

Barium Carbonate process for sulphate and metal removal from mine water

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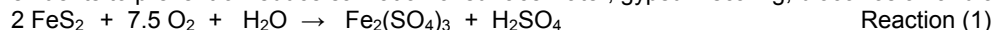
ABSTRACT

Mining is a significant contributor to water pollution. Effluents need to be treated to remove sulphate to less than 200 mg/L and for metal removal. The barium process can meet these requirements. The purpose of this study was to demonstrate the performance of the integrated barium carbonate process, consisting of the following stages: Sulphate precipitation as BaSO₄ by treatment of sulphate-rich water with BaCO₃; thermal reduction of BaSO₄ to BaS; conversion of BaS to BaCO₃ and H₂S by passing CO₂ through a solution of BaS. The stripped H₂S is converted to elemental sulphur.

Background and the results of laboratory studies are presented pertaining to the understanding of the chemical reaction conditions required for each stage of this process. These studies showed that (i) The rate of sulphate removal is influenced by the BaCO₃ concentration and the cation associated with sulphate. The rate of sulphate removal increases with increasing BaCO₃-concentration. BaCO₃ can only be used for removal of sulphate that is associated with calcium, as calcium is needed to remove the added carbonate associated with the barium cation. Sulphate removal is only marginally influenced by alkalinity. (ii) Sulphide can be stripped with CO₂ from a BaS-solution. The (CO₂ dosed/sulphide removed) ratio is close to unity for the first 50% of sulphide in solution. (iii) The stripped H₂S-gas can be absorbed into zinc acetate. (iv) BaSO₄ and CaCO₃ can be converted simultaneously to BaS and CaO, respectively. The optimum temperature is 1050°C. The CaCO₃/BaSO₄-ratio has little influence on the yield of BaS. (v) The running cost of the barium carbonate process for the removal of 2 g/L of sulphate totalled R2.28/m³, the capital redemption cost amounts to R1.08/m³ and the value of the products (water and sulphur) amount to R2.76/m³.

BACKGROUND

The scarcity of water in South Africa is exacerbated by pollution of surface and ground water resources. Mining is a significant contributor to water pollution. A major constituent of mine tailings is pyrites. When pyrites (FeS₂) is exposed to air, it is oxidized by a biologically catalyzed reaction mediated by bacteria *Thiobacillus ferrooxidans* according to Reaction 1 (Barnes, 1968). The primary pollutants of acid mine drainage are the hydrogen ion (acidity), iron, sulphate, manganese, magnesium and sometimes aluminium. Sulphate needs to be removed from effluents to prevent or reduce salination of surface water, gypsum scaling, biocorrosion and acid corrosion.



It is estimated that about 540 ML/d of acid mine water is produced in the Gauteng region alone (Volman, 1984). Mine water in the Upper Olifants River catchment in Mpumalanga (upstream of Loskop Dam) is at times discharged into local streams, resulting in local acidification and regional salination of surface water resources (Geldenhuis *et al.*, 2003). The barium process is suitable for treatment of sulphate-rich effluents.

Kun (1972) studied the removal of sulphate with barium carbonate and obtained good results. However, he identified three problems: a long retention time requirement, high concentrations of soluble barium in the treated water when more barium carbonate was dosed than stoichiometrically required and, the high cost of the barium carbonate. Volman (1984) overcame the cost problem by demonstrating that barium sulphate could be recovered and reduced efficiently and economically with coal under thermal conditions to produce barium sulphide. This compound can be used directly for the process or converted to barium carbonate. Wilsenach (1986) demonstrated the economic viability by calculating the cost of producing barium sulphide from barium sulphate.

Trusler *et al.* (1988) developed a barium carbonate method using a two-stage fluidised bed reactor system to overcome the other problems identified by Kun, namely, long retention time and the high barium concentration in the treated water. However, the barium carbonate became inactive when coated with metal hydroxide precipitates, which made it unsuitable for most mine water. Maree *et al.* (1989) noted a problem in separating barium sulphate and calcium carbonate, which co-precipitate and proposed the use of a fluidised-bed system. This system allows fast removal of sulphate with BaCO₃ due to the fact that excess BaCO₃ is in contact with the sulphate-rich water.

