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Complete sulphate removal from neutralised acidic mine drainage with barium carbonate

H. Swanepoel[1],*,**, M. de Beer* and L. Liebenberg**

* Natural Resources and the Environment, CSIR, PO Box 395, Pretoria, 0001, South Africa. E-mail: hswanepoel@csir.co.za; mdebeer@csir.co.za

** Center for Research and Continued Engineering Development, North-West University (Pretoria campus), Suite no. 93, Private Bag X30, Lynnwood Ridge, 0040, South Africa. E-mail: LLiebenberg@researchtoolbox.com

Abstract

The most widespread method used for the treatment of acidic mine drainage (AMD) is neutralisation through the addition of lime to the effluent in order to raise the pH. As a result, dissolved metals precipitate as metal hydroxides while partial sulphate removal is achieved. However, further treatment is required in order to reduce the sulphate concentration to below 500 mg/ℓ, which is the required concentration for discharge into waterways. The CSIR developed and patented the ABC (alkali-barium-calcium) Desalination process which uses barium salts to further reduce the sulphate concentration to acceptable levels with the added advantage that sulphate removal can be controlled due to the low solubility of $BaSO_4$. This paper reports on the results of an investigation to demonstrate the performance of this sulphate removal reaction. Laboratory results that draw attention to the conditions required for $BaSO_4$ precipitation are presented. A number of parameters, including temperature, initial sulphate concentration, barium-to-sulphate molar ratio and different $BaCO_3$ sources were considered. The results were also tested and verified on industrial process water. The results clearly demonstrate that the reactor temperature, initial sulphate concentration, and molar ratio of barium to sulphate have a positive influence on sulphate removal.

Key words: ABC Desalination, $BaSO_4$ precipitation, lime neutralisation, sulphate removal

INTRODUCTION

South Africa is considered a semi-arid country where water is a limited resource. Pollution of surface and groundwater sources further strains the available water resources. It is a legal requirement in terms of the National Water Act 1998 (RSA 1998) that effluent must be returned to the water resource (Section 22(2)(e)) while also reducing or preventing pollution and degradation of water resources (Section 2(h)). Typical sources of pollution include acidic mine drainage (AMD) and industrial effluents. AMD is usually characterised by high levels of acidity, heavy metals and sulphates (De Beer & Greben n.d.). Unless properly treated, the acid water cannot be legally discharged into public water sources.

The most widespread method used to treat acidic effluents, is through lime neutralisation. Lime ($Ca(OH)_2$) is added to the acid water to raise the pH. The metals are simultaneously removed as metal hydroxides and some of the sulphates as $CaSO_4$.

Initially, only partial removal of the sulphate ions (SO_4^{2-}) occurs and the sulphate concentration is reduced from about 2,500 mg/ℓ to about 1,200 mg/ℓ due to the solubility of $CaSO_4$ (Mare *et al.* 2004). According to the South African Water Quality Guidelines, acceptable sulphate levels in water bodies are 500 mg/ℓ for industrial use and 200 mg/ℓ for domestic use (DWAF 1996).

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[1] Southern African Young Water Professionals

Further treatment is therefore required to remove the excess sulphate from the effluent to render the water fit for use in industry. The CSIR developed a treatment process, known as the ABC (alkali-barium-calcium) Desalination process, which is a chemical precipitation-based technology where barium salts are used for sulphate removal. The advantage of using barium salts is that sulphate ions can be reduced to very low concentrations (close to 0 mg/ℓ) due to the low solubility of $BaSO_4$ (Perry & Green 1997).

The purpose of this study is to demonstrate the performance of sulphate removal reactions using $BaCO_3$ as the barium salt.

METHOD

Feedstock

- Synthetic $CaSO_4$ water: Prepared by dissolving analytical grade $CaSO_4$ (Merck) in distilled water. The initial sulphate concentration of the solution was controlled by varying the mass of $CaSO_4$ that was dissolved in distilled water.
- Pre-treated (neutralised) AMD.
- $BaCO_3$: Commercial $BaCO_3$ imported from China and $BaCO_3$ prepared in a batch process under laboratory conditions.

