Mine Water and the Environment (2004) 23: 195–203 © IMWA Springer-Verlag 2004

Technical Article

Treatment of Mine Water for Sulphate and Metal Removal Using Barium Sulphide

J. P. Maree[1], P. Hlabela[1], R. Nengovhela[1], A. J. Geldenhuys[1], N. Mbhele[1], T. Nevhulaudzi[1], and F. B. Waanders[2]

[1]Business Unit of Water, Environment, and Forestry Technology, CSIR, PO Box 395, Pretoria, South Africa; [2]School of Chemical and Minerals Eng, North West Univ, Potchefstroom, 2531, South Africa; corresponding author's e-mail: jmaree@csir.co.za

Abstract. The integrated barium sulphide process consists of: preliminary treatment with lime, sulphate precipitation as barium sulphate, H_2S-stripping, crystallization of $CaCO_3$, and recovery of barium sulphide. Our tests showed that during lime pre-treatment, sulphate was lowered from 2 800 mg/L to 1 250 mg/L by gypsum crystallization; metals were precipitated as hydroxides. The BaS treatment then lowered sulphate to less than 200 mg/L. Sulphide was lowered from 333 to less than 10 mg/L (as S) in the stripping stage, using CO_2 gas for stripping. The stripped H_2S-gas was contacted with Fe (III)-solution and converted quantitatively to elemental sulphur. The alkalinity of the calcium bicarbonate-rich water was reduced from 1 000 to 110 mg/L (as $CaCO_3$) after CO_2-stripping with air due to $CaCO_3$ precipitation. Fe (II), after sulphur production, was re-oxidized to Fe (III) using an electrolytic step. The running cost of the BaS process is R2.12/m^3 (US$1 = SAR6.5) for the removal of 2 g/L of sulphate.

Key words: Barium sulphide; gypsum; sulphate removal; water treatment; sulphide stripping

Introduction

Mining is a significant contributor to water pollution, due primarily to pyrite oxidation, which generates potentially high levels of acidity, metals, and sulphate. In South Africa, the large volumes of mine water generated make the problem serious; 200 ML/d of mine water flows in Gauteng, while 50 ML/d discharges into the Olifants River Catchment in Mpumalanga. South Africa requires sulphate concentrations to be less than 500 mg/L. Several processes can be considered for sulphate removal, e.g., biological sulphate removal, SAVMIN (ettringite), ecoDose, reverse osmosis, and electrodialysis. Barium can also be used for sulphate removal and has certain advantages: sulphate can be removed to specific values due to the low solubility of barium sulphate ($BaSO_4$) and the soluble barium salt, barium sulphide (BaS), can be recovered.

Kun (1972) studied the removal of sulphate with barium carbonate ($BaCO_3$) 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 $BaCO_3$ was dosed than stoichiometrically required, and the high cost of the $BaCO_3$. Volman (1984) and Maree (1989) overcame the cost problem by demonstrating that $BaSO_4$ could be reduced efficiently and economically with coal under thermic conditions to produce BaS. This compound can be used directly on site or converted to $BaCO_3$. Wilsenach (1986) demonstrated economic viability by calculating the cost of producing BaS from $BaSO_4$. Trusler et al. (1988) developed a $BaCO_3$ method using a two-stage fluidised bed reactor system to overcome the other problems identified by Kun (long retention time and high Ba levels in the treated water). However, the $BaCO_3$ became inactive when coated with metal hydroxide precipitates, which made it unsuitable for most mine water. Maree et al. (1989) also noted a problem in separating $BaSO_4$ and $CaCO_3$, which co-precipitate.

The purpose of this study was to demonstrate the performance of an integrated barium sulphide process, consisting of the following stages (Figure 1):

- Lime pre-treatment for partial sulphate removal;
- Removal of sulphate as $BaSO_4$ to below 200 mg/L by BaS treatment;
- H_2S-stripping with CO_2-gas;
- Stripping of CO_2 and $CaCO_3$ precipitation; and
- Recovery of BaS from the produced $BaSO_4$.

The specific aims were to:

- Demonstrate that sulphate can be lowered to less than 200 mg/L with BaS treatment;
- Determine optimum conditions for the following process-stages: partial SO_4 removal through lime pre-treatment, reducing $BaSO_4$ to BaS, and H_2S-stripping and processing; and
- Estimate the running cost of the process.

Materials and Methods

Feedstock

Mine water from Navigation Section of Landau Colliery was used as feed water containing 2 650

