

## Recovery of drinking water and by-products from gold mine effluents via alkali-barium-calcium processing

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### INTRODUCTION

Acid mine drainage results from active as well as decommissioned mines in the gold mining and coal mining fields. This water is highly acidic, containing sulphate, iron, aluminium, heavy metals and some radioactivity. When discharged into the environment in untreated form, the damage to human and animal health can hardly be repaired. Moreover, this water represents a loss of potentially valuable water that could be used in the water stressed South African interior.

The CSIR chemical desalination process was designed to neutralise acid mine drainage (AMD) and to recover metals and sulphate. The water treatment is integrated with a thermal sludge treatment process to recover alkali, barium and calcium from the chemical sludge. Ideally, the only reagents entering this integrated process would be AMD, coal and heat, while export products are drinking water, metal sulphides and -oxides, magnesium oxide, H<sub>2</sub>S and CO<sub>2</sub>. The H<sub>2</sub>S is concentrated and available for further processing to elemental sulphur or sulphuric

acid. The only inevitable waste products are CO<sub>2</sub> and a small fraction of the metal sludge that include heavy metals and radioactivity.

Various options were investigated: Precipitated CaCO<sub>3</sub>, a by-product from the paper industry, can be used for neutralisation of free acid followed by iron(II)-oxidation to remove Fe(OH)<sub>3</sub>. Alternatively, Ca(OH)<sub>2</sub> recovered from the thermal sludge processing can be used to remove Fe(OH)<sub>2</sub>. CaS, also recovered during sludge processing, can also be used for metal removal and further neutralisation. Alternatively, metal hydroxides are removed through further dosing of Ca(OH)<sub>2</sub> at high pH.

Either BaS or BaCO<sub>3</sub> can be used for sulphate removal (Maree *et al.*, 2004; Hlabela *et al.*, 2007). BaCO<sub>3</sub> was selected as it does not require H<sub>2</sub>S stripping from the main water stream, but from a concentrated stream in the sludge processing stage. The complete alkali-barium-calcium process consist the following reactions:

- Pre-treatment using CaCO<sub>3</sub>, or lime, for neutralisation of the free acid and precipitation of iron(III) and aluminium(III), and CaS for precipitation of the heavy metals as sulphides
 

$\text{H}_2\text{SO}_4 + \text{CaCO}_3$	□	$\text{CaSO}_4 + \text{CO}_2 + \text{H}_2\text{O}$	(1)
$\text{H}_2\text{SO}_4 + \text{Ca}(\text{OH})_2$	□	$\text{CaSO}_4 + 2\text{H}_2\text{O}$	(2)
$2\text{M}^{3+} + 3\text{CaCO}_3 + 3\text{H}_2\text{O}$	□	$2\text{M}(\text{OH})_3 + 3\text{CO}_2 + 3\text{Ca}^{2+}$ (M = FeIII, Al)	(3)
$\text{M}^{2+} + \text{H}_2\text{S}$	□	$\text{MS} + 2\text{H}^+$ (M = FeII, Mn, Ni, Co)	(4)
- Lime treatment for magnesium removal and partial sulphate removal through gypsum crystallisation,
 

$\text{Mg}^{2+} + \text{Ca}(\text{OH})_2$	□	$\text{Mg}(\text{OH})_2 + \text{Ca}^{2+}$	(5)
$\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	□	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	(6)

An alternative is to use pure (external) lime to recover a clean magnesium hydroxide downstream of the barium stage.

- pH adjustment
 

$\text{Ca}(\text{OH})_2 + \text{CO}_2$	□	$\text{CaCO}_3 + \text{H}_2\text{O}$	(7)
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- Removal of sulphate as BaSO<sub>4</sub>

$\text{Ca}^{2+} + \text{SO}_4^{2-} + \text{BaCO}_3$	□	$\text{BaSO}_4(\text{s}) + \text{CaCO}_3(\text{s})$	(8)
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An important part of the work to develop this process is the recovery of BaCO<sub>3</sub>, to be used again in the water treatment process from the

