

Application of magnesium hydroxide and barium hydroxide for the removal of metals and sulphate from mine water

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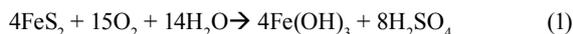
Abstract

The proposed magnesium-barium-oxide process consists of metal removal with $Mg(OH)_2$, magnesium and sulphate removal with $Ba(OH)_2$ and calcium removal with CO_2 . The raw materials, $Mg(OH)_2$ and $Ba(OH)_2$ are recovered from the $BaSO_4$ and $Mg(OH)_2$ sludges that are produced. Laboratory studies showed that metals are removed to low levels. This includes iron(II), the dominant metal ion in mine water, which is first oxidised to iron(III), whereafter it precipitates as $Fe(OH)_3$ resulting in residual levels of Fe(II) in the mine water of less than 20 mg/l. Sulphate is also removed to less than 25 mg/l. The final sulphate concentration is a function of the amount of $Ba(OH)_2$ dosed, as the amount of sulphate removed is stoichiometrically equivalent to the $Ba(OH)_2$ dosage. During CO_2 -dosing, $CaCO_3$ is precipitated to the saturation level of $CaCO_3$.

Keywords: Magnesium hydroxide; barium hydroxide; sulphate removal; water treatment

Introduction

Mining is a significant contributor to water pollution owing primarily to pyrite oxidation that generates potentially high levels of acidity, metal ions (mainly Fe), and sulphate (Reaction (1)) (Barbes and Romberger, 1968):



South Africa's Witwatersrand Basin produces 340 Ml/d of mine-water, of which 50 Ml/d is produced by the Western Basin. Most of the underground mining operations in the Western Basin were closed by 1990. By 2004 the underground voids were filled by rising water levels and acid water started to decant at the surface. Contaminated void spaces increase with time and result in: (a) less water suitable for irrigation of crops, (b) less potable water available for the growing local communities, (c) the natural drying up of rivers, and (d) stream bed losses. The water of mining origin in the Western Basin contains, on average, 4 800 mg/l sulphate, 800 mg/l Fe(II), 100 mg/l Fe(III), 230 mg/l Mn, 11 mg/l Zn, 18 mg/l Ni, 5 mg/l Co, 6 mg/l Al, 150 mg/l Mg, some radioactivity and 700 mg/l free acidity (as $CaCO_3$). This acid mine drainage (AMD) source creates a major concern in that the Cradle of Humankind, a World Heritage Site, is not far from the decant point. As of March 2010, AMD started decanting into the Krugersdorp Nature Reserve at a rate of between 10 and 60 Ml/day, with the possibility of reaching the Sterkfontein Cave System which includes the Cradle of Humankind, where the earliest known hominid fossil remains were discovered and where paleontological excavations continue (Zvinowanda et al., 2010).

It is essential that a technically sound and cost-effective solution be found for the acid mine-water problem. South Africa is water-constrained and also has a mature mining economy

with numerous mines having closed or in the process of being decommissioned. Should a solution be found that generates income, the AMD problem could be solved via economic principles rather than through government intervention by means of policies and legislated control measures.

Several processes have been considered for sulphate removal, e.g. biological removal, *SAVMIN* (ettringite) (Ramsay, 1998), *ecoDose*, reverse osmosis (Chamber of Mines Research Organisation, 1988), and electro dialysis (Pulles et al., 1996). Soluble barium salts can also be used for sulphate removal and have certain advantages in that sulphate can be removed to specific levels owing to the low solubility of barium sulphate (Volman, 1984; Maree et al., 1989; Adlem et al., 1991). Soluble barium salts, such as barium sulphide, barium chloride and barium hydroxide, are potential candidates for the treatment regime and can be regenerated at the end of the process.

