Recovery of sulphur and calcium carbonate from waste gypsum

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Abstract

Gypsum is produced as a waste product by various industries, e.g. the fertiliser industry, the mining industry and power stations. Gypsum waste disposal sites are responsible for the leaching of saline water into surface and underground water.

The aim of this investigation was to evaluate a process for converting waste gypsum into sulphur and calcium carbonate. The process evaluated consisted of the following stages: reduction of gypsum to calcium sulphide; H_2S-stripping and sulphur production. Thermal reduction showed that gypsum could be reduced to CaS with activated carbon in a tube furnace operating at 1 100 °C. The CaS yield was 96%. The CaS formed was suspended in water to form a CaS slurry. The reaction of gaseous CO_2 with the CaS slurry leads to the stripping off of H_2S gas and the precipitation of $CaCO_3$. During batch studies sulphide was stripped from 44 000 mg/ℓ to less than 60 mg/ℓ (as S).

The H_2S generated in the previous step was then reacted in the PIPco process to form elemental sulphur

Keywords: gypsum, CaS, thermal studies, H_2S stripping, sulphur, thermal reduction, $CaCO_3$ precipitation

Introduction

Brine and sludge disposal represents a major fraction of the cost during treatment of mining effluents. Gypsum-rich sludge is produced during the following water treatment activities:

- Neutralisation of acidic effluents with limestone or lime to produce gypsum and metal hydroxides (Geldenhuys et al., 2001)
- Desalination of industrial effluents from the brine when it is saturated with respect to gypsum (Van Zyl et al., 2000).

Most of the gypsum waste produced by industry is unsuitable for further use, e.g. production of plasterboard. These stockpiles create environmental concerns such as airborne dust as well as effluent problems as gypsum is slightly soluble (2 000 mg/ℓ) in water. Therefore, a need exists to develop methods to convert poor-quality gypsum into a useful product, namely sulphur.

Sulphur is an essential raw material for many manufacturing industries such as fertilisers, acids, rayon, steel, petroleum, insecticides, titanium dioxide, explosives, etc. (Cork et al., 1986). Catalytic and thermal reduction processes (Rameshni and Santo, 2005) and biological processes for sulphur recovery (Maree et al., 2004) are expensive, difficult to operate, have high fuel consumption and limited ability to control temperature and side reactions.

As far as the supply and demand for sulphur is concerned, Africa is a major importer of sulphur (Maree et al., 2005). Countries like Zambia and the DRC are importing large tons of sulphur at high cost to manufacture sulphuric acid for the reduction of oxidised ores. These costs are inflated by the cost of transportation whilst sulphur is a cheap product. South Africa alone imports 1.5 m. t of sulphur per year from the Middle East
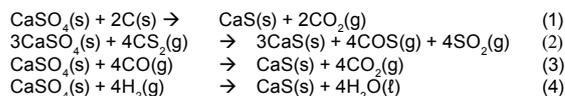
and Canada (Ratlabala, 2003). The demand for sulphur is also expected to increase in line with increased fertiliser usage and exports (Agnello et al., 2003).

In view of serious shortages of foreign exchange, it is becoming increasingly difficult for these African countries to import sulphur. Consequently, industries depending on the use of sulphur are facing shut-down unless other sources are identified. Most African countries have large amounts of waste gypsum generated by industrial activity. Even the costly sulphuric acid produced from imported sulphur mostly ends up as gypsum once used. Gypsum is a good source for the recovery of sulphur (Wewerka et al., 1982).

The recovery of sulphur and $CaCO_3$ from gypsum is economically feasible. From 1 t of gypsum it is calculated that 0.18 t of sulphur and 0.58 t of $CaCO_3$ can be recovered. From 1 t of gypsum, sulphur with a value of R180 can be recovered and $CaCO_3$ with a value of R116. The prices of sulphur and $CaCO_3$ were taken at R1 000/t and R200/t respectively. This compares favourably with the cost of the main raw material, coal. At a coal to gypsum ratio of 0.3, and a coal cost of R200/t, the cost of the coal amounts to R60/t of gypsum. This is significantly less than the combined value of R296 of sulphur and $CaCO_3$. This value would be even higher if chemically pure $CaCO_3$ were to be recovered. The price of chemically pure $CaCO_3$ amounts to R3 000/t compared to the R200/t for waste or mined $CaCO_3$.