Experimental set-up and procedure

The experimental set-up used in the laboratory is illustrated in Figure 1. A reactor with an overhead stirrer was used. The $BaCO_3$ was dosed as slurry into the $CaSO_4$ solution to initiate the sulphate removal process. During this process the pH, temperature and electrical conductivity (EC) were continuously measured using a multiple parameter probe which recorded and stored the data. Samples for sulphate ion analysis were collected at specific time intervals.

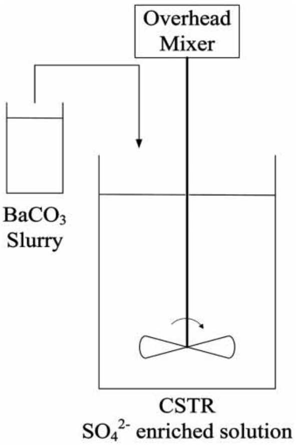

Figure 1 | Reactor set-up.

Experimental

Numerous experiments were conducted to determine the effect of different parameters on the sulphate removal process. These included the effect of initial sulphate concentration in the synthetic water, the barium-to-sulphate ion molar ratios where the barium (Ba^{2+}) was dosed as $BaCO_3$ into the sulphate ($SO_4{}^{2-}$) enriched water, and the effect of temperature on the entire sulphate removal process. Different $BaCO_3$ sources were also used to determine whether $BaCO_3$ characteristics have an effect on the sulphate removal process. The sulphate removal method was also tested and verified on pre-treated AMD.

Analytical

Samples were regularly collected and filtered through Whatman No. 1 filter paper before sulphate analyses were conducted. The sulphate ion concentration was measured by using the Turbidimetric method (APHA 1992).

RESULTS AND DISCUSSION

All the experiments were conducted by using synthetic process water with a known sulphate concentration. The sulphate removal process reaction was tracked by monitoring the EC of the solution. The reaction was considered to be complete (i.e., the sulphate removal process progressed to a point where no more sulphates would be removed from the sulphate enriched water), when the EC value remained constant over time. The sulphate concentration profile was determined through sulphate analysis. As expected, the sulphate removal profile correlates very well with the EC profile, as shown in Figure 2. In this sulphate removal experiment, all parameters were kept constant except for the mixing rate (De Beer 2010).

The sulphate removal reaction in this experiment followed the chemical reaction shown in Equation (1).

$$Ca^{2+}(aq) - SO_4^{2-}(aq) - BaCO_3(s) \rightarrow BaSO_4(s) + CaCO_3(s) \qquad (1)$$

It was found that the majority of the dissolved ions in solution were the $SO_4{}^{2-}$ ions and the Ca^{2+} ions. The dissolved Ba^{2+} ions and $CO_3{}^{2-}$ ions were at such low concentrations that they could be ignored. This observation confirmed the very low solubility of $BaCO_3$ and $CaCO_3$ in water. However,

