Treatment of Sulphate-rich Mining Effluents with the Barium Hydroxide Process and Recovery of Valuable By-products

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ABSTRACT

Soluble barium salts can be used for the treatment of sulphate-rich effluents. This study compared the technical and economical feasibility of the $BaCO_3$, BaS and $Ba(OH)_2$ processes. It was shown that acid mine water from an old coal mine in the Witbank area can be effectively treated by the barium processes. The BaS and $Ba(OH)_2$ can directly neutralise the acid water and apart from the removal of sulphate and calcium, also remove ammonia, magnesium, manganese and other heavy metals. By-products such as NaHS and sulphur can be recovered from these processes. The $Ba(OH)_2$ process is shown to be technically and economically feasible.

INTRODUCTION

The discharge of industrial effluents containing high sulphate concentrations into surface waters contributes directly to mineralization and the corrosion potential of the receiving waters. It may also result in the scaling of equipment, especially if relatively high concentrations of calcium are present. Demineralization processes such as reverse osmosis can be used for sulphate removal but they are costly; hence the need for the development of alternative processes.

Other promising processes entail the chemical removal of sulphate by means of soluble barium salts such as barium sulphide and barium carbonate[3,4,6,10,11,12]. In the barium sulphide process, BaS is added to the raw wastewater, the sulphates being removed by the crystallization of $BaSO_4$. This $BaSO_4$ is then converted back to BaS through reduction with carbon at 1 000 °C. The sulphide (from dissolved BaS) which remain in the water, is stripped off as H_2S gas which is then converted to sulphur or sodium bisulphide through biological or chemical means. In the barium carbonate process, $BaCO_3$ is added to the raw wastewater to precipitate the sulphates in the water as $BaSO_4$ and the calcium as $CaCO_3$. This $BaSO_4/CaCO_3$ mixture is then treated in a kiln at 1 000 °C where the $BaSO_4$ is converted back to BaS through reduction with carbon and the $CaCO_3$ to CaO. The BaS, which is more soluble than the CaO, is separated from the CaO by leaching with water. The BaS in solution is converted to $BaCO_3$ by stripping H_2S gas off with CO_2. The H_2S is

converted either to sodium bisulphide or elemental sulphur in a separate stage.

Each of these processes have unique disadvantages. The barium carbonate process requires a relatively long retention time for sulphate removal due to the slow dissolution rate of barium carbonate. Precipitation of barium sulphate together with calcium carbonate, necessitates a separation stage after thermic regeneration of the barium sulphate. The barium sulphide process has the disadvantage that a low concentration of H_2S-gas needs to be stripped from the total water stream that is treated, instead of a concentrated stream of H_2S-gas.

The barium hydroxide process has recently been developed to eliminate some of the steps required in the above processes[9]. In this process, $Ba(OH)_2$, (as a solid) and $Ba(HS)_2$ (in solution) are produced from BaS. $Ba(OH)_2$ is used for water treatment, while NaHS is separated from the $Ba(HS)_2$, producing $BaCO_3$. The produced $BaCO_3$ is decomposed thermically to BaO and then hydrolyzed to $Ba(OH)_2$.

Benefits associated with the barium hydroxide process are:

*   No lime dosage is required as is the case with both the barium carbonate process and the barium sulphide process.
*   No H_2S-stripping is required from the total stream as is the case with the BaS process.
* $BaSO_4$ is not precipitated together with $CaCO_3$.
*   By-products and $BaCO_3$ (which can be decomposed to produce BaO), can be recovered. Hydrolysis of the BaO produces more $Ba(OH)_2$ for water treatment.

The purpose of this study was to evaluate and compare the three barium processes for water treatment.

MATERIALS AND METHODS

Batch studies

A Phipps & Bird stirrer apparatus was used to study the kinetics of sulphate and barium removal from both synthetic solutions and industrial samples. Mine water samples as well as synthetic solutions were treated with the barium salts, $BaCO_3$, BaS and $Ba(OH)_2$. Treated samples were analyzed for sulphate, calcium, alkalinity, sulphide, barium and pH.

The following general procedure was followed during batch studies:

*   Addition of 500 mℓ sulphate rich water to the reaction beakers.
*   Addition of powdered carbon (required as reducing agent during the $BaSO_4$ reduction stage) to assist with coagulation.
*   Addition of the barium salts.
*   Stirring followed by settling of the mixtures.
*   Decanting of the supernatant.
*   Regular sampling for analyses of sulphate, calcium, alkalinity, sulphide and pH.
* H_2S-stripping from the treated water in the BaS process, using CO_2 followed by CO_2-

stripping using air.
* Complete analyses were carried out on the raw and final water.

The mine water treated with the barium salts was obtained from two sources:

* Water No. 4 - A mixture of underground acid mine drainage from an abandoned coal mine and effluent seepage water from an industrial plant in the Witbank area.
* Water No. 12 - Acid mine drainage from an abandoned coal mine in the Witbank area.

Thermic regeneration

Thermic regeneration of $BaSO_4$ to BaS was studied in a tube furnace by reducing $BaSO_4$ and a coal mixture. The molar ratio of the technical $BaSO_4$ to the carbon in the coal was 1:3. The effect of the following parameters on the efficiency of the reduction were determined:

* Temperature: The optimum temperature was determined by measuring the amount of BaS produced against time at various temperatures.
* $CaCO_3$: Thermic studies were also performed in the presence of $CaCO_3$. A mass of $CaCO_3$, stoichiometrically equal to that of the $BaSO_4$ was used.
* Shelf life of BaS.