The basic steps of the sulphur-recovery process from gypsum are:

- Reduction of gypsum to calcium sulphide using reducing agents (Matsuya and Yamane, 1981), for example, coal or activated carbon (Eq. (1)), carbon disulphide (Eq. (2)), carbon monoxide (Eq.(3)) and hydrogen (Eq.(4))
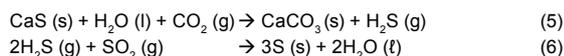
$$CaSO_4(s) + 2C(s) \rightarrow \quad CaS(s) + 2CO_2(g) \tag{1}$$
$$3CaSO_4(s) + 4CS_2(g) \rightarrow \quad 3CaS(s) + 4COS(g) + 4SO_2(g) \tag{2}$$
$$CaSO_4(s) + 4CO(g) \rightarrow \quad CaS(s) + 4CO_2(g) \tag{3}$$
$$CaSO_4(s) + 4H_2(g) \rightarrow \quad CaS(s) + 4H_2O(\ell) \tag{4}$$

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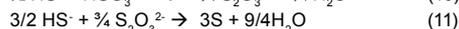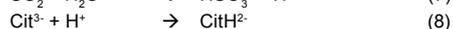- Suspending the calcium sulphide obtained from Eqs. (1) to (4) in water to form a CaS slurry. From this slurry, the H_2S is stripped off with CO_2 (Eq. (5)) and converted to elemental sulphur via the PIPco process (Eq. (6))

$$CaS\ (s) + H_2O\ (l) + CO_2\ (g) \rightarrow CaCO_3\ (s) + H_2S\ (g) \qquad (5)$$
$$2H_2S\ (g) + SO_2\ (g) \qquad \rightarrow 3S\ (s) + 2H_2O\ (\ell) \qquad (6)$$

In the PIPco process elemental sulphur is produced from SO_2 and H_2S gas (Ray et al., 1990). Comparable processes are the sodium phosphate process and the sodium citrate process (Bekassy-Molnar et al., 2005). These processes utilise a buffer (sodium phosphate and sodium citrate respectively) to absorb SO_2 which is then used as an oxidising agent in the conversion of H_2S to elemental sulphur. Due to solubility limitations these buffers only allow low concentrations of SO_2 in solution. However, in contrast, the PIPco process uses potassium citrate buffer solution to absorb SO_2 (Eqs. (7) and (8)). The potassium citrate buffer allows the solution to dissolve high concentrations of SO_2 resulting in increased sulphur recovery. The H_2S produced in Eq. (5) is bubbled through the SO_2-rich buffer solution, initially forming intermediates such as $S_2O_3^{2-}$ (Eqs. (9) to (11)), then elemental sulphur as per Eq. (6) (Gryka, 1992).

The overall reaction given by Eq. (6) consists of various steps with intermediate components (Eqs. (7) to (12)):

SO_2 absorber:
$$SO_2 + H_2O \qquad \rightarrow \quad HSO_3^- + H^+ \qquad (7)$$
$$Cit^{3-} + H^+ \qquad \rightarrow \quad CitH^{2-} \qquad (8)$$

H_2S reactor:
$$2H_2S \qquad \rightarrow \quad 2HS^- + 2H^+ \qquad (9)$$
$$\tfrac{1}{2}\,HS^- + HSO_3^- \quad \rightarrow \quad \tfrac{3}{4}\,S_2O_3^{2-} + \tfrac{3}{4}\,H_2O \qquad (10)$$
$$3/2\,HS^- + \tfrac{3}{4}\,S_2O_3^{2-} \rightarrow 3S + 9/4H_2O \qquad (11)$$

The aim of this investigation was to evaluate the various stages of the sulphur- recovery process on laboratory scale prior to full-scale implementation. Figure 1 shows the process flow-diagram of the gypsum treatment process. The following individual stages were studied:
- Production of calcium sulphide from gypsum (A)
- H_2S-stripping with CO_2 and production of $CaCO_3$ (B)
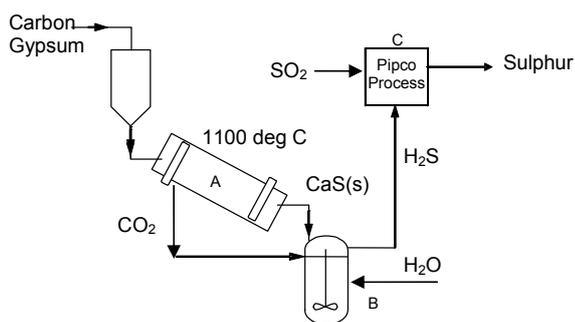- Sulphur production (C).

