a screw feeder/hopper. A load cell was used to activate and stop the feeder at the set minimum and maximum mass levels in the load cell. A mass of 20 to 22 kg of dolomite was kept in the fluidised-bed reactor. One kg of dolomite replaced 0,341 kg of water in the fluidised-bed reactor, so the amount of dolomite present in the fluidised-bed reactor at any time was given by the following equations:

Mass of dolomite in reactor (kg) $= (W - W_0)/(1{,}0 - 0{,}341)$
where:

W = mass of (cone + water + dolomite)

W_0 = mass of (cone + water) $= 66{,}73$ kg.

$\therefore$ Mass of dolomite in reactor (kg) $= 1{,}518 \times W - 101{,}3$

Experimental

Acid water was pumped through the fluidised-bed reactor continuously at a rate of 1,25 ℓ/min. The following aspects were investigated:

- Chemical composition of feed and treated water.
- Utilisation of dolomite by determining the amounts of acid neutralised and dolomite consumed in a specific time interval.
- Behaviour of impurities in dolomite in the fluidised-bed reactor by determining the dolomite content in the fluidised-bed reactor at various heights (top, middle and bottom) on a regular basis.

Analytical

Samples were collected and filtered (Whatman No 1) during continuous studies. Samples were analyzed for pH, calcium, magnesium, and acidity [5]. Alkalinity was determined by titration with hydrochloric acid to pH 4,3 and acidity by titration with sodium hydroxide to pH 8,3.

The $CaCO_3$ content of the fresh dolomite as well as in the fluidised-bed reactor was determined by dissolving 5 g of dried material in 200 mℓ of 1 N HCl. A 5 mℓ sample of the filtered solution was titrated to pH 7,0 with 0,1 N NaOH.

RESULTS AND DISCUSSION

Chemical composition

Table 2 shows typical values for the composition of the acid mine water and the simulated water.

Table 3 shows the chemical composition of acid and treated (neutralised) water. The following observations can be made: The pH increased from 2,9 to 6,4. Calcium and magnesium levels increased due to their presence in the dolomite that was used.

Table 4 shows results obtaining when neutralising artificial make-up made-up acid water.

TABLE 2: CHEMICAL COMPOSITION OF THE ACID MINE WATER AND THE SIMULATED MINE WATER.

Parameter	Concentration (mg/ℓ)			
	Sample 1	Sample 2	Sample 3	Simulated
pH	3,0	2,8	3,0	2,4
Acidity (as $CaCO_3$)	424	570	308	627
Sulphate (as SO_4)	2 233	2 468	2 369	-
Manganese (as Mn)	15,1	17,3	14,3	-
Calcium (as Ca)	357	366	373	-
Total iron (as Fe)	56,5	60,8	33,0	141
Magnesium (as Mg)	169	168	169	-

TABLE 3. CHEMICAL COMPOSITION OF THE UNTREATED AND TREATED MINE WATER.

Parameter	Concentration (mg/ℓ)	
	Untreated	Treated
pH	2,9	6,4
Acidity (as $CaCO_3$)	410	23,9
Sulphate (as SO_4)	2404	2482
Manganese (as Mn)	15,2	17,9
Calcium (as Ca)	369	451
Total iron (as Fe)	45,3	5,8
Magnesium (as Mg)	169	197

TABLE 4. CHEMICAL COMPOSITION OF THE UNTREATED AND TREATED SIMULATED WATER.

Parameter	Concentration (mg/ℓ)	
	Untreated	Treated
pH	2,4	7,1
Acidity (as $CaCO_3$)	627	47
Total iron (as Fe)	141	107

Plant performance

Figures 2 and 3 show the behaviour of various parameters during continuous treatment. Figures 2.a - 2.b apply to the on-site run, and figures 3.a - 3.b to a run on simulated mine water.