The following methods were used in the determination of the efficiency of the BaS:

* Mass loss: As the reaction products of $BaSO_4$ reduction (Reaction 1) and $CaCO_3$ decomposition (Reaction 2) are known, the percentage completion of the reaction can be monitored by loss of mass.

$$BaSO_4 + 3C \rightarrow BaS + 2CO_2 + 2CO \qquad [1]$$
$$CaCO_3 \rightarrow CaO + CO_2 \qquad [2]$$
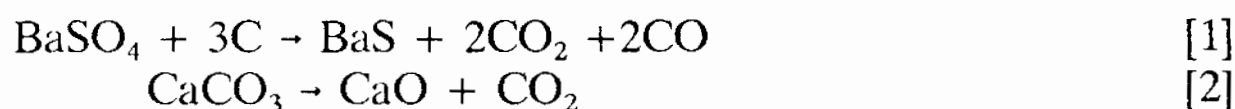
* Sulphate determination: Water soluble barium in the produced BaS was determined by measuring the amount of sulphate removed from a synthetic sulphate solution.
* Alkalinity - Calcium measurement: BaS in a solution of the BaS/CaO thermic product was calculated by the measurement of both parameters:

$$Alk = BaS + Ca(OH)_2 \text{ (when all is expressed as } CaCO_3)$$

Separation studies

In the $BaCO_3$ process, $BaSO_4$ is precipitated together with $CaCO_3$, necessitating a separation step after thermic regeneration. The dissolution of BaS and CaO in water was investigated.

Analytical

Standard methods as prescribed by APHA[1] were used in all analyses, using filtered samples.

RESULTS AND DISCUSSION

General

Tables 1 and 2 show the detailed results of treating water No. 4, and a synthetic mine water with the various barium salts ($BaCO_3$, BaS and $Ba(OH)_2$). The barium dosages applied were calculated to remove 70% of the sulphate content left in solution after neutralization with lime. Similar results were obtained in several other studies, including studies with water No. 12.

Table 1: Effect of various barium salts on the quality of water No. 4 (mine and industrial water) after neutralization with 1 342 mg/ℓ lime to a pH of 7.7

Parameter (mg/ℓ)	Chemical added (mg/ℓ)							
	Untreated	Lime	$BaCO_3$	Lime	BaS	CO_2	Lime	$Ba(OH)_2$
Dosage		1 342	7 847	1 342	6 734		1 342	12 542
SO_4 equiv.			3 816		3 816			3 816
SO_4 in sol.	7 018	5 994	2 106	5 742	1 512		5 742	501
SO_4 removed			3 888		4 230			5 241
S^{2-} (as S)					360	17		
Ca (as $CaCO_3$)	677	1 100	19	1 100	855		1 100	639
Mg (as $CaCO_3$)	1 021	838	741				66	68
Alk. (as $CaCO_3$)		90	1 370	126	2 440		126	2 766
Ac. (as $CaCO_3$)	1 831							
pH	3.1	7.7	9.4	7.7	11.3	6.4	7.7	12.2
% Ba efficiency			101.6		110.8			137.0

Table 2: Removal of sulphate with $Ba(OH)_2$ from a synthetic solution

Parameter (mg/ℓ)	Chemical added (mg/ℓ)			
	Untreated	$Ba(OH)_2$		
$Ba(OH)_2.8H_2O$ dosage		4 930	3 286	1 643
SO_4 equivalent		1 500	1 000	500
SO_4 in solution	1 966	324	799	1 361
SO_4 removed		1 642	1 166	605
Ca (as $CaCO_3$)	1 951	1 654	1 679	1 786
Ca removed		297	273	165
Alkalinity (as $CaCO_3$)	50	1 430	980	540
pH	6.4	12.0	11.9	11.6
% Barium efficiency		109.4	116.6	121.0

The efficiency of the various barium salts for sulphate removal in water Nos. 4, 12 and in the synthetic solution are summarized in Table 3, which shows that all the barium salts ($BaCO_3$, BaS and $Ba(OH)_2$) can effectively remove sulphate from neutralized acid water.

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Table 3: Efficiency of barium salts for sulphate removal.

| Water | Lime | | Efficiency (%) | | |
No.	dosage (mg/ℓ)	pH	$BaCO_3$	BaS	$Ba(OH)_2$
4	4 909	11.8	90.1	90.1	134.0
4	1 342	7.7	101.6	110.8	137.0
4*	0	2.9	24.2	95.6	107.7
12	2 760	9.4	120.5	100.7	129.0
12	1 998	7.3	100.7	105.0	131.0
Synthetic solution♦			109.4	116.6	121.0
Average♥			103.2	101.7	132.8

♥Does not include * and ♦

In the following sections aspects specific to each of the barium processes will be addressed.