Figure 1
Process flow-diagram for the sulphur-recovery process

Materials and methods

Feedstock

Gypsum: Pure $CaSO_4.2H_2O$ (Merck, AR grade) and waste gypsum from Landau Colliery prepared from the desalination stages of a mine-water treatment pilot plant were utilised in the reduction experiments.

Carbon: Activated carbon (Merck) with a carbon content of 100% was used as reducing agent.
CO_2: CO_2 gas (*Air Liquide*) was used for H_2S-stripping.
Potassium citrate solution: SO_2-rich potassium citrate buffer solution was used for the absorption of the stripped H_2S-gas.

The results of X-ray fluorescence analyses (ARL9400XP spectrometer) of the gypsum compounds are summarised in Table 1.

TABLE 1
Results of XRF analysis of pure $CaSO_4.2H_2O$ and synthetic gypsum

Compounds	Composition (%)	
	$CaSO_4.2H_2O$	Synthetic gypsum
SiO_2	0.01	0.00
TiO_2	0.02	0.00
Al_2O_3	0.01	0.00
Fe_2O_3	0.08	0.4
$Mn(OH)_2$	0.00	0.1
$Mg(OH)_2$	0.4	4.5
CaO	41.6	40.2
Na_2O	0.01	0.00
K_2O	0.01	0.00
P_2O_5	0.04	0.00
SO_3	56.0	54.8

Equipment

Thermal studies: Tube and muffle furnaces were used for thermal decomposition of gypsum. A silica tube was used for the reduction reaction and samples were contained in silica boats. Nitrogen gas was passed through the reaction tube as an inert gas in the tube furnace. In the muffle furnace no N_2 was used, therefore some oxygen was present.

H_2S-stripping at atmospheric pressure studies: Figure 2 shows the set-up used for H_2S-stripping. It consisted of three reactors connected in series, all equipped with glass spargers. The first reactor (1 ℓ) contained calcium sulphide slurry from which sulphide was stripped. The remaining two reactors (1 ℓ) contained an SO_2-rich potassium citrate buffer solution into which H_2S gas was absorbed and sulphur formed.
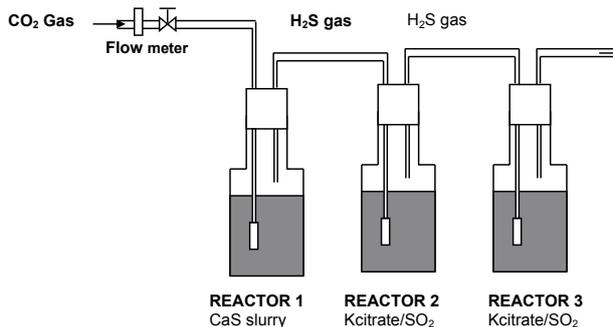

Figure 2
Schematic diagram of H_2S-stripping and absorption process

Pressurised system for H_2S-stripping studies: Figure 3 shows the 5 ℓ pressurised reactor, containing a hollow shaft stirrer capable of a maximum pressure of 300 kPa and a maximum operating temperature of 300°C, used in CaS stripping experiments.

Figure 3
Picture of the 5 ℓ jacketed, pressurised & continuously stirred reactor used in CaS stripping experiments

Experimental procedure

***Thermal studies*:** Stoichiometric amounts of gypsum (5 g) and a reducing agent (activated carbon, 1.05 g) were mixed. The mixtures were placed in silica boats and heated at elevated temperature (900°C to 1 100°C) in the tube furnace and muffle furnace for various reaction times. Reaction products from the furnace were allowed to cool in a nitrogen atmosphere.

***H₂S stripping at atmospheric pressure*:** The calcium sulphide product (approximately 60 g) from the thermal studies was dissolved in 2 ℓ of water and placed in the first reactor. The potassium citrate buffer solution dosed with SO_2 was placed in the second reactor. The CO_2 used to strip the H_2S gas was introduced into the sulphide solution via a pump. The stripped H_2S-gas was trapped in the potassium citrate buffer solution and converted to sulphur.

Pressurised system for H₂S-stripping studies: The CO_2 was fed into the pressurised & stirred reactor from the cylinder. The gas was allowed to flow at pressure through the hollow shaft, finned, mechanical stirrer and mixed with the calcium sulphide slurry. The reactor was then pressurised to the desired experimental pressure with CO_2 fed from the cylinder. The stirrer was started and the off-gas valve was opened to the flow rate specific to each experiment. At the experimental pressure and stirring rate the gas in the headspace above the slurry was also sucked back into the slurry for further reaction.

