Geochemical Study of the Interaction of Acid and Alkaline Mine Drainage with BaCO$_3$

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In this study the geochemical behaviour of BaCO$_3$ was investigated and the optimization of its use in acid (pH 2.93) and alkaline (pH 8.2) mine drainage (AMD) with high concentrations of sulfate (1250-1400 mg/L) and moderate to low metal concentrations (mainly Fe^{2+}> Al^{2+}> Mn^{2+}> Zn^{2+}) was determined. Batch experiments were conducted using a series of four interactions with BaCO$_3$:AMD ratios of 1:400 (0.1g:40mL), 1:57 (0.7g:40mL) and 1:160 (0.25g:40mL), 1:80 (0.5g:40mL) with AMD$_{alkaline}$ and AMD$_{acid}$, respectively. Each series of the experiments were composed of 15 sub-samples in which the reactions were stopped at different time intervals (0', 5', 15', 40', 2h, 6h, 12h, 24h, 36h, 48h, 72h, 96h, 120h, 144h and 168h). The neutralization process increased the pH (to 8.3 and 9.98 for AMD$_{acid/alkaline}$, respectively) through alkaline additive dissolution. The metal solubility decreased with the precipitation of BaSO$_4$ and divalent metals (Mn^{2+} and Zn^{2+}) as carbonates and poorly crystallized Fe-Al oxy-hydroxides. These precipitates acted as a sink for trace elements to the extent that the solutions reached the pre-potability requirements of water for human consumption. In all the experiments, the reactions achieved steady state conditions between 6h to 24h. The results showed 100% SO$_4^{2-}$ removal in AMD$_{acid}$ with an initial concentration of 1250 mg/L within a residence time of 6 hours. While in the AMD$_{alkaline}$ with an initial concentration of 1400 mg/, 86% SO$_4^{2-}$ removal was obtained within 24 h with lower residual barium than 0.1 g:40 mL AMD$_{alkaline}$ interaction. The results showed that this ratio was optimal and could be used in the future for remediation systems. In addition, the treatment of AMD$_{acid/alkaline}$ with BaCO$_3$ removes up to 50% salinity and conductivity. The final product was BaSO$_4$ sludge with moderate to low metal concentrations, which could even be recycled and used by other industries.

Keywords: acid alkaline mine drainage, BaCO$_3$

INTRODUCTION

The Acid Mine Drainage (AMD) generated from pyrite's oxidative dissolution, typically contains high concentration of anions (SO_4^{2-}) and metal (mostly $Fe^{3+}>Al^{3+}>Cu^{2+}>Zn^{2+}>Mn^{2+}$) which makes it a significant environmental problem for South Africa, as well as for other mining countries (Bell et al., 1998; McCarthy, 2011).

The South African AMD is characterized by a wide pH range from acid (2.6) to alkaline (8). The main reason for this fact is that the host rock contains mainly pyrite and carbonates (such as dolomite). Therefore the AMD is characterized by having high salinity (Ca>Mg>Na), hardness and heavy metal concentrations such as $Fe^{3+} > Al^{3+} > Mn^{2+}$ and moderate to low trace metal concentrations such as $Ni^{2+} > Zn^{2+} > Cu^{2+}$ (Durand, 2012).

Therefore, the conventional passive chemical systems based on a $CaCO_3$ or MgO neutralization process are not completely effective for these leachates, because: (1) the acid mine drainage treatment by $CaCO_3$ or MgO allows the neutralization and removal of heavy metals. However, it increases the salinity and hardness in the treated effluent. (2) The low solubility of $CaCO_3$ at high pH limits its use in treating acid and not alkaline drainages (Maree et al., 2004; Caraballo et al., 2011; Bologo et al., 2012). Also the active systems, such as reverse osmosis or GYP-CIX, can remove salinity and hardness. However, the high maintenance costs and the brine generated by the treatment decreases the viability of these systems (INAP, 2003).