$BaCO_3$ process

The integrated $BaCO_3$ process can be presented by the following reactions:

Neutralization : $H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4(s \& aq) + 2H_2O$ [3]

Sulphate removal : $Ca^{2+} + SO_4^{2-} + BaCO_3 \rightarrow BaSO_4 + CaCO_3$ [4]

Thermic reduction : $BaSO_4 + CaCO_3 + 3C \rightarrow BaS + 3CO_2 + CaO$ [5]

Separation of BaS & CaO : $BaS + CaO + H_2O \rightarrow Ca(OH)_2(S) + BaS(aq)$ [6]

H_2S stripping : $BaS + CO_2 + H_2O \rightarrow BaCO_3(S) + H_2S(g)$ [7]
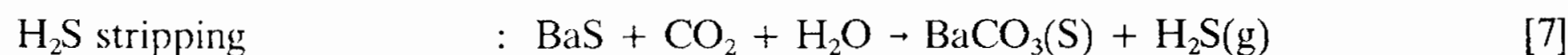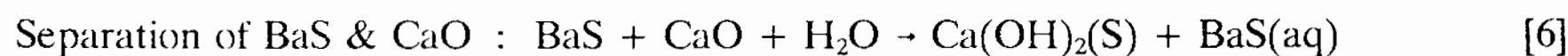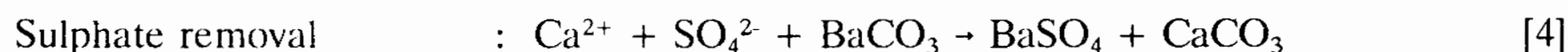
Equilibrium

Only water that is neutralized with lime can be treated with $BaCO_3$ as indicated in Table 3 (under $BaCO_3$). Figure 1a shows that where no lime was added, almost no sulphate removal occurred. Ca^{2+} ions in solution are necessary to precipitate the released CO_3 as $CaCO_3$ to keep the water unsaturated with respect to $BaCO_3$.

Reaction rate

Figures 1a and 2a show the rate at which sulphate is removed from water No. 4 when Ba dosages equal to 70% of the sulphate content were added. $BaCO_3$ dosages of less than or equal to the stoichiometric concentration of sulphate require a relatively long retention time. Maree, et al.[10] showed that an overdosage of $BaCO_3$ and a fluidized bed reactor can be used to minimize the retention time.

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Equation 4 shows that calcium and sulphate removal will take place simultaneously. Comparing Figures 1a with 1b and 2a with 2b for waters 4 and 12 respectively demonstrate this principle.
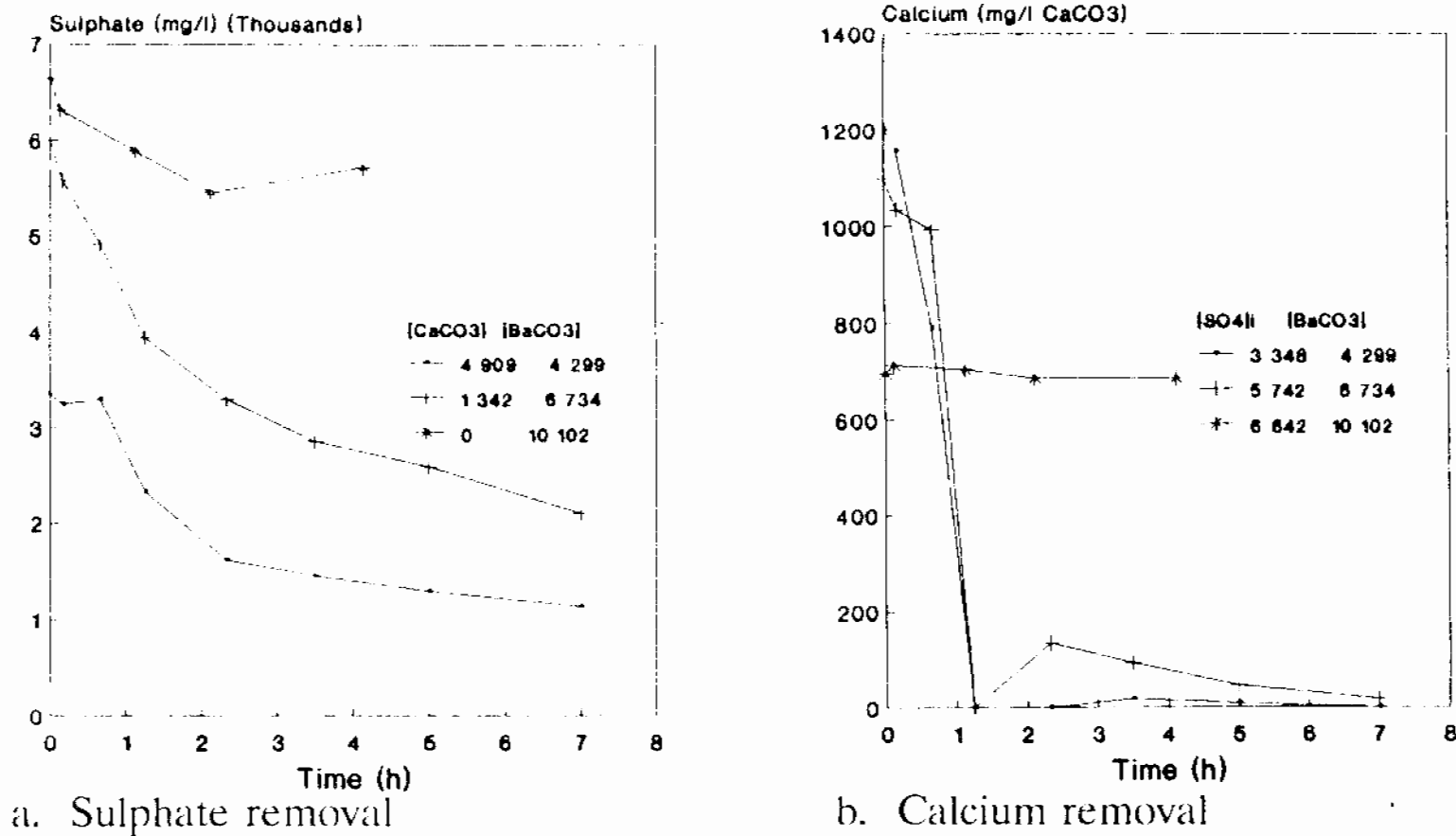

