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NEUTRALIZATION OF ACID MINE WATER WITH CALCIUM CARBONATE

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ABSTRACT

Traditionally, lime is used for the neutralization of acidic effluents. Calcium carbonate should be considered as an alternative because of considerations such as lower cost, low solubility at pH values greater than 7 and simple dosing system required. The paper describes a pilot scale study to determine the technical feasibility of neutralising sulphuric acid-rich water using fluidised bed technology.

Limestone was utilised completely when testing iron(III)-rich water, but with iron(II)-rich water, coated limestone particles accumulated in the fluidised-bed reactor. About 70% of the limestone was utilised in the case of water containing 600 mg/l iron(II).

A contact time of 4 min was sufficient for the neutralization of acid water containing 4 g/l free acid and 580 mg/l iron(III), compared to 40 min when iron(II) replaced iron(III).

KEYWORDS

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

INTRODUCTION

Neutralization of acidic streams is normally a requirement for the discharge of acidic streams into municipal wastewater treatment works to prevent corrosion of pipelines and to eliminate or reduce the concentration of toxic heavy metals, which could upset the functioning of biological systems.

Industrial effluents that require neutralization include chemical industry effluent, electroplating wastes, explosives factory and margarine/vegetable oil factory effluents, acid mine water and metallurgical plant effluent.

Traditionally, lime (calcium hydroxide) is used as neutralization agent for this purpose. Limestone (calcium carbonate) can be considered as well. By using the fluidised-bed reactor for limestone neutralization, 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, can be 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 26US$, 66US$, 100US$ and 540US$ per ton for 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 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 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).

The purpose of the study was to determine the technical and economical feasibility of the neutralization of sulphuric acid-rich water on pilot scale in a fluidised bed reactor.

Earlier findings (Clayton, *et al.*, 1990; Maree, *et al.*, 1991; Maree, *et al.*, 1992) showed that the kinetics of acid neutralization using $CaCO_3$ 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 $CaCO_3$ surface area available 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, a layer of $Fe(OH)_3$ which forms on the $CaCO_3$ surface causes K to decrease from the abovementioned value, depending on the thickness of the $Fe(OH)_3$ layer.

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. Iron(II) retarded the rate dramatically 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 the limestone neutralization process improves the quality of the water by removing free acid and acid associated with Fe(III). Sulphate is removed down to the saturation level of calcium sulphate. The pH of neutralised acid water depends on the metals that remain in solution during 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 study described in this paper was aimed at determining the contact time required between industrial and acid waters rich in iron(III) and iron(II) and the limestone bed, whether a side bleed-off stream from the limestone-bed is required in order to get rid of the impurities in the limestone and comparing the relative efficiencies of a cone-shaped and pipe-shaped fluidised-bed reactors.

MATERIALS AND METHODS

Feed water

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

Limestone

Raw limestone obtained from PPC Lime (supplier of limestone, lime and cement in South Africa) was used in the neutralization studies. The sinterstone (commercial name for limestone with a particle size of less than 5 mm) was screened and graded into various size fractions, using a series of 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 the appropriate velocity to achieve 20% bed expansion.

Pilot plants

Both a cone-shaped (Figure 1) and a pipe-shaped fluidised-bed reactor (Figure 2) were employed. 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 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%. Diaphragm pumps were used to feed acid water from a 10 kl stainless steel tank to the fluidised-bed reactors, while centrifugal pumps were used for recirculation of water in order to fluidise the limestone.

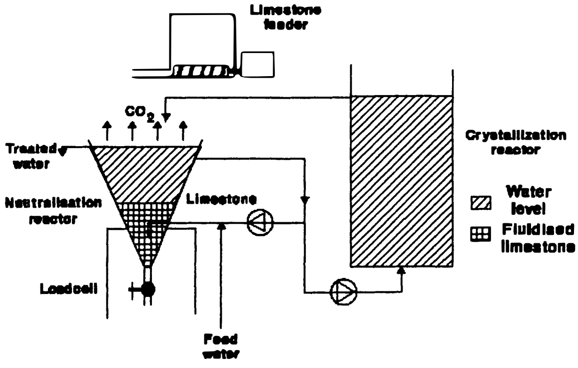


Fig. 1. Flow diagram of cone-shaped fluidised-bed and crystallisation reactors.