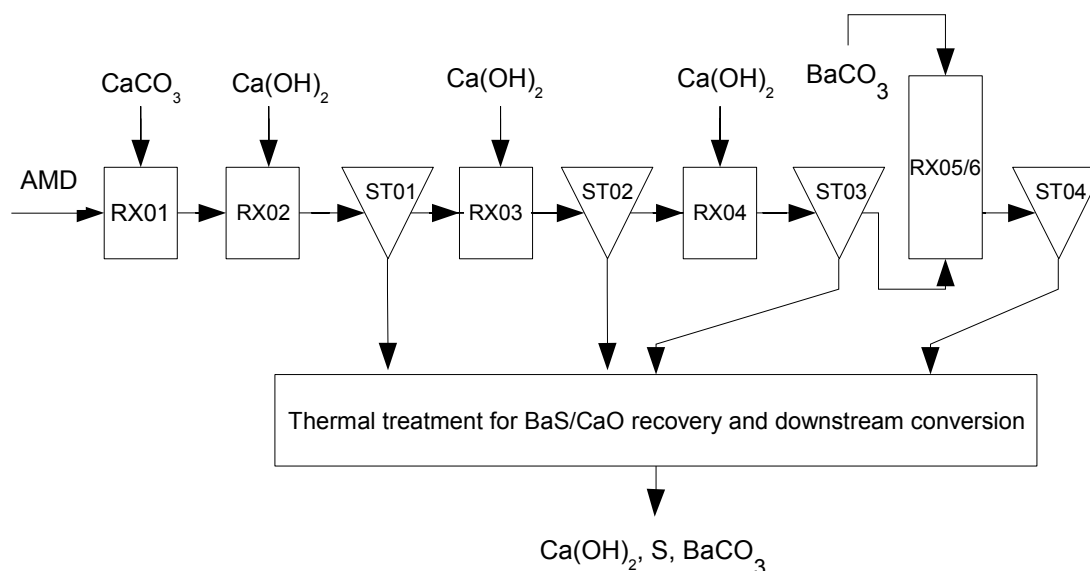
BaSO<sub>4</sub>. This article, however, only focuses on the production of a premium water quality.

## MATERIALS AND METHODS

### Feedstock

Acid mine water was pumped directly from a gold mining shaft. The water contained from

1800 to 4 600 mg/l sulphate and was fed continuously to a pilot plant with a capacity of 1 m<sup>3</sup>/h, which was run for 24h/d, 7 days/week.



**Figure 1. Block flow diagram for the CSIR chemical desalination process.**

### Equipment

A pilot plant was constructed for treatment of the water, according to the flow diagram in figure 1. Pre-treatment with CaCO<sub>3</sub>, or lime for removal of free acid and metals, lime treatment for removal of magnesium and partial removal of sulphate, and sulphate removal with BaCO<sub>3</sub> were studied by dosing combinations CaCO<sub>3</sub>, lime, and BaCO<sub>3</sub> to the plant. BaCO<sub>3</sub> was dosed in excess of stoichiometric requirements into a fluidised bed reactor, and fed with pretreated AMD until the BaCO<sub>3</sub> was completely depleted, after which the produced sludge was removed, and a fresh batch of BaCO<sub>3</sub> dosed. Sludges (metal hydroxides, gypsum/Mg(OH)<sub>2</sub> and BaSO<sub>4</sub>/CaCO<sub>3</sub>) were collected and treated in batch operation for dewatering, drying and reduction in a kiln.

### Analytical procedure

Water samples were collected at various stages in the treatment process and filtered through Whatman No 1 filter paper for sulphate, alkalinity, calcium, and Fe (II) analysis. Suspended solids (SS), acidity, and pH determinations were carried out using standard procedures (APHA, 1989). Acidity was determined by titration to pH 8.3 using a 0.1 N NaOH solution. Metals were determined with a model SpectraAA 220FS atomic absorption spectrometer (Varian Techtron Pty. LTD Springvale, Austria); linked to an auto sampler

(Varian SPS 5, sample preparation system) as well as to a computer Mecer (Photo 2). The AAS was equipped with Ca, Co, Fe, Mg, Mn and Ni hollow cathode lamps (Varian cathode lamps and photron cathode lamps) was employed for the measurement of the absorbance. The spectral slit widths of 0.5, 0.5, 0.2, 1.0, 0.2 and 0.2nm were used to isolate the 422.7, 304.4, 386.0, 202.6, 403.1 and 341.5 nm resonance lines for Ca, Co, Fe, Mg, Mn and Ni respectively.

## RESULTS AND DISCUSSION

### Water quality

Table 1 shows the chemical composition of the water of the feed and treated. Overall the total dissolved solids (TDS) content was reduced from 2 641 mg/l in the feed water to 360 mg/l in the treated water. During CaCO<sub>3</sub> treatment free acid of 370 mg/l was removed as indicated by the increase in the pH from 3.3 to 5.8. Iron(III) and aluminium(III) were removed to concentrations below 1 mg/l. During pre-treatment, with Ca(OH)<sub>2</sub> dosing, bivalent metals Fe, Ni and Co, were removed to concentrations less than 0.5 mg/l. Mn was removed to less than 4 mg/l. During further lime treatment, magnesium concentration was lowered from 145 to 1 mg/l and sulphate concentration was lowered from 1 910 mg/l (as SO<sub>4</sub>) to between 1 600 and 1 900 mg/l. Mn was also removed to less than 1 mg/l during the lime treatment stage.

During  $\text{BaCO}_3/\text{CO}_2$  treatment the pH was adjusted from 11.5 to 8.4.  $\text{Ca}^{2+}$  concentration was reduced from 75 mg/l due to  $\text{CaCO}_3$ -precipitation. During  $\text{BaCO}_3$  treatment, the sulphate concentration was reduced from 1 600 to around 10 mg/l. The concentrations to which

sulphate and metals are removed is governed by the solubility products of the various compounds. Similar good removal was achieved when water with a sulphate concentration of 4 510 mg/l was treated.