Kun (1972) studied the removal of sulphate with barium carbonate ($BaCO_3$). He identified 3 problems: a long retention time is required; high concentrations of soluble barium remain in the treated water when excess $BaCO_3$ is dosed over the required stoichiometric amount; and, the high cost of $BaCO_3$. Volman (1984) and Maree et al. (1989) overcame the cost problem by demonstrating that barium sulphate ($BaSO_4$) could be reduced efficiently and economically with coal under thermal conditions to produce barium sulphide (BaS). This compound can be used directly for the process or first converted to $BaCO_3$. Wilsenach (1986) demonstrated the economic viability of the process by calculating the cost of producing BaS from $BaSO_4$.

Trusler et al. (1988) developed an integrated process which includes the recovery of $BaCO_3$ and lime. They noted that incomplete sulphate removal with $BaCO_3$ resulted when sulphate is not completely associated with calcium ions. They overcame this problem by dosing lime for pre-removal of magnesium as $Mg(OH)_2$. Maree et al. (1989) have developed a barium carbonate process (a 2-stage, fluidised-bed reactor system) to overcome the other problems identified by Kun (1972), i.e., the long retention time and the high barium concentration in the treated water. A disadvantage of the barium carbonate process, proposed by Trusler (1988) and improved by Maree et al. (1989), is the formation of a mixed precipitate of $BaSO_4$ and $CaCO_3$. Bosman

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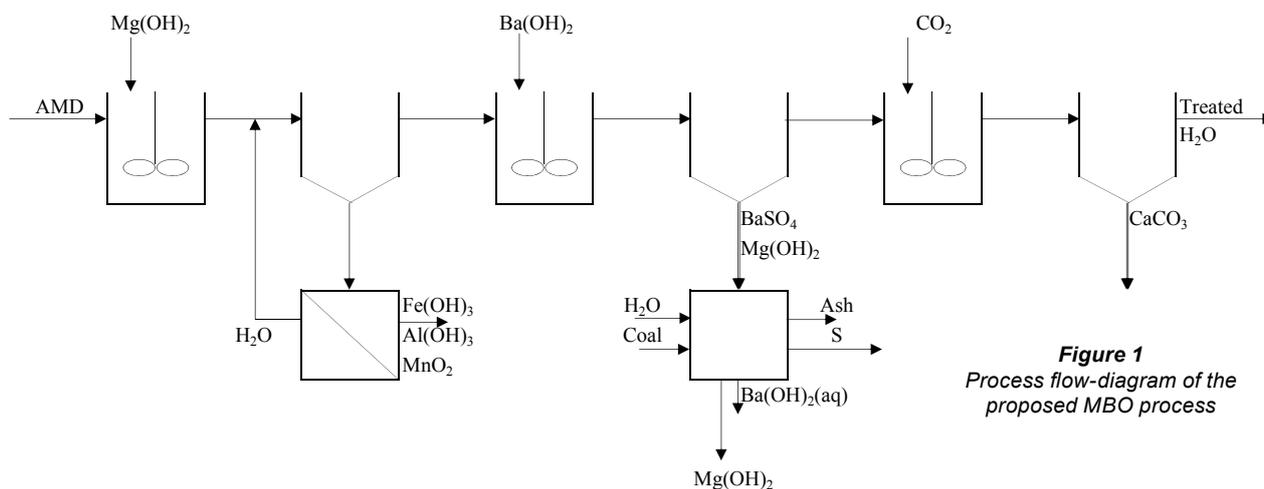


Figure 1
Process flow-diagram of the proposed MBO process

et al. (1990) and Adlem et al. (1991) overcame this problem by pre-treating the AMD with lime to remove metals before the addition of barium sulphide. BaS is highly soluble in water and can therefore readily provide Ba^{2+} ions for fast interaction with SO_4^{2-} in sulphate-rich water. Maree et al. (1990) elucidated the ability of BaS to directly remove sulphate from acid waters. Other studies have demonstrated that BaS has an advantage of producing by-products like sulphur and NaHS, which can potentially be derived from the H_2S produced during the H_2S stripping stage, and CaCO_3 from the softening stage (Maree et al., 1989; Bosman et al., 1990; Adlem et al., 1991; Du Preez and Maree, 1994). Laboratory studies were carried out by Maree et al. (2004) to demonstrate that the integrated BaS process is technically and economically viable for sulphate removal. This process consists of 4 stages. In the **thermal stage**, BaSO_4 is reduced to BaS at 1 050°C, in a kiln using coal as the reductant. In the **sulphate removal stage**, sulphate is precipitated as BaSO_4 . In the **stripping stage**, the barium sulphide is dissolved in water and reacted with CO_2 from the kiln to remove or strip off the H_2S gas. In the **softening stage**, CaCO_3 is precipitated as a result of CO_2 -stripping with air.