Based on hydrogeochemical characteristics of this type of leachate, many treatment systems have been showcased that are generally based on sulfate-reduction bioreactors. This technology, despite having been optimized in recent years, has not been able to completely remove the high concentration of SO_4^{2-} and it did not decrease salinity and hardness in these leachates (Du Preez et al. 1992; Moosa et al., 2002; 2005).

$BaCO_3$ was tested in simple batch experiments in the 70's due to its dissolution in a wider range of pH (0-9) and due to its capability to precipitate sulfate as $BaSO_4$, but it was not considered viable because the dissolution rate was very low at pH values of 7-10 (Kun, 1972). In the 80's, 90's and again in 2006, $BaCO_3$ was tested as a step in an active process to remove sulfate (Trusler et al., 1991; Hlabela et al., 2006). However, these studies did not optimize the $BaCO_3$ concentration, residence time nor provided relevant information about the geochemical behaviour of this compound and its use in AMD treatment.

Current studies have shown that $BaCO_3$ has a good dissolution rate between pH values of 0-6.5 and that the dissolution rate decreases when pH increases. In addition, it was also shown that $BaCO_3$'s dissolution rate increases with increasing temperature because of its endothermic nature. Moreover, previous studies showed variations between theoretical thermodynamics and experimental results regarding the dissolution of the $BaCO_3$ (Li & Jean, 2002).This knowledge is extended in this research which focused on addressing these issues by conducting a geochemical study with $BaCO_3$ and AMD that could explain both its behaviour as well as its potential to remediate these leachates. Understanding these processes will allow the optimization of $BaCO_3$ usage for sulfate removal and its contribution in removing salinity and hardness from acid and alkaline AMD.

METHODOLOGY

Starting materials

Acid and alkaline mine drainage

Two drainages with different hydrogeochemical characteristics from active and abandoned mines were collected from the South African provinces of Mpumalanga (25°42'20.4"S 29°59'28.4"E) and Gauteng (25°50'10.0"S 29°14'03.7"E) which were used as natural reagent solutions for batch experiments. The first drainage was an alkaline mine drainage (AMDE), whose hydrogeochemical characteristics conforms to the average of typical coal mine drainages (high sulphate, salinity and hardness concentration). The second drainage was acid mine drainage collected from an abandoned

mine (AMDK), which is characterized by high acidity and pollutant concentration (Bell et al., 1998; McCarthy, 2011). Each sample was taken on site in polyethylene tanks (ca. 260 L) for further experiments and part of each sample (1L/AMD) filtered through a 0.45 μm filter within 24 h for chemical analysis.

Alkaline material

Alkaline material used in this experiment was $BaCO_3$ (Protea Chemicals Company SA). $BaCO_3$ have a purity of 88.6%. These materials contain impurities including Fe and S as SO_4^{2-}, in negligible concentrations. Finally, a representative and homogeneous sample of 1 g was taken, which has been chemically and mineralogically analysed.

Batch experiment

Batch experiments were conducted to test the interaction of alkaline material with AMDE and AMDK at different time intervals (0min, 5min, 15 min, 40 min, 2 h, 6 h, 12 h, 24 h, 36h, 48 h, 72h, 96 h, 120 h, 144h and 168 h) in falcon tubes (50 mL) under continuous mixing in a rotary mixer at 12 rpm and room temperature. Four series of interactions were carried out using solid:liquid (w/w) ratios of 1:400, 1:57 and 1:160, 1:80 for experiments with AMDE and AMDK, respectively. Each interactions will be identified throughout the paper as E1 that refers to the interaction between 40mL of AMDE and 0.1 g $BaCO_3$; E2 to the interaction between 40mL of AMDE and 0.7 g of $BaCO_3$; K1 to the interaction between 40mL of AMDK and 0.25 g of $BaCO_3$ and K2 to the interaction between 40mL of AMDK and 0.5 of $BaCO_3$. At the end of each time interval, the tubes were removed from the rotary mixer and the supernatant was separated from the solid product by centrifugation at 4000rpm for 3min. Finally, the supernatant solutions were filtered through a 0.45μm filter and the solid product was dried at 40°C.