**Table 1. Chemical composition of feed and treated water for both low and high concentration acid mine drainage**

Parameter	Feed (mg/l)	Treated (mg/l)	Feed (mg/l)	Treated (mg/l)	Recommended
pH	3.3	7.9	3.1	7.5	
Sulphate	1910	90	4510	250	500
Chloride	44.5	49.5	37	37	200
Fluoride	8.4	0.07			
Free acidity (as $\text{CaCO}_3$ )	370	0	500	0	
Total acidity (as $\text{CaCO}_3$ )	714	0.59			
Alkalinity (as $\text{CaCO}_3$ )	0	140			
Sodium	46.5	53	96	95	150
Potassium	4.4	4.8	3	4	
Magnesium	124.6	1	113	2	
Calcium	157	75	559	30	
Silica	11	0.45	36	6	
Manganese	63.7	0.09	174	1	1
Iron(II)	228	0.03	1100	0	1
Iron(III)	2	0.00	200	0	0
Aluminium	3	0.01	6	0	1
Zinc	3.2	0.06	11	0	0.05
Nickel	5.6	0.01	18	0	0.01
Cobalt	2.1	0.02	7	0	0.01
Chromium	0.26	0.00			
Nitrate (as N)	0.41	0.46			
Ammonium (as N)	0.76	0.64			
Barium	0.2	0.5			
Uranium	0.465	0.020			
Copper	21.0	0.02			
Lead	0.03	0.01			
Total dissolved solids	2641	360			

Water with high concentrations of sodium, potassium and chloride can be treated via conventional reverse osmosis following the chemical desalination as pretreatment to remove all scale forming substances, such as metals, calcium and sulphate.

#### **Sulphate removal as gypsum**

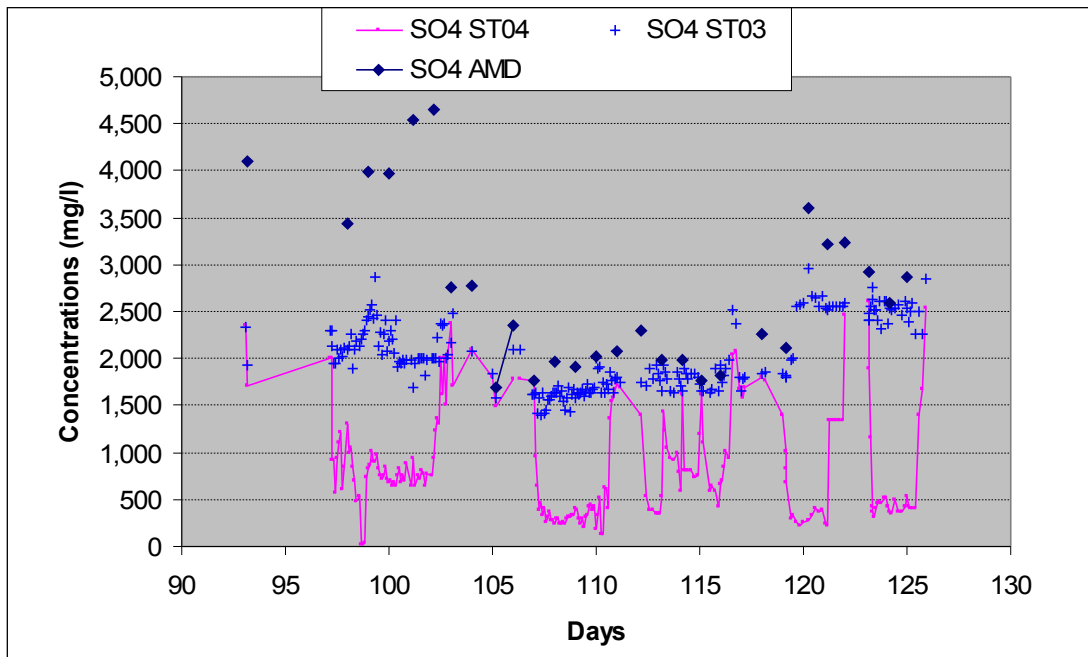
Sulphate was removed as  $\text{CaSO}_4$  in pre-treatment stages and as  $\text{BaSO}_4$  in final treatment. Whereas gypsum is normally soluble

below  $1500\text{mgSO}_4/\text{l}$ , this concentration is increased by counter-ions, e.g.  $\text{Mg}^{2+}$  and  $\text{Na}^{2+}$  in solution. The kinetics of gypsum precipitation also plays an important role in sulphate removal via gypsum. However,  $\text{BaSO}_4$  is very insoluble, and allows complete sulphate removal.

