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TECHNICAL ARTICLE

Using Calcium Carbonate/Hydroxide and Barium Carbonate to Remove Sulphate from Mine Water

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Abstract This study evaluated the effectiveness of using barium bicarbonate to remove sulphate from neutralized AMD. The $Ba(HCO_3)_2$ was produced by dosing a $BaCO_3$ solution with CO_2 to form $Ba(HCO_3)_2$. This greatly increased the barium ion concentration, which rapidly removed sulphate linked to either calcium or magnesium. Following sulphate removal, the $Ca(HCO_3)_2$ or $Mg(HCO_3)_2$ containing water can be stabilised by CO_2 stripping with air, which results in $CaCO_3$ precipitation. The $MgCO_3$ remains in solution.

Keywords Acid mine drainage · Sulphate removal · Water treatment · Solubility · Precipitation

Introduction

Background

As South Africa is urgently seeking for new options to overcome the threats of acidic mine water, this paper describes a process intensification of the existing CSIR-ABC-process (Maree 2008; Motaung et al. 2008). A desalination step has been added, leading to the name ABCD for this treatment option.

South Africa's mining industry is still a crucial part of the country's economy (Department of Mineral Resources 2014). Coal mining is very active in the Mpumalanga and Limpopo Provinces (McCarthy 2011), while gold mines are predominantly in the Gauteng Province. Most of the gold mines are now closed and contaminated mine water discharges from three mining pools (Coetzee 2013; Coetzee et al. 2003). Acid mine drainage (AMD) is of particular concern in South Africa, especially in the Gauteng Province's Witwatersrand region, where non-viable gold mines have been closing since the 1970s and only a few remain in operation. AMD occupies in Gauteng's Western Pool, whilst neutral and alkaline mine water in the Central and Eastern Pools arises from the natural neutralisation of AMD as it passes through dolomitic strata (Gomez et al. 2015). This acidic and circumneutral mine water typically has high concentrations of Fe, Al, Cu, Zn, Mn, and sulphate (Blowes et al. 2014; Castillo et al. 2015; Wolkersdorfer 2008).

Mine water pollution in South Africa has become a serious problem because of its impact on the environment, groundwater, and surface water. In the short term, the AMD has to be neutralized and, in the long-term, this neutralized water also has to be desalinated. Long-term solutions that have been considered in South Africa include

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the high density sludge (HDS) process followed by reverse osmosis (RO), ion exchange, biological processes such as the Biosure process, precipitation technologies such as the CSIR alkali-barium-calcium (CSIR-ABC) process, the magnesium-barium-hydroxide (MBO) process, the ettringite process (Expert Team of the Inter Ministerial Committee 2010), and hydrotalcite precipitation (Douglas 2014; Gusek and Figuera 2009; Kamal et al. 2014; Mullett et al. 2014; Vasquez et al. 2016).

Full-scale membrane processes are already being used in South Africa to desalinate mine water. Negative aspects associated with membrane processes include membrane scaling and high operational costs. This paper describes an additional mine water treatment method: a barium process, where scaling problems are excluded and the operational costs of desalination can be reduced if the product $BaSO_4$ can be converted back to the raw material, $BaCO_3$.

Barium Salts for Sulphate Removal

Sulphate removal with barium salts has been studied by various authors (Fig. 1). Kun (1972) was the first author to propose the use of barium salts for sulphate removal. He successfully used $BaCO_3$ (witherite), taking advantage of the low solubility of $BaSO_4$. However, the $BaCO_3$ raw material was expensive and the $BaSO_4$ sludge that was produced had to be discarded or used elsewhere. Volman (1984) overcame these drawbacks by converting the $BaSO_4$ to materials such as BaS or $BaCO_3$ that could also be used for sulphate removal. The BaS was produced by thermal reduction of $BaSO_4$ with coal at 1050 °C. His process configuration also made provision for stripping H_2S from the BaS containing water and processing it to elemental sulphur by contacting the stripped H_2S with Fe^{3+} in an acidic medium.

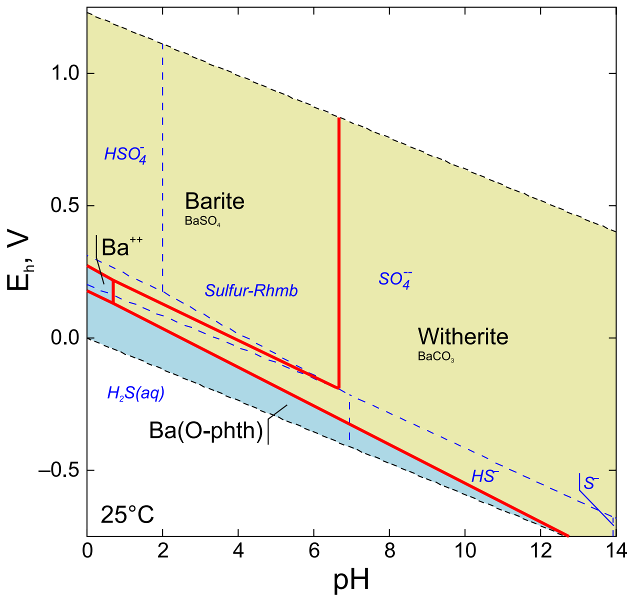

Fig. 1 Pourbaix ('stability')-diagram for Ba-S-C; $p = 1.013$ bar, $\{Ba^{2+}\} = 10^{-2}$ mol, $\{SO_4^{2-}\} = 10^{2}$ mol, $\{HCO_3^{-}\} = 10^{-1.7}$ mol. Stability field of S superimposed in thin *blue, dashed lines* and species and phases indicated in *italics* (modified Geochemist's Workbench plot)