a. Sulphate removal   b. Calcium removal

Figure 1: Treatment of water No. 4 (mixture of mine and industrial water) with $BaCO_3$ after various dosages of lime had been applied.
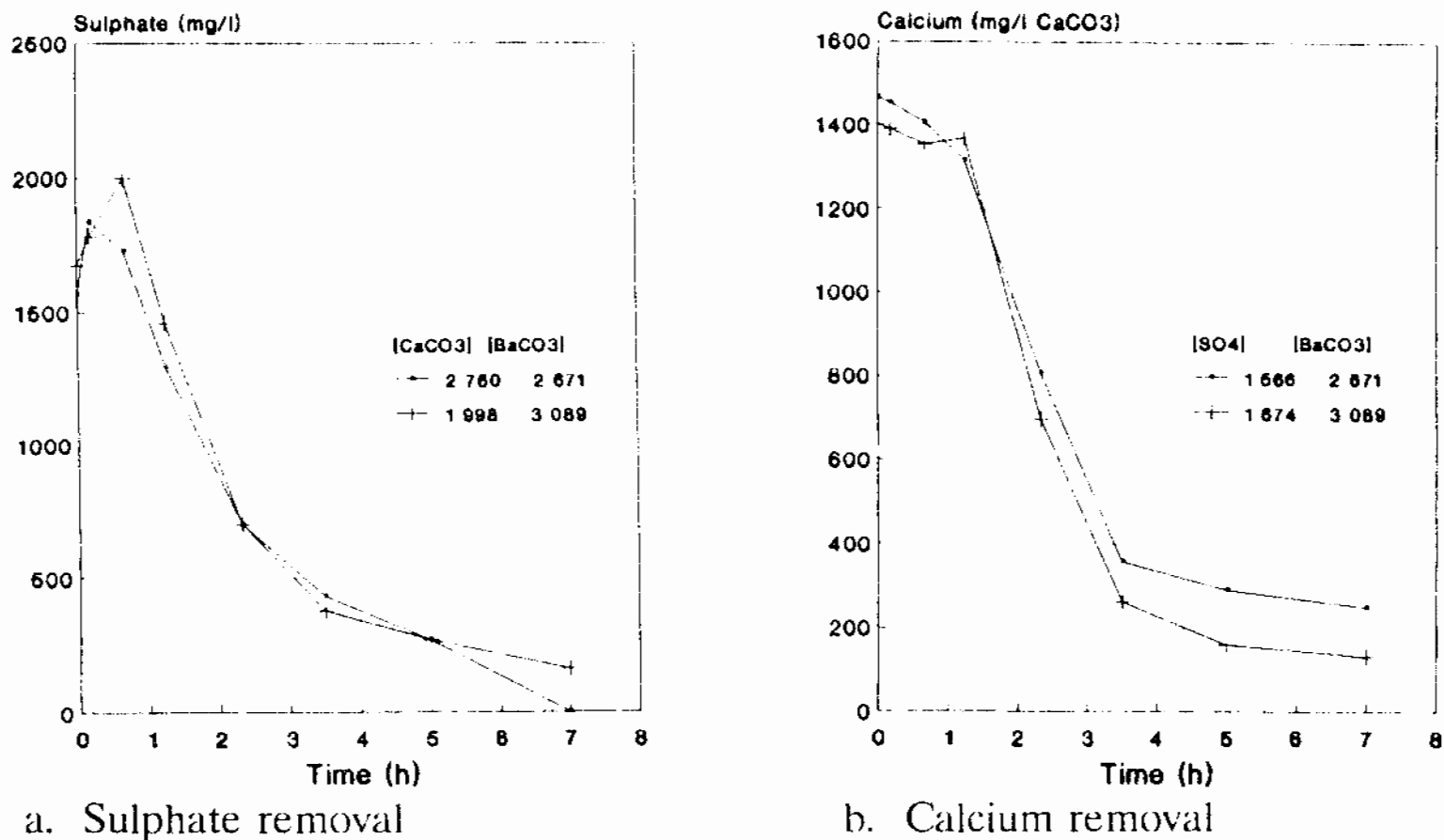