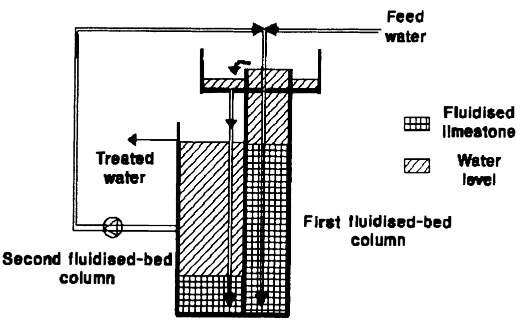


Fig. 2. Flow diagram of pipe-shaped fluidised-bed reactor.

Limestone feed system

Limestone was fed either manually or by means of screw feeder/hopper combination when using the cone reactor, and manually to the pipe reactor. 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 12 to 14 kg of limestone was kept in the cone reactor. One kg of limestone replaced 0.372 kg of water in the fluidised-bed reactor, so the amount of limestone present in the fluidised-bed reactor at any time was given by the following equation:

Mass of limestone in reactor (kg) = $(W - W_0)/(1.0 - 0.372)$
where: W = mass of (cone + water + limestone)
W_0 = mass of (cone + water).

Batch Tests

Batch studies were carried out to determine the rate of neutralization in the cone reactor and the rate of gypsum crystallisation in the crystallisation reactor. The variation of the following parameters were monitored: namely pH, sulphate, calcium, acidity and iron(II). Acidity was the most important parameter in monitoring the rate of neutralization (fast reaction), while calcium was the most important one in the case of monitoring the rate of gypsum crystallisation (slow reaction). After the addition of the acid solution to the cone fluidised-bed reactor, ungraded limestone was added.

Analytical

Samples were collected and filtered (Whatman No 1) automatically during continuous and batch studies. In the case of batch studies, samples were taken regularly and analyzed for pH, calcium, magnesium, iron(II), iron(III) and acidity (APHA, 1985). Calcium and magnesium were determined with EDTA, the alkalinity by titration with hydrochloric acid to pH 4.3 and 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 excess amount of hydrochloric acid.

TABLE 1. Design and Operational Parameters for the Two Pilot Plants

Parameter	Cone reactor height (mm)			Crystalisation reactor	Pipe reactor Stage		
	10 bottom	500 middle	1000 top		1st*	2nd*	3rd*
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

* 1st - First stage of the column-shaped reactor with a high upflow velocity due to its small diameter and recirculation.

2nd - Second stage of column-shape reactor with medium upflow velocity due to large diameter and recirculation.

3rd - Third stage of column-shape reactor with low upflow velocity due its large diameter and no recirculation.

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

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

RESULTS AND DISCUSSION

Particle size distribution and fluidisation velocity of limestone

One of the requirements of the fluidised-bed limestone neutralization process was to develop the process so that commercially available limestone, ungraded with respect to particle size, can be used as feed material. It was therefore necessary to determine the particle size distribution of the limestone (Figure 3) as well as the velocity at which it fluidises (Figure 4). Least square analyses on the curve in Figure 4 shows that the following function predicts the fluidisation velocity for a specific particle size.

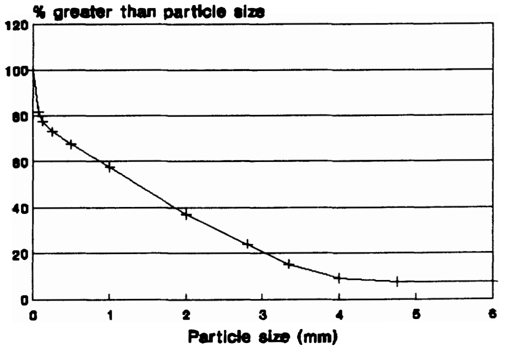


Fig. 3. Particle size distribution of sinterstone limestone.