Trusler et al. (1988) focussed on sulphate-rich water containing both Ca^{2+} and Mg^{2+}. They found that sulphate species associated with Mg^{2+} cannot be removed as $BaSO_4$ and overcame this problem by removing the Mg^{2+} upstream of the sulphate removal stage by lime treatment. In the sulphate removal stage, SO_4^{2-} was precipitated as $BaSO_4$ and Ca^{2+} as $CaCO_3$. Again, the $BaSO_4/CaCO_3$ mixture was thermally reduced in the presence of coal at 1050 °C to produce BaS from $BaSO_4$ and CaO from $CaCO_3$. The BaS was separated from CaO through solubility differences in a follow-up leaching stage.

The two-staged CSIR-ABC process (Maree 2008; Motaung et al. 2008) uses barium carbonate to remove the sulphate. The first stage involves neutralisation with $CaCO_3$ and concurrent, partial metal removal, followed by lime addition for partial removal of sulphate as gypsum, removal of iron as ferric hydroxide, and complete removal of magnesium as $Mg(OH)_2$. The final stage is the introduction of barium carbonate to precipitate the residual sulphate as barium sulphate. The sludge produced can be thermally recycled or processed into saleable products, i.e. sulphur and $CaCO_3$.

Swanepoel et al. (2012) investigated the efficiency of barium carbonate from different sources and different particle sizes on sulphate removal down to very low concentrations. They showed that particle size and shape and hence, effective surface area, have a substantial influence on the sulphate removal rate; this was evidence that $BaCO_3$ from different sources do not remove sulphate equally efficiently.

Bologo et al. (2012) and Maree (2013) proposed the magnesium-barium-hydroxide (MBO) process, where metals are removed as hydroxides with $Mg(OH)_2$, leaving $MgSO_4$ and $CaSO_4$ in solution. This was followed by SO_4^{2-}-removal with $Ba(OH)_2$, resulting in simultaneous removal of Mg^{2+} as $Mg(OH)_2$ and SO_4^{2-} as $BaSO_4$. Ca^{2+} remained in solution as $Ca(OH)_2$. $Mg(OH)_2$ can be separated from $BaSO_4$ by treating the solution with CO_2 (Rukuni et al. 2012). $Ca(OH)_2$ in solution could be removed in a separate stage as pure $CaCO_3$ by dosing CO_2. Another version of the MBO process is the ammonium-barium-hydroxide (NB) process, where ammonium hydroxide is used for neutralization and metal removal, followed by $Ba(OH)_2$ dosing for sulphate removal as pure $BaSO_4$ and NH_3 recovery at pH 13 (Maila et al. 2014).

This study is an improvement of the ABC-process in which CO_2 is added to convert the $BaCO_3$ to the more soluble $Ba(HCO_3)_2$: the alkali-barium-calcium-desalination (ABCD) process (Fig. 2). This process comprises the following stages: Stage 1, where metals are removed with $CaCO_3$ or $Ca(OH)_2$ (not part of this investigation) and Stage 2, where a barium salt is used for sulphate removal. Stage 2 has the following sub-stages: (1) formation of $Ba(HCO_3)_2$ (reaction 1a); (2) removal of sulphate as barium sulphate (reaction 1b), and, (3) precipitation of $CaCO_3$ via CO_2 stripping (reaction 2a) and/or $Ca(OH)_2$ dosing (reaction 2b). The benefits of the ABCD process are: (1) the calcium sulphate and magnesium sulphate can both be removed, and (2) the precipitated products, $BaSO_4$ and $CaCO_3$, can be recovered separately.

$$BaCO_{3(s)} + H_2O + CO_2 \rightarrow Ba\left(HCO_3\right)_{2(aq)} \quad (1a)$$

$$CaSO_{4(s)} + Ba\left(HCO_3\right)_{2(aq)} \rightarrow BaSO_{4(s)} + Ca\left(HCO_3\right)_{2(aq)} \quad (1b)$$

$$Ca\left(HCO_3\right)_2(aq) \rightarrow CaCO_{3(s)} + CO_{2(g)} \quad (2a)$$

$$Ca\left(HCO_3\right)_{2(aq)} + Ca(OH)_{2(aq)} \rightarrow 2CaCO_{3(s)} + H_2O_{(l)} \quad (2b)$$

The purpose of this study was to evaluate the ABCD process with a focus on the following aspects: (1) formation of $Ba(HCO_3)_2$, (2) SO_4^{2-} removal with $Ba(HCO_3)_2$, (3) kinetics of $BaSO_4$ precipitation with $Ba(HCO_3)_2$, and (4) softening of the $Ca(HCO_3)_2$ solution through CO_2 stripping.

Materials and Methods

Artificial, sulphate-rich water was prepared by dissolving analytical grade $MgSO_4$ (Merck) in varying concentrations in deionized water. Analytical grade $BaCO_3$ (Associated Chemical Enterprises) and CO_2 gas (Afrox) were used for the sulphate removal experiments.

Glass beakers (1000 mL) were used in the batch studies. A Knick 766 Calimatic pH meter and a Eutech Instruments CON 510 conductivity meter were used to monitor pH and electrical conductivity (EC), respectively. Overhead digitally controlled paddle stirrers (IKA RW 20) were used to stir the solutions. A turbidity meter (Eutec Instruments TN-100) was used for turbidity analyses using nephelometric turbidity units (NTU) (Instruments 2003).