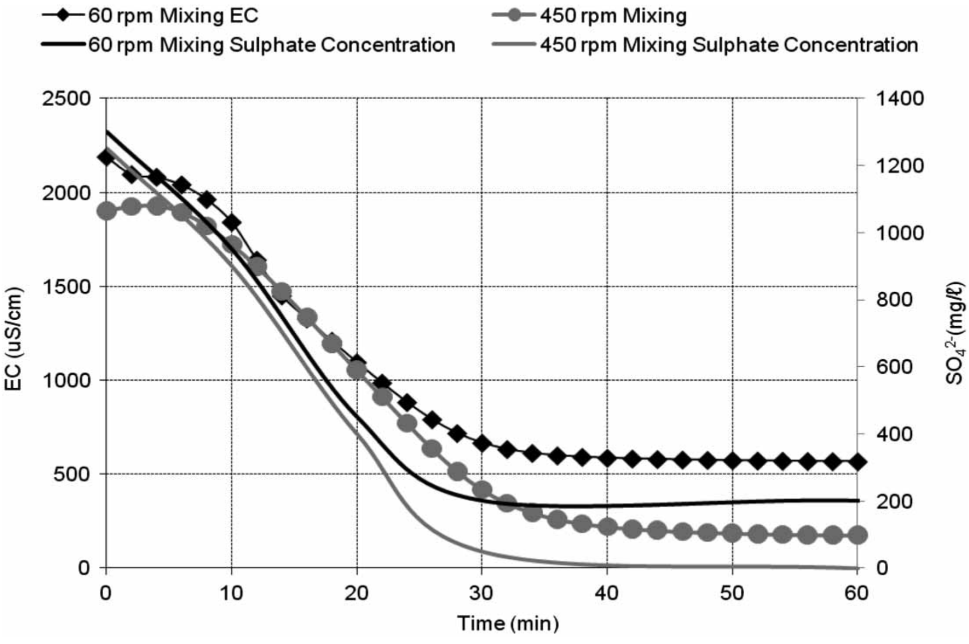

Figure 2 | Sulphate concentration and EC profile.

$BaSO_4$ is considered to be completely insoluble and therefore it will be only the $CaSO_4$ that will dissolve and form free ions in the solution (Kotz & Treichel 2003). This experiment also provides proof that EC measurement can be used to track sulphate removal since it indicates the amount of free ions in the solution.

Different $BaCO_3$ sources

All $BaCO_3$ particles are not exactly alike, as was determined by SEM photos of different $BaCO_3$ sources that were produced from a BaS carbonation reaction (De Beer 2011). Thus, an investigation was launched to determine the effect of different $BaCO_3$ sources, and therefore the $BaCO_3$ particle characteristics, on sulphate removal.

The first $BaCO_3$ source (Batch) originated from a laboratory experiment where BaS was carbonated with CO_2 gas (De Beer 2011), while the second $BaCO_3$ source was of commercial quality (China). See EC profile in Figure 3.

The commercial $BaCO_3$ imported from China took much longer to remove sulphates from the process water when compared to the laboratory batch-produced $BaCO_3$. Therefore the commercial $BaCO_3$ was deemed to be un-reactive when compared to the highly reactive batch-$BaCO_3$ which quickly removed the sulphates from the process water. This deduction was confirmed with sulphate analysis, as shown in Figure 3. It can therefore be concluded that all $BaCO_3$ sources are not equally effective in removing sulphates, which implies that the particle shape and size of the $BaCO_3$ are important characteristics for sulphate removal.

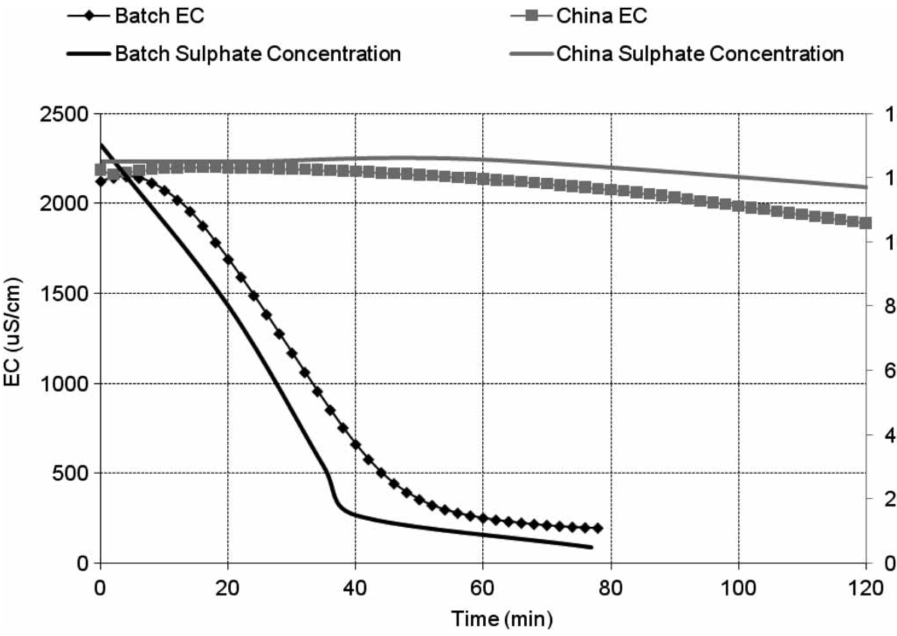

Figure 3 | Effect of barium particle size and shape.

