RECOVERY OF SULPHUR FROM WASTE GYPSUM

N.R. MBHELE[1*], W. VAN DER MERWE[1], J.P. MAREE[2] and D. THERON[3]

[1]Exxaro Resources, P.O Box 9229, Pretoria, 0001, South Africa; E-mail: ryneth.mbhele@exxaro.com
[2]CSIR, PO Box 395, Pretoria, 0001, South Africa; E-mail: jmaree@csir.co.za
[3]Sulphide Tech, Pretoria, 0001, South Africa; E-mail:dieks@pyroconsulting.co.za

ABSTRACT

Gypsum is produced as a waste product by various industries, e.g. the fertilizer industry, the mining industry and power stations. Gypsum waste disposal sites are responsible for the leaching of saline water into surface and underground water and create airborne dust. Gypsum waste is not only an environmental problem but has measurable economic value as well. However, all these environmental and economical concerns can be avoided should valuable/saleable by-products like sulphur and calcium carbonate be recovered from the low quality gypsum.

The aim of this project was to evaluate a process for converting waste gypsum into sulphur. The process evaluated consists of the following stages: reduction of gypsum to calcium sulphide; stripping of the sulphide with CO_2 gas and the production of sulphur.

Thermal reduction study showed that gypsum can be reduced to CaS with activated carbon in a tube furnace operating at 1100 ºC. The CaS yield was 96%. The CaS formed was slurried in water. The reaction of gaseous CO_2 with the CaS slurry leads to the stripping of sulphide to form H_2S gas and the precipitation of $CaCO_3$. The H_2S generated was then reacted with SO_2 in the PIPco processes to form elemental sulphur.

Sulphur with the purity between 95% and 99% was recovered from waste gypsum in this study.

1. 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:

- Neutralization 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 (2000 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 fertilizers, 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 oxidized 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 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)),

$$CaSO_4(s) + 2C(s) \rightarrow CaS(s) + 2CO_2(g) \qquad (1)$$

- Suspending the calcium sulphide obtained from Eq. (1) in water to form a CaS slurry. From this slurry, the H_2S is stripped off with CO_2 (Eq. (2)) and converted to elemental sulphur via the PIPco process (Eq. (3))

$$CaS\ (s) + H_2O\ (l) + CO_2\ (g) \rightarrow CaCO_3\ (s) + H_2S\ (g) \qquad (2)$$

$2H_2S\ (g) + SO_2\ (g) \rightarrow 3S\ (s) + 2H_2O\ (\ell)$ (3)

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 utilize a buffer (sodium phosphate and sodium citrate respectively) to absorb SO_2 which is then used as an oxidizing 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. (4) and (5)). The potassium citrate buffer allows the solution to dissolve high concentrations of SO_2 resulting in increased sulphur recovery. The H_2S produced in reaction 2 is bubbled through the SO_2 rich buffer solution, initially forming intermediates such as $S_2O_3^{2-}$ (Eqs.(7) to (8)), then elemental sulphur as per Eq. (8) (Gryka, 1992).

The overall reaction given by equation 3 consists of various steps with intermediate components (Eqs. (4) to (8)).

SO_2 absorber: $SO_2 + H_2O \rightarrow HSO_3^- + H^+$ (4)
$Cit^{3-} + H^+ \rightarrow CitH^{2-}$ (5)
H_2S reactor: $2H_2S \rightarrow 2HS^- + 2H^+$ (6)
$\frac{1}{2} HS^- + HSO_3^- \rightarrow \frac{3}{4} S_2O_3^{2-} + \frac{3}{4} H_2O$ (7)
$3/2\ HS^- + \frac{3}{4} S_2O_3^{2-} \rightarrow 3S + 9/4 H_2O$ (8)

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)
- Sulphide stripping with CO_2 to form H_2S and production of $CaCO_3$ (B)
- Sulphur production (C)