All samples were filtered (Whatman No. 1), including those for the alkalinity and acidity determinations, as otherwise the unreacted alkali may have interfered in the analyses. Concentrations of SO_4, alkalinity, acidity, and pH determinations were conducted using standard procedures (APHA 2012). Flame atomic absorption spectroscopy (Spectra AA, 220FS; Varian Techtron (Pty) Ltd) was used for Ca and Mg analysis. Alkalinity was determined by titration of the solution to pH 4.3 using 0.1 N HCl. CO_2 was passed through a gas diffuser with a pore size of 50 µm in a 500 mL glass beaker containing a $BaCO_3$ slurry.

Batch studies were carried out by mixing variable amounts of $MgSO_4$, $BaCO_3$, and CO_2 at time, $t=0$. The mixtures were stirred at 250 rpm (rotations per minute) and the sulphate removal rates were monitored by analysing filtered 50 mL samples (at 2, 5, 10, 15, 30, and 60 min) for sulphate, acidity, alkalinity, pH, and EC.

The effects of the following parameters were investigated by varying one parameter at a time:

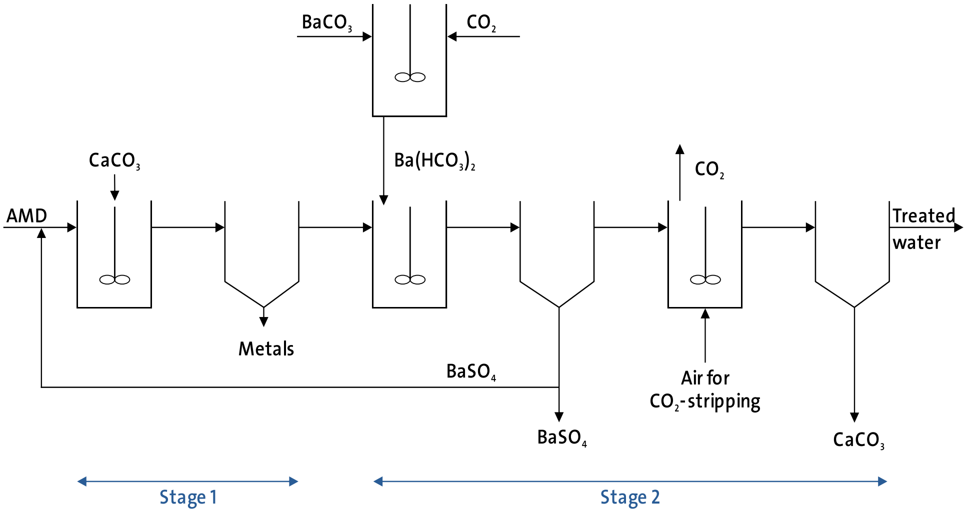

Fig. 2 Process flow-diagram for the ABCD process

- *Solubility of $BaCO_3$ in the presence of CO_2* The effect of CO_2 dosing on Ba^{2+} in solution was investigated by collecting samples at 5 min intervals.
- *SO_4-concentrations* The effect of initial SO_4 concentration (1, 2 g L^{-1}) on SO_4 removal was measured over time.
- *CO_2-flow-rate* The effect of CO_2 flow-rate (10, 15, 20, 25 mL min^{-1}) on the SO_4 removal rate was measured over time. Alkalinity and pH were also monitored.
- *$BaCO_3$-concentration* The effect of the $BaCO_3/SO_4^{2-}$ molar ratio (0, 0.5, 0.9, 1.0, 2.0) on SO_4 removal was monitored over time.
- *$CaSO_4$ vs. $MgSO_4$* The effect of SO_4 associated with $CaSO_4$ and $MgSO_4$ species on SO_4 removal over time was investigated.
- *Temperature* The effect of temperature (5, 10, 20, 25 °C) on SO_4 removal was investigated as described earlier.

Results and Discussion

Solubility

Due to its higher solubility, $Ba(HCO_3)_2$, made by passing CO_2 gas through a $BaCO_3$-solution at a pH 9.5–10, was used for sulphate removal instead of $BaCO_3$. An OLI systems (2015) model and OLI analyser Studio 9.0 (Table 1) were used to model the differences in solubility. The results (at 25 °C and 1013 hPa) were 22 mg of $BaCO_3$ and 1686 mg of $Ba(HCO_3)_2$ in solution (Table 1), similar to what was found by Busenberg and Plummer (1986). The same trend was exhibited experimentally, with 40 mg $BaCO_3$ and 1577 mg $Ba(HCO_3)_2$ in solution (Fig. 3; Table 2). The changes in pH and alkalinity (Fig. 3) after 20 min was due to the introduction of CO_2 as the $BaCO_3$(s) dissolved to produce $Ba(HCO_3)_2$(aq). The pH in the $Ba(HCO_3)_2$ solution dropped from 8.9 to 6.4 and alkalinity increased gradually from 0 to 10 mmol L^{-1} due to the conversion of solid $BaCO_3$ to soluble $Ba(HCO_3)_2$.