The following observations can be made: The pH of the acid water was raised from just below 3 to values greater than 6. During on-site studies the acidity was removed from 400 mg/ℓ (as $CaCO_3$) to less than 25 mg/ℓ (as $CaCO_3$). Studies on simulated water showed that the acidity was reduced from about 620 mg/ℓ to less than 50 mg/ℓ. This can be represented by the following reaction:

$$2H_2SO_4 + MgCa(CO_3)_2 \rightarrow CaSO_4(aq) + MgSO_4(aq) + 2CO_2 + 2H_2O \qquad (2)$$

Total iron was reduced from 45 mg/ℓ to 6 mg/ℓ during on-site studies (Table 2), while it was reduced from 141 to 107 mg/ℓ during treatment of simulated water (Table 3). For complete removal of iron (II), pre-oxidation of iron(II) to iron(III) in an aeration pond is recommended (Reaction 3), as iron(III) precipitates immediately as $Fe(OH)_3$ during limestone neutralisation [4].

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

During neutralisation of mine water (on-site) the calcium content increased on average from 370 to 450 mg/ℓ (as $CaCO_3$) (Table 2) and the magnesium content from 169 mg/ℓ to 197 mg/ℓ.

Dolomite utilisation

Figures 4.a. and 4.b. show that for dolomite the utilisation efficiency was between 60 and 70%. This is the result of manual feeding and poor sedimentation. Poor sedimentation of dolomite particles can be ascribed to turbulence in the cone part of the Sala pump, which was used as a settler. When the plant is fed continuously by a feeder-hopper system and sedimentation is improved, utilisation efficiencies above 90% will be achieved. This was shown in previous neutralisation tests [3,4].

Dolomite impurities

Some types of limestone/dolomite contain high-density impurities, that tend to built up in the fluidised-bed reactor, and eventually suppresses neutralisation, while the density of the impurities of other types are low and is washed out with the effluent. Figure 5 shows the composition of the reactor contents at different depths. The impurities tend to concentrate at the top of the fluidised-bed reactor and does not accumulate at the bottom. Therefore, no removal of impurities would be required from the fluidised-bed reactor for the dolomite used in this investigation.

The effect of iron(II)

Previous research [4] showed that iron(II) in the feedwater slowed the neutralisation process and decreased the limestone utilisation efficiency. Due to the relatively low iron(II) concentrations in acid water used in this study, the influence of iron on the neutralisation process was found to be negligible.

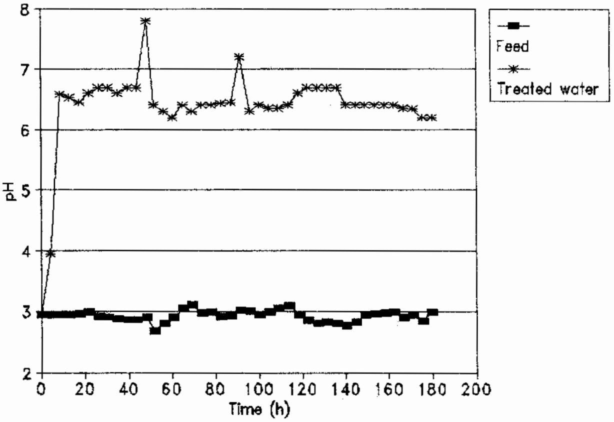

Figure 2.a Behaviour of pH during dolomite neutralisation (on-site).

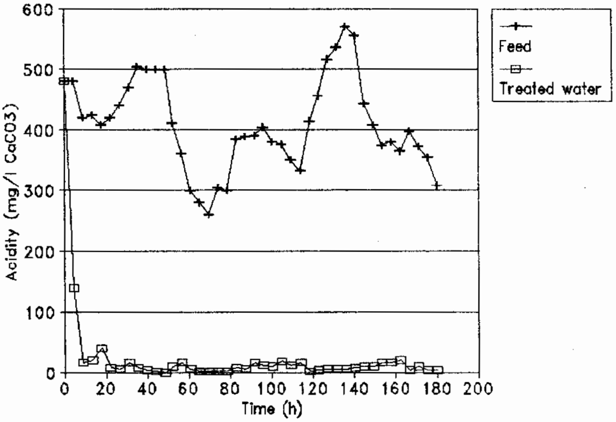

Figure 2.b Behaviour of acidity during dolomite neutralisation (on-site).