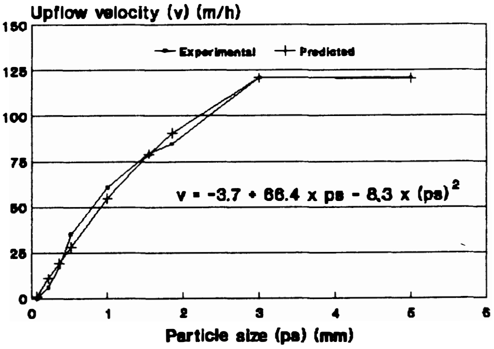
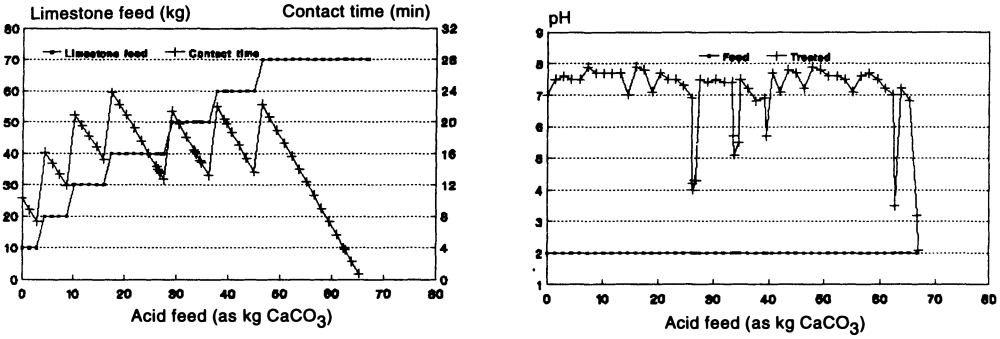


Fig. 4. Fluidisation velocity of limestone (PPC Sinterstone from Lime Acres) as a function of particle size.

Neutralization of iron(III)-rich water

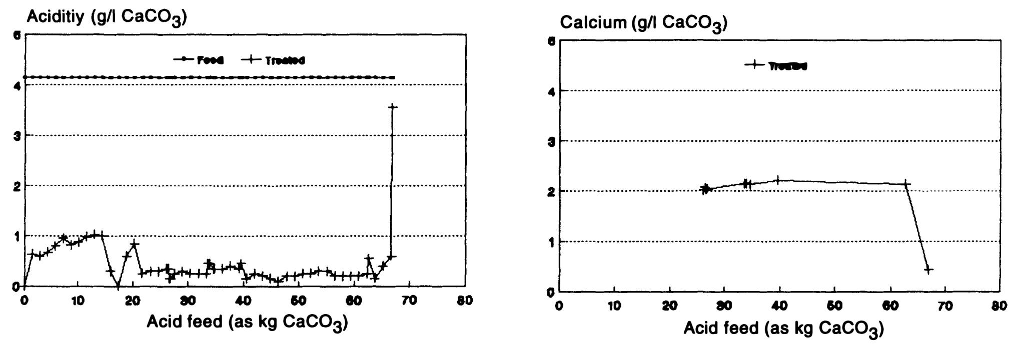
Figure 5 shows the results when artificial mine water containing 4 g/l H_2SO_4 (as $CaCO_3$) and 582 mg/l Fe(III) was neutralised with ungraded sinterstone in the cone-shaped fluidised-bed reactor. The conditions during the studies were as follows:

- Feed rate of acid water = 1 l/min
- Limestone addition = 10 kg/addition
- Assumed limestone concentration during fluidisation = 1 kg/l
- Contact time = (10 kg ÷ 1 kg/l) ÷ 1 l/min = 10 min