a. Sulphate removal   b. Calcium removal

Figure 2: Treatment of water No. 12 (acid minewater) with $BaCO_3$ after various dosages of lime had been applied.
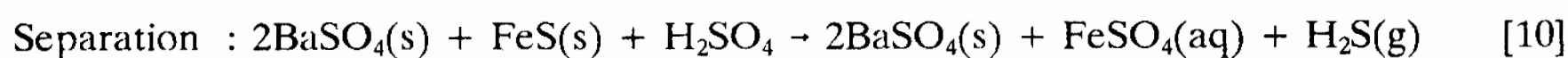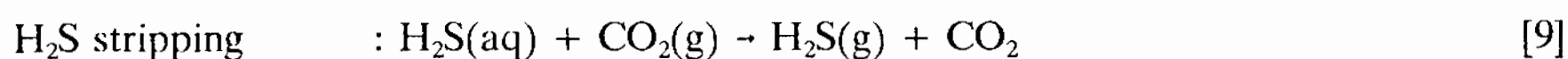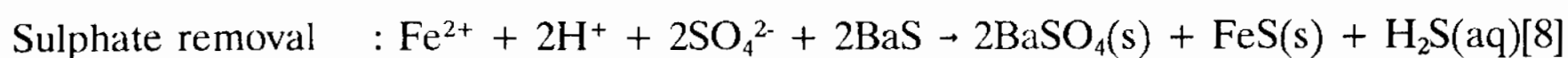
BaS process

The BaS process can be used for the treatment of acid water before or after neutralization. Direct neutralization of acid water with BaS has the following benefits:

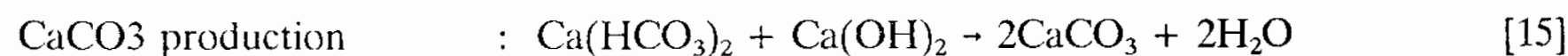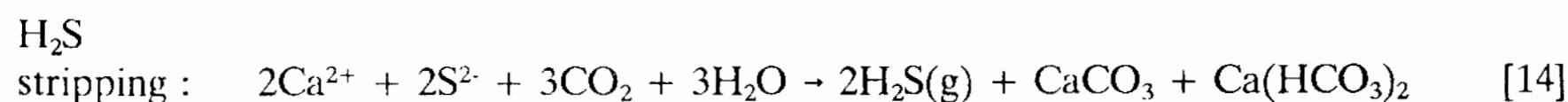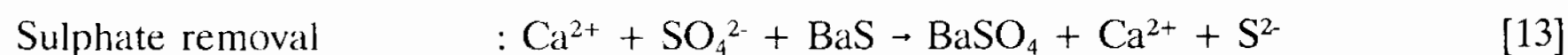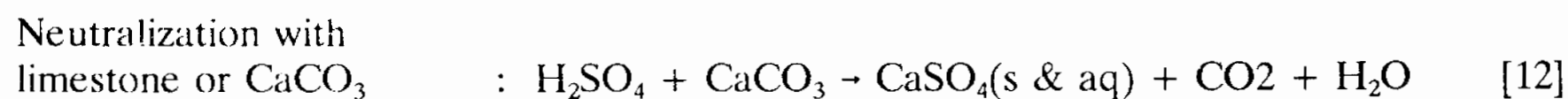**4th International Mine Water Congress, Ljubljana, Slovenia, Yugoslavia, September 1991**

* A greater quantity of by-product can be recovered from sulphate as it is not precipitated as gypsum.
* An additional treatment step, of neutralization with lime or limestone, is eliminated.
* The disposal of sludge (mainly gypsum) is eliminated to a large extent.

When metal containing acid water is treated, metal sulphides precipitate together with the $BaSO_4$. Metals such as aluminium, iron and silica can form barium metal complexes which are insoluble in water, reducing the barium recovery of the process. Metal sulphides can be separated from the $BaSO_4$ by acid leaching or by oxidizing the sulphide of the metal sulphides to H_2SO_4 through the use of iron oxidizing bacteria. Valuable metals can be recovered from the acid solution if economically feasible.[3,9,10]

The integrated BaS process (Route I) can be presented by the following reactions when iron containing acid water is treated directly:

Sulphate removal : $Fe^{2+} + 2H^+ + 2SO_4^{2-} + 2BaS \rightarrow 2BaSO_4(s) + FeS(s) + H_2S(aq)$ [8]

H_2S stripping : $H_2S(aq) + CO_2(g) \rightarrow H_2S(g) + CO_2$ [9]

Separation : $2BaSO_4(s) + FeS(s) + H_2SO_4 \rightarrow 2BaSO_4(s) + FeSO_4(aq) + H_2S(g)$ [10]

Thermic reduction : $BaSO_4 + CaCO_3 + 3C \rightarrow BaS + 3CO_2 + CaO$ [11]
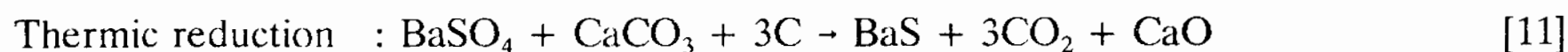
The BaS process, if operated in such a way that neutralization is carried out with lime or limestone, can produce another valuable by-product, namely pure $CaCO_3$ with a high value (up to R3 000/ton). This (Route II) process is presented by the following reactions:

Neutralization with limestone or $CaCO_3$: $H_2SO_4 + CaCO_3 \rightarrow CaSO_4(s \& aq) + CO2 + H_2O$ [12]

Sulphate removal : $Ca^{2+} + SO_4^{2-} + BaS \rightarrow BaSO_4 + Ca^{2+} + S^{2-}$ [13]

H_2S stripping : $2Ca^{2+} + 2S^{2-} + 3CO_2 + 3H_2O \rightarrow 2H_2S(g) + CaCO_3 + Ca(HCO_3)_2$ [14]

CaCO3 production : $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ [15]

Thermic reduction : $BaSO_4 + CaCO_3 + 3C \rightarrow BaS + 3CO_2 + CaO$ [16]

H_2S-stripping

In the case of the barium sulphide process, H_2S gas needs to be stripped from the total effluent. H_2S was stripped to values below 20 mg/ℓ (as S) (Table 1). Residual sulphide can be removed by precipitating it with iron as FeS.

