

Water Softening in the Barium Sulphide Process for Sulphate Removal

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ABSTRACT

Sulphate-rich effluents and acid mine "rock" drainage is produced at mines when pyritic ores are mined. These effluents can cause environmental pollution, contributing directly to the mineralization of receiving waters. The barium sulphide process can be used for treatment of these effluents and for the recovery of valuable by-products like sulphur and CaCO₃. The integrated BaS process consists of sulphate removal, H₂S stripping, water softening and BaSO₄ reduction. This study evaluated the water softening stage of the integrated BaS process.

The Ca(HCO₃)₂-rich water, which was the product of the H₂S stripping stage, was successfully softened using a bubble and a packed bed reactor. The rate of CaCO₃ crystallization is influenced by air flow rate, CaCO₃ seed crystal concentration and addition of alkali. A typical treated effluent was softened to calcium, alkalinity, and pH values of between 420-200 mg/l (as CaCO₃), 460-160 mg/l (as CaCO₃) and 8.4-7.5 respectively. Initial values were 2100 mg/l (as CaCO₃), 2200 mg/l (as CaCO₃) and 6.8 respectively. The bubble reactor is more effective for the crystallization and separation of CaCO₃ than the packed bed reactor.

INTRODUCTION

Sulphate need to be removed from industrial effluents rich in sulphate. Acid mine waters contain high concentrations of dissolved heavy metals and sulphate, and can have pH values as low as 2,5. These conditions have a detrimental effect on aquatic plant and fish life when discharged untreated into public streams^[4,5]. Acid mine drainage also causes ground water pollution.

Neutralised Acid Mine Drainage still exceeds the South African Effluent Act limit of 250mS/m or 2000 mg/l dissolved solids^[13] and may not be discharged into public streams (Water Act 54 of 1956 and Water Amendment Act 96 of 1984).

The BaS process is suitable for the treatment of such effluents and consists of the following stages:

BaS dissolution, sulphate removal, sulphide stripping, sulphur production, water softening, and BaSO₄ reduction^[3,7].

The BaS-process has some distinct advantages. Acid waters can be treated directly with barium sulphide. The process removes ammonia, magnesium, manganese and other heavy metals as their sulphide and hydroxides due to the high pH after BaS dosage. A further advantage is that by-products like sulphur and NaHS can be produced from the H₂S produced in the process, and CaCO₃ from the softening stage.

Acid mine water, slimes dam effluent, uranium raffinate and power station cooling water has been treated successfully with BaS to remove sulphate^[3,7].

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Volman^[2] and Adlem et al^[1] showed that $BaSO_4$ can be thermally reduced to BaS at a temperature of $1050^\circ C$. Bosman et al^[3] showed that the integrated process is economically feasible. The capital cost of the BaS process is \$479 000/MI/d, the net operating cost amounting to 27 c/m³ (including the revenue from sulphur sales). Toxicity is a concern when barium salts are used for water treatment. Murray^[9] showed that $BaSO_4$ is practically insoluble in all circumstances present in the total BaS process and will not cause toxicity problems.

The use of BaS , $BaCO_3$, and $Ba(OH)_2$ for the treatment of SO_4 -rich water has been described in various studies^[1,3,7]. The BaS -process was selected as the most attractive one due to the following features:

- A short retention time is required for sulphate removal compared to the barium carbonate process, which requires a relatively long retention time due to the slow dissolution rate of barium carbonate.
- No lime dosing is required to equalise the sulphate and calcium concentrations that enable the barium carbonate in the barium carbonate process to react.
- Only barium sulphate precipitates during barium sulphide addition and not a mixture of barium sulphate and calcium carbonate as in the case of barium carbonate treatment. A barium sulphate/calcium sulphate complex forms with barium hydroxide treatment.
- It enables the recovery of high quality calcium carbonate as a by-product, as it is precipitated in a separate stage.
- A few stages are required as barium sulphide can be used directly for water treatment after conversion from the barium sulphate in a kiln.

A flow sheet for the integrated BaS -process is given in Figure 1.