Chemical analysis

The following parameters were analysed on site from the collected samples to avoid the dissolution effects of the CO_2 (g) and O_2 (g): pH, Electrical Conductivity (EC), salinity (Sal), redox potential (Eh) and temperature (T). The pH, EC, Sal and T were measured with the ExStix®II multi-probe, while Eh was with ExStix®II ORP (Pt and Ag/AgCl electrodes) probe. The Eh measurements were then corrected to standard hydrogen electrode (SHE). Samples were filtered and acidified to pH < 2 with HNO_3 (2%) and stored at 4°C for further chemical analysis at the Institute for Ground Water Studies, University of the Free State. Sulfate concentrations were analysed by a portable Hach spectrophotometer (model DR/900 colorimeter) according to the turbidimetric method described in the Hach Procedures Manual-Method Sulfate 608. Fe^{2+} and Fe_{Total} were determined after filtration (0.45 μm) with a Hach spectrophotometer (model DR/900 colorimeter) according to the colorimetric method described in the Hach Procedures Manual-Method Ferrous iron 255 and FerroVer 265. All these chemical analysis also were carried out on site.

The neutralization potential of $BaCO_3$ was determined by treating a sample with a known excess of standardized hydrochloric acid subjected to heat treatment (95°C). Finally, the amount of neutralizing bases expressed in tons $CaCO_3$ equivalent/thousand tons of material was determined from the amount unconsumed acid by titration with standardized sodium hydroxide (Jackson, 1958).

The $BaCO_3$ was digested by an *aqua regia* solution ($1HCl:1HNO_3:1H_2O$) at 90°C for 1 h up to its complete dissolution (Pérez-López et al., 2010). Total Element Concentration (TEC) from the digestion, as well as the sub-samples, were analysed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Jarrel Ash Atom comp 975). The mineralogical characterization of the final experimental products was carried out by X-ray diffraction (XRD, powder method) using a Panalytical Empyrean diffractometer under following conditions: slit fixed at 10mm, Cu/ Kα monochromatic radiation, 40mA and 45 kV. Samples were run at a speed of 2°θ /min (5-70˚). The spectrum was obtained by Highscore software. In addition, solid samples were also studied using a scanning electron microscope equipped with an energy dispersive system (SEM–EDS; JEOL model GSM 6610).

Geochemical modelling

Precipitation of newly formed solid phases by the $BaCO_3$ dissolution could control the fate of the metal concentrations in both the acid and alkaline mine drainage, studied by the batch experiment. The results of the hydrogeochemical analysis from supernatant of each reaction (sub-sample) were modelled by PHREEQC-2 geochemical speciation model (Parkhurst and Appelo, 2005) using MINTEQ thermodynamic database (Allison et al., 1991) to predict the aqueous speciation of leachates and saturation indices of solid phases in the experiments [SI=log(IAP/KS) where IAP is the ion activity product and KS is the solubility constant]. Zero, negative or positive SI values indicate that the solutions are saturated, undersaturated and supersaturated, respectively, with respect to a solid phase.

RESULT AND DISCUSSION

Characterization of the starting materials

Acid and alkaline mine drainage (AMD)

Results of hydrogeochemical characterization of the AMDs are reported in Table 1. The main difference between the two mine water samples is the pH. The pH values of AMDE and AMDK were 8.2 and 2.93, respectively. In the case of AMDK, low pH values were related to the low carbonate concentration in the host rock, which contain high sulphide concentration. Its intense oxidation and subsequent dissolution of pyrite, produces a large amount of acidity. In the case of the AMDE it had circum-neutral to alkaline pH-values due the low content of sulphide minerals and the presence of carbonate or basic silicate minerals (Banks et al., 2002). The carbonate dissolution also contributes to lowering the water quality by increasing the hardness and salinity, which also affects the ecosystem.