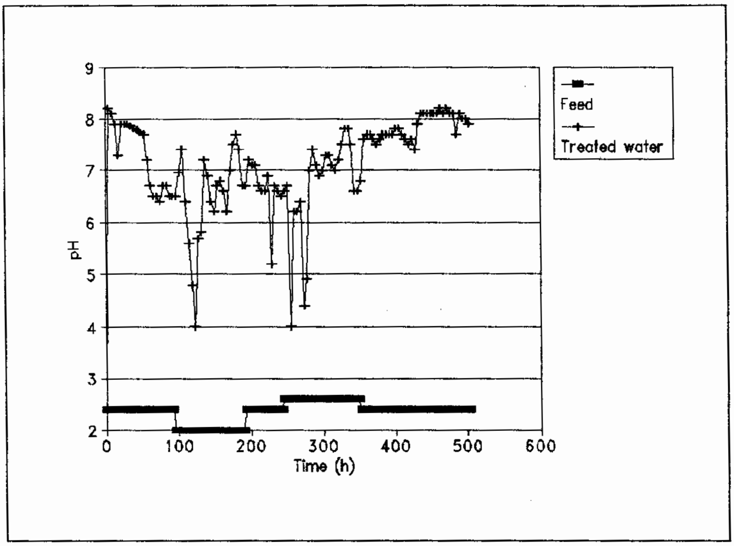

Figure 3.a Behaviour of pH during dolomite neutralisation (simulated water).

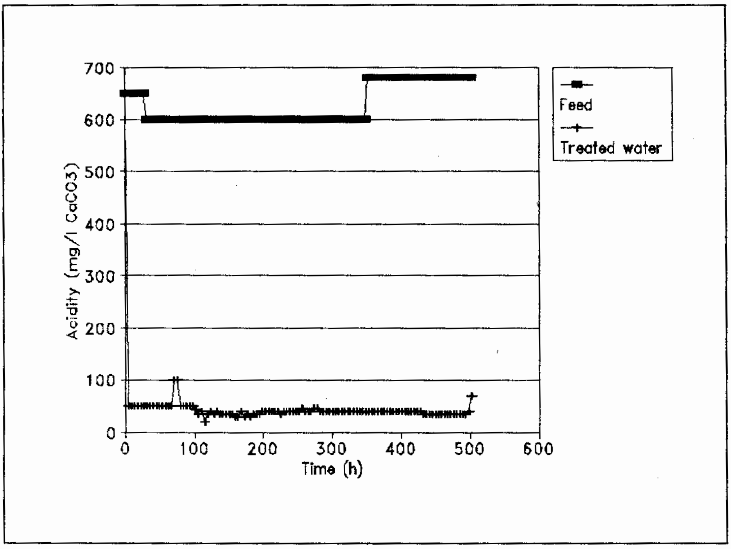

Figure 3.b Behaviour of acidity during dolomite neutralisation (simulated water).

