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PILOT-SCALE NEUTRALISATION OF UNDERGROUND MINE WATER

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ABSTRACT

Traditionally acid mine water is neutralised with lime ($Ca(OH)_2$). Limestone ($CaCO_3$) is a cheaper alternative for such applications. This paper describes an investigation aimed at demonstrating that underground mine water can be neutralised with limestone in a fluidised-bed. The contact time required between the limestone and the acid water, chemical composition of water before and after treatment, and economic feasibility of the fluidised bed neutralisation process are determined. A pilot plant with a capacity of 10kl/h was operated continuously underground in a gold mine. The underground water could be neutralised effectively using the limestone process. The pH of the water was increased from less than 3 to more than 7, the alkalinity of the treated water was greater than 120 mg/l (as $CaCO_3$) and the contact time required between mine water and limestone was less than 10 min (the exact contact time depends on the limestone surface area). Chemical savings of 56.4% can be achieved compared to neutralisation with 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. The acid water is formed largely through bacterial oxidation of pyrites when exposed to oxygen and water. The oxidation reaction can be represented as follows (Barnes, 1968):

$$2FeS_2 + 7\tfrac{1}{2}O_2 + H_2O \dashrightarrow Fe_2(SO_4)_3 + H_2SO_4 \qquad (1)$$

Its chemical composition makes the discharge of untreated acid mine waterss into public streams impossible. Such waters have a detrimental effect on aquatic plant and fish life due to low pH levels and the presence of low concentrations of radioactive uranium. Acid mine drainage may also cause groundwater pollution and is corrosive to pipelines transporting it. To date only lime, sodium hydroxide and sodium carbonate have been used for neutralisation. These chemicals have the disadvantage that they require accurate dosing to prevent under or over application. Since the flow rate of underground mine water may vary by a factor of 10 (Pulles *et al.*, 1994), lime/soda ash systems can only function well if dosing rates are adjusted accordingly. The result of inadequate dosing control is that water from low to high pH values (3 to 10 respectively) is pumped through the vertical mine water pipelines, resulting in either corrosion as a result of the low pH, or scale formation (gypsum) as a result of high calcium concentrations in typical mine water. Since large quantities of lime are required, neutralisation of effluents such as the above is a costly operation.

The CSIR has developed a fluidised-bed neutralisation process which uses limestone or dolomite as the neutralising agent (Maree and du Plessis, 1993). This process overcomes the dosing problem as limestone will only dissolve as long as the water is undersaturated with respect to $CaCO_3$. The saturation usually occurs at a pH between 6 and 8.

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

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

MATERIALS AND METHODS

Feed water and limestone

The pilot plant was positioned at level 50 (1.3 km below the surface) North Shaft of the Western Areas Gold Mining Company. Acid water from the gold mining operations was treated. The mine discharges 70 Ml/d to the surface to keep away from the mining operations. The underground water originates from rain that seeps into dolomite compartments in the first 200 to 300 m below the soil surface, and also from dust suppression activities at the mining face. The study was carried out underground to demonstrate that the fluidised-bed process can be operated under typical operating conditions in areas where limited space is available, and that no sophisticated dosing equipment is required. Limestone obtained from various sources was used in the investigation (Table 1).

Table 1. Characteristics of limestone used during the pilot-plant study

Limestone type	Purity (% as $CaCO_3$)	Particle size range (mm)	Bulk density (kg/ℓ)	Void %
Tvl A	83	2-5	1.24	57.5
Cape A	97	0.1-4	1.43	49.8

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

Pilot plant

The pilot plant used could be operated at a variable capacity of 1 to 10 kl/h (Fig. 1). It consisted of a fluidised-bed reactor, a recirculation clarifier, a limestone silo and a recycle pump. The purpose of the recirculation clarifier was to allow fine limestone particles washed out from the fluidised-bed reactor to settle and return to the fluidised-bed reactor via the recycle pump. Table 2 summarises the design and operational parameters for the system. After startup, the feed rate was gradually increased from 1.0 to 7.2 kl/h. The recycle flow rate was 35 kl/h. Between 100 and 180 kg of limestone (Tvl A) was present in the reactor at any time. The recirculation rate was set to fluidise the limestone. A compressed air pump was used to feed acid water to the plant.