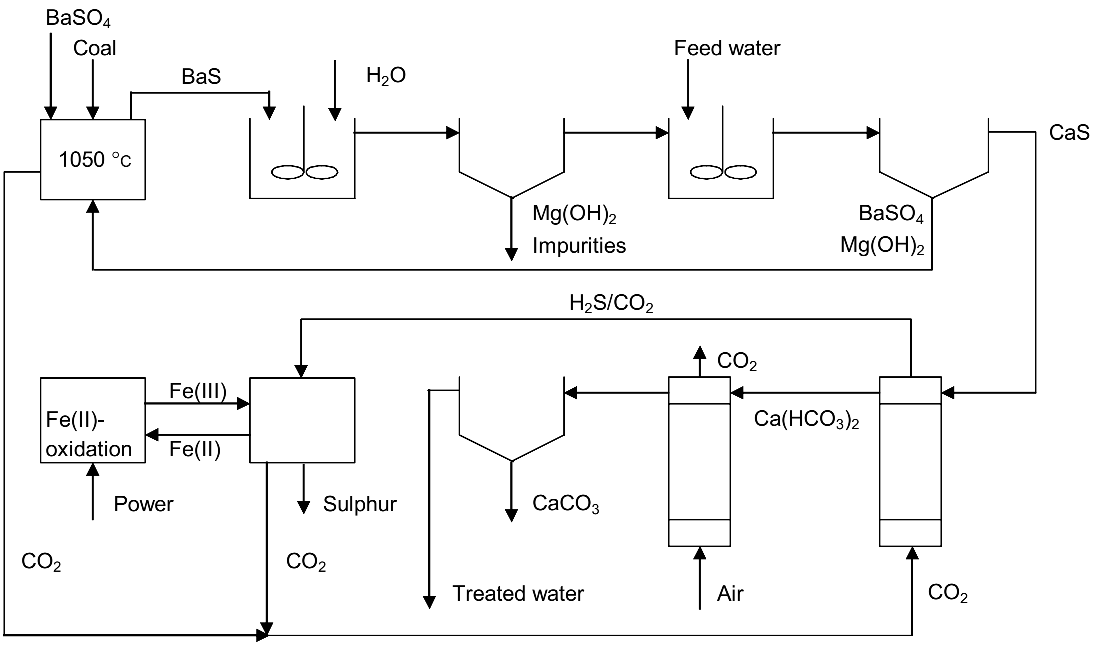


Figure 1. Process flow diagram for the barium sulphide process (pre-treatment with lime not shown)

mg/L SO_4 and 167 mg/L Mg (complete chemical analyses shown later) during continuous pilot-scale studies. Lime (Lime Distributors) and BaS (G&W Base Minerals) were used for pH adjustment and sulphate removal, respectively. For the H_2S-stripping studies, synthetic sulphide-rich feed water with sulphide concentrations between 700 and 800 mg/L was used. CO_2 gas (supplied by Afrox) was used for H_2S-stripping. A $Fe_2(SO_4)_3$ solution (11 g Fe/L) was used for absorption of the stripped H_2S-gas. During the thermic studies, chemically pure $BaSO_4$ and industrial grade $BaSO_4$ (supplied by G & W Base Minerals) were used for the BaS recovery studies.

Equipment

Figure 1 shows the laboratory-scale plant that was used for sulphate removal with BaS. The laboratory-scale plant used for H_2S-stripping and H_2S-processing to elemental sulphur is shown in Figures 2 and 3. Table 1 shows the volume and dimensions of the various reactors depicted in Figures 1, 2, and 3. The tube had a diameter of 40 mm and was 530 mm long.

A packed bed reactor and a venturi system were used for H_2S-stripping and H_2S-absorption into a Fe (III) solution, using configurations A (Figure 2) and B (Figure 3) respectively. In configuration A, the sulphide solution was fed continuously to the packed-bed reactor (stripping stage), and allowed to drip down the packing material (25 mm diam. Raschig rings), while H_2S-free CO_2-gas, flowing from bottom to top, was recycled via the H_2S-absorption stage. In the H_2S-absorption stage, H_2S was contacted with Fe (III) solution at a pH of 2.5, to produce elemental sulphur (Reaction 1). The Fe (III) solution was replaced batchwise, as required.

$$H_2S + 2Fe^{3+} \rightarrow S + 2Fe^{2+} + 2H^+ \qquad (1)$$

In configuration B, the sulphide solution was recycled in batch mode. CO_2-rich gas was incorporated into the solution via a venturi system, hence contacting it with the sulphide-rich water for H_2S-stripping (stripping stage). The stripped H_2S-rich gas was passed through a packed bed-reactor to which the Fe (III) solution was continuously fed for sulphur production.

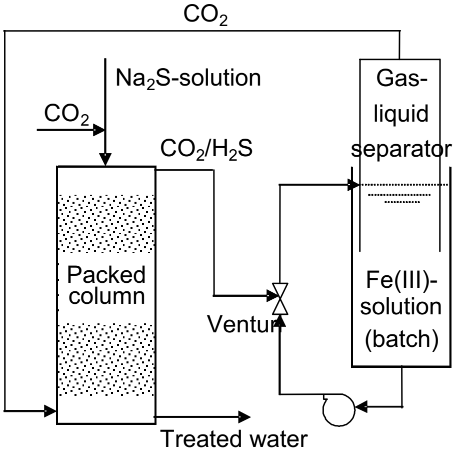
The packed column consisted of a 0.8-m randomly packed bed, with 25-mm Pall-rings used as packing material. A 240-mm diam. Perspex cylinder (adsorption) was used and Perspex plates were used to support the packing and to aid in flow distribution in the column. A Perspex plate with evenly distributed holes was installed at the top of the column to ensure adequate distribution of the liquid feed. The venturi was used for gas recirculation between the stripping and the absorption stages. A centrifugal pump (capacity, 1 m^3/h) was used to recycle Fe (III) (configuration 1) or sulphide (configuration 2) solution via the venturi. Table 1 shows the dimensions of the various units. CO_2 was transferred from a CO_2-cylinder to a CO_2 float tank from which it was pumped at a set flow rate with a peristaltic pump at NTP (normal temperature and pressure) to the H_2S-stripping stage.