After the H_2S stripping stage the water is rich in $Ca(HCO_3)_2$ and needs a further softening stage.

Traditionally, softening is applied through $Ca(OH)_2$ dosing.

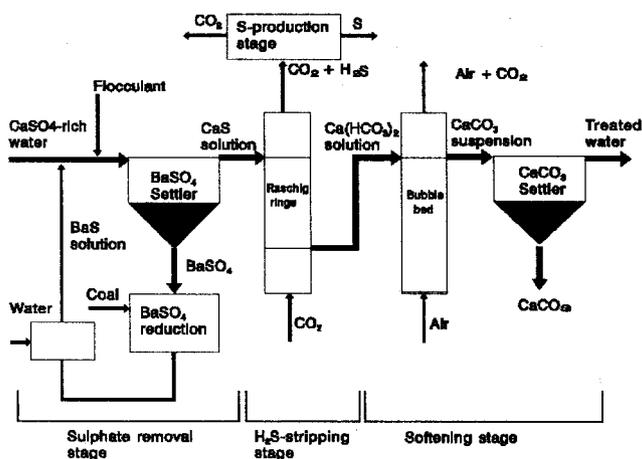
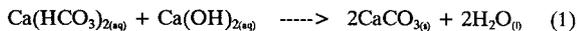
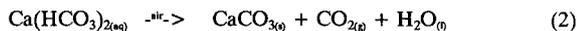


Figure 1. Schematic diagram of the integrated BaS process.

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The aim of this study was to achieve softening of hard water through a novel process in which no lime is used. Softening is achieved through CO₂ stripping^[8].



The effects on the softening process of the following were investigated:

- Water quality before and after the water softening stage.
- Feed rate of air on the rate of crystallisation in the water softening stage.
- Surface area on rate of crystallisation in the water softening stage.
- Alkalinity addition on the rate of crystallisation in the water softening stage.
- Residual sulphide on the kinetics of the water softening stage.
- Reactor type on rate of crystallisation in water softening stage.

MATERIALS AND METHODS

Apparatus

A packed bed and a bubble reactor were operated to evaluate softening of water by removing CO₂ from the effluent by means of air stripping. The preparation and use of each apparatus are described below.

Packed bed reactor

The reactor (Fig. 2) with an inside and outside diameter of 188 and 200 mm respectively was packed to a height of 1000 mm with ceramic Raschig rings. Rings were 25 mm long with an inside and outside diameters of 17 and 25 mm respectively. A fan was installed at the top of the reactor to extract CO₂-rich air.

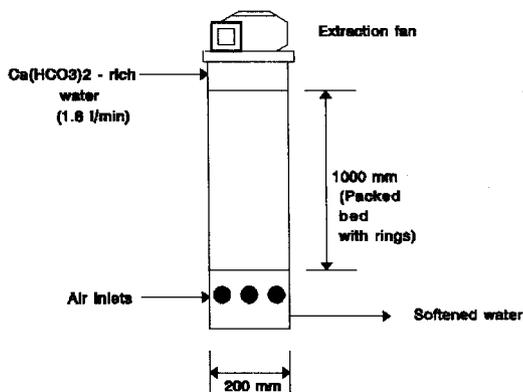


Figure 2. The packed bed reactor used for water softening.

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Bubble reactor

The reactor (Fig. 3) height was 550 mm (liquid) with inside and outside diameters of 145 mm and 150 mm respectively. Air was fed to the reactor through a diffuser at the bottom of the column. Available compressed air was used and flow rates were measured manually.

Feedstock

Synthetic solutions equivalent to 2 g/l of sulphate were prepared using $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaHCO_3 . Ten litre quantities were treated in batch studies in the two reactor configurations.

Analytical

Chemical analyses of samples were carried out according to Standard Methods^[2]. The pH of all samples was measured and they were analysed for calcium, alkalinity and acidity using titrimetric methods.