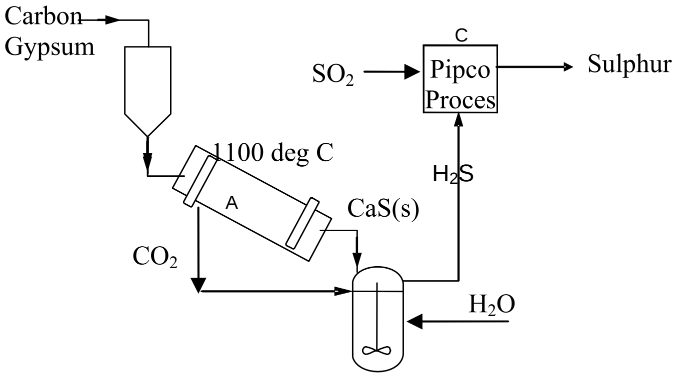

Figure 1. Process flow-diagram for the sulphur recovery process

2. MATERIALS AND METHODS

Feedstock

Gypsum. Pure $CaSO_4.2H_2O$ (Merck, AR grade), Anglo gypsum from Landau Colliery prepared from the desalination stages of a mine water treatment pilot plant and Foskor gypsum obtained from Foskor prepared from the leaching of calcium phosphate with sulphuric acid were utilised in the reduction experiments.

Carbon. Activated carbon (Merck) with a carbon content of 100% was used as a 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. XRF results of pure $CaSO_4.H_2O$, Anglo gypsum and Foskor gypsum

	Composition (%)		
Compounds	**Pure gypsum**	**Anglo gypsum**	**Phosphogypsum**
SiO_2	0.01	0.01	0.17
TiO_2	0.01	0.00	0.00
Al_2O_3	0.01	0.01	0.01
Fe_2O_3	0.00	0.09	0.05
MnO	0.00	0.12	0.00
MgO	0.00	4.37	0.00
CaO	41.6	34.74	37.47
Na_2O	0.01	0.01	0.01
K_2O	0.01	0.00	0.01
P_2O_5	0.04	0.13	0.78
SO_3	56.0	50.48	53.76
Loss On Ignition	0.89	9.10	6.64
Total $CaSO_4$	97.6	85.2	91.2

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 and clay crucibles. Nitrogen gas was purged as an inert gas through the reaction tube prior to the heating sequence to drive off any air entrained between solid particles. Then it was passed through the reaction tube in the furnace during the experiments.

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

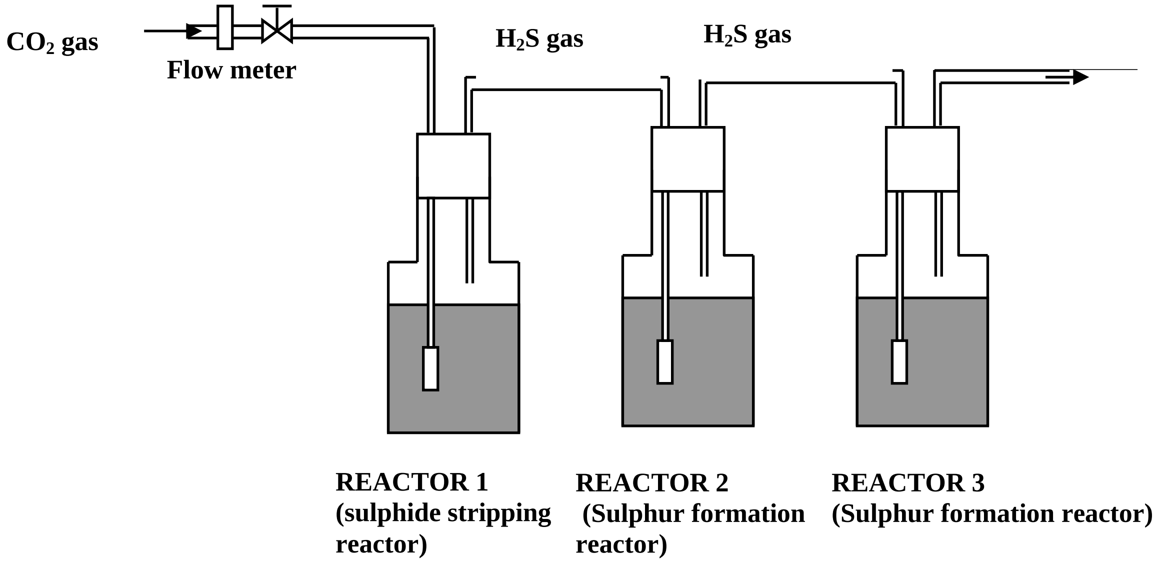

Figure 2. Schematic diagram of H_2S-stripping and sulphur formation process.