General Experimental Procedures

Pre-treatment and BaS-treatment were investigated in both continuous and batch studies. In the continuous

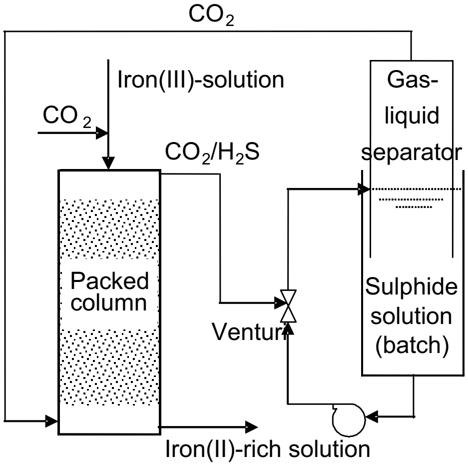
Table 1. Volume and dimensions of various reactors

Item	Volume (L)	Diameter (mm)	Height (mm)
BaS treatment stage			
BaS storage tank	10	235	235
BaS treatment reactor	10	235	235
Clarifier ($BaSO_4$)		450	
H_2S-stripping/processing			
Packed bed-reactor packed with 25 mm Pall-rings	39	250	800
Venturi reactor	40	300	800



Configuration A

Figure 2. H_2S-stripping and processing



Configuration B

Figure 3. H_2S-stripping and processing

experiments, feed water (2 650 mg/L SO_4, 83 mL/min), lime slurry (10%, 3 mL/min), BaS slurry (57.7 g/L, 3 mL/min), and a flocculant (Flocculant 3095) (3 mL/min) were fed to the system shown in Figure 2. Sludge was recycled from the underflow of the two clarifiers to the completely-mixed reactors at a rate of 83 mL/min. Sludge was withdrawn periodically to maintain the solids content in the lime treatment reactor at 40 g/L and in the BaS-treatment reactor at 32 g/L.

Batch studies were carried out on the BaS treated water for H_2S-stripping and softening. H_2S-stripping was achieved by bubbling CO_2 through the water; softening was achieved by dosing the water with 5 g/L $CaCO_3$ and stripping the CO_2 with air.

H_2S stripping and processing were investigated in configuration A (Na_2S fed continuously to the packed bed-reactor and contacted with Fe (III) solution was passed through a venturi system in batch mode). Na_2S was contacted with CO_2-gas with varied concentrations and flow rates. Sulphide removal was monitored in the feed water, after the feed pipe, at the inlet of the packed bed-reactor and the treated water. The Fe (II) concentration was monitored in the Fe (III) solution that was handled in batch mode.

In configuration B (Fe (III) solution fed to the packed bed-reactor and contacted with stripped H_2S-gas from the venturi system), Fe (III) solution was fed at various flow rates. The resulting Fe (II) was monitored in the feed and treated streams of the Fe (III) solution. The sulphide concentration was monitored in the sulphide solution, which was handled in batch mode.

Thermal studies involved mixing and reacting $BaSO_4$ (industrial grade and pure $BaSO_4$) and coal at elevated temperatures in a tube or muffle furnace for various reaction periods. Solid samples were collected and analyzed for mass loss, sulphide content, and ability to remove sulphate.

Experimental Program

The BaS-treatment stage feed water and treated water were analyzed (Table 2) and the following parameters were investigated in the subsequent stages:

H_2S-stripping and processing stage

- Reactor type (packed bed-reactor and 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

Thermic studies stage

- C: BaSO4-ratio (2, 2.5, and 3)
- Type of furnace (Tube and Muffle)
- Temperature (900ºC to 1100ºC)
- Reaction time (15, 30, 60, and 120 min).

Analytical

Samples were collected regularly and filtered through Whatman No 1 filter paper. Sulphate, sulphide, alkalinity, calcium, Fe (II), mixed liquor suspended solids, volatile suspended solids, acidity, and pH determinations were carried out according to standard procedures (APHA 1985). Calcium was assayed using atomic absorption spectrophotometry. Sulphide (a product from the thermic studies) was determined by mortaring the product, and analyzing it using the iodine method in a 0.5 g/100 mL BaS solution.

Results and Discussion

Water Quality

Table 2 shows the feed water composition before and after treatment with lime and BaS. It was noted that:

- During pre-treatment with lime, sulphate decreased from 2 650 mg/L to 1 250 mg/L, reflecting the solubility product of gypsum. Magnesium and other metals were completely removed.
- During BaS-treatment, sulphate was lowered to the stoichiometric BaS-limit (1 000 mg/L).
- During H_2S-stripping with CO_2 gas, sulphide was lowered from 320 to < 20 mg/L (Figure 4).
- During the softening stage, 890 mg/L of $CaCO_3$ (993 – 103 mg/L $CaCO_3$) precipitated due to CO_2 stripping with air (Figure 5). The pH increased from 5.7 to 7.2 as the CO_2 was stripped, resulting in $CaCO_3$ precipitation (since the solubility of $CaCO_3$ decreases with increasing pH).

H_2S Stripping and Processing Stage

Sulphide can be removed by CO_2 stripping to less than 20 mg/L (Figure 4). To obtain engineering design criteria for full-scale implementation, the effects of various parameters on the rate of H_2S-stripping were determined, using configuration A (Figure 2). By feeding a sodium sulphide solution and a CO_2-gas stream, counter current, on a continuous basis through to a packed bed reactor, it was noted that by passing the sulphide solution through two stages in series at a CO_2/Na_2S feed load of 1.4 g CO_2/g S, sulphide was lowered from 834 to 434 mg/L in stage 1, and from 376 to 77 mg/L (as S) in stage 2 (Table 3). By providing a third stage, sulphide could have been decreased to less than 20 mg/L. The aim, however, with this investigation was to identify optimum process conditions to allow the minimum number of process stages for complete sulphide removal. Sulphide is quantitatively converted to sulphur as indicated by the correspondence between the actual and theoretical values for the ratio: load of Fe (II)