Experimental programme

Thermal studies: The effects of the following parameters were investigated:
- Reaction time (5 min, 20 min, 30 min and 60 min)
- Temperature (900°C, 1 000°C, 1 050°C and 1 100°C, 1 150°C)
- Carbon to gypsum molar ratio (0, 0.025, 0.5, 1, 2 and 3)
- Particle sizes of gypsum (1 250 μm, 630 μm and 380 μm)
- State of reactant mixture (pellets or powder)
- Type of furnace (muffle furnace (oxygen present) or tube furnace (oxygen deficient).

***Sulphide stripping studies*:** The effect of CO_2 flow rate (520 mℓ/min and 1 112 mℓ/min) at atmospheric pressure was investigated. The following parameters were also studied using the pressurised system:

- CO_2 flow rate (2.22 ℓ/min and 3.34 ℓ/min)
- Temperature (25°C and 600C)
- Pressure (100 kPa and 200 kPa)
- Mixing intensity (500 r/min and 1 000 r/min)

Analytical procedure

The calcium sulphide and other compounds formed during the process were analysed using an automated Siemens D501 XRD spectrometer. The titration procedure to determine the concentration of sulphite (SO_3^{2-}) and thiosulphate ($S_2O_3^{2-}$) was developed by Pfizer and is accurate to ± 0.01mol/ℓ (Gryka, 2005). The purity of sulphur recovered was analysed using the LECO Combustion Techniques.

Iodine was used to oxidise SO_3^{2-} to SO_4^{2-} (Eq. (12)) and $S_2O_3^{2-}$ to $S_4O_6^{2-}$ (Eq. (13)) to give a combined titration Value A. $S_2O_3^{2-}$ only was determined by adding formaldehyde to precipitate SO_3^{2-} to give a titration Value B. The difference between Values A and B (C) is equivalent to the SO_3^{2-} concentration.

$S_2O_3^{2-}$ is calculated from:
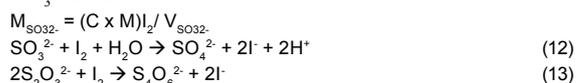
$$(V \times 2M)_{S2O32-} = (B \times M)_{I2}$$
$$M_{S2O32-} = (B \times M)_{I2} / 2V_{S2O32-}$$

where:
- V – volume of solution
- B – I2 titration volume
- M – concentration in moles/ℓ

and SO_3^{2-} from:

$$M_{SO32-} = (C \times M)I_2 / V_{SO32-}$$
$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2I^- + 2H^+ \tag{12}$$
$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \tag{13}$$

Results and discussion

Thermal studies

Table 2 shows the effects of various reaction parameters on the CaS yield during the thermal conversion of gypsum to CaS using pure gypsum.

TABLE 2
Results of XRD analyses of the reaction products of carbon and pure gypsum

Expt. number	Parameter	Value	Percentage		
			CaSO₄	CaS	CaO
1	Time (min)	5	49	45	7
		20	0	96	4
		60	0	93	5
2	Temperature (°C)	900	84	15	1
		1 000	8	88	4
		1 100	0	96	4
3	C/CaSO₄ mole ratio	0	100	0	0
		0.25	93	0	7
		0.5	74	0	25
		1	48	13	38
		2	2	88	10
		3	0	96	4
4	Particle size of gypsum (μm)	380	0	80	11
		630	22	56	10
		1 250	86	1	14

The following parameters were kept constant: temperature = 1 100 °C, time = 20 min, mole ratio (carbon: gypsum) = 3: 1, activated carbon and tube furnace unless otherwise stated.

Exp. No.	Parameter	Value	Percentage					
			$CaSO_4$	CaS	MgO	CaO	$MgAl_2O_4$	$Ca_2Al_2SiO_7$
1	State of reactant mixture	Powder	0	90	9	1	0	0
		Pellet		92	8	0	0	0
2	Furnace type	Tube	0	92	8	0	0	0
		Muffle	5	80	6	0	3	6

The following parameters were kept constant: temperature = 1100 °C, mole ratio (carbon: gypsum) = 3: 1, time = 20 min, activated carbon and a tube furnace unless otherwise stated.

Effect of time: Expt. 1 (Table 2) showed that good conversion yields (> 96%) were achieved after a reaction time of 20min. After a reaction time of 5 min, the yield was only 45%.

Effect of temperature: Expt. 2 (Table 2) showed that for a carbon: gypsum mole ratio of 3:1, after a reaction time of 20 min, the conversion percentage increased from 15% at 900 °C to 96% at 1 100 °C. This could be due to the high activation energy required for the reduction of calcium sulphate to calcium sulphide.