Hlabela et al. (2007) demonstrated that BaCO_3 can be used effectively for sulphate removal after pre-treatment of the AMD with lime for removal of metals, including magnesium, as metal hydroxides.

The purpose of the present study was to demonstrate, using a laboratory study, the performance of an alternative, integrated magnesium hydroxide and barium hydroxide process (MBO Process) for treatment of acid mine-water. The provisionally patented process (Maree and Louw, 2010) consists of the following stages (Fig. 1):

- Magnesium hydroxide, for neutralisation and metal removal
- Barium hydroxide, for sulphate and magnesium removal
- CO_2 , for CaCO_3 precipitation
- Recovery of Ba(OH)_2 via BaS from the BaSO_4 produced

The specific aims were to demonstrate that:

- Metals can be completely removed with Mg(OH)_2
- Sulphate concentration can be lowered to less than 200 mg/l
- Magnesium concentration can be lowered to less than 10 mg/l with Ba(OH)_2
- The high pH water can be stabilised with CO_2

The processing of BaSO_4 and Mg(OH)_2 in the sludge to recover the process raw materials, Ba(OH)_2 and Mg(OH)_2 , were investigated separately.

Materials and methods

Feedstock

Waters from a coal mine and a gold mine were used as feed waters containing 2 400 – 4 800 mg/l sulphate (for chemical analyses, see Tables 1 and 2). Magnesium hydroxide and barium hydroxide were used for pH adjustment and sulphate removal, respectively. CO_2 gas (Afrox) was used for pH adjustment after sulphate removal.

The following chemicals were used in this study: Barium hydroxide ($\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$, analytical reagent, Merck) and calcium hydroxide (97% Ca(OH)_2 , Rochelle Chemicals, Johannesburg); Mg(OH)_2 (CP grade, May and Baker Ltd, Dagenham, England), air (HP compressed; Afrox, South Africa), and CO_2 (Afrox, South Africa).

Equipment

Neutralisation with Mg(OH)_2 and sulphate removal with Ba(OH)_2 were studied using stirred beakers.

Experimental procedure

Feed water was mixed in a beaker (5 l), aerated for iron(II) oxidation and stirred (30 min) for completion of the oxidation/precipitation reactions. The sludge was allowed to settle and the clear water decanted. Ba(OH)_2 was mixed with the decant water (1000 ml glass beakers). Stabilisation of the Ba(OH)_2 treated water was achieved by passing CO_2 through the water.

Experimental programme

The following parameters were investigated: metal removal with Mg(OH)_2 , magnesium and sulphate removal with Ba(OH)_2 , and calcium removal with CO_2 .

Analytical

Samples were collected regularly and filtered (Whatman No. 1). Sulphate, alkalinity, Fe(II), mixed liquor suspended solids (MSS), volatile suspended solids (VSS), acidity, and pH were determined according to standard procedures (APHA, 1989). Calcium and magnesium were assayed using atomic absorption spectrophotometry.