Later Maree *et al.* (2004) investigated an integrated barium sulphide process and found that, (1) during lime treatment, the sulphate concentration was decreased from 2 800 mg/L to less than 1 200 mg/L due to gypsum precipitation. Metals were precipitated as hydroxides. During BaS treatment, sulphate concentration in the effluent fell to less than 200 mg/L through BaSO₄-precipitation. (2) Sulphide was decreased from 333 mg/L to less than 10 mg/L (as S) in the stripping stage, using CO₂ gas. (3) The stripped H₂S-gas was contacted with Fe (III) solution and converted quantitatively to elemental sulphur. A disadvantage with the latter system is that the H₂S gas needs to be stripped from the total water stream being treated.

This drawback led to the proposal of the integrated barium carbonate process. The purpose of this study was to demonstrate the performance of such a process, consisting of the following stages: (1) Pre-treatment with lime for

magnesium removal, (2) Removal of sulphate as barium sulphate by dosing barium carbonate, (3) processing of the sludge to recover BaCO₃ and CaO (dewatering and thermal processes) and H₂S sulphide stripping and sulphur production.

The specific aims were to evaluate the integrated BaCO₃-process as shown in Figure 1, determine the effect of various parameters on the rate of sulphate removal with BaCO₃ (alkalinity, pH, BaCO₃-concentration, MgSO₄ concentration, MgCl₂ concentration), evaluate H₂S stripping with CO₂, determine the effect of various parameters on the reduction of BaSO₄ to BaS (CaCO₃-concentration, temperature, time, carbon/BaSO₄ ratio) and estimate the running cost of the process.

MATERIALS AND METHODS

Feedstock

Artificial feed water containing 1 400 mg/L sulphate and supplemented with magnesium was used during batch studies. Barium carbonate (Merck) was used for sulphate removal. For H₂S-stripping studies, a 6% BaS (Merck) solution was used. CO₂ gas (supplied by Afrox) was used for H₂S-stripping. A 2 N zinc acetate (Merck) solution was used for absorption of the stripped H₂S-gas. During the thermal studies, chemically pure BaSO₄ (Saarchem) were used for the BaS recovery studies.

Equipment

Sulphate removal with BaCO₃ was studied by using 1000 mL beakers and a 6 paddle stirrer. H₂S-stripping was studied by using the laboratory set-up as shown in Figure 1. It consists of H₂S-stripping and H₂S-absorption stages. Thermal studies were carried out by using an tube furnace (Elite) and a muffle furnace (Lenton) permitting temperatures up to 1200°C. The mass of the BaSO₄/CaCO₃ mixture was determined before and after thermal treatment.

Procedures

Sulphate removal was studied by adding BaCO₃ to 1000 mL beakers, containing 1 400 mg/L SO₄²⁻ (2.508 g/L CaSO₄). The contents were stirred at 150 rpm. The reduction in the sulphate concentration was monitored by sampling at 30 min, 60 min, 120 min, 180 min and 240 min intervals.

Sulphide-stripping was studied by placing a BaS solution in the stripping reactor (500 mL) and a zinc acetate solution in the absorption reactor. CO₂ from a gas bottle was purged through the BaS solution and from there it was passed, together with the stripped H₂S, to the zinc acetate solution.

Thermal studies were carried out by reacting mixtures of BaSO₄, CaCO₃ and coal at elevated temperatures (950 to 1150 °C) in the tube furnace and the muffle furnaces to produce BaS and CaO. Solid samples were collected and analyzed for mass loss, sulphide content, and alkalinity.

Experimental programme

The effects of the following parameters were investigated:

Water treatment

- BaCO₃ concentration (2 873 mg/L, 5 746 mg/L, 14 365 mg/L and 28 729 mg/L) on the sulphate removal and hence determination of the reaction order.
- Alkalinity and pH on the reaction rate when different amounts of Ca(OH)₂ (0, 74 mg, 370 mg and 1 480 mg or 0 mg/L, 100 mg/L, 500 mg/L, 1000 mg/L and 2000 mg/L when expressed as CaCO₃ respectfully) were added to each beaker containing 1 400 mg/L sulphate and treated with BaCO₃ (2 298 mg)..
- Different magnesium concentrations (0 mg/L, 100 mg/L and 300 mg/L Mg, for both MgCl₂ and MgSO₄·6H₂O) in a solution when a solution containing a total sulphate concentration of 1 400 mg/L is treated with BaCO₃ (2 298 mg).