Effect of carbon: gypsum mole ratio: Expt. 3 (Table 2) showed that when no carbon was added, no CaS was formed. The addition of 2 and 3 moles carbon, respectively, showed high percentage conversion of gypsum to calcium sulphide (88% and 96% respectively).

Effect of particle size: Expt. 4 (Table 2) showed that the formation of the reduced product calcium sulphide, is dependent upon the particle size of gypsum, the smaller the particle size, the higher is the conversion under specific conditions. This can be ascribed to higher reactant surface areas for smaller particle size.

Table 3 shows the effects of various reaction parameters on the CaS yield during the thermal conversion of gypsum to CaS using synthetic gypsum:

From Table 3, the XRD results showed that the use of pellets results in a 92% conversion, while the use of powder yielded a 90% conversion. Therefore the reactant mixture in the form of pellets instead of powder only increased conversion by 2%. The 2% difference between the pellets and the powder cannot be seen as significant. Pellets may have a larger accessible bulk surface area for heat transfer than the powder, but the powder has a higher overall surface area.

The results in Table 3 further showed that the tube furnace (92%) is more efficient in converting gypsum to CaS than the muffle furnace (80%). The presence of oxygen in the muffle furnace resulted in the formation of several oxygen-containing compounds such as $MgAl_2O_4$ and $Ca_2Al_2SiO_7$. However, the tube furnace purged with nitrogen does not favour production of oxygen-containing compounds.

Sulphide stripping and absorption studies

Effect of CO_2 flow rate on the formation of intermediate compounds

Figures 4 to 7 and Tables 4 and 5 show the results, as well as the experimental conditions, when sulphide was stripped with 100% CO_2 from a CaS slurry, followed by absorption of the stripped H_2S gas in a SO_2-rich potassium citrate solution. The effect of
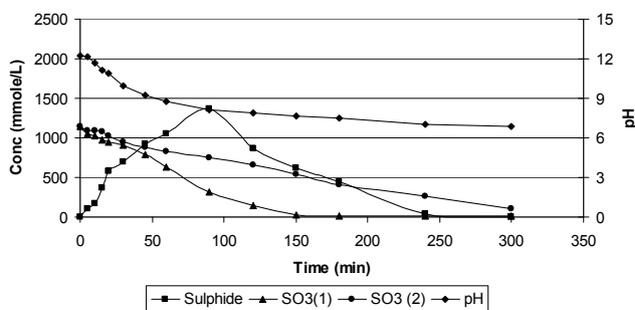
Figure 4
Sulphide stripping with CO_2 at a flow rate of 520 mℓ/min (concentrations vs. time)
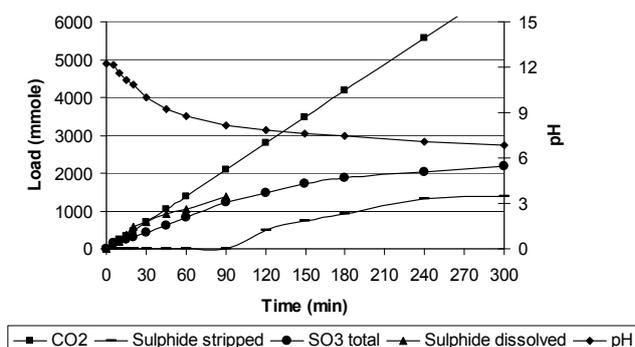
Figure 5
Sulphide stripping with CO_2 at a flow rate of 520 mℓ/min (load vs. time)

CO_2 flow rate was investigated by conducting an experiment at 520 mℓ/min and at 1 112 mℓ/min.