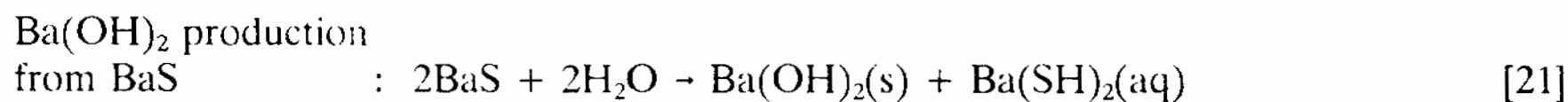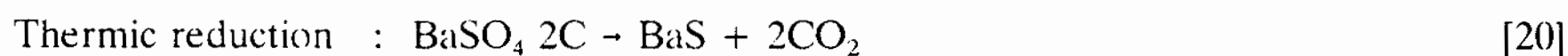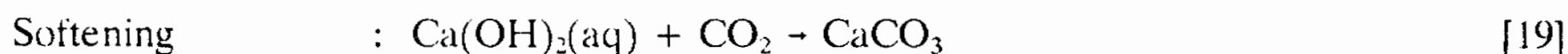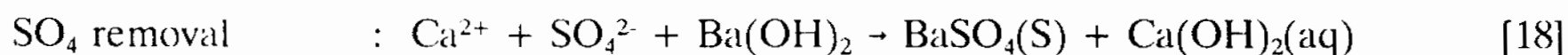$$S^{2-} + Fe^{2+} \rightarrow FeS$$ [17]

Magnesium removal

Magnesium is also removed with the BaS process when water is not pretreated with lime. In directly treated acid water, magnesium was removed from 435 to 176 mg/ℓ. As magnesium removal is a function of pH, not all was removed at the pH of 9.4. A higher percentage removal of sulphates with BaS will result in a higher pH and better magnesium removal.

Ba(OH)$_2$ process

As metal hydroxides are more difficult to dissolve than metal sulphides, the Ba(OH)$_2$ process is considered to be more suitable for treating neutralized water, than to treat acid water where metal hydroxides will precipitate.

The Ba(OH)$_2$ process eliminates the disadvantages associated with the water treatment stages of both the BaCO$_3$ and BaS processes. No long retention time is required for sulphate removal as is the case with the BaCO$_3$ process. When compared to the BaS process, no H$_2$S stripping is required from the total water stream. In fact, it has the unique benefit that no stripping stage is required to recover NaHS from sulphide.

The integrated Ba(OH)$_2$ process can be presented by the following reactions:

SO$_4$ removal   : $Ca^{2+} + SO_4^{2-} + Ba(OH)_2 \rightarrow BaSO_4(S) + Ca(OH)_2(aq)$ [18]

Softening   : $Ca(OH)_2(aq) + CO_2 \rightarrow CaCO_3$ [19]

Thermic reduction   : $BaSO_4\ 2C \rightarrow BaS + 2CO_2$ [20]

Ba(OH)$_2$ production
from BaS   : $2BaS + 2H_2O \rightarrow Ba(OH)_2(s) + Ba(SH)_2(aq)$ [21]

NaSH production   : $Ba(SH)_2(aq) + Na_2CO_3(aq) \rightarrow BaCO_3(s) + 2NaHS(aq)$ [22]

Ba(OH)$_2$ production
from BaCO$_3$: $BaCO_3 + heat \rightarrow BaO + CO_2$ [23]
$\qquad\qquad\qquad\quad BaO + 2H_2O \rightarrow Ba(OH)_2$ [24]
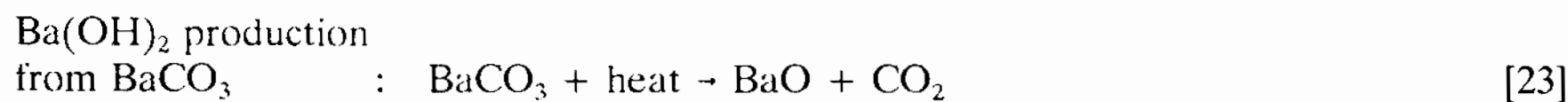
The BaCO$_3$ produced can be converted to Ba(OH)$_2$ as indicated by reactions 23 and 24. The choice whether both Ba(OH)$_2$ and BaCO$_3$ should be used in one process, or only Ba(OH)$_2$, should be made by considering the various advantages associated with each approach.

Disadvantages of dosing both Ba(OH)$_2$ and BaCO$_3$:

*   An additional dosing unit for BaCO$_3$ is required which makes provision for a long contact time due to the slow rate of the reaction.
*   H$_2$S needs to be stripped from a concentrated chemical solution.
*   A larger kiln would be required as CaCO$_3$ needs to be decomposed to CaO together

with $BaSO_4$ reduction.