H₂S-stripping

- Reactor type (packed bed with venturi system)
- CO₂-concentration (20% to 100%)
- CO₂ : Sulphide ratio
- Feed rate of CO₂ rich stream (0.2 to 1.0 L/min)
- Retention time of sulphide solution (Feed rate of sulphide rich stream (0.5 to 2 L/min))
- Efficiency of sulphide reaction with Fe (III) solution

Thermal Studies

- CaCO₃/BaCO₃ ratio
- Reaction times in a tube furnace and muffle furnace
- Temperature in tube furnace
- C/BaSO₄-ratio
- Type of furnace (tube and muffle furnaces)
- Mass in a muffle furnace

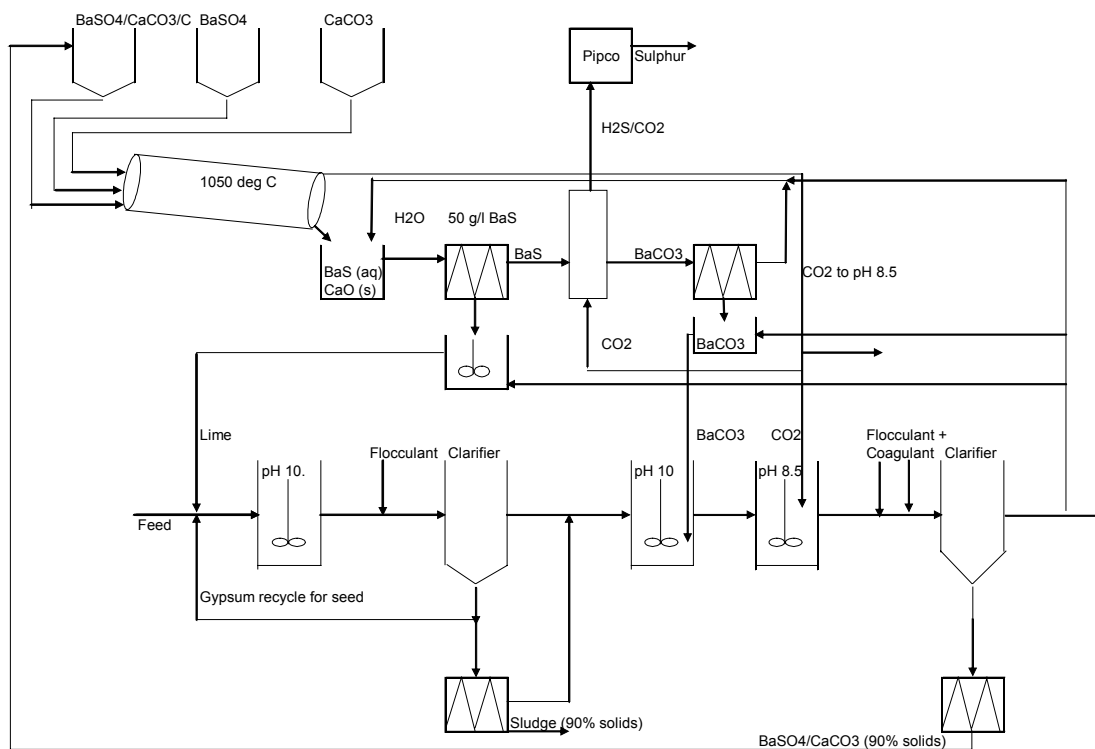


Figure 1: Process flow diagram for the integrated barium carbonate process

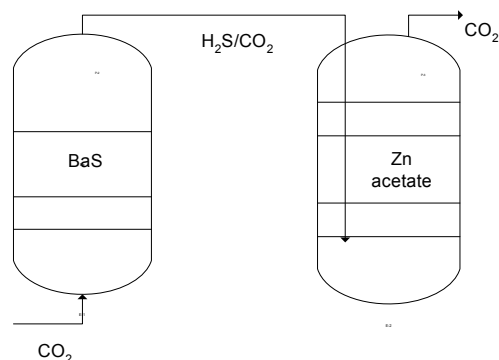


Figure 2: Schematic diagram for H₂S-stripping

Analytical

Samples were collected and filtered through Whatman No 1 filter paper for sulphate, sulphide, alkalinity, calcium, Fe (II) analysis. Mixed liquor suspended solids (MLSS), volatile suspended solids (VSS), acidity, and pH determinations were carried out to standard procedures (APHA, 1985). Calcium was assayed using atomic absorption spectrophotometry. Acidity was determined by titration to pH 8.3 using NaOH. Sulphide (in the product from the thermal studies) was determined by mortaring and dissolving 0.5g of the product in 100 mL deionized water followed by the iodine method for sulphide analysis (APHA, 1985).