Experimental Procedure

Thermal studies:

The stoichiometric amounts of the gypsum samples were thoroughly mixed by hand with activated carbon to obtain a homogeneous sample with the composition as constant as possible. The mixture was placed in a silica boat/clay crucible and heated at elevated temperatures in the tube furnace for various reaction times. The Anglo gypsum and Foskor gypsum were dried first at 150°C to remove excess moisture (anhydrous gypsum) as they tend to form lumps when wet and thereafter grounded to a fine powder. Nitrogen gas (50ml/min) was passed through the reaction tube as an inert gas in the furnace. Reaction products from the furnace were allowed to cool in a nitrogen atmosphere.

Sulphide stripping and sulphur formation:

The calcium sulphide product (produced from Foskor gypsum and Anglo gypsum, approximately 60g) from the thermal studies was dissolved in 2ℓ of water, placed in the first reactor and stirred. The potassium citrate buffer solution dosed with SO_2 was placed in the second and third reactor. The CO_2 used to strip the H_2S gas was introduced into the sulphide solution via a a rotameter. The stripped H_2S gas was trapped into the 2M potassium citrate buffer solution rich in SO_2. The reaction between the two gases resulted in the formation of sulphur. Sulphur was formed in the potassium citrate solution. The solution was then filtered, sulphur was dried at room temperature and sent for analysis..

Analytical Procedure

The calcium sulphide and other compounds formed during the process were analysed using an automated Siemens D501 XRD spectrometer and sulphide concentration were carried out manually according to procedures described in Standard Methods (APHA, 1985).

The titration procedure to determine the concentration of sulphite (SO_3^{2-}) and thiosulphate ($S_2O_3^{2-}$) (reaction 7) was developed by Pfizer and is accurate to ± 0.01mol/ℓ (Gryka, 2005). The sample solutions were mixed with water, starch and formaldehyde and titrated with Iodine (reaction 9 and 10)

$$SO_3^{2-} + I_2 + H_2O \rightarrow SO_4^{2-} + 2I^- + 2H^+ \qquad (9)$$

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \qquad (10)$$

The purity of sulphur recovered was analysed using the LECO Combustion Techniques.

3. 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.

Table 2. Results of XRD analysis of the reaction products of carbon and gypsum compounds

Expt. number	Parameter	Value	$CaSO_4$	CaS	CaO	MgO	$Ca_5(PO_4)_3OH$
1	Time (min)	5	49	45	7	0	0
		20	0	96	4	0	0
		60	0	93	5	0	0
2	Temperature (°C)	900	84	15	1	0	0
		1000	8	88	4	0	0
		1100	0	96	4	0	0
3	$C/CaSO_4$ mole ratio	0	100	0	0	0	0
		0.25	93	0	7	0	0
		0.5	74	0	25	0	0
		1	48	13	38	0	0
		2	2	90	8	0	0
		3	0	96	4	0	0
4	Particle size of Gypsum (µm) Foskor gypsum	380	0	80	15	0	0
		630	22	56	18	0	0
		1250	86	1	12	0	0
5	Gypsum compounds	Pure	4	91	4	0	0
		Anglo	8	76	7	7	0
		Foskor	7	81	6	0	2

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

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

Effect of temperature. Experiment 2 (Table 2) indicated a marked improvement in the yield of the reduced mass as temperature was raised from 900 ºC to 1100 ºC. The results further showed that for a carbon: gypsum mole ratio of 3:1 and a reaction time of 20 min, the conversion percentage increased from 15 at 900 ºC to 96% at 1100 ºC. This could be due to the high activation energy required for the reduction of calcium sulphate to calcium sulphide, (Zhitkov et al., 1972). Saeed (1983) showed that the reaction between carbon and $CaSO_4$ to CaS takes place between 750 ºC and 1100 ºC.