Table 2. Chemical composition of feed water and after treatment with BaS

Parameter	Concentration				
	Feed	Lime	BaS	H_2S stripping	Softening
$Ca(OH)_2$-dosage (g/L)		1.89			
BaS-dosage (g/L)			1.76		
Gypsum dosage (g/L)		5			
$CaCO_3$ dosage (g/L)					5
Alkalinity addition (g/L)		2554	1041	3595	
pH	1.6	12	11.9	5.7	7.2
Sulphate (mg/L SO_4)	2650	1250	250	255	250
Sulphide (mg/L S)	0	320	<20	<20	<20
Alkalinity (mg/L $CaCO_3$)	-1900	960	2276	993	103
Alkalinity increase (mg/L)		2860	1316	4176	
Calcium (mg/L Ca)	43	950	981	460	139
Magnesium (mg/L Mg)	166.5	<0.1	<0.1	1.70	1.8
Iron (mg/L Fe)	8.53	<0.01	<0.01	<0.01	<0.01
Aluminium (mg/L Al)	9.3	0.14	0.23	0.16	0.19
Manganese (mg/L Mn)	10.6	<0.03	<0.03	<0.03	<0.03
Copper (mg/L Cu)	9	<0.05	0.06	0.06	0.07
Lead (mg/L Pb)	8.9	<0.1	<0.1	<0.1	<0.1
Zinc (mg/L Zn)	16	<0.05	<0.05	<0.05	<0.05
Nickel (mg/L Ni)	11.2	<0.03	<0.03	<0.03	<0.03
Cations (meq/L)	57.28	47.50	40.97	23.00	6.95
Anions (meq/L)	55.21	45.24	50.73	25.17	7.27

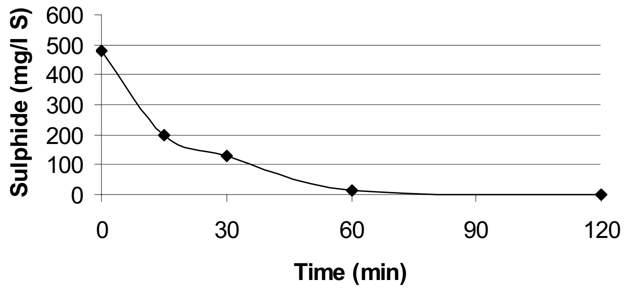


Figure 4. H_2S-stripping with CO_2

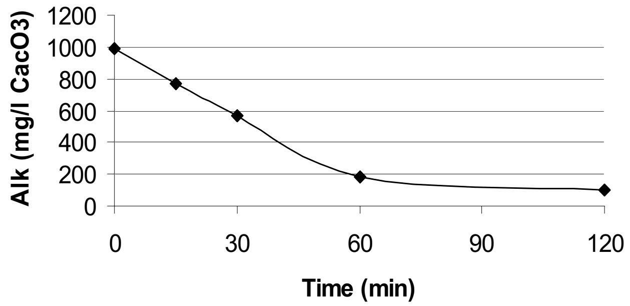


Figure 5. CO_2 stripping with air and $CaCO_3$ precipitation

produced/load of sulphide removed (3.65 g Fe/g S (average of 3.60 and 3.70) versus 3.49). More than one stripping stage was needed for complete sulphide removal as less CO_2 was dosed than theoretically required (1.75 g CO_2/g S (average of 1.70 and 1.79) versus 2.75). The theoretical ratios for load of CO_2 consumed/load of sulphide removed (2.75) and load of Fe (II) produced/load of sulphide removed (3.49) were calculated from Reactions 2 and 3.

$$H_2S + 2Fe^{3+} \rightarrow S + 2Fe^{2+} + 2H^+ \quad (2)$$

$$2CO_2 + S^{2-} + 2H_2O \rightarrow 2HCO_3^- + H_2S \quad (3)$$

Table 4 shows the effect of the Na_2S feed rate on the sulphide removal. Better sulphide removal was achieved with a lower Na_2S feed rate (higher HRT). At a feed rate of 0.5 L/min (HRT = 59 min), 217 mg/L of sulphide was removed, compared to only 154 mg/L at a feed rate of 2 L/min (HRT = 15 min). The results in this experiment were however negative in the sense that the pH of the treated water was higher than 8 (9.0), even though the actual value of dCO_2/dNa_2S of 14.53 was higher than the theoretical value of 2.75. This negative result can be ascribed to the fact that CO_2 was not completely utilized due to too little contact time with the Na_2S-solution. In the next experiments, this problem was solved by passing the Na_2S/CO_2 mixture through a 5 m pipe with a diameter of 20 mm (6.3 L volume). At a feed rate of 1 L/min, the hydraulic retention time in the 5 m pipe amounted to 6.3 min.

Table 5 shows the effect of CO_2 flow rate on the sulphide removal at a constant Na_2S flow rate of 1 L/min.