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

CT = Bed volume/Q
= $A.h_B/Q$
ACT = Bed interstitial volume/Q
= $(A.h - V)/Q$

$= (A.h_B - m_S/\ {}_S)/Q$
$= (A.h_B/Q).(1 - m_S/(\ {}_S.A.h_B))$
$= CT.(1 - m_S/(\ {}_S.A.h_B))$
$HRT = A.h_T/Q$
where: ρ_s = solid density (2.85 kg/l)
ρ_b = bulk density
CT = contact time between limestone and water
ACT = actual contact time between limestone and water
C_S = limestone concentration in the bed of the reactor
A = bed cross-sectional area
h_B = height of limestone bed in fluidised-bed reactor during fluidisation
V_S = volume of solids
Q = flow rate
m_S = mass of solids
ρ_S = density of solids
HRT = hydraulic retention time
h_T = height of fluidised-bed reactor.

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

$C_S = m_S/(A.h_B)$
$= 1$ kg/l, during fluidisation,
$ACT = 0.65 \times CT$

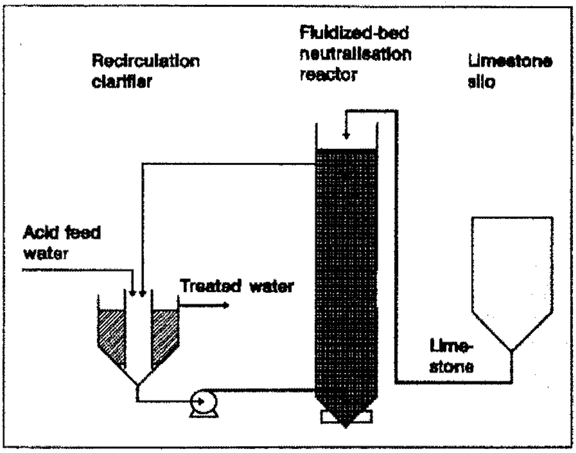

Figure 1. Schematic diagram of the limestone neutralisation plant.

Limestone feed system

Limestone was stored in a 1 000l silo with a cone shaped bottom. The feed rate of the limestone was controlled with a commercial vibrator. A load cell was used to activate and stop the feeder. The mass of limestone in the fluidised-bed reactor was allowed to fluctuate over a range of 20 kg. The amount of limestone present in the fluidised-bed reactor at any one time was calculated by the following equations:

$$\text{Mass of limestone in reactor (kg)} = (M_T - M_{OW})/0.65 \qquad (2)$$

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

$M_t = M_W + M_S$
$= (V-X).\rho_W + X.\rho_S$

$$
\begin{aligned}
 &= V.\rho_W - X.\rho_W + X.\rho_S \\
X &= (M_t - V.\rho_W)/(\rho_S - \rho_W) \\
M_S &= \rho_S.X \\
 &= \rho_S.(M_t - V.\rho_W)/(\rho_S - \rho_W) \\
 &= (M_t - V.\rho_W)/(1 - \rho_W/\rho_S) \\
 &= (M_t - M_{OW})/(1 - \rho_W/\rho_S)
\end{aligned}
$$

where: M_t = mass of water and limestone
M_W = mass of water in reactor when limestone is present
M_{OW} = mass of water in reactor when no limestone is present
M_S = mass of limestone
V = empty volume of reactor
X = volume of water replaced by limestone
ρ_S = density of limestone
ρ_W = density of water
If ρ_S = 2.85 g/l and ρ_W = 1.0 g/l
then M_S = $(M_t - M_{OW})/0.65$

Continuous studies

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

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

Table 2. Design and typical operational parameters for the pilot plant

Parameter	Fluidised-bed reactor	Recirculation clarifier
Feed rate (kℓ/h)	3	3
Recycle rate (kℓ/h)	35	35
Diameter (mm)	355	-
Cross-sectional area (m^2)	0.099	0.98
Height (m)	4.0	0.8
Empty volume (kℓ)	0.396	0.864
Upflow velocity (m/h)	354	3
Limestone charge (kg)	140	-
Contact time (min)	2.8	-
Actual contact time (min)	1.8	-

Batch studies

Batch studies were carried out in beakers by adding a specific amount of limestone to 1l of stirred mine water in order to determine the following:

- The effect of limestone concentration on the neutralisation rate.
- Rate of neutralisation when using different limestone types (Tvl A and Cape A).