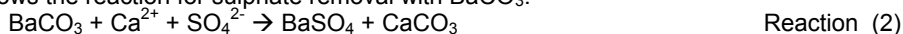
RESULTS AND DISCUSSION

Sulphate removal

Figures 3 to 7 show the effect of the following parameters, respectively: BaCO₃ concentration, alkalinity and magnesium concentration.

The effect of BaCO₃ concentration on the reaction rate

Reaction 2 shows the reaction for sulphate removal with BaCO₃.



The rate of sulphate removal increased with increased BaCO₃ concentration (Figure 3). The reaction order was determined by plotting the log of the reaction rates of sulphate removal for different BaCO₃ concentrations against the log of different BaCO₃ concentrations. This was found to be first order (Figure 4) and this further proves that the rate of the reaction is dependant on the BaCO₃ concentration (rate order >0).

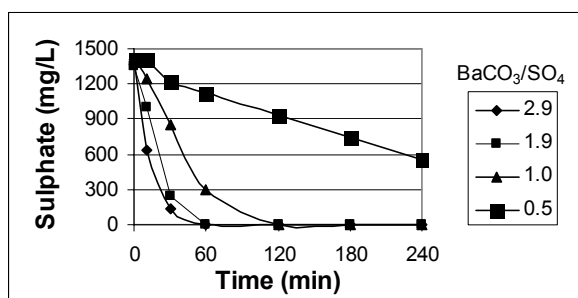


Figure 3: Effect of BaCO₃-concentration on the level of sulphate removal

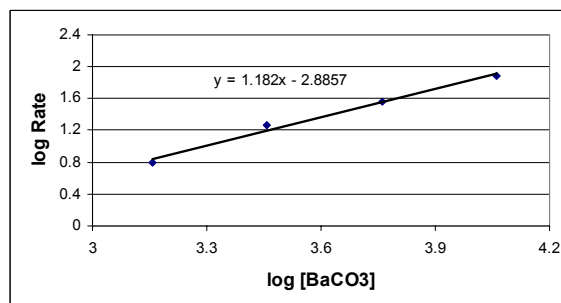


Figure 4: The reaction order of sulphate removal by BaCO₃

The effect of alkalinity on reaction rate

The rate of sulphate removal decreased slightly with increasing alkalinity (Figure 5). This could be ascribed to the decrease in solubility of BaCO₃ with increasing alkalinity and concomitant increasing pH.

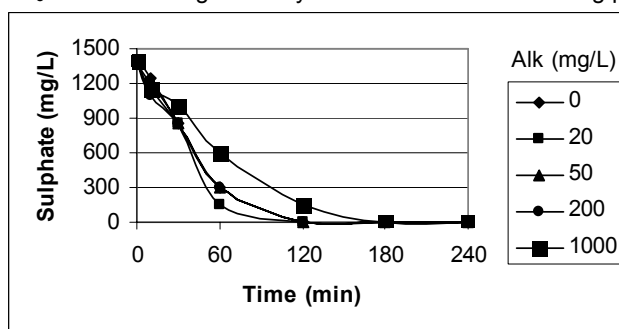


Figure 5: Effect of alkalinity on the rate of sulphate removal

The effect of magnesium on sulphate removal

Trusler (1988) showed that sulphate can only be precipitated as BaSO₄ with BaCO₃ after magnesium is removed (e.g. through lime treatment). This aspect was re-investigated with the focus on the anion associated with magnesium (e.g. chloride or sulphate).

Figure 6 shows the results when a CaSO₄/MgSO₄ solution was used for sulphate removal with BaCO₃ (sulphate associated with magnesium). The sulphate concentration was 1350 mg/l while the Mg concentrations were 0, 100 and 300 mg/L, respectively.

Figure 7 shows the results when a CaSO₄/MgCl₂ solution was used (sulphate not associated with magnesium). The sulphate concentration was again 1350 mg/L while the Mg concentration was 0 mg/L, 100 mg/L and 300 mg/L, respectively. In the case of CaSO₄/MgSO₄

(Figure 6), only sulphate associated with calcium was removed, while in the case of CaSO₄/MgCl₂ (Figure 7), all the sulphate was removed, irrespective of the magnesium concentration. This shows that magnesium only influences the level of sulphate removal if it is associated with sulphate.