Effect of carbon: gypsum mole ratio. Experiment 3 (Table 2) showed that when no carbon was added, no CaS was formed. The addition of carbon to gypsum at 1:1 moles ratio showed that only 20 % of gypsum was converted to CaS. The percentage conversion results further showed that CaO formation is favoured by a carbon: gypsum mole ratio of 1:1. Gypsum to CaO conversion of 38 % was obtained. However, increasing the ratio of carbon to 2 and 3 moles to a given amount of gypsum showed high percentage conversion of gypsum to calcium sulphide (90 and 96 %, respectively). The above results indicated that a reducing agent is needed for the thermal reduction of gypsum to CaS. The high percentage conversion for 1:2 moles corresponds to the stoichiometric amounts for the reaction of gypsum and carbon as indicated by reaction 11 (Reddy, et al 1967)

$$CaSO_4(s) + 2C(s) \rightarrow CaS(s) + 2CO_2(s) \qquad (11)$$

Effect of particle size. Experiment 4 (Table 2) showed that the formation of the reduced product calcium sulphide, is dependent upon the particle size of gypsum. When the gypsum particle size was 380 µm, the gypsum to CaS conversion was 80%. Increasing the particle size to 1250 µm resulted in a decrease in the conversion. Better yield of CaS with 380 µm gypsum can be ascribed to higher surface areas offered by the smaller particle size for interaction.

Effect of different gypsum compounds. Experiment 5 (Table 2) showed that 91% of gypsum was converted to CaS when pure gypsum was used. The lower conversion percentages (76% and 81%) obtained when Anglo gypsum and Foskor gypsum were reduced to CaS can be ascribed to the impurities contained in the two gypsum compounds

Reaction Mechanism for Sulphide Stripping

Behaviour of sulphide, calcium, alkalinity and pH during the sulphide stripping process

Figure 3 shows the behaviour of sulphide, calcium, alkalinity and pH during the sulphide stripping process. The initial CaS concentration was 1083 mmole/L and CO_2 flow rate was 520 mL/min.

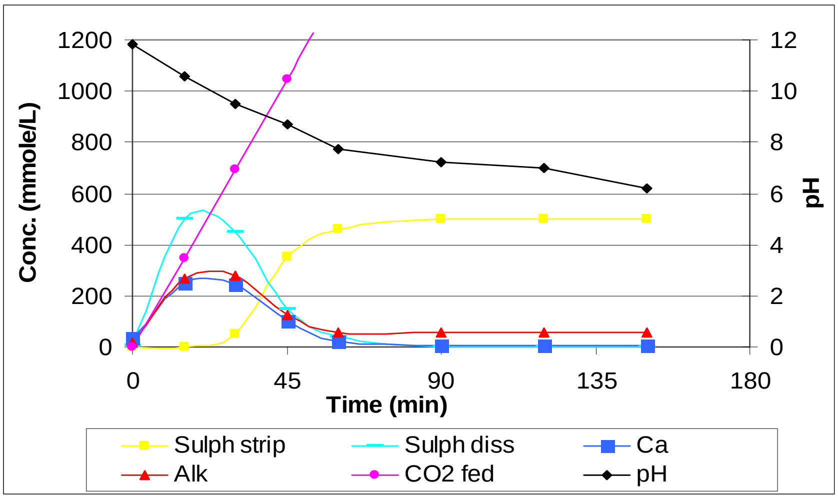

Figure 3. Behaviour of Ca and Sulphide during sulphide stripping process

- ***Sulphide dissolved and stripped***

The graphs show that during the first 30 min of the experiment, as CO_2 was added into the CaS slurry, CaS dissolves to form $Ca(HS)_2$ (proposed intermediate, reaction 12). As more CO_2 (after 30 min) was added then the sulphide in the form of $Ca(HS)_2$ is stripped off as H_2S gas (reaction 13). The graphs further showed that from the 1083 mmole/L of sulphide as CaS that was initially slurried, only 510 mmole/L sulphide dissolved and stripped with CO_2. An investigation was carried out to explain why only 510 mmole/L of sulphide dissolved and stripped. The results will be discussed in Figure 4.

$$2CaS\ (s) + CO_2\ (g) + H_2O\ (aq) \rightarrow CaCO_3\ (s) + Ca(HS)_2\ (aq) \quad (12)$$

$$Ca(HS)_2\ (aq) + CO_2\ (g) + H_2O\ (aq) \rightarrow CaCO_3\ (s) + 2H_2S\ (g) \quad (13)$$

- ***Calcium and Alkalinity***

The calcium graph shows that 250 mmole/L of calcium was in solution and the alkalinity (an indication of the CO_3^{2-} concentration) was 270 mmole/L. The concentrations of the two components (calcium and carbonate) are almost half the value of sulphide as $Ca(HS)_2$ in solution (510 mmole/L). From reaction 12 it can be noted, $Ca(HS)_2$ is equivalent to 2 mole sulphide as CaS but to 1 mole $CaCO_3$. The above finding proofs the formation of $Ca(HS)_2$. Furthermore, the low Ca concentration shows that $CaCO_3$ precipitates out due to its low solubility at pH values of 7.5 and higher.