* Provision must be made for separation of BaS and CaO.

Disadvantages of dosing only $Ba(OH)_2$:

A second, smaller kiln is required in addition to the one required for the reduction of $BaSO_4$ to BaS, which can decompose $BaCO_3$ to BaO.

Magnesium removal

Magnesium is very efficiently removed by the $Ba(OH)_2$ process as demonstrated in Table 1. The $Ba(OH)_2$ increases the pH of the water to approximately 12. At a pH of 11.4 and higher, magnesium precipitates completely as $Mg(OH)_2$.

Co-precipitation of $CaSO_4$

An interesting aspect of the $Ba(OH)_2$ process is that coprecipitation of $CaSO_4$ takes place together with $BaSO_4$ to a greater extent than in case of the $BaCO_3$ and BaS processes. Table 3 shows that on average, $BaCO_3$ and BaS remove an amount of sulphate stoichiometrically equal to the salt dosed. In the case of $Ba(OH)_2$, 32.8% more sulphate was removed than the stoichiometric equivalent of barium dosed. This can be explained by the fact that gypsum co-precipitates with $BaSO_4$ to form a complex $Ba_xCa_ySO4_{x+y}$, similar to the formation of $Ca_xMg_yCO3_{x+y}$ complexes as described by Benjamin et al.[2]. This behaviour of $Ba(OH)_2$ has the advantage that 30% less barium than stoichiometrically required, needs to be dosed for sulphate removal.

Thermic reduction of $BaSO_4$

The results of thermic reduction studies of $BaSO_4$ to BaS appear in Figure 3. It is clear from Figure 3 that the optimum temperature for reduction is between 1 000 and 1 100 °C. This confirms observations made previously[5,8]. More than 90% conversion of $BaSO_4$ to BaS was achieved.
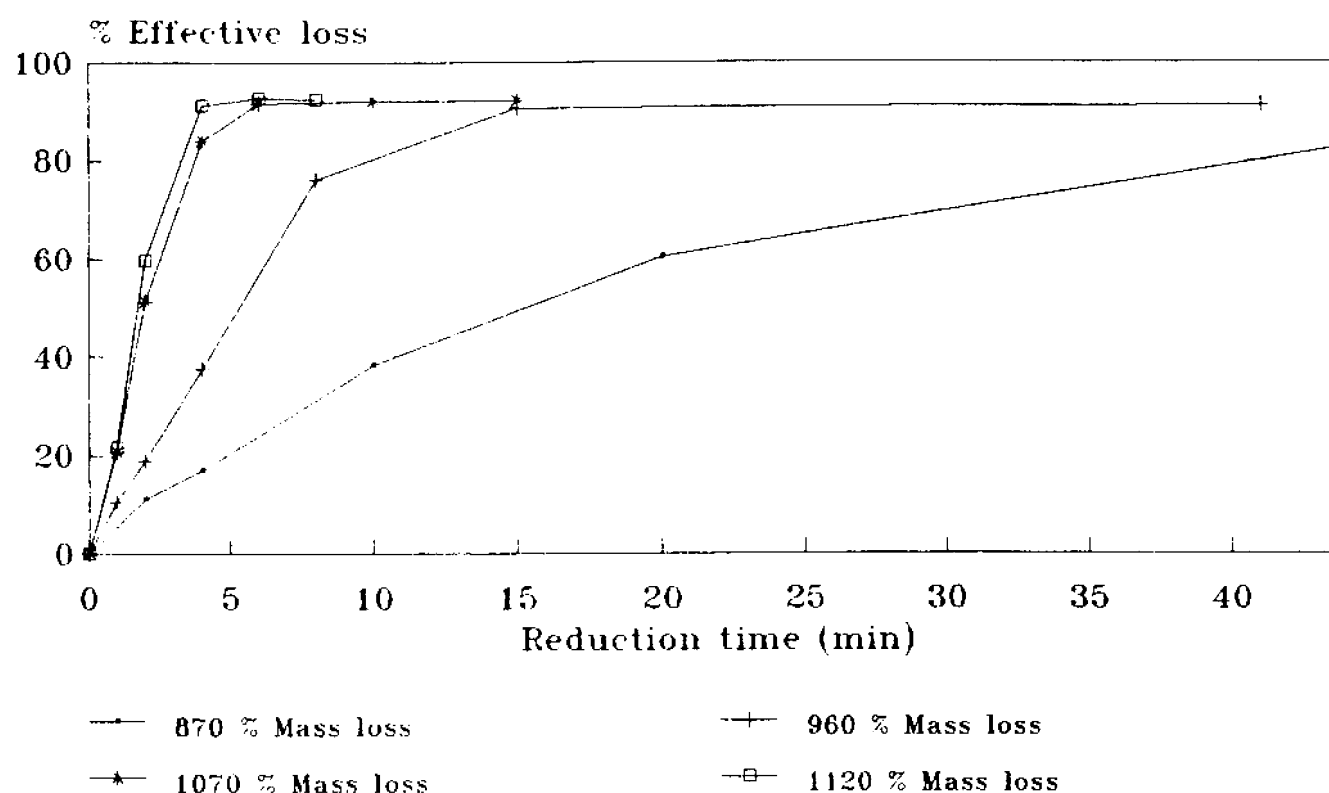

Figure 3: The effect of temperature on the reduction of $BaSO_4$ and a coal mixture $(BaSO_4 : C \rightarrow 1 : 3)$

Table 4 shows the efficiency of BaS production under various conditions and measured by various methods. The average efficiency determined based on mass reduction was 97.5%, compared to 90.9% in the case of indirect measurements. This can be explained by the fact that insoluble barium complexes could have formed due to the presence of impurities in the coal such as Al_2O_3, SiO_2 or Fe_2O_3. It appears that $CaCO_3$ has no influence on the efficiency of $BaSO_4$ reduction.