Table 3. Sulphide removal in two stages in series at 100% CO_2, a Na_2S feed rate of 0.90 L/min, a HRT of 32.7 min, and a gas recycle rate of 22.9 L/min

Parameter	Stage1	Stage2
CO_2/Na_2S-feed ratio (g CO_2/g S)	0.77	1.40
Na_2S feed rate (L/min)	0.90	0.90
CO_2 feed rate (L/min)	0.29	0.24
Sulphide in feed (mg/L S)	834	376
Sulphide in treated water (mg/L S)	434	77
Sulphide removed (mg/L)	400	299
pH in feed	9.05	7.0
pH in treated water	7.02	6.2
dCO_2/dNa_2S ratio (g CO_2/g S)		
Theoretical	2.75	2.75
Actual	1.70	1.79
$dFe(II)/dH_2S$		
Theoretical	3.49	3.49
Actual	3.60	3.70

Table 4. Effect of retention time (Na_2S feed rate) on sulphide removal, at 100% CO_2, and a gas recycle rate of 18.1 L/min

Parameter			
Na_2S feed rate (L/min)	2.00	1.00	0.50
CO_2/Na_2 feed ratio (g CO_2/g S)	2.77	1.85	1.51
Na_2S feed rate (L/min)	2.00	1.00	0.50
CO_2 feed rate (L/min)	2.09	0.66	0.26
HRT (min)	14.7	29.5	58.9
Sulphide in feed (mg/L S)	742	704	688
Sulphide, treated water (mg/L S)	588	496	470
Sulphide removed (mg/L)	153.6	208	217.6
pH in feed water	12.18	12.15	12.17
pH in treated water	9.00	8.41	8.47
dCO_2/dNa_2S ratio (g CO_2/g S)			
Theoretical	2.75	2.75	2.75
Actual	14.53	7.28	5.37
$dFe(II)/dH_2S$			
Theoretical	3.49	3.49	3.49
Actual	1.80	0.98	8.90

By increasing the CO_2 flow rate from 0.19 L/min to 0.83 L/min, the sulphide removal increased from 342 to 474 mg/L and residual sulphide in solution decreased from 134 to 0 mg/L (as S). The corresponding ratios of CO_2 feed load/Na_2S feed load increased from 0.78 to 3.46. The stoichiometric value required for this ratio is 2.75 (Reaction 3). This demonstrates that complete sulphide removal can be achieved by dosing excess CO_2, compared to what is stoichiometrically required. In this experiment, 30% excess CO_2 was dosed. By dosing excess CO_2, H_2S-stripping is favoured as the pH is reduced to less than 7 due to free CO_2 in solution. The rate of sulphide stripping also increase with lower pH values as the ratio of H_2S/S_T ($S_T = S^= + HS^- + H_2S$) increase with decreasing pH values. At pH 7 and less, a greater fraction of sulphide species is in the H_2S form.

Table 5. Effect of the CO_2 feed rate on sulphide removal with 29.5% CO_2, an HRT of 100 min, a Na_2S feed rate of 1 L/min, and a gas recycle rate of 18.1 L/min

Parameter			
CO_2 feed rate (L/min)	0.19	0.40	0.83
CO_2/Na_2S feed ratio (g CO_2/g S)	0.78	1.68	3.46
Sulphide in feed (mg/L S)	476	464	473
Sulphide after pipe (mg/L S)	378	265	73.6
Sulphide, treated water (mg/L S)	134	25	0
Sulphide removed (mg/L)	342	438	473
pH in feed water	8.40	8.48	8.95
pH after pipe	7.02	6.62	6.38
pH in treated water	7.10	7.06	6.54
dCO_2/dNa_2S ratio (g CO_2/g S)			
Theoretical	2.75	2.75	2.75
Actual	1.02	1.77	3.46
dFe(II)/dH_2S			
Theoretical	3.49	3.49	3.49
Actual	0.88	1.13	1.91

Table 6. Effect of CO_2 concentration on sulphide removal with an HRT of 29.5 L/min, a Na_2S feed rate of 1 L/min, and a gas recycle rate of 18.1 L/min

Parameter			
CO_2-concentration (%)	20	53	100
CO_2/Na_2S feed ratio (g CO_2 /g S)	1.37	1.61	1.46
CO_2 feed rate (L/min)	0.51	0.56	0.49
Air feed rate (L/min)	2	0.5	0
Sulphide in feed (mg/L S)	739	678	665
Sulphide after pipe (mg/L S)	640	538	486
Sulphide, treated water (mg/L S)	460	393	278
Sulphide removed (mg/L)	278	284	387
pH in feed water	9.54	12.30	12.34
pH after pipe	8.62	8.22	7.36
pH in treated water	8.12	8.03	7.97
dCO_2/dNa_2S ratio (g CO_2/g S)			
Theoretical	2.75	2.75	2.75
Actual	3.60	3.86	2.49
dFe(II)/dH_2S			
Theoretical	3.49	3.49	3.49

Table 7. Effect of gas recirculation rate on sulphide removal at a Na_2S feed rate of 1 L/min, 100% CO_2, and an HRT of 29.5 min

Parameter			
Gas recycle rate (L/min)	19.6	13.1	9.1
CO_2-concentration (%)	19.63	13.09	9.06
CO_2/Na_2S feed ratio (g CO_2/g S)	0.78	1.34	1.17
CO_2 feed rate (L/min)	0.26	0.48	0.41
Sulphide in feed (mg/L S)	665	697	681
Sulphide after pipe (mg/L S)	666	374	377
Sulphide in treated water (mg/L S)	227	371	304
Sulphide removed (mg/L)	438.4	326.4	12.34
pH in feed water	12.10	12.30	7.36
pH after pipe	7.55	7.55	7.97
pH in treated water	7.81	7.64	
dCO_2/dNa_2S ratio (g CO_2/g S)			
Theoretical	2.75	2.75	2.75
Actual	1.19	2.88	2.70
dFe(II)/dH_2S			
Theoretical	3.49	3.49	3.49
Actual	1.76	2.23	3.73

Excess CO_2 gas would be available in many applications: during barium treatment, CO_2 is produced at the rotary kiln where BaS is recovered from $BaSO_4$; with the biological sulphate removal process, CO_2-gas is produced by the heating unit; during limestone neutralization of acid water, CO_2 is produced due to $CaCO_3$ dissolution. The CO_2 in these CO_2-rich gasses can be utilised for H_2S-stripping by contacting the CO_2-rich gas with the sulphide rich stream in a spray tower or a packed-bed reactor.