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3\ (s) \quad (14)$$

- ***pH***

The pH graph indicates that when CO_2 is added into CaS slurry, the pH drop from 11.8 to 6.2. And it was further concluded that above pH 10, sulphide is in solution as $Ca(HS)_2$ and below pH 10 it is present as H_2S gas (reaction 12 and 13, respectively) .

Sulphide dissolved and in suspension

Figure 4 shows the experiment conducted with the aim to explain why only half of the initial sulphide slurried was measured (as dissolved and stripped) during stripping process in the previous experiment (Figure 3). The investigation was carried out using CaS slurry with an initial concentration of 1200 mmole/L and CO_2 gas at a flow rate of 520 mL/min. During the experiments, sample were taken and analysed. The sulphide analysis was done from the clear solution (filtrate) and from the mixed solution (filtrate and solids).

The results from the two solutions showed that:

When sulphide was measured from the clear solution, only 650 mmole/L sulphide concentration was analysed as dissolved sulphide, however when sulphide was analysed from the mixture, 1175 mmole/L of sulphide was in suspension. The graph further showed that from the initial CaS concentration of 1200 mmole/L, 1175 mmole/L of sulphide was stripped off with CO_2 gas. The different of 25 mmole/L sulphide might have escaped during the experiment. The finding indicates that during the stripping of sulphide from CaS slurry with CO_2 gas, sulphide dissolve in solution as $Ca(HS)_2$ (aq) and also present as a solid $Ca(HS)_2$ (s). This shows the low solubility of $Ca((HS)_2$.

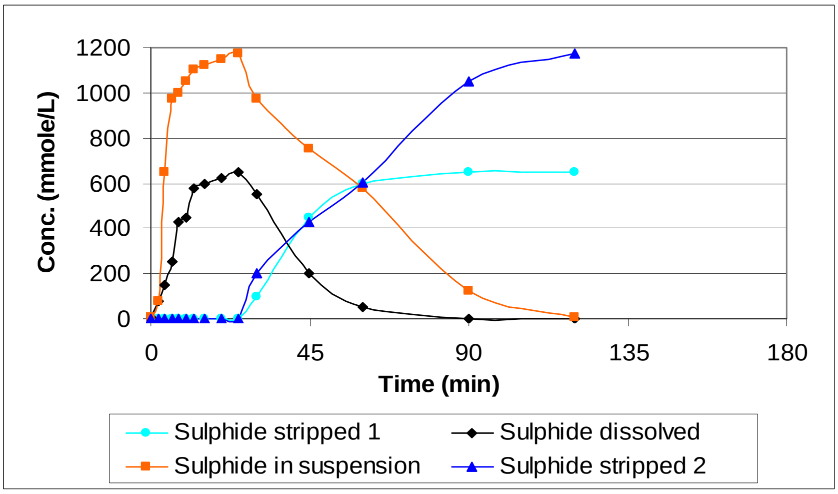

Figure 4 . Dissolved and in suspension sulphide analysis

Sulphur Production Via the Pipco Process

Figures 5 to 8 show the results when sulphide was stripped with CO_2 from a CaS (recovered from Anglo and Foskor gypsum) slurry, followed by absorption of the stripped H_2S gas in a SO_2-rich potassium citrate solution for sulphur formation. The effect of CO_2 flow rate (520 mL/min and at 1112 mL/min) on the formation of intermediate compounds during sulphur production was investigated

Figure 5 shows the relationship between the concentrations of the various species formed during sulphur production with 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. The CaS has a low solubility as indicated by a low value of 3.0 mmole/L before the addition of CO_2 gas. During CO_2 addition the pH dropped from 12.2 to 8.2. The sulphide concentration in the slurry reactor dissolve until it reached a maximum concentration of 1 375 mmole/L due to the formation of $Ca(HS)_2$. With further CO_2 addition, the pH dropped further to 6.9 and sulphide was stripped completely. The stripped H_2S reacted with the SO_3^{2-} in the potassium citrate solution rich in SO_2 reactors.