Where sulphate is of low concentration (say 1600 to 2000 mg/l) in the AMD, very little gypsum would be removed in the primary treatment stages. This could be further optimised

to prevent as far as possible any gypsum formation, e.g. through not maintaining a sludge underflow from clarifier back to reactors. At low concentrations, some gypsum is still formed at a long hydraulic retention time (RX04 = 4 - 5 hours) to the thermodynamic equilibrium concentration. The exact quantification of gypsum prevention must be further evaluated for this specific water. It should be possible to minimise the formation of gypsum in the neutralisation and metal removal stages still further. The period from day 120 – 125 (Figure 4) shows that increases in sulphate concentration was largely following increases in

the AMD sulphate concentration, suggesting that the reactors removed a mass per time unit, and not to equilibrium conditions, which is a function of active precipitation sites, which occurred after the reactors had been running with a low sulphate concentration AMD. This shows that the removal of sulphate as gypsum is not only a function of the thermodynamic equilibrium, but that sludge conditioning and rate of precipitation are important aspects that could be used to either inhibit or stimulate the precipitation of gypsum.



**Figure 2: Sulphate removal through various stages with low concentration AMD.**

The slow reactions that govern the sizes of the main reaction vessels are gypsum crystallisation (Reaction 5),  $\text{CaCO}_3$  crystallisation (Reaction 7) and dissolution of  $\text{BaCO}_3$  (Reaction 8). The rate of sulphate removal by gypsum crystallisation may be predicted by Equation 9 (Maree *et al.*, 2004).

$$d[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]/dt = k[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}](S)[C - C_0] \quad (9)$$

where  $d[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}]/dt$  represents the rate of crystallisation,  $k$  the reaction rate constant,  $[\text{CaSO}_4 \cdot 2\text{H}_2\text{O}](S)$  the surface area of the seed crystals,  $C$  the initial concentration of calcium sulphate in solution and  $C_0$  the saturated concentration of calcium sulphate in solution. The higher the gypsum concentration in solution, the higher is the rate of gypsum crystallization. This motivates for the introduction of sludge recirculation during the lime dosing stage if gypsum removal is required, or no sludge

recirculation if sulphate is required to stay in solution.

During  $\text{CO}_2$  addition for pH adjustment,  $\text{CaCO}_3$  crystallization occurred, as indicated by the decrease in the calcium concentration. According to Loewenthal and Marais (1986), the saturation, under-saturation and super-saturation states of  $\text{CaCO}_3$  are theoretically identified by the activity product of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  species that compares with the solubility product constant,  $k_{sp}$ , for  $\text{CaCO}_3$ . Above the solubility product,  $\text{CaCO}_3$  will precipitate from solution and below,  $\text{CaCO}_3$  will dissolve. The rate of precipitation or dissolution is described by the following equation:

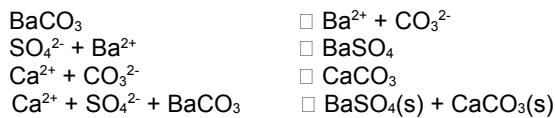
$$-d[\text{Ca}^{2+}]/dt = kS\{(\text{Ca}^{2+})^{1/2}(\text{CO}_3^{2-})^{1/2} - k_{sp}^{1/2}\}^2 \quad (10)$$

where  $k$  is the precipitation rate constant,  $S$  the surface area of  $\text{CaCO}_3$  growth/dissolution sites

and (Loewenthal and Marais, 1986) the activity in mol/l. The rate of precipitation depends on  $k$ ,  $S$  and the term within curly brackets. Although  $k$  is affected to an unknown extent by crystal structure,  $S$  is dependent on the size, mass and structure of the crystals. By controlling  $S$  and the degree of super-saturation, the rate of precipitation or dissolution of  $\text{CaCO}_3$  can be determined.

### BaCO<sub>3</sub>-treatment stage

Reaction (8), the removal of sulphate with  $\text{BaCO}_3$ , is the result of the following sequence of reactions:



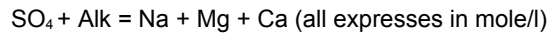
The low solubility of  $\text{BaCO}_3$  allows a low concentration of free  $\text{Ba}^{2+}$  ions in solution to react with  $\text{SO}_4^{2-}$ . Reaction (8) can only continue to produce  $\text{Ba}^{2+}$  if the  $\text{CO}_3^{2-}$  that is produced, is removed from solution through  $\text{CaCO}_3$ . Previous laboratory studies showed that the rate of sulphate removal increased with increased  $\text{BaCO}_3$  concentration. The reaction order was determined by plotting the log of the reaction rates of sulphate removal against the log of different  $\text{BaCO}_3$  concentrations and was found to be first order.

The solubility of  $\text{BaCO}_3$ , like  $\text{CaCO}_3$ , decreases with increasing pH values. Therefore it is expected that the rate of sulphate removal will be slower at higher pH levels, due to lower  $\text{Ba}^{2+}$  concentrations in solution.

The rate of  $\text{CaCO}_3$  precipitation (Reaction 7) governs the rate of  $\text{BaSO}_4$  precipitation (Reaction 8).  $\text{BaCO}_3$  can only dissolve as fast as  $\text{Ca}^{2+}$  is removed from solution through  $\text{CaCO}_3$ -crystallisation. The rate of sulphate removal with  $\text{BaCO}_3$  is related to the  $\text{CaCO}_3$ -concentration.