Figure 4 shows the relationship between the concentrations of the various species vs. time when CO_2 was added at a flow rate of 520 mℓ/min. The initial CaS concentration in the slurry was 2 167 mmole/ℓ and the pH of the slurry was 12,2. CaS has a low solubility as indicated when zero CO_2 was added. During CO_2 addition the pH dropped from 12.2 to 8.2. The sulphide concentration in the slurry reactor reached a maximum concentration of 1 375 mmole/ℓ (44 000 mg/ℓ S) due to the formation of $Ca(HS)_2$ in solution (Eq.(14)). The difference of 792 mmole/ℓ $Ca(HS)_2$ (2 167 to 1 375) was present as a solid due to its solubility. With further CO_2 addition, the pH dropped down to 6.9 and sulphide was stripped completely (to less than 60 mg/ℓ S) (Eq. (15)). The stripped H_2S reacted with the SO_3^{2-} in the SO_2/citric acid reactors. The SO_3^{2-}-concentration in Reactor 1 dropped sharply, while that in Reactor 2 dropped slowly. The fast drop in Reactor 1 can be ascribed to the formation of sulphur (Eq. (17)) and possibly due to some of the SO_2 being stripped with CO_2.
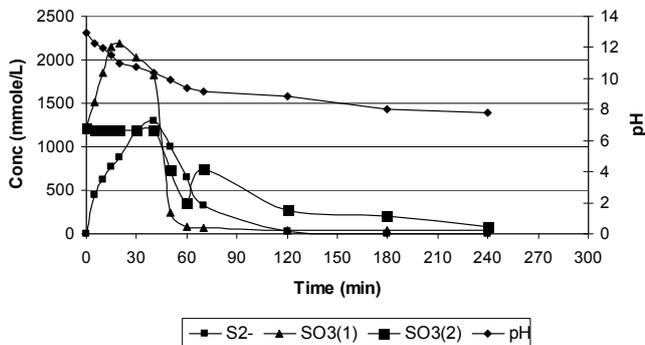
Figure 6
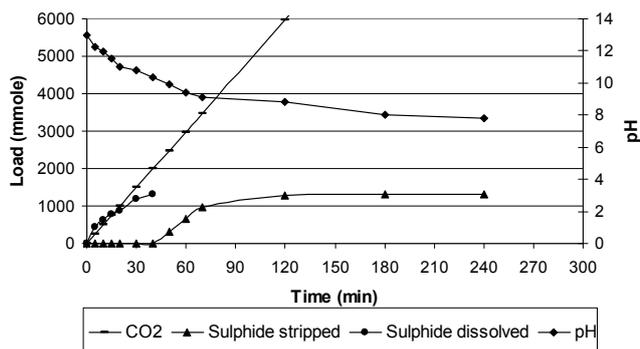*Sulphide stripping with CO_2 at a flow rate of 1 112 mℓ/min (concentrations vs. time)*
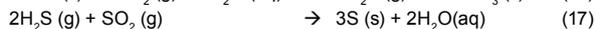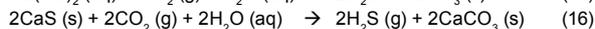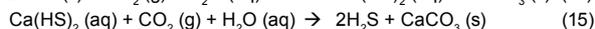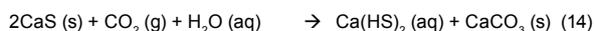

Figure 7
Sulphide stripping with CO_2 at a flow rate of 1 112 mℓ/min (load vs. time)

The slow drop in the SO_3^{2-}-concentration in Reactor 2 can be ascribed to SO_2-stripping with CO_2.

Figure 5, shows the relationship between load removed or formed of the various parameters as a function of time. It is noted that:

- 2 167 mmole CaS was initially slurried
- 1 375 mmole of the formed $Ca(HS)_2$ was in solution and the balance as a solid as the solubility of $Ca(HS)_2$ was exceeded
- 2 180 mmole SO_3^{2-} was removed, which is more than the CaS that had been slurried. This shows that a portion of the SO_2 is stripped with CO_2. This observation explains why the Pipco process needs to be operated under excess H_2S-conditions.

$$2CaS\ (s) + CO_2\ (g) + H_2O\ (aq) \rightarrow Ca(HS)_2\ (aq) + CaCO_3\ (s) \quad (14)$$
$$Ca(HS)_2\ (aq) + CO_2\ (g) + H_2O\ (aq) \rightarrow 2H_2S + CaCO_3\ (s) \quad (15)$$
$$2CaS\ (s) + 2CO_2\ (g) + 2H_2O\ (aq) \rightarrow 2H_2S\ (g) + 2CaCO_3\ (s) \quad (16)$$
$$2H_2S\ (g) + SO_2\ (g) \rightarrow 3S\ (s) + 2H_2O(aq) \quad (17)$$

This finding is of importance as it shows that Ca $(HS)_2$ can possibly be recovered as a valuable product.
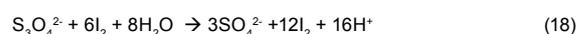
The experiment described above for 520 mℓ/min CO_2 was repeated for a CO_2 flow of 1 112 mℓ/min (Figs. 6 and 7 and Table 5). Similar conclusions were made except for the behaviour of SO_3^{2-} in the SO_2/citrate reactor. The following similar observations were made:

- 2 167 mmole CaS was initially slurried
- 1 300 mmole remained in solution as $Ca(HS)_2$, and the balance was in solid form as $Ca(HS)_2$
- 2 310 mmole SO_3^{2-} was removed which is also more than

expected from the amount of CaS that was slurried. This shows that a portion of the SO_2 is stripped with CO_2.