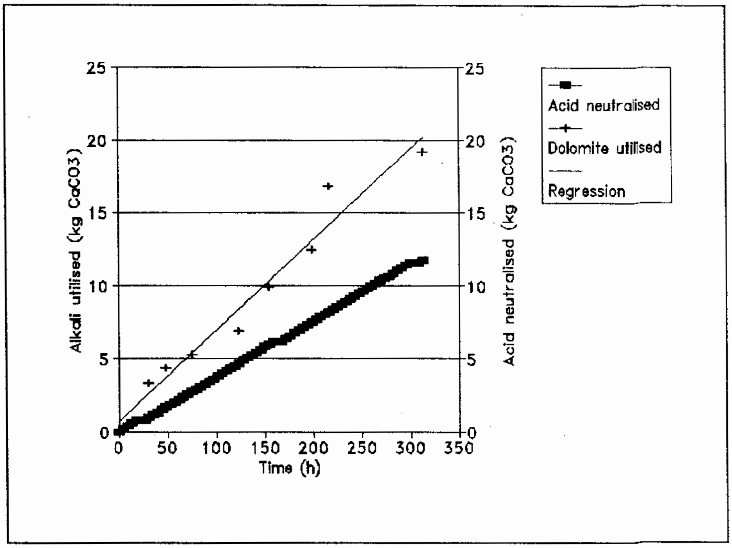

Figure 4.a Efficiency of acid removal and dolomite utilisation (on-site).

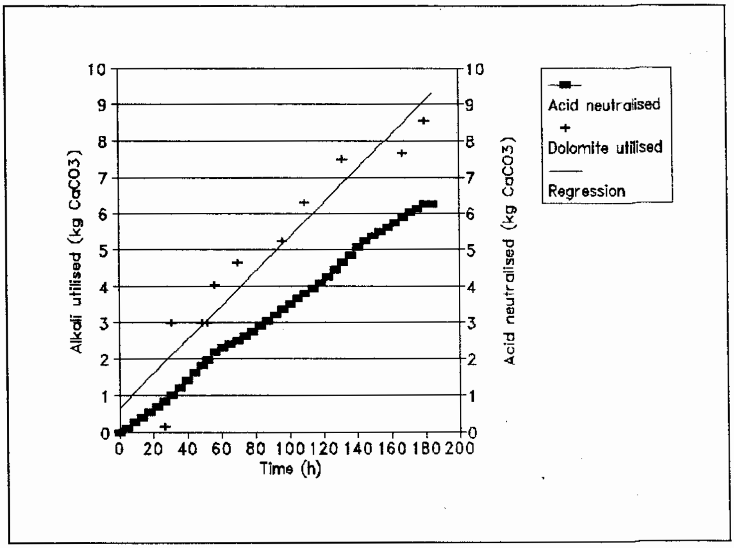

Figure 4.b Efficiency of acid removal and dolomite utilisation (simulated water).

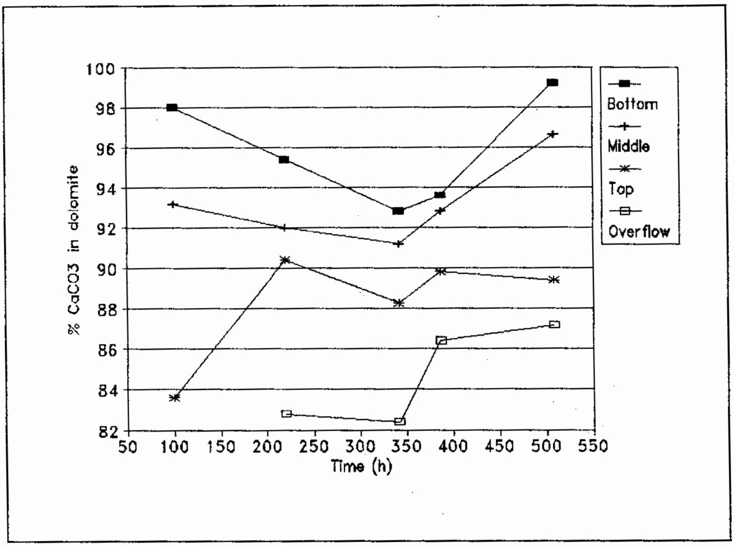

Figure 5. Dolomite purity gradients at different depths in the fluidised-bed reactor.

CONCLUSIONS

The chemical composition of acid mine water can be improved by treating it with the dolomite neutralisation process:

- The pH can be increased from 2,5 to 6,5.
- The acidity can be reduced from 600 to less than 50 mg/ℓ (as $CaCO_3$).

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