The higher the  $\text{CaCO}_3$  crystal concentration, the faster is the rate of sulphate removal. A fluidised-bed reactor will provide a high  $\text{CaCO}_3$  crystal concentration.

$\text{CaCO}_3$  has a low solubility at slightly alkaline pH (8.3 and higher).  $\text{Ca}(\text{OH})_2$  has a solubility of 1100 mg/l and will result in a pH up to 13. After treatment the main components in wastewater would be:



One may accept that this ion balance would determine the effluent quality and that calcium plays an important role with magnesium, because sodium is near constant and not removed at any stage. High sulphate would keep calcium in concentration, even at ideal pH (8.3) for  $\text{CaCO}_3$  precipitation. Inversely, high calcium, due to high pH, could to some extent even prevent the removal of sulphate via  $\text{BaSO}_4$ .

During lime treatment sulphate was reduced from 1 800 to 1 500 mg/l due to gypsum crystallisation. Magnesium was also removed due to  $\text{Mg}(\text{OH})_2$  precipitation.

By by-passing sulphate-rich water from ST03 to ST04, residual barium after the column reactor was removed to 0.5 mg/l (as Ba).

The relation between sulphate from the barium treatment process overflow, and that of the final effluent (from ST04) after blending the column overflow with a bypass stream from the pre-treatment are shown in figures 3, 4, 5 and 6. Where the barium process operates to specification, the effluent concentration fluctuates with the influence of sulphate fluctuations in the pre-treatment (and raw water quality). Lower bypass rates would prevent such fluctuation. Where the barium treatment process fails, the effluent sulphate is a direct result of this.

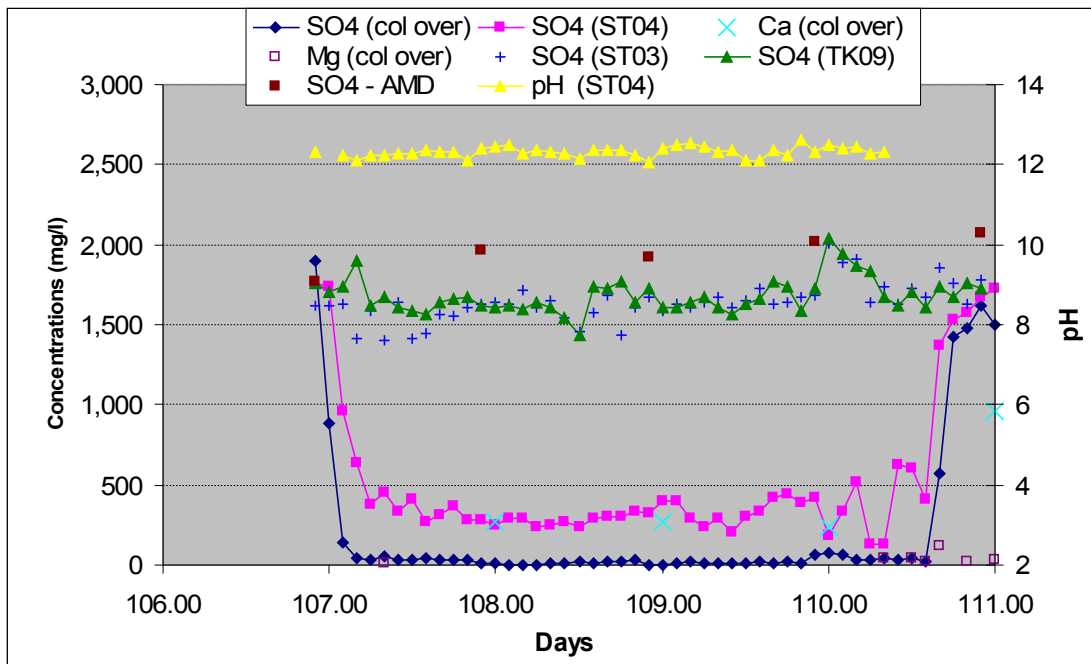


Figure 3: Barium batch process results – sulphate removal.