Barium ion-to-sulphate ion molar ratios

The effect that the barium–to–sulphate molar ratio has on the sulphate removal process was also investigated, as shown in Figure 4.

In this experiment, the initial sulphate concentration was kept constant while the $BaCO_3$ dosage varied. In the cases where the barium was under-dosed, i.e., where the barium-to-sulphate ratio was less than stoichiometric ($[Ba^{2+}]/[SO_4{}^{2-}] < 1$), only partial sulphate removal was achieved. However,

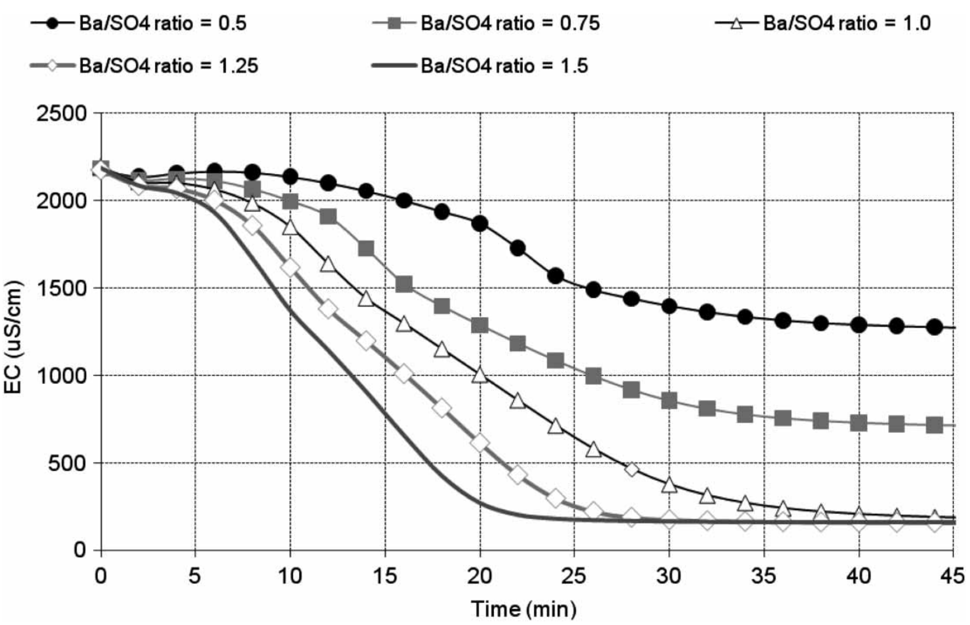

Figure 4 | The effect of barium-to-sulphate molar ratio.

when the barium was over-dosed, i.e., where the barium-to-sulphate ratio was greater than stoichiometric ($[Ba^{2+}]/[SO_4{}^{2-}] > 1$), complete sulphate removal was achieved. Figure 4 indicates that over-dosed barium accelerates the sulphate removal process. This is beneficial since a shorter reaction time requires a smaller reactor, which leads to lower construction costs.

However, a disadvantage of over-dosing with barium is the excess barium in the waste stream. This is highly undesirable and of major concern since barium is very toxic (Science Lab 2011a). It is understood that $BaCO_3$ is highly insoluble, but even at low concentrations the barium in the waste stream may have serious environmental impacts. $BaSO_4$ is also toxic but it is the least toxic salt of barium due to its insolubility (Science Lab 2011b). Special care should be taken to ensure that the product and waste streams do not contain barium particles. Thus, stoichiometric barium dosing will deliver the best results.

Effect of initial sulphate concentration

A stoichiometric amount of barium was dosed ($Ba^{2+}/SO_4{}^{2-} = 1$) into the sulphate rich water. The results are shown in Figure 5.

A limited amount of $CaSO_4$ (gypsum) could be dissolved in distilled water since the solubility constant (k_{sp}) of gypsum is 4.9×10^{-5} at 25 °C. This implies that approximately 2,500 mg/ℓ gypsum can be dissolved into water at 25 °C (Kotz & Treichel 2003). This is supported by the fact that the initial EC was the same for concentrations of 1,600 mg/ℓ and 2,000 mg/ℓ (Figure 5).