Analytical

Samples were collected regularly and filtered automatically through Whatman No 1 filter paper. Samples were analysed for pH, calcium, magnesium, iron and acidity (APHA, 1985). Treated samples were filtered through Whatman No 540 before being analysed. Alkalinity was determined by titration with sodium hydroxide to pH 7.0. CO_2gas was allowed to escape freely from solution while waiting in the sampler. pH, acidity and alkalinity analyses were carried out.

RESULTS

Table 3 shows the composition of the water before and after limestone neutralisation in the pilot plant, while Fig. 2 and Fig. 3 show the temporal behaviour of pH and acidity during continuous treatment respectively. Fig. 4 shows the effect of different types of limestone on the rate of neutralisation.

DISCUSSION

General performance

From the pH and acidity values (Figs. 2 and 3) it is noted that, with the exception of 5 occasions during the first 360 h of operation of the pilot plant, an effluent with consistently acceptable pH and low acidity was produced. The exceptions were due to failure of the electronically controlled recycle pump. During power fluctuations the speed control cut out and the pump had to be restarted manually. This problem was eventually overcome by overriding the electronic speed control unit.

Chemical composition of feed water

During the study, the sulphate content in the feed water varied between 500 and 800 mg/l, acidity between 300 and 400 mg/l (as $CaCO_3$), iron between 5 and 20 mg/l, and pH between 2.7 and 3.0.

Chemical composition of treated water

Table 3, Figs. 2 and 3 show the composition of the water before and after limestone neutralisation. On average the pH increased from 2.8 to 7.8. The pH value of 7.8 was measured after CO_2 was allowed to escape freely from solution. The pH of the water prior to the escape of CO_2 was 5.5. In a full-scale plant, dissolved CO_2 will escape from solution freely in the settler, or otherwise CO_2 will be stripped with air between the neutralisation and settling stages.

Acidity decreased by 97% and can be ascribed to the following reaction:

$$CaCO_3 + H_2SO_4 \dashrightarrow CaSO_4 + CO_2 + H_2O \tag{3}$$

The stability of the treated water with respect to calcium carbonate is determined by the pH, calcium and alkalinity values of the treated water. The alkalinity of the treated water was 120 mg/l (as $CaCO_3$) owing to the escape of CO_2 from solution. This is a benefit as the increased buffer capacity contributes to stabilising the pH of the water (Table 3). The calcium concentration increased during treatment from 100 to 175 mg/l (as Ca) due to the dissolution of limestone (Table 3). Using the Stasoft Computer Programme (Friend and Loewenthal, 1992), it is noted that the treated water (pH = 7.8; Ca = 175 mg/l as Ca; Mg = 70 mg/l as Mg; Na = 16 mg/l as Na; Cl = 11 mg/l as Cl; SO_4 = 600 mg/l as SO_4; Alkalinity = 120 mg/l as $CaCO_3$ and Total Dissolved Solids = 944 mg/l) is oversaturated to the extent of 31.3 mg/ as $CaCO_3$. This scaling tendency of the treated water is desirable as it will assist in protecting pipelines against chemical corrosion. It is expected that the over saturation level of $CaCO_3$ can be controlled by controlling the contact time between limestone and water in the reactor.

Sulphate in the water passed through the process unchanged. This was expected as the sulphate concentration can only be reduced when the solubility product of gypsum is exceeded. Normally this will occur for waters with a low ionic strength at sulphate concentrations of 2 200 mg/l, which is well above the concentrations between 500 and 800 mg/l observed in this study (Table 3).

The iron concentration in the treated water was less than 1 mg/l (Table 3). This can be ascribed to most of the iron in the feed water being in the iron(III) state and the treated water pH of 7.8. The iron concentration in the treated water is determined by the oxidation state of the iron and its solubility at the pH obtained after neutralisation. Iron(II) is readily soluble at pH values up to 7.5, while the solubility of iron(III) decreases sharply at pH levels of 3 and higher.