The following different observations were made for the different CO_2 flow rates: The increase in SO_3^{2-}-concentration during the initial period (Fig. 6) can be ascribed to the formation of an intermediate compound when H_2S is contacted with the SO_2/citrate solution. The intermediate compound is oxidised to sulphate from a much lower valence (valence of S species) when contacted with iodine, compared to SO_3^{2-}, which has a valence of +4. The intermediate could be $S_3O_4^{2-}$, with a valence of +2. Reaction 18 shows the reaction of $S_3O_4^{2-}$ with iodine. This was determined by way of elimination of the reactions with iodine of the various sulphur species.

- $S_2O_3^{2-}$ is oxidised to $S_4O_6^{2-}$ (Eq.(13)) and the latter will not be further oxidised with iodine
- SO_3^{2-} is oxidised to SO_4^{2-} (Eq. (12))
- Thus, $S_3O_4^{2-}$ is the only remaining sulphur species and can only be oxidised to SO_4^{2-}.

$$S_3O_4^{2-} + 6I_2 + 8H_2O \rightarrow 3SO_4^{2-} + 12I_2 + 16H^+ \quad (18)$$

TABLE 4
Sulphide stripping with CO_2 at a flow rate of 520 mℓ/min

Parameter	CaS reactor		SO_2/Citric Reactor 1		SO_2/Citric Reactor 2	
Time (min)	0	300	0	300	0	300
Citric acid (g/ℓ)			768		768	
KOH (g/ℓ)			673		673	
CO_2 (mℓ/min)	520					
CaS (mmole/ℓ)	1 944					
Sulphide(mmole/ℓ)	1 944	64				
SO_3^{2-} (mmole/ℓ)			1 145	130	1 145	100
pH	12.2	6.9				

TABLE 5
Sulphide stripping with CO_2 at a flow rate of 1 112 mℓ/min

Parameter	CaS reactor		SO_2/Citric Reactor 1		SO_2/Citric Reactor 2	
Time (min)	0	240	0	240	0	240
Citric acid (g/ℓ)			768		768	
KOH (g/ℓ)			673		673	
CO_2 (mℓ/min)	1 112					
CaS (mmole/ℓ)	1 944					
Sulphide(mmole/ℓ)	1 944	16				
SO_3^{2-} (mmole/ℓ)			1 215	80	1 215	350
pH	12.9	7.8				

Effect of CO_2 flow-rate, temperature, pressure and hydrodynamics

Table 6 and Figs. 8 to 11 show the effect of various parameters on the rate of sulphide stripping when carried out in a pressurised unit. It was noted that:

- The rate of sulphide stripping increased with increasing CO_2 flow rates (Fig. 8). This was expected and is also confirmed by the results reported in the previous section.
- The rate of sulphide stripping increased with increased temperature (Fig. 9).

TABLE 6
Experimental conditions for the data reported in Figs. 8 to 11

Parameters	Pressure (kPa)	Temp (ºC)	Flow (ℓ/min)	Stirring rate (r/min)
CO₂ flow	100	25	**2.22 (40%)**	1 000
	100	25	**3.34 (60%)**	1 000
Pressure	**100**	25	3.34	1 000
	200	25	3.34	1 000
Temperature	100	**25**	3.34	1 000
	100	**60**	3.34	1 000
(Mixing intensity (r/min)	100	25	2.22	**500**
	100	25	2.22	**1 000**

Reactor volume = 5 ℓ
CaS mass = 250 g

The results indicate that at higher temperature, more CaS dissolves into solution as $Ca(SH)_2$ and more sulphide is stripped off with CO_2 gas. At lower temperature less CaS dissolved therefore and low sulphide was stripped.

- The rate of sulphide stripping increased with increasing stirring rate. The finding could be due to the higher rate of CaS dissolution at faster speed (Fig. 10).
- The rate of the sulphide stripping increased with a decrease in pressure (Fig. 11). This can be attributed to the solubility of CO_2 gas and H_2S gas that increased at an increased pressure.