Effect of temperature

The effect of temperature on sulphate removal was investigated on reactive $BaCO_3$ that was produced in the laboratory. The batch reactors were kept at a constant temperature (14, 21 or 33 °C) for the duration of the experiments with the help of temperature baths. The effect of temperature on the sulphate removal process is shown in Figure 6.

At higher temperatures the EC value dropped quickly and stabilised. The initial EC value for the higher temperature experiment (33 °C) was also higher than that of the two other experiments

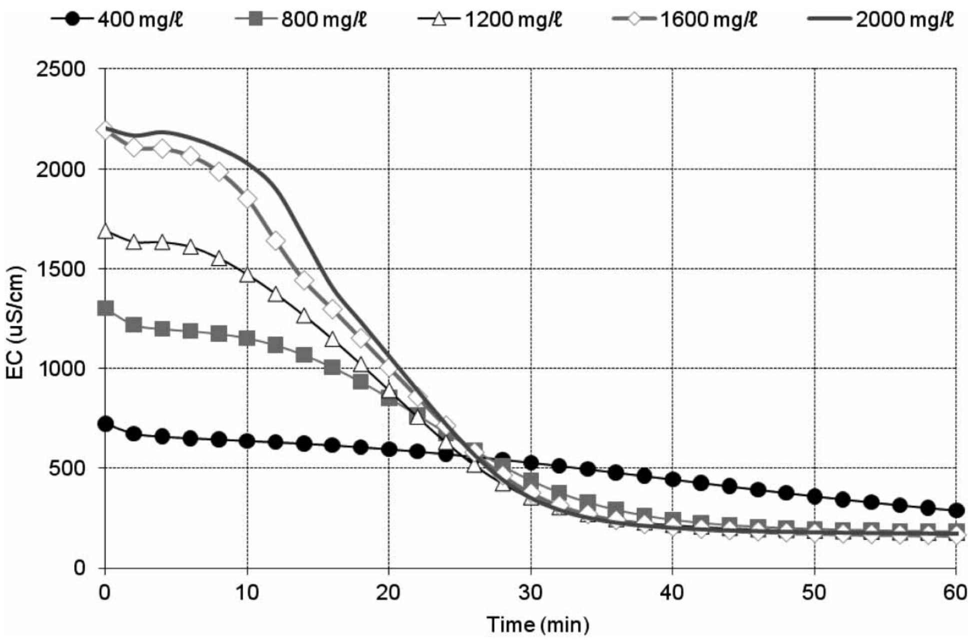

Figure 5 | The effect of the initial sulphate concentration.

conducted at lower temperatures. The experiment done at the lowest temperature (14 °C) took significantly longer to decrease the EC before it settled at the same EC value as before. The middle temperature profile (21 °C) was neatly situated between these two profiles and settled at almost the same EC value as the previous two.

It is known that temperature affects the solubility of compounds (Kotz & Treichel 2003). With temperature increase, compounds solubility increases too (Perry 1997). In this system the solubility constant (k_{sp}) for $BaCO_3$ was 2.58×10^{-9} at 25 °C while k_{sp} for $CaSO_4$ was 4.93×10^{-5} at 25 °C (Kotz & Treichel 2003). This confirms the results of Figure 6.

The correlation between temperature and sulphate removal was evident: the higher the reactor temperature, the faster the sulphate removal rate. Even if the initial reactor temperature was slightly