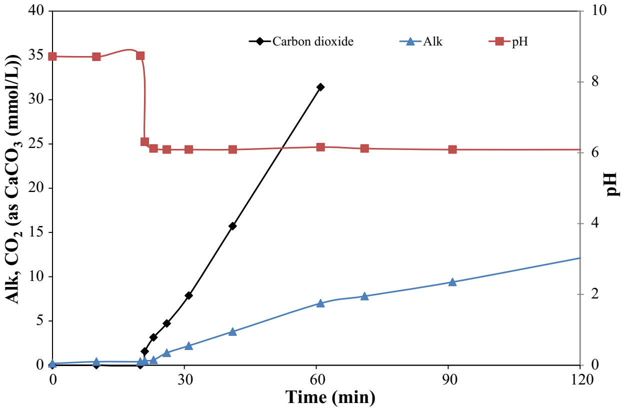

Fig. 3 Effect of CO_2 dosing on the solubility of $BaCO_3$. Experimental conditions: 50 g L^{-1} $BaCO_3$; 0 or 25 mL min^{-1} CO_2 introduced via a 50 µm pore size diffuser; 25 °C; 250 rpm

Table 1 Results of the *OLI* model with $BaCO_3$ and $BaCO_3+CO_2$ and calculated solubilities of $BaCO_3$ and $Ba(HCO_3)_2$

Species	Concentrations (mol L^{-1})	
	$BaCO_3$	$BaCO_3/CO_2$
Ba^{2+}	1.08×10^{-4}	7.85×10^{-3}
$BaCO_3$ (aq)	1.42×10^{-6}	1.41×10^{-6}
$Ba(HCO_3)_2$	7.47×10^{-8}	6.93×10^{-4}
$BaOH^+$	2.64×10^{-8}	1.61×10^{-10}
HCO_3^-	7.84×10^{-5}	1.64×10^{-2}
CO_3^{2-}	3.01×10^{-5}	1.11×10^{-6}
CO_2 (aq)	2.25×10^{-8}	3.39×10^{-2}
OH^-	7.85×10^{-5}	1.097×10^{-8}
H^+	1.33×10^{-10}	1.207×10^{-6}
pH	9.89	5.97
Sum of Ba cations (mmol L^{-1} Ba)	1.10×10^{-4}	8.54×10^{-3}
Sum of of Ba cations (mg L^{-1} $BaCO_3$ or $Ba(HCO_3)_2$)	21.7	1686.1

Sulphate Removal

We compared the efficiency of sulphate removal by the ABC process with that of $Ba(HCO_3)_2$ (ABCD process) generated by adding CO_2 to $BaCO_3$, in treating an $MgSO_4$ solution (Fig. 4). The sulphate concentration was reduced effectively with $Ba(HCO_3)_2$, from 11 to 1 mmol L^{-1} (1050–96 mg L^{-1}) SO_4^{2-} within 15 min. The $BaCO_3$ only reduced sulphate to 8 mmol L^{-1} over the same period of time. The solubility difference between the two plays a substantial role in the lowering of the sulphate concentration, since more Ba^{2+} ions are available to react with the sulphate.

To investigate if the initial sulphate concentration may have affected the sulphate removal efficiency, initial concentrations of 1 and 2 g L^{-1} of SO_4 were used. The experimental results showed that these initial sulphate concentrations had no effect on the ultimate sulphate concentrations that were achievable (Fig. 5). The effect of carbon dioxide flow rate on sulphate removal from a $MgSO_4$ solution with $BaCO_3$ was also investigated (Fig. 6). The higher the flow rate, the faster the sulphate removal due to the increased formation of $Ba(HCO_3)_2$.

The rate of sulphate removal also increased as the $Ba(HCO_3)_2/SO_4^{2-}$ mole ratio was increased (Fig. 7). At ratios of 0.5:1 and 0.9:1, incomplete sulphate removal took place, as expected. At a molar excess of 2:1, complete sulphate removal was achieved within 30 min. In practice, the

Table 2 Results of the CO_2-flushing experiment

CO_2 (mL min^{-1})	Time (min)	Alkalinity (mmol L^{-1})	pH	Electrical conductivity (mS cm^{-1})	CO_2 (mmol L^{-1})
0	0	0.2	8.90	0.12	–
0	10	0.4	8.86	0.18	–
0	20	0.4	8.99	0.19	–
25	20.5	0.5	8.99	0.18	0.56
25	22	0.6	9.03	0.18	2.23
25	25	1.4	8.45	0.22	5.58
25	30	2.2	7.83	0.32	11.16
25	40	3.8	7.26	0.55	22.32
25	80	7.0	6.62	1.08	66.96
25	95	7.8	6.48	1.13	83.71
25	110	9.4	6.50	1.16	100.5
25	140	12.2	6.48	1.28	133.9

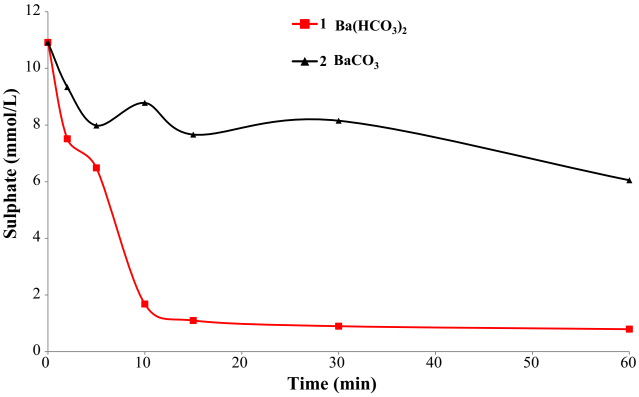

Fig. 4 Comparison of $BaCO_3$ and $Ba(HCO_3)_2$ for sulphate removal (3.7 g L^{-1} $BaCO_3$; 25 °C; 250 rpm; excess CO_2)