The SO_3^{2-}concentration in Reactor 1 dropped sharply, while in Reactor 2 dropped slowly. The fast drop in Reactor 1 can be ascribed to the formation of sulphur and possibly due to some of the SO_2 being stripped with CO_2. The slow drop in the SO_3^{2-}-concentration in Reactor 2 can be ascribed to SO_2-stripping with CO_2.

From figure 6, which shows the relationship between load removed or formed of the various parameters as a function of time, it is noted that:

- 2167 mmole CaS was initially slurried
- 1375 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 (as discussed in Figure 4)
- 2180 mmole SO_3^{2-} was removed ((which shows the formation of Sulphur) refer to equation 7 and 8)), which is more than the concentration of CaS that was 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.

The experiment described above for 520 mL/min CO_2 was repeated for a CO_2 flow rate of 1112 mL/min (Figures 7 and 8). Similar conclusions were made except for the behaviour of SO_3^{2-} in the SO_2/citrate reactor. The following similar observations were made:

- 2167 mmole CaS was initially slurried,
- 1300 mmole dissolved in solution as $Ca(HS)_2$, and the balance was in solid form as $Ca(HS)_2$.
- 2310 mmole SO_3^{2-} was removed which is 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 (Figure 7) can be ascribed to the formation of an intermediate compound when H_2S is contacted with the SO_2/citrate solution.

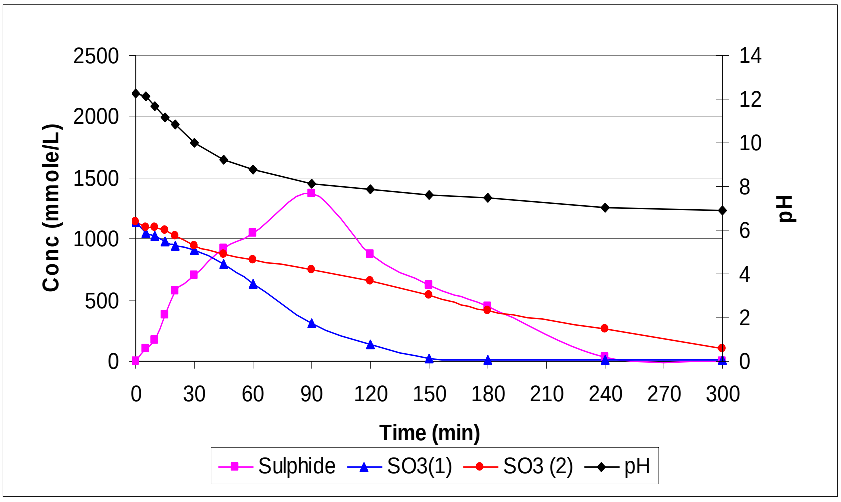

Figure 5. Sulphide stripping with CO_2 at a flow rate of 520 mL/min (concentrations versus time).

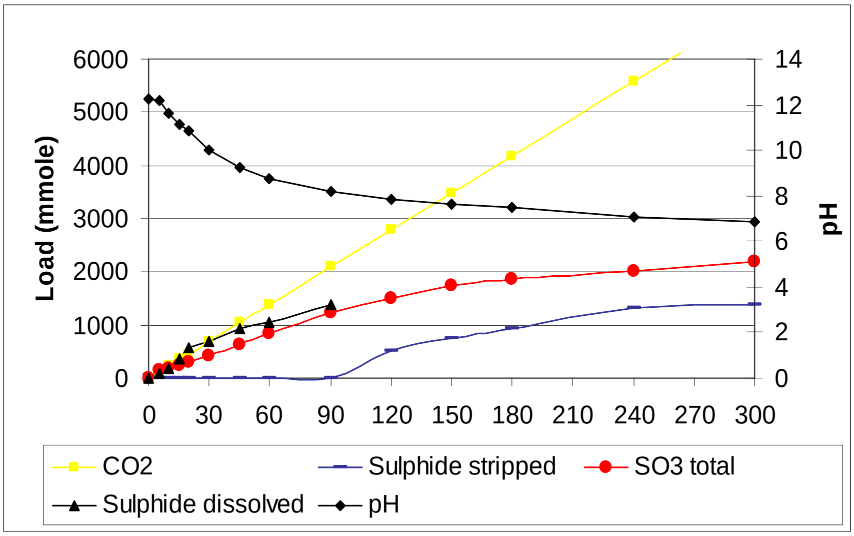

Figure 6. Sulphide stripping with CO_2 at a flow rate of 520 mL/min (load versus time).