Table 1 Significant physicochemical parameters of the acid and alkaline mine drainages

	AMDE	AMDK
pH	8.2	2.93
EC (mS m^{-1})	209	170
Redox potential (mV)	295	415
Ca (mg/L)	256.0	169.84
Mg (mg/L)	138.9	66.34
Na (mg/L)	12.18	41.30
Ba (mg/L)	0.040	0.028
Fe (mg/L)	0.042	34.24
Al (mg/L)	0.019	44.89
Sulfate (mg/L)	1250.0	1400
Mn (mg/L)	0.023	10.11
Zn (mg/L)	0.016	1.31

Alkaline materials

The neutralization potential of $BaCO_3$ obtained was 525 tons $CaCO_3$ equivalent / thousand tons of material. The neutralization potential of $BaCO_3$ is lower than calcite which has a high neutralizing capacity of 937.5 tons $CaCO_3$ equivalent / thousand tons of materials. However, the calcite is scarcely soluble at circum-neutral pH (6-7), while $BaCO_3$, despite having a low solubility at circum-neutral pH (6-7) is able to dissolve at pH values of up of 8-9. Total Element Concentration (TEC) confirmed the product data from Protea Chemicals, which indicated that the most significant impurities were S and Fe with values of 0.30% (total sulfur as SO_4^{2-}) and 0.004% (Fe total). The average particle size was 1-3 μm.

Preliminary batch experiments were carried out to test the dissolution capacity of the $BaCO_3$ in alkaline and acid mine drainage. The results obtained in these experiments showed a sulfate removal percentage of 90% on average and an increase to pH of 9. The $BaCO_3$ had a higher dissolution at lower pH such as 4-5, whereas, at higher pH such as 8.9 the dissolution of $BaCO_3$ was slower. However, the dissolution of $BaCO_3$ after 24 h showed the same behaviour in both AMDK and AMDE, indicating that the pH does not decrease the dissolution of $BaCO_3$ after 24 h