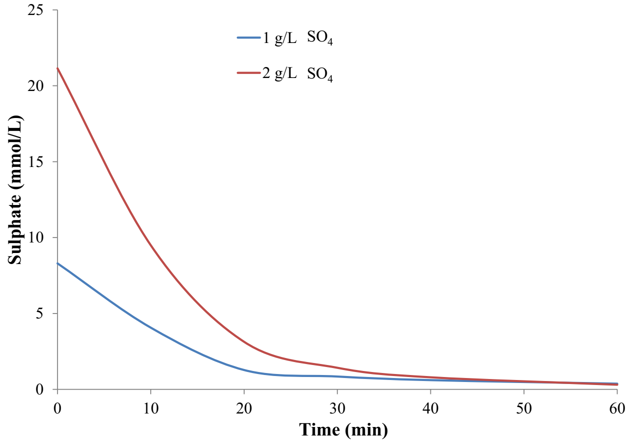

Fig. 5 Effect of SO_4^{2-} concentration on sulphate removal from $MgSO_4$ solution ($Ba(HCO_3)_2/SO_4$ mole ratio = 0.9; 250 rpm; 25 mL min^{-1} CO_2)

aim would be to dose a ratio of 1:1 or slightly higher to minimize the use of $Ba(HCO_3)_2$ and consequently $BaCO_3$ and CO_2 (Fig. 7).

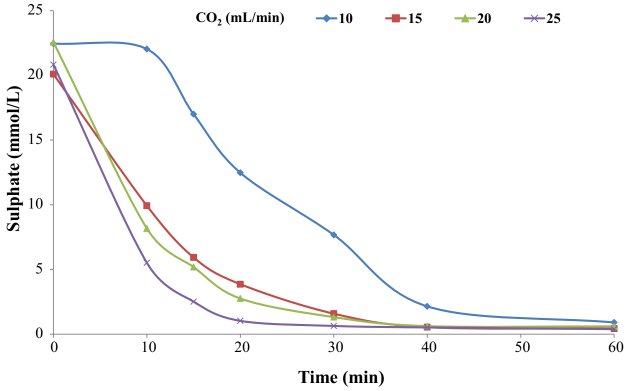

Fig. 6 Effect of CO_2 addition on the removal of sulphate from $MgSO_4$ solution (CO_2 flow-rates were 10, 15, 20 and 25 mL min^{-1})

When solutions of $CaSO_4$ and $MgSO_4$, were reacted with $Ba(HCO_3)_2$, the sulphate–magnesium species were removed slightly faster than the sulphate–calcium species (Fig. 8).

The effect of temperature on the sulphate removal rate (Reaction 1b) is shown in Figs. 9, 10, 11 and Table 3.

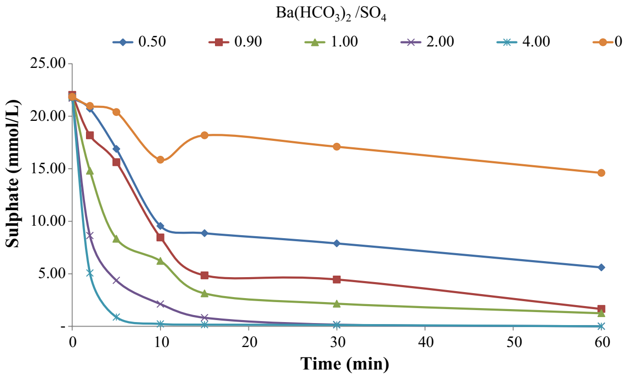

Fig. 7 Effect of $Ba(HCO_3)_2$ concentrations on the sulphate removal from $MgSO_4$ solution (CO_2 excess; 25 °C; 250 rpm)

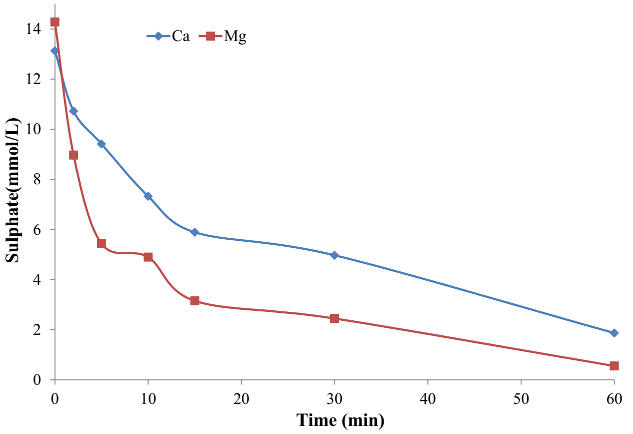

Fig. 8 Comparison of $Ba(HCO_3)_2$ for sulphate removal from $CaSO_4$ and $MgSO_4$ solutions ($BaCO_3/SO_4=0.9$; 25 °C; 250 rpm; excess CO_2)

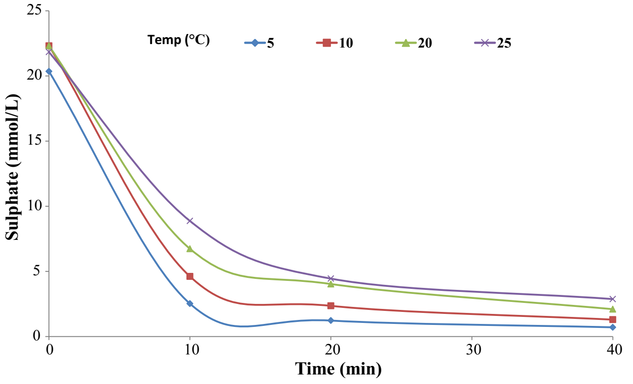

Fig. 9 Effect of temperature on the removal of sulphate. $Ba(HCO_3)_2/SO_4$ mole ratio = 0.9; 250 rpm; 25 mL min^{-1} CO_2