Parameter	Stage			
	Feed	Mg(OH) ₂	Ba(OH) ₂ ·8H ₂ O	CO ₂
Dosage (mg/l)		0.25	7.35	
Mg(OH) ₂ utilisation (mole/mole)		279.1		
Barium dosage/SO ₄ feed (mole/mole)			0.9	
Barium dosage/SO ₄ removed (mole/mole)			0.968	
pH	3.4	8.3	12.0	7.6
Sulphate (mg/l SO ₄)	2 487	2 493	181	181
Chloride (mg/l Cl)	35	37	33	31
Alkalinity (mg/l CaCO ₃)		30	1 305	180
Acidity (mg/l CaCO ₃)	200			
Sodium (mg/l Na)	71.5	87.9	101.3	101.5
Potassium (mg/l K)	30.4	36.8	36.8	27.2
Magnesium (mg/l Mg)	147.0	292.2	30.7	8.7
Calcium (mg/l Ca)	467.3	462.3	454.4	39.7
Barium (mg/l Ba)	0.04	0.04	0.90	0.80
Aluminium (mg/l Al)	20.00	1.00	2.00	1.00
Silicon (mg/l Si)	12.66	5.87	1.18	1.26
Titanium (mg/l Ti)	0.21	0.21	0.20	0.18
Chromium (mg/l Cr)	0.20	0.20	0.18	0.17
Manganese (mg/l Mn)	8.98	7.09	0.26	0.26
Iron(II) (mg/l Fe)	100.00	0.00	0.00	0.00
Iron(III) (mg/l Fe)	20.00	0.00	0.00	0.00
Cobalt (mg/l Co)	0.00	0.00	0.00	0.00
Nickel (mg/l Ni)	0.03	0.00	0.00	0.00
Copper (mg/l Cu)	0.05	0.00	0.00	0.00
Zinc (mg/l Zn)	1.12	0.00	0.00	0.00
Lead (mg/l Pb)	0.51	0.33	0.41	0.34
Total dissolved solids (mg/l)	3 406	3 434	1 286	454
Fe(OH) ₃ (mg/l)		230		
Mn(OH) ₂ (mg/l)		3.1	11	
Zn(OH) ₂ (mg/l)		2		
Ni(OH) ₂ (mg/l)		0		
Co(OH) ₂ (mg/l)		0		
Al(OH) ₃ (mg/l)		55		
BaSO ₄ (mg/l)			5 611	
Mg(OH) ₂ (mg/l)			628	
CaCO ₃ (mg/l)				1 037
Suspended solids (mg/l)	0	289	6250	1 037
Anions (-) (meq/l)	52.81	53.58	30.81	8.24
Cations (+) (meq/l)	52.56	53.23	31.04	8.16

Results and discussion

Water quality and chemical reactions

The MBO study can be applied to the treatment of acid mine-water. Tables 1 and 2 show the chemical composition of the feed waters before and after treatment with Mg(OH)₂, Ba(OH)₂ and CO₂, for effluents from coal and gold mines, respectively. The total dissolved solids (TDS) content in the case of coal mine-water was 3 406 mg/l in the feed water, 3 434 mg/l after Mg(OH)₂ treatment, 1 286 mg/l after Ba(OH)₂ treatment and 454 mg/l after CO₂ addition (Table 1). Similarly, in the case of gold mine effluent, the overall TDS content was lowered from 6 954 mg/l in the feed water to 416 mg/l, following treatment

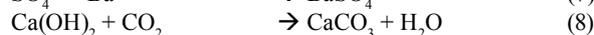
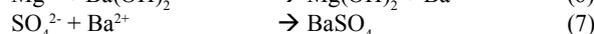
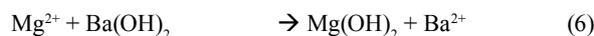
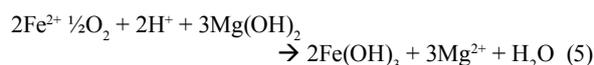
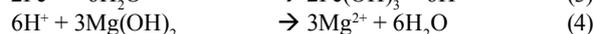
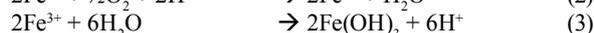
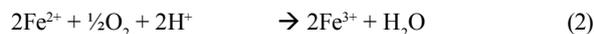
with the MBO process (Table 2). During Mg(OH)₂ treatment, free acid and all of the metal concentrations, excluding that of calcium and magnesium, were lowered to below allowable limits for drinking water in South Africa (SANS 241:2006). The lowering of the TDS in the case of Mg(OH)₂ treatment was mainly due to the oxidation of Fe²⁺ to Fe³⁺ (Reaction (2)) and precipitation as Fe(OH)₃ (Reaction (3)). Similarly, Mn²⁺ was oxidised to Mn⁴⁺ and precipitated as MnO₂. The other metals, Al³⁺, Co²⁺, Zn²⁺, Pb²⁺, Co²⁺ and Ni²⁺, precipitated as metal hydroxides. This was owing to the low solubility-products for Fe(OH)₃ (2.64 × 10⁻³⁹); Al(OH)₃ (8.5 × 10⁻²³); Mn(OH)₂ (2.06 × 10⁻¹³); Cu(OH)₂ (2.20 × 10⁻²⁰); Zn(OH)₂ (7.71 × 10⁻¹⁷); Pb(OH)₂ (1.42 × 10⁻²⁰); Co(OH)₂ (1.09 × 10⁻¹⁵) and Ni(OH)₂ (5.47 × 10⁻¹⁶) (Sillen and Martell, 1964; Lide, 1992).