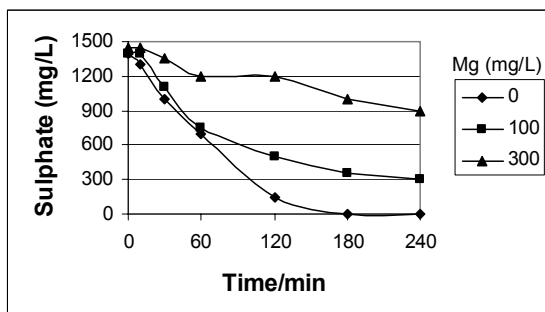


Figure 6: The effect of MgSO₄-concentration (0, 100 and 300 mg/L Mg) on the level of sulphate removal.

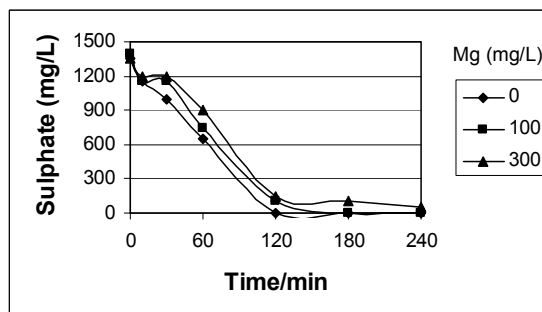


Figure 7: Effect of MgCl₂-concentration (0, 100 and 300 mg/L Mg) on the level of sulphate removal.

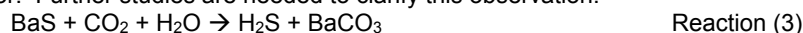
The above finding can be explained by the following: BaCO₃ needs to dissolve partially in order to provide Ba²⁺ ions to precipitate sulphate as BaSO₄. Because of the low solubility of BaCO₃, both the Ba²⁺ and CO₃²⁻ ions in solution need to be removed to allow further dissolution of BaCO₃. Ba²⁺ is removed through precipitation of

BaSO₄, while the CO₃²⁻ ion need to be removed through precipitation as CaCO₃. If the water that needs to be treated with BaCO₃ for sulphate removal, contains Mg²⁺ or Na⁺ that are associated with sulphate, a sulphate concentration stoichiometric equal to the sum of the Mg²⁺ and Na⁺ concentrations will remain in solution. This is due to the high solubility of both Mg and Na carbonate salts.

H₂S-stripping and absorption

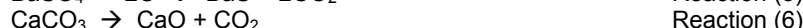
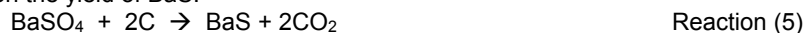
Figures 8 and 9 show the results when sulphide was stripped with 100% CO₂ from a 60 g/L BaS solution. It was noted that:

- H₂S can be removed effectively by stripping with CO₂. Figure 8 shows that sulphide was stripped from 330 mg/L to 75 mg/L (as S) within 90 min (Figure 8). The rate limiting factor was the CO₂ feed rate. In other experiments where excess CO₂ was dosed, sulphide was removed to less than 10 mg/L (as S). In the barium carbonate process it is not required to remove sulphide to low levels as the sulphide solution is recycled.
- Figure 9 shows that the mole ratio (CO₂ fed/H₂S-stripped) = 1, for the period when the pH was > 12 (Reaction 3) and it increased to 2 or higher when the pH dropped to < 12 (Reaction 4). It is therefore recommended that H₂S-stripping be operated in the pH range > 12 at BaS concentrations of 60 g/L to ensure minimum CO₂ consumption.
- The stripped H₂S was completely absorbed zinc acetate solution. However no sulphide was detected in the zinc acetate solution during the first 15 min of CO₂ stripping, although sulphide removal occurred in the stripping reactor. This was possibly due to the formation of a sulphur complex that first forms in the sulphide absorption reactor. Further studies are needed to clarify this observation.



Thermal Studies

In the BaCO₃ process, a mixture of BaSO₄ and CaCO₃, needs to be treated thermally for the production of BaS and CaO. Reaction 5 shows the conversion of BaSO₄ to BaS and Reaction 6 the conversion of CaCO₃ to CaO. Table 1 and Figures 10 to 13 show the effect of various parameters (time, mass, temperature ratio of CaCO₃/BaSO₄) on the yield of BaS.