Hydrogeochemical study of BaCO3 dissolution with AMD

The hydrogeochemical evolution as a function of time of the physicochemical parameters such as pH, Eh, EC, Sal, as well as sulfate concentration in the four ratio (w/v) interactions are shown in Figure 1. The neutralization potential of $BaCO_3$ allowed the pH to increase from 2.93 to 8.27 for the K1 and K2 interactions (0.25 and 0.5 g of $BaCO_3$), and from pH 8.2 to 9.98 on average for the E1 and E2 interactions (0.1 and 0.7 g of $BaCO_3$), respectively. The Eh values decreased from 295 to 67 mV and from 415 to 128 mV on averages, whereas EC decreased to 942 $\mu S/cm$ and 1091 $\mu S/cm$ (variation $\pm 5\%$), for the E1-E2 and K1-K2 interactions, respectively. The decrease in EC values reflects an improvement in the quality of AMDs that was confirmed by the decrease in sulfate concentration in the solution. In the experiments with AMDK all these parameters achieved a steady state in 6 h in both interactions (K1 and K2). The behaviour of $BaCO_3$ was different for the interactions with AMDE (E1 and E2), where a steady state was achieved after 24 h. The sulfate concentrations decreased slowly after 24 h (E 1 and E2 reached 280 and 120 ppm after of 168 h) without achieving a steady state, while in the K1 and 2 interactions, the sulfate concentration was completely removed after 24 h. $BaCO_3$ dissolution was faster in the K2 interaction where the pH increased from pH 2.93 to 6.79 and the interaction was almost immediate. However the Sal and EC evolution was slower.
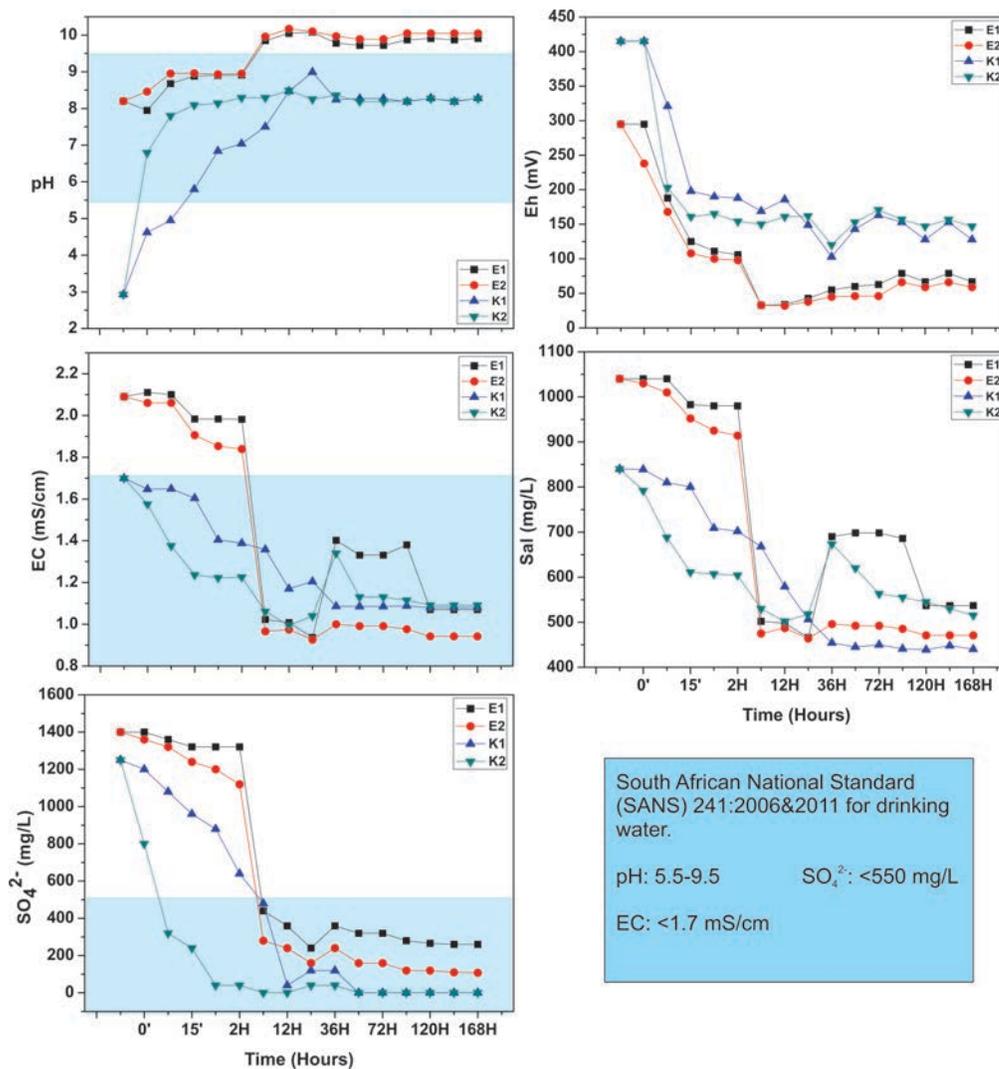
Figure 1 Temporal evolution of the physicochemical parameters from 0 to 168 h and its relation with drinking water standard (SANS 241)

The evolution of metals and sulfates are closely related to the dissolution rate and the concentration of $BaCO_3$ (Figure 2). Therefore, optimization and understanding of its behaviours is vital to assess its remediation potential. The interaction with a concentration of $BaCO_3$ larger than 0.1g (E1) showed higher concentration of dissolved Ba^{2+} at the end of the experiment (0.33, 6.7, 4.1 mg/L in E2, K1 and K2, respectively) which did not react during the experiment. Therefore, the concentration of $BaCO_3$ used in E1 can be considered as the optimum to be used in passive and active systems with a residence time of 24 hours, at most, to get an 86% sulfate removal rate.