Table 2
Chemical composition of feed and treated water when gold mine effluent was treated with Mg(OH)₂, Ba(OH)₂ and CO₂

Parameter	Stage			
	Feed	Mg(OH) ₂	Ba(OH) ₂ .8H ₂ O	CO ₂
Dosage (mg/l)		1.38	14.16	
Mg(OH) ₂ utilisation (mole/mole)		0.960		
Barium dosage/SO ₄ feed (mole/mole)				
Barium dosage/SO ₄ removed (mole/mole)			0.985	
pH	2.5	8.6	12.2	7.7
Sulphate (mg/l SO ₄)	4 890	4 398	24	24
Chloride (mg/l Cl)	37	37	37	37
Alkalinity (mg/l CaCO ₃)		20	1 607	369
Acidity (mg/l CaCO ₃)	500			
Sodium (mg/l Na)	186.0	189.9	182.0	168.0
Potassium (mg/l K)	39.0	18.7	5.6	7.3
Magnesium (mg/l Mg)	147.0	718.1	0.0	5.2
Calcium (mg/l Ca)	500.0	571.9	578.2	46.6
Barium (mg/l Ba)	0.00	0.00	0.2	0.00
Aluminium (mg/l Al)	10.00	1.00	2.00	1.00
Silicon (mg/l Si)	40.16	2.10	0.41	0.97
Titanium (mg/l Ti)	0.16	0.22	0.23	0.20
Chromium (mg/l Cr)	0.18	0.22	0.21	
Manganese (mg/l Mn)	116.7	33.76	0.00	0.00
Iron(II) (mg/l Fe)	920.0	0.00	0.00	0.00
Iron(III) (mg/l Fe)	20.00	0.00	0.00	0.00
Cobalt (mg/l Co)	11.20	0.12	0.00	0.00
Nickel (mg/l Ni)	18.29	0.00	0.00	0.00
Copper (mg/l Cu)	0.00	0.00	0.00	0.00
Zinc (mg/l Zn)	7.46	0.00	0.00	0.00
Lead (mg/l Pb)	0.52	0.41	0.41	0.50
Total dissolved solids (mg/l)	6 954	5 978	1 377	416
Fe(OH) ₃ (mg/l)		1 798		
Mn(OH) ₂ (mg/l)		134	55	
Zn(OH) ₂ (mg/l)		11		
Ni(OH) ₂ (mg/l)		29		
Co(OH) ₂ (mg/l)		17		
Al(OH) ₃ (mg/l)		26		
BaSO ₄ (mg/l)			10 616	
Mg(OH) ₂ (mg/l)			1 723	
CaCO ₃ (mg/l)				1 329
Suspended solids (mg/l)	0	2 016	12 394	1 329
Anions (-) (meq/l)	102.92	93.07	33.67	8.91
Cations (+) (meq/l)	102.98	98.12	37.28	10.52