Conclusions

The reduction of gypsum to CaS takes place at a temperature of 1 100°C. A good conversion was obtained when a reducing agent was used. Controlling the amount of carbon added, relative to the amount of gypsum, higher reduction was achieved when the molar ratio gypsum to carbon was 1:3. The smaller particle size of gypsum yielded higher reduction percentages due to the higher reactant surface areas for smaller particles. The reaction time between gypsum and carbon was also found to be shorter. The optimum time found was 20 min.

The use of pellets resulted in better conversion of gypsum to CaS than the use of powder mixture. Depending on the presence of oxygen in the muffle furnace, the reaction mixture obtained after heating at 1 100°C consisted of oxygen-containing compounds. The tube furnace which had been purged with nitrogen yielded no oxygen-containing compounds. The thermal decomposition of gypsum to CaS should, therefore be carried out in an oxygen-deficient environment.

The H_2S stripping studies led to the following conclusions:
- H_2S gas can be stripped with CO_2 from a CaS slurry with the simultaneous production of $CaCO_3$
- Sulphur can be produced from the stripped H_2S. Sulphur with a purity of between 95 and 99% was produced.

Acknowledgements

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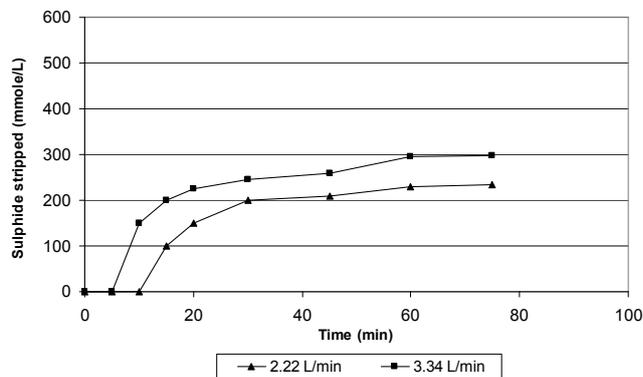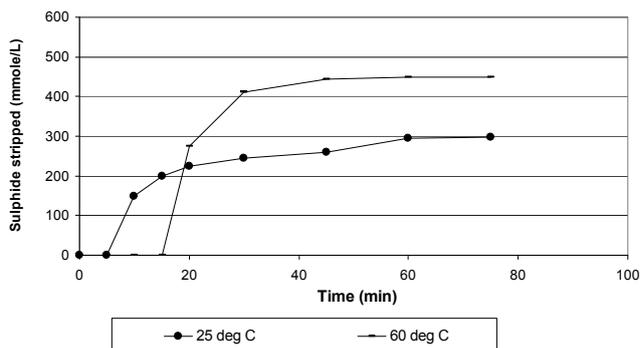
Figure 8
Effect of CO_2 flow rate on H_2S-stripping

Figure 9
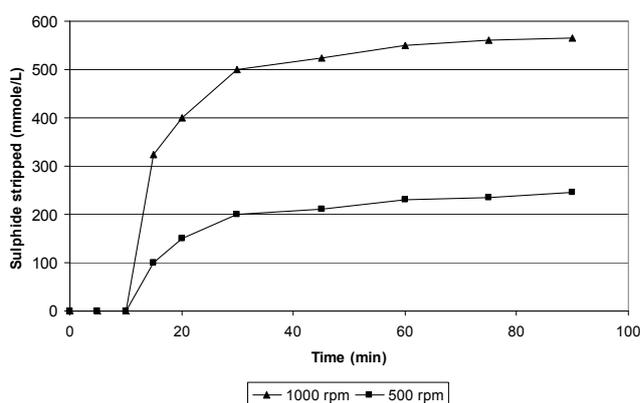*Effect of temperature on H_2S-stripping*

Figure 10
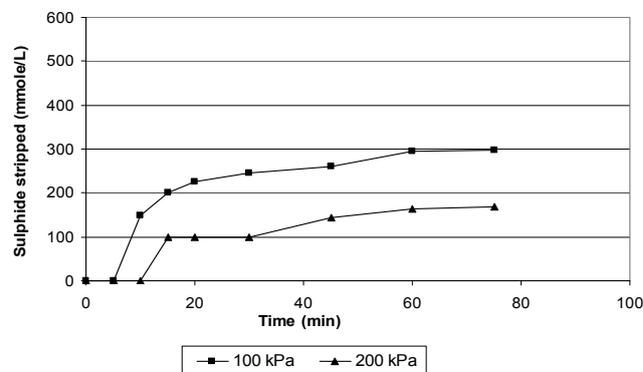*Effect of hydrodynamics on H_2S-stripping*

Figure 11
Effect of pressure on H_2S-stripping

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