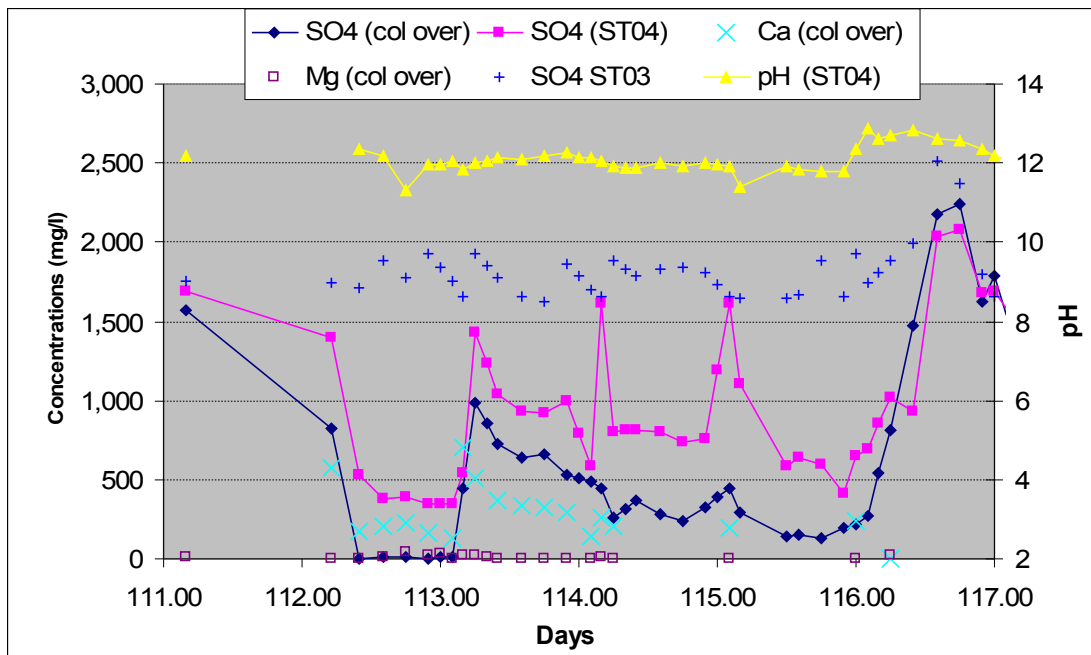
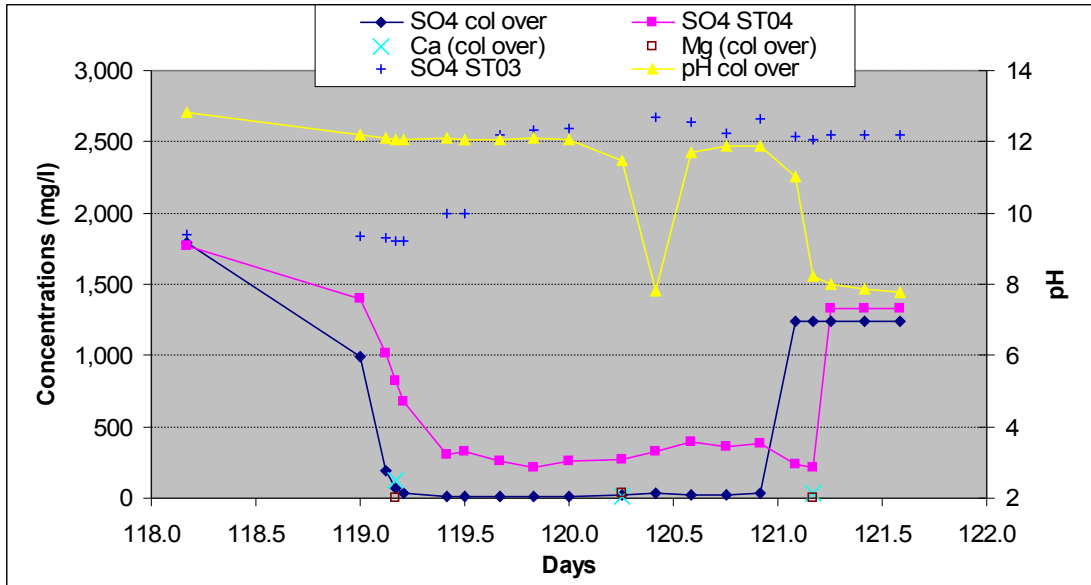


Figure 4: Barium batch process – poor calcium and sulphate removal trends at sustained high pH.

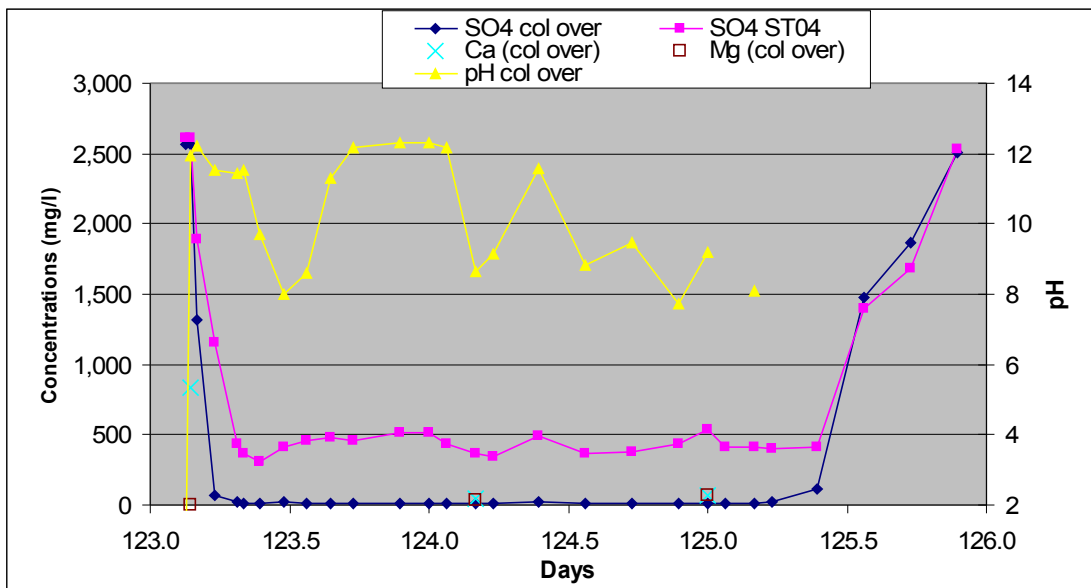
The failure of the barium treatment process (Figure 4, after day 113) could be ascribed to the high concentrations of calcium. This trend between sulphate from the column overflow and a high calcium concentration is most evident in Figure 4. The high calcium concentrations in turn result from the upstream dosing (magnesium