The precipitated BaSO₄ and Mg(OH)₂ can be made to settle rapidly by dosing coagulants. Coagulant dosing can be avoided by controlling the precipitation process to yield particles with improved settling rates. Hlabela (2009) showed that a multiple point, in-line dosing system can produce flocs within the size range 10 - 100 µm. In the final step, the calcium concentration in the feed water was lowered from 454 mg/l down to 40 mg/l (as Ca⁺) by stabilising the water with CO₂ (Reaction (8)). During CO₂ addition for pH adjustment, CaCO₃ crystallisation occurred, as indicated by the decrease in the calcium concentration. According to Loewenthal et al. (1986), the saturation, under-saturation and super-saturation states of CaCO₃ are theoretically identified by the activity product of Ca²⁺ and CO₃²⁻ that is comparable to the solubility

product constant, k_{sp} , for CaCO₃. Above the solubility product, CaCO₃ will precipitate from solution, and below, CaCO₃ will dissolve. The rate of precipitation or dissolution is described by Eq. (9), where k is the precipitation rate-constant, S , the surface area of CaCO₃ growth/dissolution sites, and the parameters in square brackets, activities 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 (term in curly brackets), the rate of precipitation or dissolution of CaCO₃ can be determined (Loewenthal et al., 1986).



$$-d[\text{Ca}^{2+}]/dt = kS\{[\text{Ca}^{2+}]^{1/2}[\text{CO}_3^{2-}]^{1/2} - k_{sp}^{-1/2}\}^2 \quad (9)$$

where:

k = precipitation rate-constant,

S = surface area of CaCO_3 growth/dissolution sites and the terms in square brackets, activities in mol/l.

The rate of sulphate removal through BaSO_4 crystallisation is influenced by the sulphate concentration in solution and the BaSO_4 seed crystal concentration. It was observed that sulphate removal was stoichiometrically equivalent to the $\text{Ba}(\text{OH})_2$ dosage, as indicated by $[\text{Ba}^{2+} \text{ dosage}]/[\text{SO}_4 \text{ removed}]$ (mol/mol) ratios of 1.05, 0.97 and 1.02, respectively (Table 3). As expected, higher residual Ba^{2+} concentrations were in solution with lower residual SO_4^{2-} concentrations. This is due to the low solubility product of BaSO_4 and the rate of BaSO_4 crystallisation at low seed-crystal concentrations. The practical implication is that about 200 mg/l free sulphate should remain in solution to limit Ba^{2+} concentration to less than 2 mg/l in solution, the guideline value for drinking water as laid down by the USEPA (2011). Optimum conditions also need to prevail to allow rapid BaSO_4 -crystallisation, such as providing a solid BaSO_4 presence in the reactor by means of sludge recirculation.

Barium ions react with sulphate ions forming a white precipitate of BaSO_4 . Figure 2 shows an increase in the sulphate removal rate with increased barium hydroxide concentration (molar ratios of 0.8, 0.85, 0.9 and 1) in the solution. From chemical Reaction (7), 1 mole of barium reacts with 1 mole of sulphate. Therefore, it is clear that the more barium ions available in solution the more sulphate ions are removed from the solution. Sulphate removal followed normal stoichiometry. Therefore, it is sufficient to use a 1:1 mole ratio of dissolved barium to sulphate for almost complete removal of sulphate from wastewater.

The effect of BaSO_4 seeds added to AMD before the addition of $\text{Ba}(\text{OH})_2$ was investigated. The results are shown in Fig. 3. From these results it was observed that the presence of a small amount of barium sulphate seed did not have any significant effects on the removal of sulphate.

Four different experiments were carried out using increasingly rapid stirring rates. The results are shown in Fig. 4. It was also observed (Fig. 4) that the removal-rate initially increased

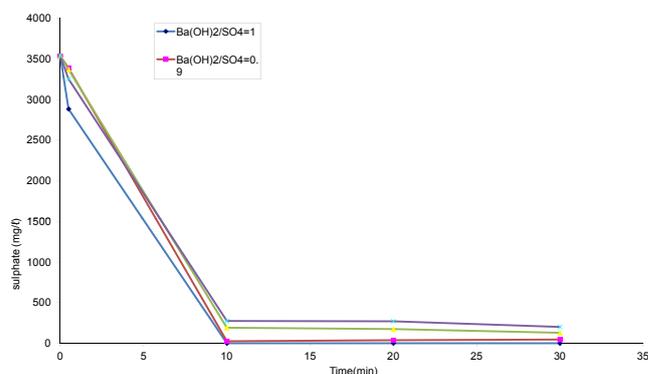


Figure 2
Effect of $\text{Ba}(\text{OH})_2/\text{SO}_4$ mole ratio on the removal rate of sulphate