Table 4: Efficiency and stability of $BaSO_4$ reduction under thermic conditions

| Background of BaS | | | % |
Age	$CaCO_3$	Method used	Efficiency
Fresh	Present	Mass reduction	98.7
Fresh	Absent	Mass reduction	96.3
Fresh	Present	SO_4 removed with Ba	91.7
Fresh	Absent	SO_4 removed with Ba	86.2
Fresh	Present	Alk - Ca	91.6
Fresh	Absent	Alk - Ca	94.2
Old	Absent	SO_4 removed with Ba	65.0

BaS/CaO separation

In the $BaCO_3$ process, a mixture of BaS and CaO is produced during the thermic treatment of $BaSO_4/CaCO_3$ in the presence of coal. As CaO is less soluble than BaS, it can be separated from the BaS by dissolution of the BaS/CaO mixture in water. Figure 4 shows the percentage of dissolution of BaS and CaO in water at different concentrations (expressed as $CaCO_3$).
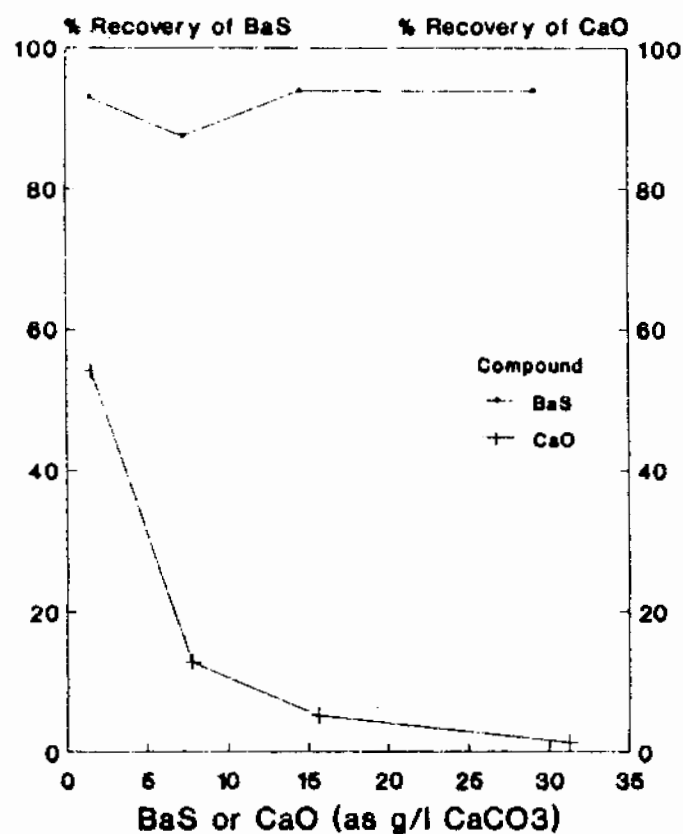

Figure 4: Solubility of BaS and CaO at different solid to liquid ratio's

It is shown that at a concentration of 1.5 g/ℓ, 54% of the CaO is in solution, against only 1,3% at a concentration of 31 g/ℓ. In the case of BaS, there is no decrease in the percentage of BaS that dissolves in the range 1 to 30 g/ℓ. These results confirm the feasibility of separating BaS and CaO using their different solubilities, as suggested by Trusler[11].

CONCLUSIONS

Sulphate removal

All the barium processes ($BaCO_3$, BaS and $Ba(OH)_2$) can be used for complete removal of sulphate provided that the water is neutralized with lime. In the case of the BaS and $Ba(OH)_2$ processes, acid water can be treated directly with the barium salts without neutralization. These processes also remove ammonia, magnesium, manganese and other heavy metals as a result of the high pH that is achieved prior to CO_2 treatment. The $Ba(OH)_2$ process causes significant coprecipitation of $CaSO_4$, improving sulphate removal by 30% above the other processes.

By-products

Sulphur can be recovered from the H_2S produced in all the processes. In the BaS process, H_2S need to be stripped from the total water stream treated. In the $BaCO_3$ and $Ba(OH)_2$ processes, H_2S needs to be stripped from a concentrated BaS solution. NaHS can also be produced in all of barium processes. In the $BaCO_3$ and BaS processes, the H_2S stripped from the water with CO_2 gas, needs to be selectively absorbed into a NaOH solution. In the $Ba(OH)_2$ process, no stripping of H_2S is required and therefore, it is the most suitable process should NaHS production be of a high priority due to its high value. In the case of the BaS and $Ba(OH)_2$ processes, $CaCO_3$ of a high purity is produced in a separate stage after the $BaSO_4$ precipitation stage. The benefits of this are that a minimum $BaSO_4$ load is put on the kiln and that $CaCO_3$ with a high purity has a value of about R3 000/t.

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