The hydrogeochemical behaviour of the cations, such as Ca^{2+}, Mg^{2+} and Na^+ over time was similar, between E1 and E2, as well as between K1 and K2. Ca decreased drastically within 6h, the removal reached 97 % in the E interactions, but in K interactions took 120 h to reach 51% of Ca^{2+} removal. The concentration of Na^+ only decreased 18 % in K interactions.

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The evolution of metals during the experiment will only be described and discussed with regards to the K interactions, due to the insignificant concentration of metals in AMDE. The concentration of metals in AMDK was as follow, $Al^{3+} > Fe^{3+} > Mn^{2+} > Zn^{2+}$ (44.89 > 34.24 > 10.1 > 1.3, respectively). The removal of Fe^{3+}, Al^{3+} and Zn^{2+} were 100%. However the removal of Mn was 66% in 24 h and 86% in 120 h.

Parameters such as EC, Sal and hardness decreased in all the interactions to values below the allowable limits for drinking water (SANS 241, 2006; 2011) (Figure 1). The removal of SO_4^{2-}, Ca^{2+} and heavy metals was the main reason for those parameters to decrease. Most of the passive systems are not able to remove Ca^{2+}, but increase its concentration (such as the systems based on $CaCO_3$), however this system has demonstrated its effectiveness in removing anions (SO_4^{2-}) and cations (mainly Fe^{3+}, Al^{3+}, Mn^{2+}, Zn^{2+} and Ca^{2+}) which is also reflected in the concentration of Sal and EC of the drainage.
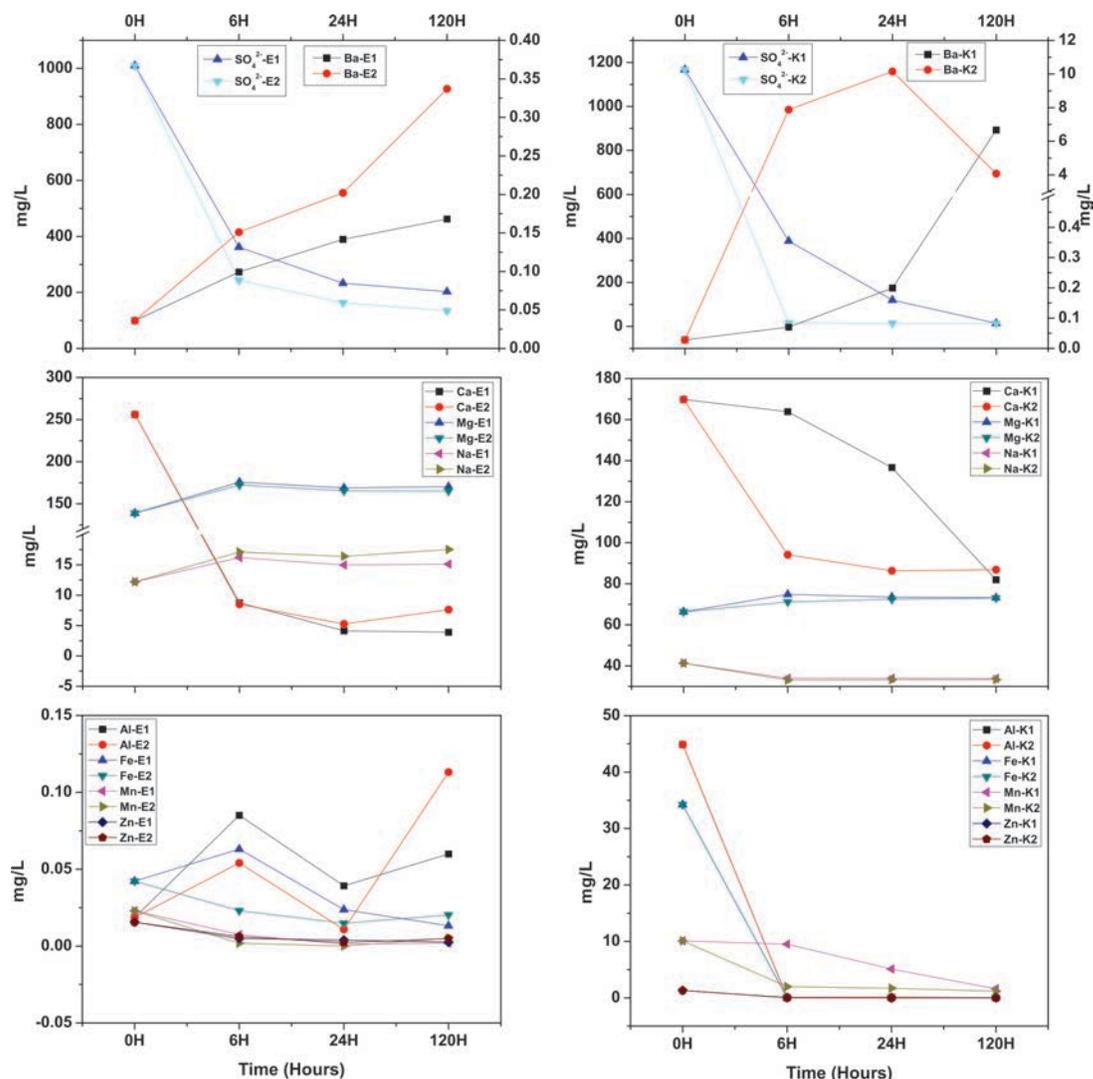
Figure 2 Temporal evolution of cations and anions from 0 to 168 h