It was noted that:

- The BaS yield is directly related to the reaction time (Figure 10). A reaction time of 15 min was needed when 5 g of BaSO₄ and a stoichiometric amount of CaCO₃ was reacted with 50% excess carbon in a tube furnace (Figure 10). A reaction time of 60 min was needed when 300 g of BaSO₄ a equal stoichiometric amount of CaCO₃ were reacted with 50% excess carbon in a muffle furnace (Figure 10). Both cases show that the BaS yield is a function of time. The fact that a longer time was needed in the case of the muffle furnace is because of the smaller ratio of surface area/mass of reactants.

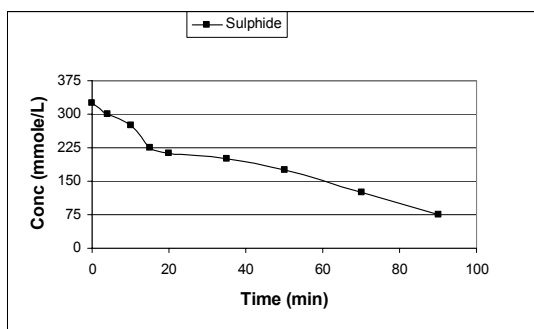


Figure 8: Sulphide concentration during H₂S-stripping with CO₂.

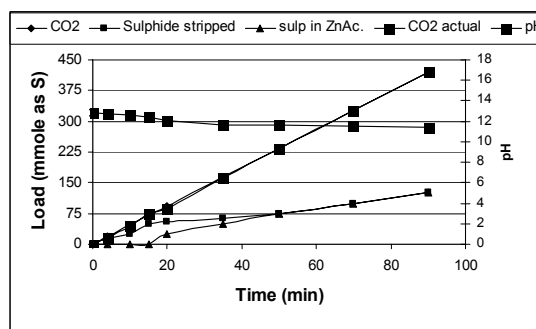


Figure 9: Relationship between various parameters during sulphide stripping with CO₂.

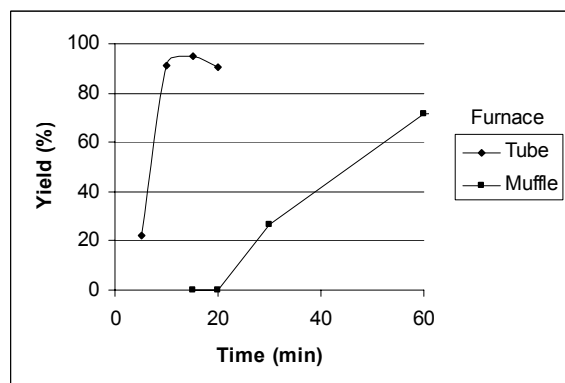
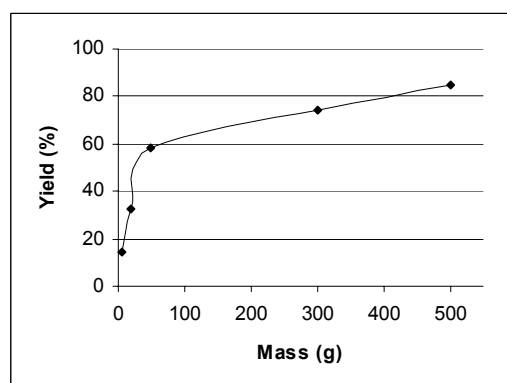
- In the muffle furnace, the yield of BaS increased with increased mass of BaSO₄ (Figure 11). In the case of only 5 g BaSO₄, the yield of BaS was only 14.7%, compared to 84.4% for a BaSO₄ mass of 500 g (Table 1, BaSO₄ mass). This finding can be ascribed to the degree of how oxygen in the air is replaced with CO₂ produced in the reaction. The empty volume of the muffle furnace is 25.8 L. At 25°C, 25.8 L air contains 5.2 L O₂ (or 7.4 g O₂). At 1000°C the total volume of gas in the furnace (25.8 L) contains only 1.73 g O₂. This mass of 1.73 g O₂ is equivalent to 6.28 g of BaSO₄. Therefore, in the case of 5 g BaSO₄, sufficient O₂ is available from the hot air in the furnace to react with the coal. The result is a low yield of only 14.7%. With higher masses of BaSO₄, and higher masses of carbon, the original air in the muffle furnace is complete replaced with the CO₂ produced, resulting in higher BaS yields.

- The optimum temperature for BaSO₄ reductions is in the range 950°C to 1050°C (Figure 12).