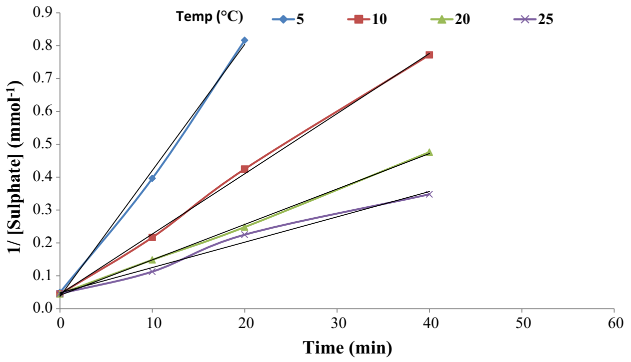

Fig. 10 Second-order graphs for sulphate removal

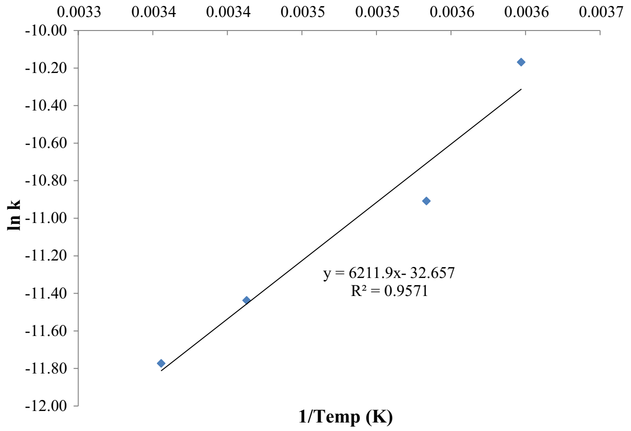

Fig. 11 Activation-energy determination for the removal of sulphate ($Ba(HCO_3)_2/SO_4$ mole ratio = 0.9; 250 rpm; 25 mL min^{-1} CO_2)

The sulphate removal rate increased at lower temperatures (Fig. 9), which can be explained by the higher solubility of CO_2 at lower temperatures, and consequently more dissolved $Ba(HCO_3)_2$. Figure 9 shows that it is a second-order reaction, as indicated by the straight line graphs of $1/[SO_4]$ plotted against time over the temperature range of 5–25 °C. The reaction constant k was calculated for the various temperatures from the slope of the graphs in Fig. 9. The activation energy, E, and the pre-exponential factor A were calculated from the slope and the y-intercept of the graph (Fig. 10) as 51.65 kJ mol^{-1} and 6.56×10^{-12}, respectively. The initial reaction rates were determined as 1.78, 1.77, 1.56, and 1.30 mmol/(L min^{-1}) at 5, 10, 20, and 25 °C, respectively.

The Arrhenius equation allows the estimation of the reaction constant, k, at different temperatures (Stumm and Morgan 1996) and explains the different reaction rates:

$$k = Ae^{-E_a/RT} \tag{3}$$

where T = temperature (K), E_a = 51.65 kJ mol^{-1} (activation energy), and $R = 8.314$ J mol^{-1} K^{-1} (gas constant) and

Table 3 Effect of temperature on the rate of sulphate removal with $Ba(HCO_3)_2$

Time, *T* (min)	Temperature (°C)			
	5	10	20	25
$[SO_4]$ (mg L^{-1})				
0	1954	2142	2142	2096
10	242	443	647	852
20	118	226	387	427
40	68	124	202	276
60	47	99	112	143
$[SO_4]$ (mmol L^{-1})				
0	20.35	22.31	22.31	21.83
10	2.52	4.61	6.73	8.87
20	1.23	2.36	4.03	4.44
40		1.3	2.1	2.87
$1/[SO_4]$				
0	0.05	0.04	0.04	0.05
10	0.4	0.22	0.15	0.11
20	0.82	0.42	0.25	0.23
40		0.77	0.48	0.35
k (mol^{-1} min^{-1})	3.83×10^{-5}	1.83×10^{-6}	1.08×10^{-6}	7.71×10^{-6}
ln k	−10.169	−10.908	−11.438	−11.774
$1/T$ (K^{-1})	0.00360	0.00353	0.00341	0.00336
R (J·mol^{-1} K^{-1})	8.314			
E/R	6211.9			
E (kJ·mol^{-1})	51.65			
ln A	−25.75			
A	6.5602×10^{-12}			

6.56×10^{-12} (constant from the activation energy graph; Fig. 11).

Softening of Treated Water

After sulphate removal with $Ba(HCO_3)_2$, the water contains $Ca(HCO_3)_2$, which increases its hardness. Consequently, the final step of the *ABCD* process is the use of air to strip the CO_2 and initiate $CaCO_3$ precipitation (Reaction 2a). The rate of $CaCO_3$ crystallization is related to the amount of $CaCO_3$ seed crystals present (Fig. 12). The calcium concentration was reduced from 18 mmol L^{-1} (720 mg L^{-1} as Ca) to 3 mmol L^{-1} (120 mg L^{-1} as Ca). This corresponds with a decrease in TDS from 2916 mg L^{-1} [as $Ca(HCO_3)_2$] to 300 mg L^{-1} (as $CaCO_3$). In practice, a $CaCO_3$ fluidised-bed reactor would provide the appropriate conditions.