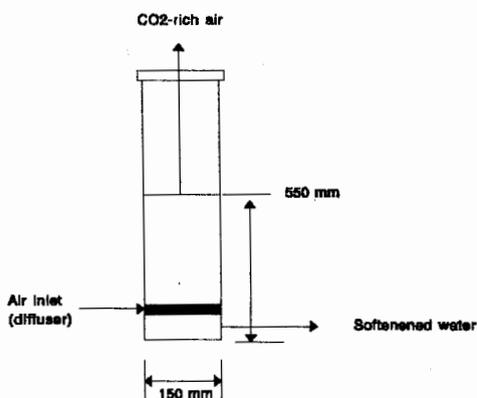


Figure 3. The bubble bed reactor used for water softening.

Experimental

Three main reactor configurations were employed in the evaluation. They were the bubble reactor aerated by air through a diffuser and the packed bed reactor run with and without the fan. Air was allowed to flow freely through the reactor through several large inlet holes. Aeration was caused by the fan on top of the packed bed reactor. As the fan was sensitive to back pressure no accurate measurement of its flow could be made.

In all the packed bed investigations a recycle rate of 1.8 l/min was employed. Investigations with the fan respectively on and off were done to evaluate the effect of recycling air on the kinetics of water softening. CaCO_3 seeds were added in all cases.

The flow rate of air fed to the bubble reactor through a diffuser from a compressed air outlet was 20 and 75 l/min.

Effluent was aerated after the dosing of different amounts of CaCO_3 seeds to determine the effect of surface area on the crystallization of CaCO_3 in the water softening stage. Different

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quantities of lime and NaOH were added to seeded effluents to evaluate the effect of alkalinity. A single evaluation was carried out by aerating an effluent containing approximately 200 mg/ℓ sulphide (as SO₄).

RESULTS AND DISCUSSION

Water quality

Table 1 shows that water quality improved significantly by aeration in the two reactor types. Calcium was removed to below 440 mg/ℓ (as CaCO₃) and alkalinity to below 460 mg/ℓ (as CaCO₃). The pH values increased to between 7.5 and 8.4.

The effluent quality described in Table 1 can be achieved within a retention time of 60 minutes during which up to 90% of the hardness in the water is removed. Similar water qualities were achieved with both reactor types, showing both the packed bed and bubble reactor to effectively strip CO₂ from the Ca(HCO₃)₂ rich water.

Table 1. Water quality of effluent before and after treatment in the packed and bubble bed reactors.

Treatment method	Calcium as (mg/ℓ CaCO ₃)	Alkalinity (mg/ℓ CaCO ₃)	pH	Acidity as (mg/ℓ CaCO ₃)
Untreated	2100	2200	6.8	80
Packed bed	400 - 200	440 - 280	7.5 - 8.1	111 - 26
Bubble bed	420 - 200	460 - 160	8.0 - 8.4	13 - 0

Figure 4 shows the relationship between calcium, alkalinity, acidity and pH observed in batch studies. Calcium and alkalinity were removed in stoichiometric quantities as expected. Acidity displayed a slightly downward trend during the initial stage of the batch experiments as free CO₂ was stripped from solution. The pH increased as expected.

Air flow rate

The rate of CO₂ transfer depends on the difference in partial pressure of CO₂ across the air-water interface, water surface exposed to the gas and the degree of turbulence^[6]. An increase in surface renewal of CO₂ oversaturated water, by aeration, increases the transfer rate and the time for the water to reach CO₂ equilibrium with the air. The equilibrium between dissolved and atmospheric CO₂ at a specific partial pressure is given by Henry's law as:

$$[\text{CO}_2] = K'_{\text{CO}_2} P_{\text{CO}_2} \quad [1]$$

where K'_{CO_2} is the temperature dependant Henry's Law Constant, and P_{CO_2} is the partial pressure of CO₂ in the atmosphere^[6].

As expected from the above principles higher aeration flow rates improved the rate of hardness removal from seeded effluent in the bubble reactor (Fig. 5). At a retention time of 60 minutes calcium was removed from 2100 mg/ℓ (as CaCO₃) to 190 mg/ℓ (as CaCO₃) at a flow rate of 75 ℓ/min and to 300 mg/ℓ at a flow rate of 20 ℓ/min.