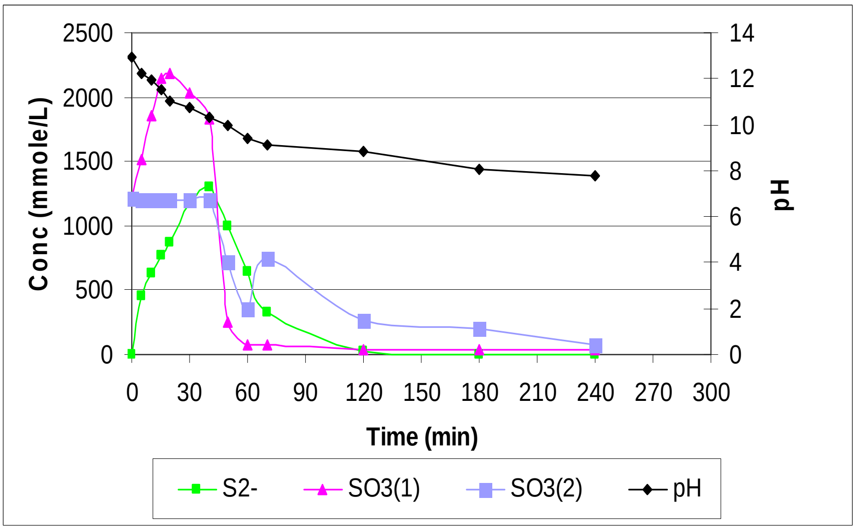

Figure 7. Sulphide stripping with CO_2 at a flow rate of 1112 mL/min (concentrations versus time).

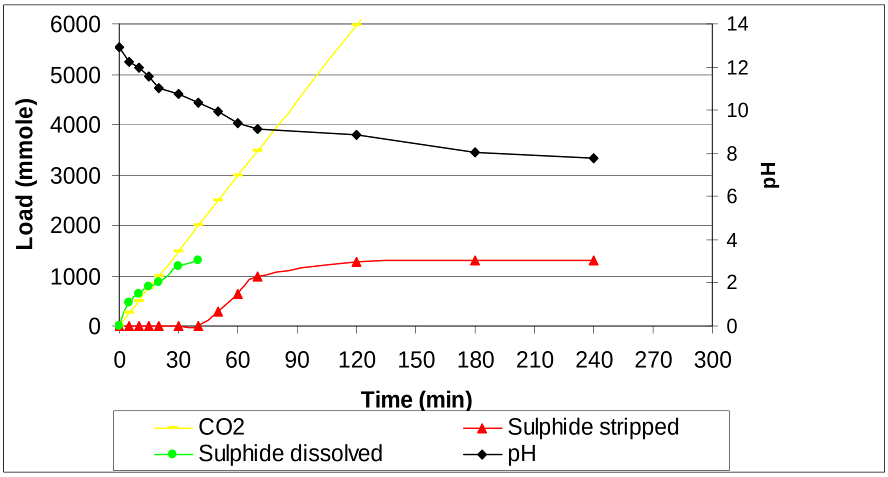

Figure 8. Sulphide stripping with CO_2 at a flow rate of 1112 mL/min (load versus time).

Purity of Sulphur Recovered

The LECO Combustion Techniques used to analyse the purity of Sulphur showed that Sulphur with the purity between 95 and 99% was recovered.

To identify the other elements formed during the recovery of sulphur process, XRF analyses was conducted on the sulphur samples. The results are indicated in Table 3.