- The ratio $\text{CaCO}_3/\text{BaSO}_4$ has little influence on the yield of BaS (Figure 13). A 94.7 % BaS yield was obtained when the stoichiometric $\text{CaCO}_3/\text{BaSO}_4$ mole ratio was zero (no CaCO_3). This value dropped to only 86.3% for a stoichiometric $\text{CaCO}_3/\text{BaSO}_4$ mole ratio = 1. This shows that BaSO_4 - reduction to BaS and CaCO_3 decomposition to CaO can take place simultaneously.

Table 1: Effect of various parameters on the thermal conversion of BaSO_4 to BaS

Experiment	Value	Conversion	Experimental conditions					
			Mass loss (%)	Time (min)	Temp ($^{\circ}\text{C}$)	BaSO_4 (g)	Activated Carbon (g)	CaCO_3 (g)
Time (min)	Tube	21.9	5	1050	5	0.77	2.15	Tube
		91.1	10	1050	5	0.77	2.15	Tube
		94.8	15	1050	5	0.77	2.15	Tube
		90.2	20	1050	5	0.77	2.15	Tube
	Muffle	0.0	15	1050	300	46.35	128.8	Muffle
		0.0	20	1050	300	46.35	128.8	Muffle
		26.8	30	1050	300	46.35	128.8	Muffle
		71.7	60	1050	300	46.35	128.8	Muffle
Temp ($^{\circ}\text{C}$)	800	0.0	20	900	5	0.77	2.15	Tube
	900	68.4	20	950	5	0.77	2.15	Tube
	950	90.2	20	1000	5	0.77	2.15	Tube
	1000	91.1	20	1050	5	0.77	2.15	Tube
	1050	94.8	20	1100	5	0.77	2.15	Tube
$\text{CaCO}_3/\text{BaSO}_4$	0	94.7	20	1050	5	0.77	0	Tube
	0.2	94.0	20	1050	5	0.77	0.43	Tube
	0.5	87.4	20	1050	5	0.77	1.07	Tube
	1	86.3	20	1050	5	0.77	2.15	Tube
BaSO_4 mass	5	14.7	60	1050	5	0.77	2.15	Muffle
	20	32.9	60	1050	20	3.09	8.58	Muffle
	50	58.4	60	1050	50	7.73	21.46	Muffle
	500	84.4	60	1050	500	77.25	214.6	Muffle

**Figure 10: The effect of time on the % yield conversion****Figure 11: The effect of mass on the yield BaS**

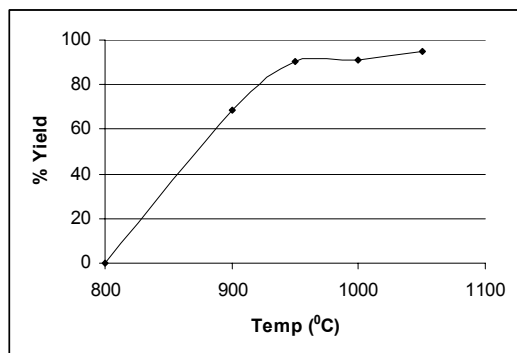


Figure 12: The effect of temperature on the yield of BaS.

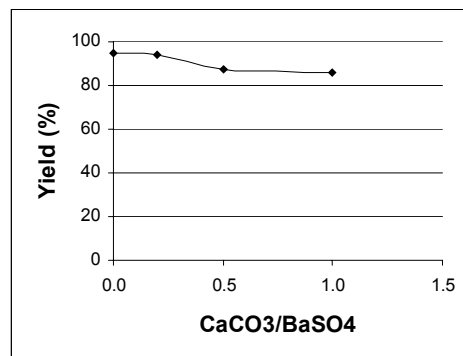


Figure 13: The effect of CaCO₃/BaSO₄ ratio on the % conversion

Economic feasibility

Tables 2 to 4 show the economic feasibility of the treatment of 20 ML/d of sulphate rich water. Table 2 shows the chemical composition of feed and treated water, Table 3, the mass and composition of sludge produced and Table 4, the running cost, estimated capital cost and value of by-products. It was noted that the total running cost amounts to R1.28/m³ of treated water, compared to the value of R2.78/m³ for the products (water and sulphur). The capital redemption cost was estimated at R1.08/m³.