During the CO_2 stripping, the Ca^{2+}-concentration decreased due to precipitation of $CaCO_3$. The degree of saturation or under-saturation of $CaCO_3$ is expressed by the saturation index (SI), which is the quotient of the ion-activity product (IAP) of the Ca^{2+}- and CO_3^{2-}-species and the solubility product (k_{sp}) for $CaCO_3$ (Loewenthal and Marais 1976; Stumm and Morgan 1996). Consequently, when the $SI > 0$, $CaCO_3$ should precipitate and when the $SI < 0$, it should dissolve. The rate of this process is described by the following equation:

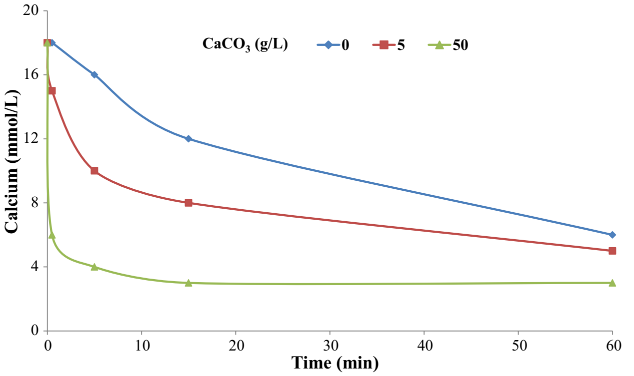

Fig. 12 Effect of $CaCO_3$ seed crystals on the removal of calcium (25 °C; 250 rpm; excess air)

$$-\frac{d\{Ca^{2+}\}}{dt} = kS\sqrt{\{Ca^{2+}\}\{CO_3^{2-}\}} - \sqrt{k_{sp}}^{\,2} \tag{4}$$

On the right-hand side of the equation, k, is the precipitation rate constant; S is the surface area of the $CaCO_3$

growth/dissolution sites; k_{sp}, the solubility product for $CaCO_3$, and $\{Ca^{2+}\}$ and $\{CO_3{}^{2}\}$ the activities of the calcium and carbonate ions, respectively (Loewenthal et al. 1986).

The degree of super-saturation is given by the terms within the curly brackets. The precipitation rate depends on the surface area (*S*) and the degree of super-saturation. Although the rate constant (*k*) is affected to an unknown extent by the crystal structure, *S* depends on the size, mass, and structure of the crystals. The rate of precipitation or dissolution of $CaCO_3$ can be determined by controlling *S* and the degree of super-saturation.

$Ca(HCO_3)_2$ can also be removed by dosing $Ca(OH)_2$ to form $CaCO_3$. This would be more attractive than CO_2 stripping, from a CO_2 emission point of view. In the case of CO_2 stripping, the amount of CO_2 released is less than the CO_2 produced when $Ca(OH)_2$ is manufactured from limestone. In the latter case, CO_2 is produced from converting $CaCO_3$ to CaO plus the amount of coal required to be burned for the thermal process.

Conclusions

This study showed that it is possible to precipitate sulphate as $BaSO_4$ from mine water with $Ba(HCO_3)_2$. This $SO_4{}^{2-}$-removal reaction with $Ba(HCO_3)_2$ is a second-order reaction with an activation energy of 51.65 kJ mol^{-1}. The $Ba(HCO_3)_2$ can be formed by mixing the $BaCO_{3(s)}$ with CO_2. This lowers the pH to about 7, compared to the $BaCO_3$-solution, which has a pH of 9–10. The rate of $SO_4{}^{2-}$ removal is faster with $Ba(HCO_3)_2$ than with $BaCO_3$ due to the higher solubility of the former.

The ABCD process enables sulphate removal from Mg^{2+}-rich waters without prior removal of Mg^{2+}, as is required with the ABC process, because the ABCD-process uses the more soluble $Ba(HCO_3)_2$. This allows $BaSO_4$ sludge to be recovered separately from $CaCO_3$. A practical limitation associated with the ABCD process is that in addition to $BaCO_3$, a CO_2 source is required to convert the $BaCO_3$ to $Ba(HCO_3)_2$. Another limitation is that an overdosage can occur with $BaCO_3$, once all of the $SO_4{}^{2-}$ has been removed. Residual $Ca(HCO_3)_{2(aq)}$ remaining after $SO_4{}^{2-}$ removal can be removed by $CO_{2(g)}$ stripping. Further studies with a variety of real mine waters need to be conducted to study the effects of potentially competing reactions.