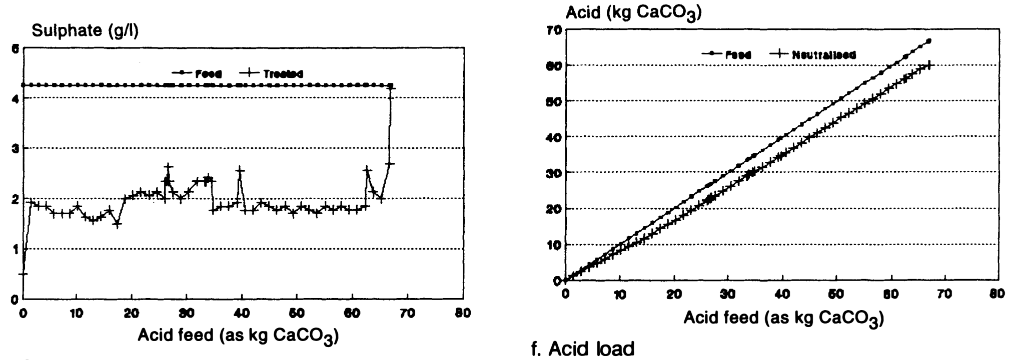
a. Limestone feed and contact time

b. pH



c. Acidity

d. Calcium



e. Sulphate

f. Acid load

Fig. 5. Behaviour of various parameters during neutralization of iron(III)-rich water in a fluidised-bed reactor.

The following are concluded from Figure 5:

- The contact time varied between 10 and 22 min as limestone was fed and consumed due to the neutralization reaction (Figure 5a).

- The pH rose from 2.2 to 7.5 during the course of the experiment (Figure 5b). The drop in pH for short periods occurred 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 neutralization. By comparing the pH in Figure 5b, after 62 kg of acid (as $CaCO_3$) was fed, with the corresponding contact time in Figure 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.

- Acidity decreased from 4200 mg/l to 200 mg/l except during start-up and termination (Figure 5c). The acid water was not completely neutralised in the beginning due to too little fluidisation of the bed, while at the end neutralization was stopped due to the fact that feeding of limestone was terminated.

- Calcium increased to 1900 mg/l (as $CaCO_3$) due to the dissolution of limestone according to the following reaction (Figure 5d):

$$Ca^{2+} + SO_4{}^{2-} \text{-->} CaSO_4 \qquad (2)$$

- Sulphate was removed from 4200 to 2000 mg/l as a result of gypsum crystallisation as shown in equation 1 (Figure 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 5f shows that the amount of acid that was fed to the reactor was almost equal to the amount of acid removed in the reactor due to limestone neutralization, which indicates almost complete neutralization. At 70 kg of limestone fed, 60 kg of acid was removed, which represents an 86% utilisation of limestone. This represents an almost 100% efficiency as limestone contains only 86% to 90% $CaCO_3$.

Waste sludge

When feeding iron(III)-rich water, the limestone is completely utilised while the ferric hydroxide sludge 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.

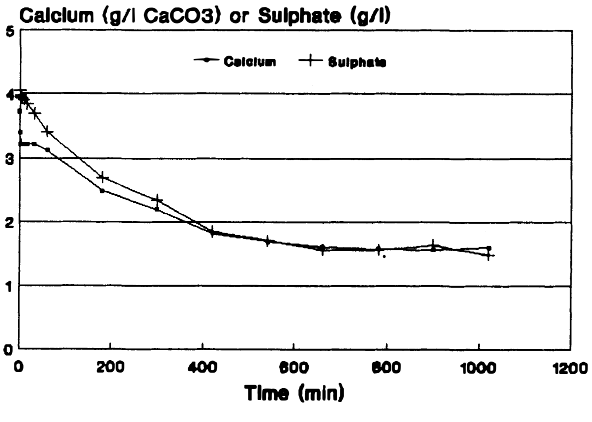


Fig. 6. Crystallisation rate of calcium sulphate under batch conditions.