removal) and non-removal of calcium due to sustained high pH in the column reactor.

A much improved process performance is seen in figure 5, where pH was controlled somewhat.



**Figure 5: Improved pH control for stable sulphate and calcium removal (effluent sulphate from ST04 much lower than specification).**



**Figure 6: Improved pH control for stable sulphate and calcium removal (effluent sulphate controlled to specification through increased flow rate).**

An excess  $\text{BaCO}_3$  dosed resulted in near complete sulphate removal. Due to the large excess of  $\text{BaCO}_3$  in contact with the sulphate water, sulphate is immediately removed to 0 mg/l sulphate. The large initial excess of  $\text{BaCO}_3$  results in a low fraction of  $\text{BaCO}_3$  that is not utilised. Excess  $\text{BaCO}_3$  that is collected together with the product,  $\text{BaSO}_4$  and  $\text{CaCO}_3$ , does not need to be exposed to high sulphate water, e.g. In counter current stream, to utilise the unused  $\text{BaCO}_3$ . The sulphate removal process was improved with the aim to increase the rate of sulphate removal with  $\text{BaCO}_3$ . This was done by

dosing  $\text{CO}_2$  together or before  $\text{BaCO}_3$  addition instead of after it.

The preferred option at full scale must always be to run the barium treatment process at pH 8.3 as it also allows for Ca removal as  $\text{CaCO}_3$ . This is shown by the difference in performance between figures 3, 4, 5 and 6. Removal of all magnesium upstream of the barium stage improves and stabilises sulphate removal. However, the removal of magnesium increases the calcium concentration, which has to be removed. Where this is not the case due to high pH, the high calcium concentration associates with sulphate

in solution, leading to poor sulphate removal even in the BaCO<sub>3</sub> process. With low calcium and magnesium, the sulphate effluent from the barium treatment process is near zero.

BaCO<sub>3</sub>/BaSO<sub>4</sub> in the expanded bed entered the settling zone on top of the column (RX05, RX06) depending on the initial loading rate. The barium sludge settled out in the cone but formed a sludge blanket of increasing thickness towards the outer peripheral. This barium sludge did not

fully participate in the reaction. Table 4 summarises various barium treatment batches and utilisation efficiencies. The deviation in utilisation efficiency is due to:

- Suspended solids in the barium column reactor overflow (refer fig 13)
- Finite sample analysis of dynamic system
- Inaccuracies in measurement of flow rates and sulphate.

Table 4. Barium carbonate utilisation efficiency

	Period	BaCO <sub>3</sub> utilisation, based on SO <sub>4</sub> <sup>2-</sup> removal	Comments
	Day 66 – 69	103%	First experiments during semi-continuous dosing
	Day 93 – 97	Not determined	First batch experiment
	Day 97 – 106	62%	Overflow occurred, due to high solids loading
Figure 3	Day 106 – 110	78%	High pH
Figure 4	Day 112 – 118	69%	High pH, Ca <sup>2+</sup>
Figure 5	Day 119 – 121	86%	High pH
Figure 6	Day 123 – 126	114%	pH stabilisation. Sensitive to small flow rate variations.

Figure 7 shows that the sulphate removal stops abruptly when BaCO<sub>3</sub> is fully utilised. The upward slope at the end of the barium carbonate batch is not a slow removal rate, but due to the treated water buffering the concentration increase effect of incoming high sulphate water (i.e. solely a dilution/concentration effect). This is an important finding for the operating philosophy of full scale plants: once sulphate starts increasing, the BaCO<sub>3</sub> is fully utilised.

Figure 7 also shows good correspondence between the theoretical solids load (based on

sulphate removal) and the suspended solids concentration as measured at different depths in the column. Stabilisation of pH upstream of the barium treatment process also prevents anomalies in final effluent concentration, such as high concentrations of calcium and metals. The effluent sulphate concentration to meet SANS 241 class II is < 600 mg/l. The sulphate can be adjusted upward through higher bypass ratios around the barium treatment process, without fear of discharging high concentrations of either calcium or other metals to the final effluent.