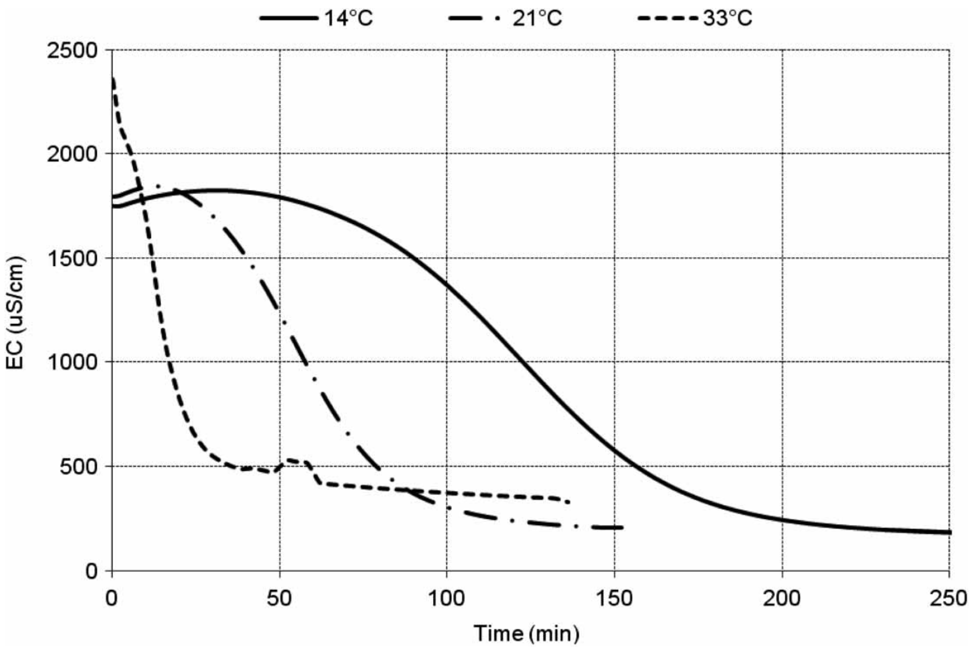

Figure 6 | The EC profile due to the effect of temperature.

higher (e.g., 21 °C instead of 14 °C) the reaction rate could be increased remarkably (as can be seen from the slope of the graphs in Figure 6). The sulphate removal reaction is thus sensitive to temperature changes.

The opposite is also true. If the reactor temperature is slightly cooler (e.g., by 7 °C) than the optimal temperature, the reaction rate would be much slower, resulting in longer retention times causing the process effluent to deviate from the desired quality. This is a problem for the process control since careful temperature control will be required. A slight change in temperature can influence the product quality.

Process water

From here on, the experiments were conducted with industrial process water. The same process water at two different treatment stages was used. The first extraction point was at a pH of 12 after lime neutralisation and gypsum crystallisation (magnesium precipitation occurred here as well). The second extraction point was at a pH of 7, after pH adjustment of the previously mentioned water. Reactive $BaCO_3$ was used to remove sulphate from these process fluids.

$BaCO_3$ can only be used to remove the sulphate from the process fluid that is associated with calcium, as calcium is needed to remove the added carbonate ions associated with the barium cation. The sulphates that are associated with magnesium and sodium will stay in solution (Hlabela *et al.* n.d.). Thus, sulphate can only be precipitated as $BaSO_4$ by using $BaCO_3$ after magnesium is removed.

From laboratory results it is clear that this sulphate removal process works well on AMD. The EC does not decrease as low as the synthetic sulphate-enriched water due to other ions being present in the water. Though the sulphate concentration for the pH 7 experiment decreased from 2,350 mg/ℓ to less than 50 mg/ℓ, and for the pH 12 experiment it decreased from 2,400 to 250 mg/ℓ. The difference in these final sulphate concentrations could be explained by the $BaCO_3$ solubility variation with pH. $BaCO_3$ is more soluble at lower pH levels and thus better sulphate removal could be achieved (Hlabela *et al* n.d.).

CONCLUSION AND RECOMMENDATIONS

It was found that EC measurements can be used to track the progress of sulphate removal successfully. This correlation helped with interpreting the data generated in the experiments that were conducted. The following conclusions were made:

- Not all $BaCO_3$ particles are equally effective in removing sulphate ions from AMD; the particle characteristics have an influence on the reaction. A more detailed investigation is recommended.
- Under-dosing of $BaCO_3$ results in partial sulphate removal. Over-dosing will achieve complete sulphate removal, but excess barium ions will remain in the effluent water which is highly undesirable due to its toxicity. Thus, it is recommended to use stoichiometric dosing of $BaCO_3$.
- A limited amount of sulphate will be dissolved into the process water due to the solubility of gypsum.
- The sulphate removal reaction is sensitive to temperature; a small change can influence the final product quality.
- This sulphate removal process works well on AMD.

ACKNOWLEDGEMENTS

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