Figure 6 shows the rate at which gypsum crystallises from the neutralised water if sufficient time is provided. About 160 min is required to reduce sulphate from 4000 to 1700 mg/l, the solubility level of gypsum under the specific conditions.

Neutralization 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 with 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 neutralization of iron(II)-rich water.

Contact time. 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, it was determined that:

* The pH of the treated water was increased from 4,0 to 7,8.
* The acidity decreased from 750 to 300 mg/l (as $CaCO_3$).
* The iron(II) content decreased from 225 to 75 mg/l.

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:

$$2Fe^{2+} + O_2 + 2H^+ \text{-->} 2Fe^{3+} + 2OH^- \qquad (3)$$

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 neutralization. Thus, by allowing sufficient contact time in the fluidised-bed reactor, iron can be removed sufficiently.

Hydraulic retention 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, neutralization of iron(II)-rich water was investigated in two systems, namely the cone fluidised-bed reactor (Figure 1) and the pipe reactor (Figure 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 2 shows the effect of hydraulic retention time on the efficiency of the neutralization 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.

It was also noted that by keeping the contact time constant (by means of continuous limestone dosing), 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. It is assumed that partial coating of the limestone particles occurs 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.

TABLE 2. Effect of Contact Time and Hydraulic Retention Time on Neutralization of Iron(ii)-rich Water

Parameter	Untreated	Treated				
		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

More coated particles were noticed in the pipe reactor than in the case of the cone reactor, and the pH of the treated water was lower than that of the cone. The difference in pH 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 consumed (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 'Neutralization of iron(III)-rich water'). It is therefore concluded that limestone utilisation is influenced by the iron(II) content of the water, rather 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.

Neutralization of coal mine water (from the Witbank area)

The purpose of this section was to demonstrate the feasibility of the limestone neutralization process on an industrial water. The selected water for this purpose is a mixture of acid mine water from an old coal mine and an industrial effluent with high concentrations of sulphate, sodium and chloride. The following conditions existed during the experiment:

Feed rate = 350 ml/min
Contact time = Decease gradually from 57 to 43 min
Hydraulic retention time = 800 min
Temperature = 40.0 °C
Limestone addition = 20.0 kg
Reactor type = Cone.

TABLE 3. Chemical Composition of Coal Mine Water Before and After Limestone Neutralization

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)	7 250	6 000
Chloride (as Cl^-)	502	498
Ammonia (as N)	186	186
Calcium (as $CaCO_3$)	1 300	1 350
Magnesium (as $CaCO_3$)	1 043	1083
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	1 667
Potassium (mg/ℓ K)	484	521
Nickel (mg/ℓ Ni)	1.0	0.7

The following are concluded from the experiment (Table 3):

* The contact time varied between 57 and 43 min as limestone was fed and consumed due to the neutralization reaction.

* The pH was increased from 3.0 to 8.0 during limestone neutralization.

* Acidity decreased from 2 400 mg/l to 600 mg/l . 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 neutralization, 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 4) and crystallised as gypsum.

$$CaCO_3 + H_2SO_4 \text{-->} CaSO_4 + CO_2 + H_2O \quad (4)$$

* Sulphate was reduced from 7 400 to 6 000 mg/l as a result of gypsum crystallisation as shown in equation 1.
high sulphate level in the treated water compared to the previous studies can be ascribed to the sodium conte
the untreated water. Sulphate associated with sodium in the untreated water will remain in solution durin
neutralization process. Only sulphate associated with free acid or metals, that will precipitate during neutraliza
can be removed as calcium sulphate.

CONCLUSIONS

The following conclusions are drawn from the study.

A fluidised-bed reactor with multiple stages of increasing diameters is preferred for the limestone neutralization 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 neutralization process.

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.

A contact time of 4 min is sufficient for the neutralization 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, when iron(II) replaces iron(III).

A contact time of 4 min proved sufficient for the neutralization of acid water containing 4 g/l free acid and 580 mg/l iron(III), while a contact time of at least 40 min was required when iron(II) replaced iron(III).

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