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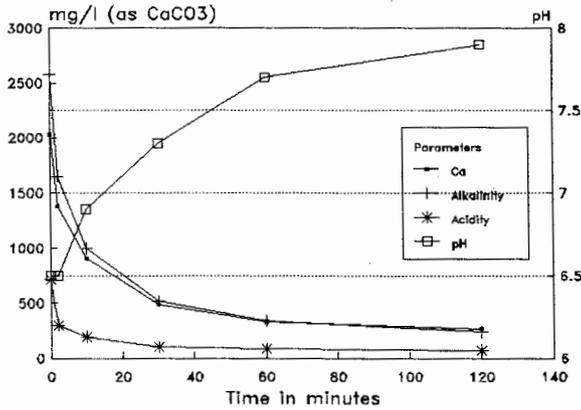


Figure 4. Evaluation of the behaviour of various parameters in the packed bed reactor during the softening stage (50000 mg/t CaCO₃ seed crystals were added).

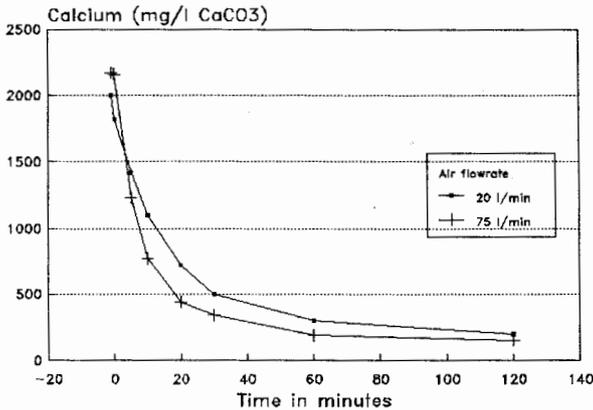


Figure 5. Comparison of the effect of air flow rate on the crystallisation rate of CaCO₃ in the water softening stage in the bubble reactor (500 mg/t CaCO₃ seed crystals were added).

CaCO₃ concentration

Figure 6 shows that at a retention time of 60 minutes calcium was removed from 2200 mg/l (as CaCO₃) to 330 mg/l (as CaCO₃) with 0 mg/l seed crystals, 200 mg/l (as CaCO₃) with 500 mg/l seed crystals and to 190 mg/l with 5000 mg/l of crystal seeds. pH values ranged from 7.9 to 8.4.

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This confirms the findings of Nancollas and Reddy et al^[10,11].

Nancollas and Reddy studied the kinetics of CaCO₃ crystallization and showed that the rate of crystallization is directly proportional to the surface area of the seed crystals and the square of the oversaturated fraction of CaCO₃ in solution.

$$\frac{d[Ca^{+2}]}{dt} = -K \cdot S \cdot ([Ca^{+2}] \cdot [CO_3^{-2}] - K_{sp} / f_D^2) \quad [2]$$

Where

- [Ca⁺²] = molar concentration of Ca⁺² ions (mol/l)
- [CO₃⁻²] = molar concentration of CO₃⁻² ions (mol/l)
- K = rate constant for calcite crystallization (l/(mol.min))/(mg seed/l)
- S = total surface area of seed crystals
- K_{sp} = solubility product for CaCO₃ (mol².l²)
- f_D² = activity factor for divalent ions

Equation [2] needs modification before application to the process under evaluation. The equilibrium calcium concentration in solution varies as a function of the amount of CO₂ that has been stripped off.

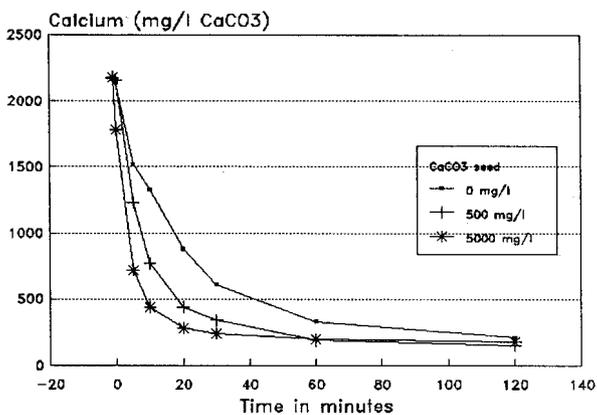


Figure 6. Effect of surface area on the rate of CaCO₃ crystallization in the water softening stage in the bubble reactor (air flow rate: 75 l/min).