CONCLUSIONS

1. The rate of sulphate removal is influenced by the BaCO₃ concentration and the cation associated with sulphate. The rate of sulphate removal increases with increasing BaCO₃-concentration. BaCO₃ can only be used for removal of sulphate that is associated with calcium, as calcium is needed to remove the carbonate associated with the barium cation. Sulphate removal is only marginally influenced by alkalinity.
2. Sulphide can be stripped with CO₂ from a BaS-solution. The (CO₂ dosed/Sulphide removed) ratio is equivalent to 1 for the first 50% of sulphide passed through the solution.
3. The stripped H₂S-gas can be absorbed into zinc acetate.
4. BaSO₄ and CaCO₃ can be converted simultaneously to BaS and CaO, respectively. The optimum temperature is 1050°C. The (CaCO₃/BaSO₄) ratio has little influence on the yield of BaS.
5. The running cost of the barium carbonate process for the removal of 2 g/L of sulphate totalled R2.28/m³, the capital redemption cost amounted to R1.08/m³ and the combined values of the products (water and sulphur) R2.76/m³.

Parameter	Unit	Feed	Lime	BaCO ₃	CO ₂
Flow rate (ML/d)		20.0			
pH		3.1	10.0	10.0	8.5
Acidity	mg/L CaCO ₃	473.0			
Total Dissolved Solids	mg/L	3103.0	3319.4	769.4	489.4
Calcium	mg/L	426.6	902.4	152.4	72.4
Magnesium	mg/L	164.0	1.0	1.0	1.0
Sodium	mg/L	71.0	71.0	71.0	71.0
Potassium	mg/L	7.0	7.0	7.0	7.0
Iron	mg/L	81.0	1.0	1.0	1.0
Manganese	mg/L	23.0	1.0	1.0	1.0
Aluminium	mg/L	16.0	1.0	1.0	1.0
Free acid	mg/L CaCO ₃	239.1	0.0	0.0	0.0
Sulphate	mg/L	2274.7	2000.0	200.0	200.0
Chloride	mg/L	35.0	35.0	35.0	35.0
Alkalinity	mg/L CaCO ₃	0.0	300.0	300.0	100.0
Cations	Meq/L	48.4			
Anions	Meq/L	48.4			

Table 2: Chemical composition of feed and treated water

Chemical	Unit	Value
Fe(OH) ₃	kg/h	127.5
Al(OH) ₃	kg/h	36.1
Gypsum	kg/h	410.1
Mn(OH) ₂	kg/h	29.5
Mg(OH) ₂	kg/h	325.9
Total sludge (100% solids)	kg/h	929.1

Table 3: Sludge production

Parameter	Unit	Value
Lime		
Lime dosage (100% CaCO ₃)	mg/L	1448
CaCO ₃ intake (Purity = 87%, 5% losses)	kg/h	727
Lime usage (87% CaCO ₃)	kg/h	1456
Ca(OH) ₂ recovered (as CaCO ₃)	kg/h	562
CaCO ₃ recovered	kg/h	167
BaSO₄		
BaSO ₄ sludge (100%)	kg/h	3641
BaSO ₄ losses (5%)	kg/h	182
Coal		
Coal for CaO	kg/kg CaCO ₃	0.27
Coal usage for CaO	kg coal/h	393
Heat of Formation	MJ/kg BaSO ₄	2.03
Coal Energy value	MJ/kg coal	28
Coal for Energy (80% utilization efficiency)	kg/kg BaSO ₄	0.09
Coal for BaSO ₄ -reduction	kg/kg BaSO ₄	0.22
Coal usage for BaS	kg/kg BaSO ₄	0.31
Coal usage for BaS	kg coal/h	1190
Coal usage for CaO + BaS	kg coal/h	1583
Chemical prices		
BaSO ₄ Price	R/t	1650
CaCO ₃ Price	R/t	220
Coal Price	R/t	180
Running cost		
CaCO ₃ cost	R/m ³	0.19
BaSO ₄ cost	R/m ³	0.36
Coal cost	R/m ³	0.34
KOH & Citric acid	R/m ³	0.03
Operators, Electricity, Maintenance, etc	R/m ³	0.36
Total Running cost	R/m ³	1.28
Capital cost		
Capital	R	-50000000
Capital redemption cost (10%/year, 120 months)	R/m ³	R 1.08
Value of products		
Sulphur	kg/h	500.00
Price	R/t	450.00
Sulphur value (5% losses)	R/m ³	0.26
Water value	R/m ³	2.50
Value of products	R/m ³	2.76

Table 4: Capital cost, running cost and value of by-products of the BaCO₃-process

Note: US\$1.00 = ZAR6.50, July 2005

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