- Table 6 shows the effect of the CO_2 concentration on sulphide removal. By increasing the CO_2 concentration from 20 to 100%, sulphide removal was increased from 278 to 387 mg/L (as S). In the case where 100% CO_2 was dosed, the theoretical and actual values for dCO_2/dNa_2S were similar (2.75 versus 2.53).

- Table 7 shows the effect of the gas recycle rate on sulphide removal. Increasing the gas recycle rate from 9.1 to 19.6 L/min improved sulphide removal from 304 to 438 mg/L. In this experiment, sulphide was also not completely removed as the dCO_2/dNa_2S feed ratio was only slightly higher than what is stoichiometrically required for the second and third runs and even less than that for the first run.

- It was demonstrated above that a packed bed reactor (configuration A, Figure 2) can be used for sulphide stripping. In this configuration, it appeared that the absorption stage, where H_2S-rich gas was contacted with Fe (III) solution in a venturi system, was effective due to good contact between gas and liquid phase. With the apparent good performance of the venturi system for H_2S absorption, it was decided to also evaluate the suitability of the system for H_2S stripping. The same equipment that was used for configuration A (Figure 2) was used for configuration B (Figure 3), except that the venturi system was used for sulphide stripping in batch mode, and the packed bed-reactor was used for H_2S-absoption into the Fe (III) solution under continuous conditions. Table 8 and Figure 6 show the effect of Fe (III) feed rate on sulphide removal. It was noted that:

- Better sulphide removal was achieved by increasing the Fe (III) feed rate. This is ascribed to partial absorption of H_2S at low Fe (III) feed rates in the closed circuit of configuration 2, and indicates that the packed bed reactor does not function as well as the venturi system for H_2S absorption into the Fe (III) solution.

- The experimental (actual) dFe(II)/dH_2S ratio was similar to the theoretical value of 3.49 (Reaction 2). This shows that all of the Fe (III) introduced into the packed bed reactor was consumed by H_2S-absorption.

Table 8. Effect of the Fe (III) flow rate on sulphide removal, in tests where the gas recycle rate was 18.1 L/min

Parameter				
Fe^{3+}-feed rate (L/min)	1.00	1.00	3.00	4.00
Time (min)	Sulphide (mg/L S)			
	816	1056	704	784
15	768	944	560	720
30	688	880	432	416
45	592	816	336	224
60	432	768	224	32
75	320	672	96	
90		480	94	
Time (min)	pH			
0	11.35	12.13	12.84	12.9
15	10.19	11.79	10.04	8
30	8.44	10.24	8.03	11.1
45	7.65	8.93	7.04	6
60	7.41	8.05	7.23	8.34
75	7.23	7.83	7.13	7.70
90		7.74	7.08	7.30
	dCO_2/dNa_2S ratio (g CO_2/g S)			
Theoretical	2.75	2.75	2.75	2.75
Actual	8.40	8.06	8.02	7.99
	$dFe(II)/dH_2S$			
Theoretical	3.49	3.49	3.49	3.49
Actual	2.87	3.49	3.15	3.12

The results showed that H_2S-stripping and H_2S-absorption is favoured by intensive mixing. Intensive mixing supports mass transfer of H_2S from liquid to gas phase in the case of H_2S-stripping and from gas to liquid phase in the case of H_2S-absorption. The venturi device was more efficient than the packed bed reactor, which we ascribed to the high pressure (300 kPa) and the high velocity (50 m/sec) of gas and liquid particles. Based on this observation, it was decided that a Turbulator, which consists of a motor that directly (no gear box) drives a disc via a hollow shaft, should be used during scale-up. The Turbulator allows mixing between the gas and liquid phase by sucking in air through the hollow shaft that rotates at 2000 rpm. The velocity at the outer limit of the disc is 15 m/sec (diameter = 0.15 m; rpm = 2 000).

Thermal Studies

The cost of the BaS process is largely determined by the cost of recovering BaS from $BaSO_4$. Barium sulphide is produced by reacting $BaSO_4$ with coal at a temperature of 900°C and higher.

$$BaSO_4 + 2C \rightarrow BaS + 2CO_2 \qquad (4)$$

Table 9 shows the effect of various parameters on BaS yield during the thermic conversion. Note that:

- The conversion efficiency reduced with time when a Muffle furnace was used (Experiment 1). This is ascribed to the large volume of air surrounding the reaction vessel. Initially, $BaSO_4$ is converted to BaS due to reducing conditions created by the conversion of coal to CO and CO_2. When the carbon is exhausted, the BaS reacts with oxygen at the high temperature to form $BaSO_4$. Therefore, all further studies (Experiments 2-8) were carried out in a tube furnace. The air was also purged with nitrogen to eliminate oxidizing conditions.