A retention time of 30-60 minutes is possible using CaCO₃ seeds in the water softening stage. This would ensure an effluent quality of less than 400 mg/l calcium as CaCO₃. Formation and growth of CaCO₃ crystals will not only improve the retention time of the softening stage, but the

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CaCO₃ potentially can be harvested to sell as valuable by-product.

Reactor configurations

Figure 7 shows that the kinetics for the precipitation of CaCO₃ is very similar in all the variations of the packed bed and bubble reactors. Table 2 gives the conditions for these runs.

In the packed bed reactor, aeration by the Raschig rings effectively softened the water by removal of CaCO₃. No significant improvement was achieved by employing a fan at the top of the reactor. At a retention time 60 minutes calcium was removed from 2100 mg/l to 330 and 400 mg/l as CaCO₃ with the fan on and off respectively.

In the bubble reactor calcium was removed to 150 mg/l (as CaCO₃) at a retention time of 60 minutes with an air flow of 75 l/min. This is slightly better than the packed bed reactor that removed calcium to 330 mg/l at the same retention time.

Table 2. The running conditions for obtaining the results for the packed bed and bubble reactors.

	Bubble	Bubble	Packed bed	Packed bed with fan	Control
Feed rate air(ℓ/min)	20	75	none	NA	none
CaCO ₃ (mg/ℓ)	500	500	5000	5000	5000
Recycle rate (ℓ/min)	none	none	1.8	1.8	1.8

In the control the effluent was recycled in a ten litre container, with no aeration, removing calcium to a level of 1270 mg/l as CaCO₃ at 60 minutes.

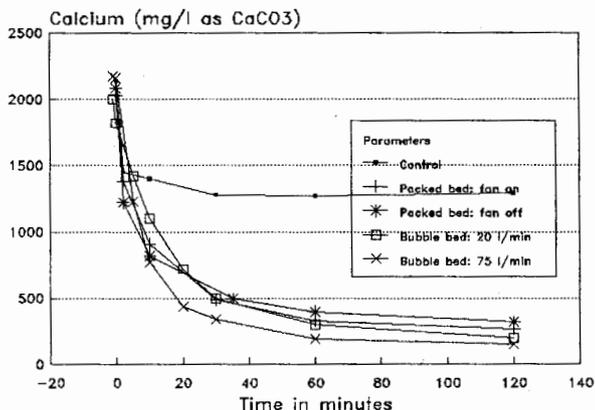


Figure 7. The effect of the different reactor configurations on the kinetics of the water softening stage.

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Although the kinetics in Figure 7 is similar the packed bed reactor and the bubble reactor are not directly comparable (Table 2). The packed bed reactor is considered unsuitable for water softening as CaCO_3 precipitates onto the Raschig rings and seed crystals are removed from solution. This implies high running costs and the loss of potentially valuable CaCO_3 .

The reactors' running parameters differed significantly, but the bubble bed produced better results with ten times less seed crystals than the packed bed reactor. In the bubble reactor it will be easier to take advantage of the surface area of seed crystals and the surface renewal rate of water oversaturated with CO_2 to improve the kinetics of CaCO_3 crystallization.

Alkalinity addition

Figure 8 shows the effect of alkalinity added through NaOH and Ca(OH)_2 on the calcium removal efficiency of the bubble reactor.