Uranium in water contributes to radioactivity and is therefore considered a hazardous material which requires strict control. Uranium content was reduced on average from 1 100 g/l to 190 g/l. This performance is similar to that of conventional lime treatment (Duggan, 1995).

Table 3. Chemical composition of feed and treated water during pilot-plant study

Parameter	Chemical composition		Removal (%)
	Feed	Treated	
pH	2.8	7.8	
Acidity (mg/ℓ $CaCO_3$)	300 - 400	12	97
Alkalinity (mg/ℓ $CaCO_3$)	negative	120	
Sulphate (mg/ℓ SO_4)	500 - 800	500 - 800	0
Calcium (mg/ℓ Ca)	100	175	
Iron (mg/ℓ Fe)	5 - 20	< 1	95
Uranium (μg/ℓ U)	1 100	190	83

Contact time

Figures 2 and 3 show the temporal behaviour of pH and acidity of the feed and treated water for the laboratory- and pilot-scale plants respectively. During this period the contact time between the limestone and the water was gradually decreased (Fig. 2) so that the minimum contact time required could be determined. At the end of the experiment, when the contact time was only 0.62 min, complete neutralisation was still achieved. The limestone utilisation rate per unit reactor volume was 0.48 kg $CaCO_3$/(kl.min). This high rate is ascribed to the high surface area of the limestone used. Owing to limited capacity of the feed pump, it was not possible to study the performance of the plant at even lower contact times under continuous conditions. A batch experiment was therefore carried out to give an indication of the minimum contact time. Figure 4 shows the rate of neutralisation under batch conditions when the feed water was treated with two different types of limestone. The minimum contact times for Cape A and Tvl A were 0.060 and 0.014 min respectively (Table 4). The difference is ascribed to the difference in particle size of the two products. The rate of neutralisation is directly proportional to the surface area of the limestone (Clayton *et al.*, 1990).

$$-dC/dt = k.S.C \qquad (4)$$

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

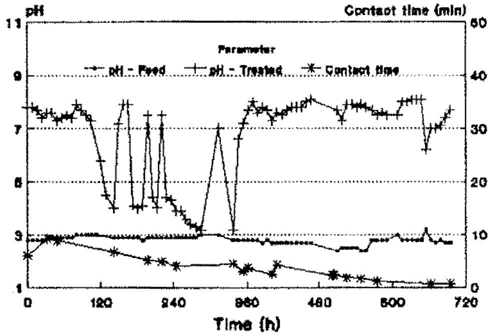

Figure 2. PH-levels when acid water is neutralised with limestone.

It is concluded that the feed rate of 7.2 kl/h employed was below the maximum possible. A contact time of 0.62 min was used in the pilot plant compared with the 0.014 min of the beaker test obtained with Tvl A limestone. The experimentally determined neutralisation rate of a specific limestone, and the acid content in the feed water, can be used to size the reactor empirically (Table 5). A contact time of 2 min is required when Tvl A or Cape A limestone is used. The surface area of more crystalline limestone products is less and hence the rate of neutralisation would be slower. It is recommended that the fluidised-bed reactor be designed for a contact time of 10 min to accommodate the use of such limestone types.

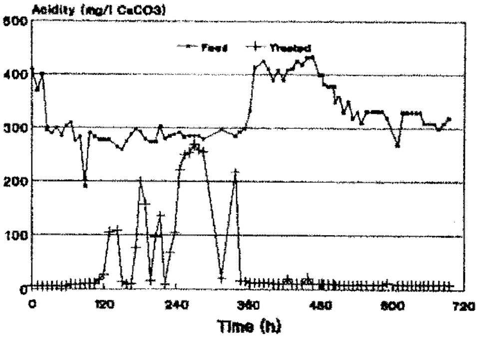

Figure 3. Acidity removal when acid water is neutralised with limestone.

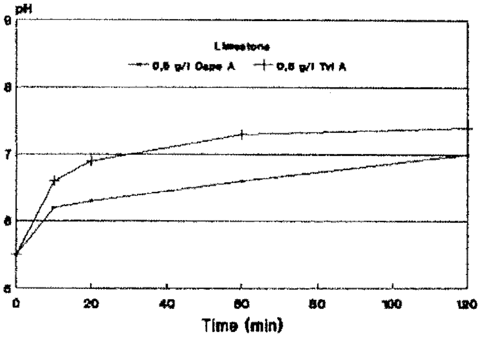

Figure 4. Effect of different limestone types on the rate of neutralisation.