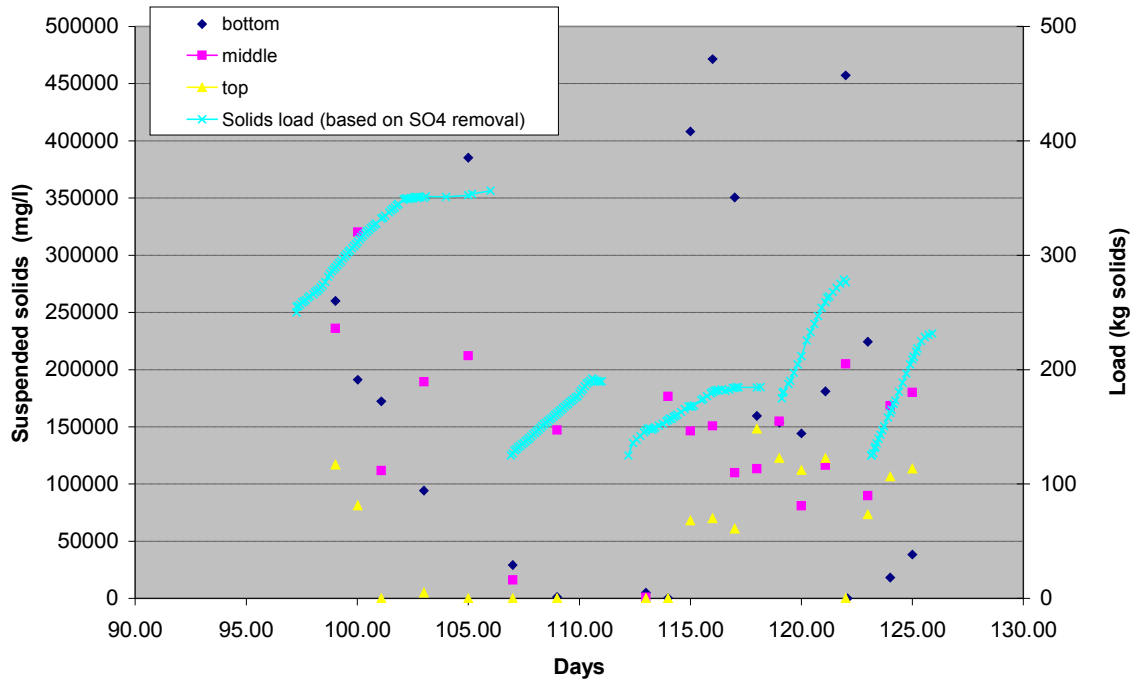


Figure 7. Solids concentration at different levels in the barium column reactor, compared with the removal of  $\text{BaSO}_4/\text{CaCO}_3$  concentrations. Solids were measured at depth. The sulphate removal was used to calculate the concentration of  $\text{BaSO}_4/\text{CaCO}_3$ .

## CONCLUSIONS AND OUTLOOK

The following conclusions were made from this study:

- The CSIR Chemical (Alkali-barium-calcium) desalination process can be used for neutralisation of AMD and lowering of the total dissolved solids content from 7 600 mg/l to 400 mg/l.
- Metals can be removed effectively through precipitation with lime.
- The rate of sulphate removal during gypsum crystallisation is influenced by the gypsum seed crystal concentration, as well as the concentration of counter ions.
- The rate of sulphate removal during  $\text{BaCO}_3$  treatment is influenced by pH,  $\text{CaCO}_3$  solids and  $\text{BaCO}_3$  solids concentrations.
- $\text{BaCO}_3$  reactor design should be further optimised to
  - Prevent carry over of fine particles in order to maximise  $\text{BaCO}_3$  recovery
  - Maintaining sludge batches separate to a specific reactor operating in parallel to get maximum  $\text{BaCO}_3$  utilisation.

It is believed that  $\text{BaCO}_3$  starts as large particles, dissolving gradually in contact with sulphate while  $\text{BaSO}_4$ -particles start as fines

and could potentially grow in to crystals. Fines tend to escape the column set-up.

- The internalisation of most of the sludge lessens the environmental impact of the treatment process. Separation of the different metal sludges seems technically possible, but not yet economical. The ideal of an industrial ecology, where no wastes remain and all possible value is extracted from wastewater, seems to remain, in the current socio-political environment, still mostly an ideal.

Future work will focus on the thermal reduction of  $\text{BaSO}_4/\text{CaCO}_3$  to produce  $\text{BaS}$  and  $\text{CaO}$ . The downstream processing of this product should be integrated with the barium stage reactor design in the water treatment plant. If a fine  $\text{BaCO}_3$  precipitant is formed that could react quick enough with the sulphate in solution, a plug flow reactor with clarifier may be considered. If however, the  $\text{BaCO}_3$  production can be optimised to form larger granules, then a fluidised bed reactor may be most effective in the barium stage.

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