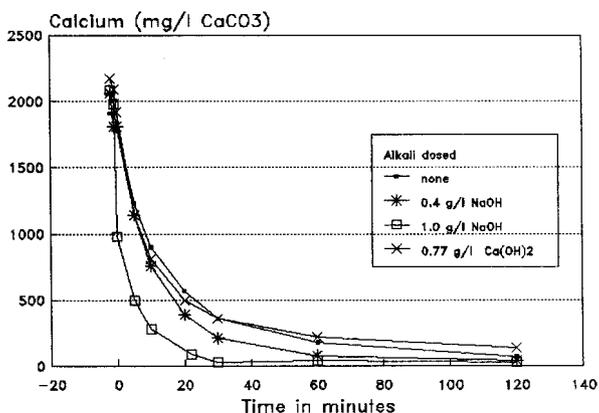


Figure 8. Effect of alkalinity addition on the rate of CaCO_3 crystallization in the water softening stage in the bubble reactor (air flow rate: 21 l/min, 500 mg/l CaCO_3 seed crystals).

The rate of CaCO_3 crystallization was improved by higher dosages of NaOH . Addition of 0, 0.4 and 1.0 g/l NaOH removed calcium from 2100 mg/l (as CaCO_3) to a level of 360, 200 and 40 mg/l (as CaCO_3) at a retention time of $t=30$ minutes. Improvement of the rate of CaCO_3 crystallization by the higher NaOH dosages was the result of a sharp increase in alkalinity and pH. This increased the degree of supersaturation of CaCO_3 in the solution.

According to Loewenthal and Marais^[6] the rate of establishment of an equilibrium between solids and solutes is a complex function of many factors including the degree of oversaturation, mixing conditions and availability of crystal growth sites. One of these factors, degree of supersaturation was enhanced effectively with the addition of 1 g/l of NaOH to the effluent before stripping.

The rate of CaCO_3 crystallization was not affected significantly by the addition of lime. Figure 8 shows that the rate of calcium removal was slower for the dosage of 0.77 g/l Ca(OH)_2 (equivalent to 0.83 g/l NaOH) than for the dosage 0.4 g/l NaOH and very similar to the rate

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achieved with no alkali dosage. This limited influence can be ascribed to the low solubility of $\text{Ca}(\text{OH})_2$ (1.5g/l). Its lower solubility could have affected the rate of dissolution negatively.

The addition of alkaline reagents did not produce good results except at high dosages of NaOH. This means that the water softening stage will operate cost-effectively by employing simple aeration in a packed bed or bubble reactor.

Residual sulphide

Figure 9 shows that the presence of sulphide has no significant effect on the rate of CaCO_3 crystallization.

No special measures will be necessary to remove residual sulphide from the effluent coming from the H_2S stripping reactor.

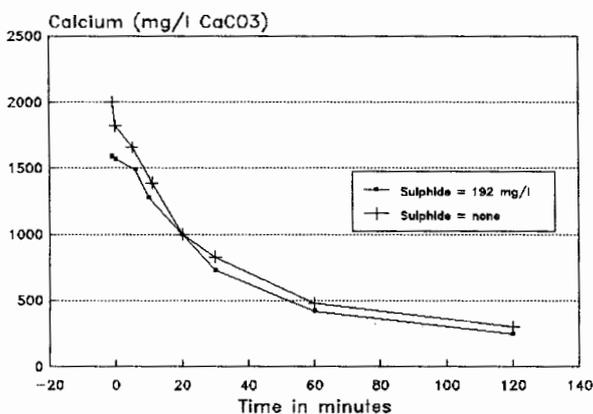


Figure 9. Effect of residual sulphide on the crystallization rate of CaCO_3 in the water softening stage (500 mg/l CaCO_3 seed crystals).

CONCLUSIONS

- The water softening stage of the BaS-process can reduce the calcium content of treated effluents to values as low as 200 mg/l (as CaCO_3).
- The rate at which hard water is softened is influenced by the flow rate of the air used to strip CO_2 from the solution and the concentration of CaCO_3 seed crystals added. The presence of sulphide does not influence the rate.
- The bubble reactor is preferred above the packed bed reactor for the process as in the latter case, CaCO_3 scale accumulates on the packing material resulting in higher running costs and loss of valuable CaCO_3 .

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