Table 4. Minimum contact time required for various limestones

Limestone		Reaction time (min)	Contact time (min)[*1]
Source	Concentration (g/ℓ)		
Cape A	0.5	120	0.060
Tvl A	0.5	28	0.014

[*1] Contact time = Reaction time x limestone concentration in beaker/limestone concentration in fluidised-bed reactor (~ 1 kg/ℓ).

ECONOMIC FEASIBILITY

The economical feasibility of the installation of a limestone neutralisation plant is based on the figures in Table 5 and the following assumptions:

- The running and overhead costs associated with limestone neutralisation are the same as for lime neutralisation.

- The plant life is 15 years and capital is redeemed at an interest rate of 16%.
- The capacity of the plant is 1 000 kl/h.

Table 5. Sizing of fluidised-bed reaction

Parameter	Value
Acid concentration	450 mg/ℓ (as $CaCO_3$)
Limestone type	Tvl A, Cape A or any other limestone with similar properties
Particle size (mm)	0.5 - 4
Feed rate (kℓ/h) (q)	1 000
Recycle rate (kℓ/h) (q_{Rec})	3 000
q_{Rec}/q	3
$[Acid]_{Feed}$ (mg/ℓ $CaCO_3$) (F)	450
$[Acid]_{Treated}$ (mg/ℓ $CaCO_3$) (T)	20
Design contact time (active part) (min)	10
Hydraulic retention time (min) (HRT)	16.8
Reactor volume (active part) (kℓ) (V^*)	166.7
Upflow velocity (m/h) (v)	120
Area (m^2) (A = (q + $_{qRec}$)/v)	33
Diameter (m)	6.51
Length (m) (V/A)	5.0

* (V = q (kℓ/h) x HRT (min) ÷ 60)

Table 6 shows that lime with a current cost of SA R1 182 085/a can be replaced by limestone with an expected cost of SA R515 294/a (Figure in South African Rand). This represents a saving of 56.4% per unit lime.

Table 6. Calculation of cost associated with limestone and lime

Parameter	Lime	Limestone
Flow rate (kℓ/h)	1 000	1 000
[Acid] to be neutralised (mg/ℓ $CaCO_3$)	450	450
Purity	85 % (as $Ca(OH)_2$	85 % (as $CaCO_3$)
Utilisation efficiency (%)	90	90
Dosage (kg/kℓ)	435	588
Usage (t/a)	3 813	5 153
Delivered price (SA R/t)	310	100
Cost (SA R/a)	1 182 085	515 294
Saving (SA R/a)		666 791
Percentage saving		56.4

Table 7. Capital and running cost of a limestone and lime neutralisation plant

Item	Amount (SA R)	
	Limestone	Lime
Capital cost	1 131 772	1 131 772
Running cost:		
Capital redemption cost (15 years, 16 %)	199 468	199 468
Limestone	515 294	1 182 085
Electricity	114 048	68 429
Labour	1 560	1 560
Total running	830 370	1 451 542
Total running (c/kℓ)	9.5	16.6

Table 7 shows that:

- The equipment and construction cost for the limestone plant is SA R1 131 771 (R40 919/Ml/d).
- The capital redemption cost of the plant is SA R199 468/a.
- The running cost (limestone, electricity, labour and capital redemption) of the plant amounts to SA R830 370/a (9.5 c/kl), which compares favourably with that of a lime plant, namely 16.6 c/kl.

* (V = q (k /h) x HRT (min) 60)

CONCLUSIONS

The results allow the following conclusions to be made:

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

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

- Chemical savings of 56.4% can be achieved by using limestone rather than lime. The capital and construction cost of a plant with a capacity of 24 M /d amounts to R1 131 772. The running cost (limestone, electricity, labour and capital redemption) of the plant amounts to R830 370/year (9.5 c/kl). This compares favourably with the running cost of lime neutralisation, which amounts to R1 451 542 (17 c/kl).

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