Table 3. XRF results for Sulphur sample

Elements	**Conc. Impurities**
K	820ppm
Fe	91ppm
Ca	184ppm
Mg	170ppm
Si	20ppm
Co	40ppm
Cr	60ppm
Ni	56ppm

Economic Feasibility

The recovery of sulphur and $CaCO_3$ ($CaCO_3$ studies not included in this study) from gypsum based on laboratory and pilot studies (pilot results not included in this study), seems to be economically feasible. From 1 ton of gypsum it was calculated that 0.18 ton of sulphur (Value = R180) and 0.58 t of $CaCO_3$ (Value = R145) can be recovered. The prices of sulphur and $CaCO_3$ were taken at R500/t and R250/t, respectively. This compares favourable with the cost of the main raw material, coal. At a coal to gypsum ratio of 0.3, and a coal cost of R400/t, the cost of the coal amounts to R120/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 $CaCO_3$ is recovered. The price of chemically pure $CaCO_3$ amounts to R3 000/t compared to the R250/t for waste or mined $CaCO_3$.

4. CONCLUSIONS

The thermal reaction of gypsum to CaS in a tube furnace and nitrogen atmosphere takes place between 900 °C and 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 1:2 and 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 impurities contained in Anglo and Foskor gypsum seems to lower the CaS yields as compared to pure gypsum.

The H_2S stripping studies showed that sulphide can be stripped with CO_2 from a CaS-slurry to form H_2S with the simultaneous production of $CaCO_3$

From the PipCo process, pure yellow sulphur with the purity between 96% and 99% was recovered. The main element that was formed as an impurity was potassium.

5. REFERENCES

Apha, 1985. Standard Methods for the Examination of Water and Wastewater treatment. 12th ed. American Public Health Association. New York.

BEKASSY-MOLNAR E, MARKI E and MAJEED JG (2005) Sulphur dioxide absorption in air lift tube absorbers by sodium citrate buffer solution. *Chem.Eng. Process,* **44** (9) 1039-1046

CORK DJ, JERGER DE and MAKA A (1986) Biocatalytic production of sulphur from process waste streams. *Biotechnol. Bioeng*. **16** 149-162.

GELDENHUYS AJ, MAREE JP, DE BEER M and HLABELA P (2001) An integrated limestone/lime process for partial sulphate removal. *Proc. Environmentally Responsible Mining Conference, South Africa*. September. CSIR, Pretoria, South Africa.

GRYKA GE (1992) System for Recovering Sulphur from Gases Especially Natural Gas. PIPco, Inc., Southport, CT (USA).

GRYKA GE (2005) Titration for HSO_3 and HS_2O_3, Personal Communication. PIPco, Inc., Southport, CT (USA).

MAREE JP, GREBEN HA and DE BEER M (2004) Treatment of acid and sulphate-rich effluents in an integrated biological/chemical process. *Water SA* **30** (2) 183-189.

MAREE JP, THERON D, NENGOVHELA NR, HLABELA PS (2005) Sulphur from smelter gases and sulphate –rich effluents. *J. S. Afr. Inst.Min.Metall.* **105** 1-4.

MATSUYA S and YAMANE M (1981) Decomposition of gypsum bonded investment. *J. Dent. Res.* **60** (8) 1418-1423.

RAMESHNI M and SANTO S (2005) Production of Elemental Sulphur from SO_2. RSR (Ramenshi SO_2 Reduction*). WorleyParsons*. Arcadia, California 91007 (USA).

RATLABALA ME (2003) An Overview of South Africa's Mineral Based Fertilizers. Department of Minerals and Energy, Government of South Africa.

RAY WG, ARBO JC and GRYKA GE (1990) Process for Recovery of Sulphur from a Gas Stream. US Patent 5,057,298, assigned to PIPco Inc., Southport, CT (USA).

Reddy, P.P., Ratinam, M., Sundaram, N. and Satyanarayananan, A.K. 1967. Studies on the reduction of gypsum to calcium sulphide. Chemical age of India, **18 (4):** 282.

VAN ZYL HC, MAREE JP, VAN NIEKERK AM, VAN TONDER GJ and NAIDOO C (2000) Collection, treatment and re-use of mine water in the Olifants River Catchment. *SAIMM* **101** (1) 41 - 46.

Zhitkov, V.V. and Jukov, V.Y., 1972. USSR. Tr. Vses. nauchissled. Inst. Tesllyul-bum. RUSS. 61-99