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References

APHA (American Public Health Association) (2012) Standard Methods for the examination of water and wastewater, 22nd edn. American Water Works Assoc, Water Environment Federation, Washington DC

Blowes DW, Ptacek CJ, Jambor JL, Weisener CG, Paktunc D, Gould WD, Johnson DB (2014) The geochemistry of acid mine drainage. In: Turekian HD, Holland KK (eds) Treatise on geochemistry, 2nd edn. Elsevier, Oxford, pp 131–190

Bologo V, Maree JP, Carlsson F (2012) Application of magnesium hydroxide and barium hydroxide for the removal of metals and sulphate from mine water. Water SA 38(1):23–28

Busenberg E, Plummer LN (1986) The solubility of $BaCO_3$(cr) (witherite) in CO_2-H_2O solutions between 0 and 90 °C, evaluation of the association constants of $BaHCO_3{}^{+}$(aq) and $BaCO_3$(aq) between 5 and 80 °C, and a preliminary evaluation of the thermodynamic properties of Ba^{2+}(aq). Geochim Cosmochim Acta 50(10):2225–2233. doi:10.1016/0016-7037(86)90077-3

Castillo J, Gomez-Arias A, Posthumus J, Welman-Purchase M, Heerden Ev (2015) Geochemical study of the interaction of acid and alkaline mine drainage with $BaCO_3$. In: Brown A et al (eds) Agreeing on solutions for more sustainable mine water management. Gecamin, Santiago/Chile, pp 1–12 (electronic document). http://www.IMWA.info/docs/imwa_2015/IMWA2015_Castillo_290.pdf

Coetzee H (2013) Flooding of the underground mine workings of the Witwatersrand gold fields. Proc, Reliable Mine Water Technology, IMWA conf, pp 937–942

Coetzee H, Horstmann U, Ntsume G, Croukamp L (2003) The potential environmental impact of the decant of water from Witwatersrand. Proc, 8th International Congr on Mine Water and the Environment, Johannesburg, pp 201–217

Department of Mineral Resources (2014) South Africa's mineral industry 2012/2013. 30th edn. Pretoria

Douglas GB (2014) Contaminant removal from acidic mine pit watervia in situ hydrotalcite formation. Appl Geochem 51:12–22

Expert Team of the Inter Ministerial Committee (2010) Mine water management in the Witwatersrand gold fields with special emphasis on acid mine drainage—report to the inter-ministerial committee on acid mine drainage. Council for Geoscience, Pretoria

Eutech Instruments (2003) Instruction manual TN-100/T-100 portable turbidity meter. Eutech Instruments, Singapore

Gomez-Arias A, Castillo J, Welman-Purchase M, Posthumus J, Heerden Ev (2015) Evidences of effective treatment of alkaline mine drainage with $BaCO_3$. In: Brown A et al (eds) Agreeing on solutions for more sustainable mine water management. Gecamin, Santiago/Chile, pp 1–12 (electronic document), http://www.IMWA.info/docs/imwa_2015/IMWA2015_Castillo_290.pdf

Gusek JJ, Figuera LA (2009) Mitigation of metal mining influenced water, vol 2, The Soc of Mining, Metallurgy and Exploration (SME), Littleton, CO, USA

Kamal NM, Sulaiman SK (2014) Bench-scale study of acid mine drainage treatment using local neutralisation agents. Malays J Fund Appl Sci 10(3):150–153

Kun LE (1972) A report on the reduction of the sulphate content of acid mine drainage by precipitation with barium carbonate. Internal report, Anglo American Research Laboratories

Loewenthal RE, Marais GvR (1976) Carbonate chemistry of aquatic systems: theory and application. Ann Arbor Science Publ, Ann Arbor, MI, USA

Loewenthal RE, Wiechers HNS, Marais GvR (1986) Softening and stabilization of municipal waters. Water Research Commission Report, Pretoria

Maila MD, Maree JP, Cele LM (2014) Acid mine water neutralisation with ammonium hydroxide and desalination with barium hydroxide. Water SA 40(3):521–528. doi:10.4314/wsa.v40i3.16

Maree JP (2008) Modified $BaCO_3$ process, South Africa patent 2008/4014, CSIR

Maree JP (2013) Treatment of sulphate rich water—MBO process. US Patent 8557124, Tshwane Univ of Technology

McCarthy TS (2011) The impact of acid mine drainage in South Africa. S Afr J Sci 107:5–6

Motaung S, Maree J, De Beer M, Bologo L, Theron D, Baloyi J (2008) Recovery of drinking water and by-products from gold mine effluents. Int J Water Res Dev 24(3):433–450

Mullett M, Fornarelli R, Ralph D (2014) Nanofiltration of mine water: impact of feed pH and membrane charge on resource recovery and water discharge. Membranes 4:163–180

Rukuni TT, Maree JP, Zvinowanda CM, Carlsson FHH (2012) Separation of magnesium hydroxide and barium sulphate from a barium sulphate—magnesium hydroxide mixed sludge by carbonation: the effect of temperature. J Civil Environ Eng 2(116):16–28

Stumm W, Morgan JJ (1996) Aquatic chemistry—chemical equilibria and rates in natural waters, 3rd edn. Wiley and Sons, New York City

Swanepoel H, De Beer M, Liebenberg L (2012) Complete sulphate removal from neutralised acidic mine drainage with barium carbonate. Water Pract Technol 7(1):1–8

Trusler GE, Edwards RI, Brouckaert CJ, Buckley CA (1988) The chemical removal of sulphates. Proc, 5th National Mtg of the S Afr Inst Chem Eng, Pretoria, pp W3-0–W3-11

Vasquez Y, Escobar MC, Neculita CM, Ziv Arbeli Z, Roldan F (2016) Biochemical passive reactors for treatment of acid mine drainage: effect of hydraulic retention time on changes in efficiency, composition of reactive mixture, and microbial activity. Chemosphere 153:244–253

Volman R (1984) The use of barium sulphide to remove sulphate from industrial effluents. MS Thesis, Univ of Stellenbosch, South Africa

Wolkersdorfer C (2008) Water management at abandoned flooded underground mines—fundamentals, tracer tests, modelling, water treatment. Springer, Heidelberg