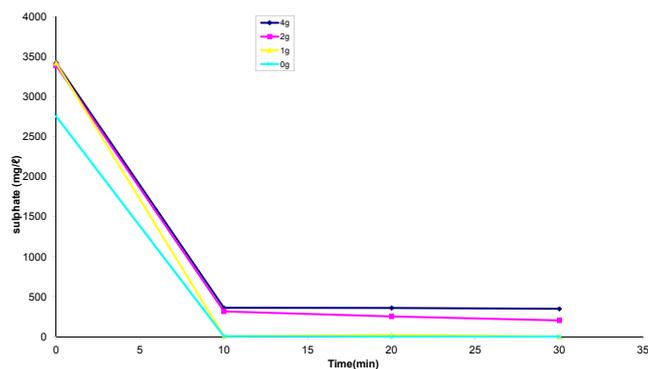


Figure 3
Effect of BaSO_4 seed crystals on the removal rate of sulphate

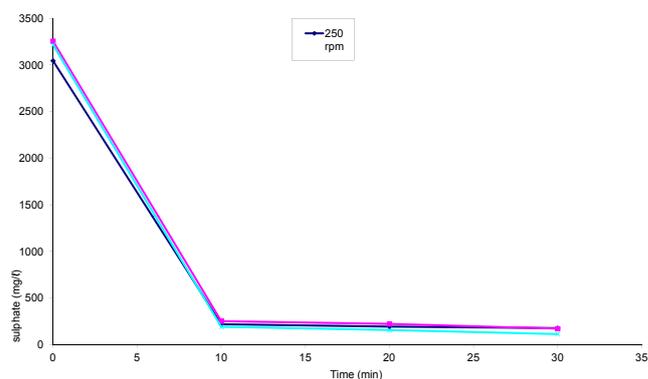


Figure 4
Effect of stirring rate on the removal rate of sulphate

linearly and subsequently flattened to become abruptly constant, showing a complete removal of sulphate. The stirring rates in the range 250-800 r/min did not show any significant differences in the removal rates of sulphates.

Table 3			
Efficiency of sulphate removal with $\text{Ba}(\text{OH})_2$			
Parameter (units as indicated)	Value of parameter		
Barium dosage/ SO_4 in feed (mol/mol)	0.80	0.90	1.00
$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ dosage (g/l)	6.55	7.35	8.17
Sulphate in feed water (mg/l)	2 600	2 493	2 493
Sulphate in treated water (mg/l)	704	181	41
Barium in treated water (mg/l)	0	0.14	85
Barium dosage/ SO_4 removed (mol/mol)	1.05	0.97	1.02

An advantage of using $Mg(OH)_2$ for neutralisation and metal removal is that the precipitated metal hydroxides are not mixed with gypsum. A sludge of higher density was produced which settles to the bottom faster. The sludge from the $Mg(OH)_2$ stage consisted of $Fe(OH)_3$, $Al(OH)_3$, MnO_2 and $Zn(OH)_2$. The 'Ba(OH)₂ sludge' consisted of 70% $BaSO_4$ and 30% $Mg(OH)_2$.

Conclusions

With the MBO study at a laboratory scale, it was demonstrated, that:

- $Mg(OH)_2$ precipitated metals as metal hydroxides. Iron(II) was first oxidised to iron(III) before being precipitated.
- $Ba(OH)_2$ precipitated sulphate as $BaSO_4$ and magnesium as $Mg(OH)_2$. Sulphate removal was stoichiometrically equivalent to the $Ba(OH)_2$ dosage.
- CO_2 precipitated calcium as $CaCO_3$.

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