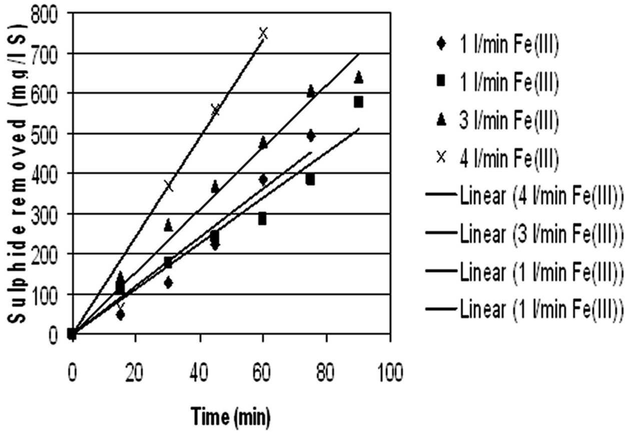


Figure 6. Effect of Fe (III) flow rate on sulphide removal

- A short reaction time (15 min) is sufficient to obtain a high yield of BaS at a temperature of 1050 °C (Experiment 2). Figure 7a shows the conversion of $BaSO_4$ to BaS as a function of time.
- The reaction starts at 900°C and its rate increases with temperature. At 1100°C, a conversion of 100% was achieved within 15 minutes (Experiment 3, Figure 7b).
- The minimum C/$BaSO_4$ mole ratio required for complete reduction is 2, which indicates that the reaction (Experiment 4, Figure 7c) proceeds according to equation 4.
- Better values are achieved with activated carbon than with coal, which may be due to impurities in the coal.
- Both analytical grade and industrial grade $BaSO_4$ (supplied by a supplier) provided good yields of BaS (Experiment 7).
- $Mg(OH)_2$ does not interfere with the reduction reaction of $BaSO_4$ to BaS (Experiment 8).

The methods used for conversion measurements (mass loss, sulphide and sulphate precipitation) compare well. The sulphide values were lower than the mass loss values, which can be ascribed to sulphide losses during dissolution, which was confirmed by a sulphide odour. The product was also tested for the ability to remove sulphate (Experiment 5). Although the sulphate method is not as accurate as the other methods, a value of the same order was achieved.

Running Cost

The running cost of the barium sulphide process amounts to R2.12/m^3 (U.S. $1 = South African Rand 6.50) for the removal of 2 g/L of sulphate (table 10). This excludes the value of the water (R2/m^3) and the

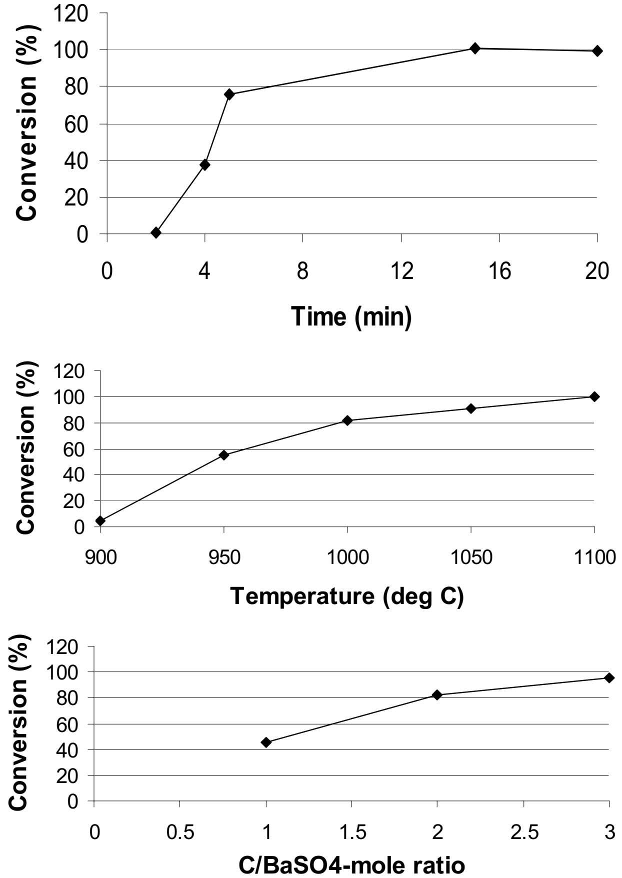


Figure 7. Effect of time, temperature, and C/$BaSO_4$ molar ratio on the conversion of $BaSO_4$ to BaS

by-products, sulphur (R0.30/m^3) and calcium carbonate (R3.33/m^3). The cost of CO_2 that is needed for H_2S-stripping is included in the running cost. CO_2 is recovered from the off gas from the kiln. Coal is used as energy source as well as the reducing agent.

Conclusions

1. During lime treatment, sulphate was lowered from 2 800 mg/L to 1 20 mg/L due to gypsum formation. Metals were precipitated as hydroxides. During BaS treatment, sulphate was lowered to less than 200 mg/L by $BaSO_4$ precipitation.

2. Sulphide was decreased from 333 to less than 10 mg/L (as S) in the stripping stage, using CO_2 gas.

3. The stripped H_2S-gas was contacted with Fe (III) solution and converted quantitatively to elemental sulphur.

4. The alkalinity of the calcium bicarbonate rich water was reduced from 1 000 to 110 mg/L (as $CaCO_3$) after CO_2 stripping with air due to $CaCO_3$ precipitation.

5. Fe (II), after sulphur production, was re-oxidized to Fe (III) using an electrolytic step.

6. The running cost of the barium sulphide process for the removal of 2 g/L of sulphate totalled R2.12/m^3.

Table 9. Effect of various parameters on the thermic conversion of $BaSO_4$ to BaS

Expt./Parameter	Value	Conversion (%)			Experimental conditions						
		Mass loss	Sulphide analysis	SO_4 precip.	Time (min)	Temp °C	C/$BaSO_4$	Carbon	$BaSO_4$	$Mg(OH)_2$/ $BaSO_4$	Furnace
1. Time (min)	15	75.3			15	1050	3	Coal	Pure	0	Muffle
	30	63.8			30	1050	3	Coal	Pure	0	Muffle
	60	60.6			60	1050	3	Coal	Pure	0	Muffle
2. Time (min)	2	1.1	0		2	1050	3	Activated	Industrial	0	Tube
	4	37.5	35.5		4	1050	3	Activated	Industrial	0	Tube
	5	75.6	74.4		5	1050	3	Activated	Industrial	0	Tube
	15	101	96.3		15	1050	3	Activated	Industrial	0	Tube
	20	99.6	94.6		20	1050	3	Activated	Industrial	0	Tube
3. Temp. (°C)	900	5			20	900	3	Activated	Industrial	0	Tube
	950	54.7	50.7		20	950	3	Activated	Industrial	0	Tube
	1000	81.6	79.4		20	1000	3	Activated	Industrial	0	Tube
	1050	90.4	86.5		20	1050	3	Activated	Industrial	0	Tube
	1100	100	96.3		20	1100	3	Activated	Industrial	0	Tube
4. C/$BaSO_4$-molar ratio	1	45.5	40.1		20	1050	1	Activated	Industrial	0	Tube
	2	82.1	77.7		20	1050	2	Activated	Industrial	0	Tube
	3	95.3	82.8		20	1050	3	Activated	Industrial	0	Tube
5. Carbon	Activated	101.6	94.6		30	1050	3	Activated	Industrial	0	Tube
	Coal	94.6	93	90	30	1050	3	Coal	Industrial	0	Tube
6. Carbon	Activated	89.3	82.8		20	1050	3	Activated	Industrial	0	Tube
	Coal	84.4	79.4		20	1050	3	Coal	Industrial	0	Tube
7. Barium	Pure	107.1	99.7		30	1050	3	Activated	Pure	0	Tube
	Industrial	101.6	94.6		30	1050	3	Activated	Industrial	0	Tube
8.$Mg(OH)_2$/ $BaSO_4$	0	89.3	86.2		20	1050	3	Activated	Industrial	0	Tube
	0.7	93.2	78.4		20	1050	3	Activated	Industrial	0.7	Tube
	1.7	97.6	76		20	1050	3	Activated	Industrial	1.7	Tube
	4.3	96.9			20	1050	3	Activated	Industrial	4.3	Tube

Table 10. Running costs of the barium sulphide process and value of the products (water, sulphur and calcium carbonate)

Item	**Cost (R/m^3)**
Feed sulphate (mg/L)	2200.00
Treated sulphate (mg/L)	200.00
$BaSO_4$ production (kg/m^3)	5.22
Barium losses (%)	5.00
$BaSO_4$ purity (%)	93.00
$BaSO_4$ required (kg/m^3)	0.26
$BaSO_4$ price (R/t)	2630
$BaSO_4$ cost (R/m^3)	0.69
Carbon content of coal (%)	70.00
C:$BaSO_4$ ratio	3.00
Coal required (kg/m^3)	1.07
Coal price (R/t)	150.00
Coal cost (R/m^3)	0.16
Iron oxidation (kg/m^3)	2.33
Energy requirement:	
$BaSO_4$ reduction (MJ/kg)	2.03
Iron oxidation (kW/kg Fe)	1.07
Energy requirement:	
$BaSO_4$ reduction (kW/m^3)	2.94
Iron oxidation (kW/m^3)	2.50
Electricity cost (R/kWh)	0.16
Energy cost (R/m^3)	
Kiln	0.47
Iron oxidation	0.40
Drives, pumps, etc.	0.20
Labour	0.20
Total running cost (R/m^3)	2.12
Products	**Value**
Water value (R/m^3)	2.00
Sulphur (R/m^3)	0.60
Sulphur yield (%)	90
Price (R/t)	500.00
Sulphur value (R/m^3)	0.30
$CaCO_3$ (kg/m^3)	1.67
$CaCO_3$ yield (%)	80
Price (R/t)	2000.00
$CaCO_3$ value (R/m^3)	3.33
Total value (R/m^3)	5.63

Acknowledgements

We sincerely thank the following organizations for financial support: The National Research Foundation, which provided funding for CSIR projects on neutralization and sulphate removal through their Technology and Human Resources for Industry Programme; and the CSIR, who provided substantial financial support for the research programme.

References

APHA (1985) Standard Methods for the Examination of Water and Wastewater. 12th Edit, American Public Health Assoc, NY

Kun LE (1972) A report on the reduction of the sulphate content of acid mine drainage by precipitation with barium carbonate. Internal report, Anglo American Research Laboratories, Project D/3/W/1

Maree JP, Bosman DJ, Jenkins GR (1989) Chemical removal of sulphate, calcium and heavy metals from mining and power station effluents. Proc, 1st Biennial Conf of the Water Inst of Southern Africa, Cape Town

Maree, JP (1989) Treatment of water (BaS process), Republic of South Africa (Patent No. 90/1889), 28 November), Canada (Patent No. 2 012 266 8) and United States of America (Patent No. 5,035,807).

Trusler GE, Edwards RI, Brouckaert CJ, Buckley CA (1988) The chemical removal of sulphates. Proc, 5th National Mtng of the S.A. Institute of Chemical Engineers, Pretoria, W3-0 – W3-11

Volman R (1984) The use of barium sulphide to remove sulphate from industrial effluents. M.Sc. Thesis (Chem. Eng), Univ of Stellenbosch

Wilsnach IT (1986) Cost estimate for barium sulphate reduction. Internal report, Div of Water Technology, CSIR, Project 620/2616/6

Received June 17, 2004; revised manuscript submitted Sept. 30, 2004; accepted Oct. 24, 2004