The precipitates collected at the end of the experiment from E1 and K1 interactions, were analysed by XRD (Figure 3). The analyses showed mainly mineral phases related to the dissolution of $BaCO_3$ as well as to the precipitation of sulfate and Ca^{2+}. The geochemical processes involved in the increased of pH, as well as the sulfate, Ca^{2+}, Mg^{2+} removal, including Fe^{3+}, Al^{3+}, Mn^{2+} and Zn^{2+} has been represented by the following equations:

1. Representation of dissolution of $BaCO_3$ in AMD:

$$BaCO3s \rightarrow Ba2+(aq)+CO32-(aq) \tag{1}$$
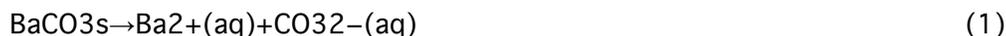
2. pH values were increased by releasing OH$^-$ radicals and formation of CO_2 that could act as a buffer to control the increase of pH .

$$CO32-aq+ H2Ol \rightarrow HCO3-aq+ OH-aq \tag{2}$$

$$HCO32-aq+ H2Ol \rightarrow H2CO3-aq+ OH-aq \tag{3}$$

$$H2CO32-aq \rightarrow CO2aq+ H2O(l) \tag{4}$$

3. The increased pH values would allow the trivalent and divalent metals precipitation as oxy-hydroxides and/or oxy-hydroxysulfate of Fe^{3+} and Al^{3+} and carbonates of Mn^{2+} of Zn^{2+}, respectively. In addition, the presence of carbonates and bicarbonates in solution would promote the Ca^{2+} and Mg^{2+} removal as carbonates and thus reduce the hardness of these AMDs.

$$Me+HCO3- \rightarrow MeCO3+H+ \tag{6}$$

$$Me+H2CO3- \rightarrow MeCO3+2 H+ \tag{7}$$

The estimated percentage of those mineral phases were, according to the contact time (0h, 6h and 168 h), as follow: E1: 0h: witherite (71.2%) > calcite (15.9%) > barite (12.9%); 6h: barite (63.8%) > witherite (26.5%) > calcite (9.7%); 168h: barite (65.7%) > calcite (19.2%) > witherite (16.9%). K1: 0h: witherite (76.2%) > barite (13.5%) > calcite (10.3%); 6h: witherite (71.4%) > barite (18.9%) > calcite (9.6%); 168h: witherite (53%) > barite (28.5%) > calcite (18.5%).
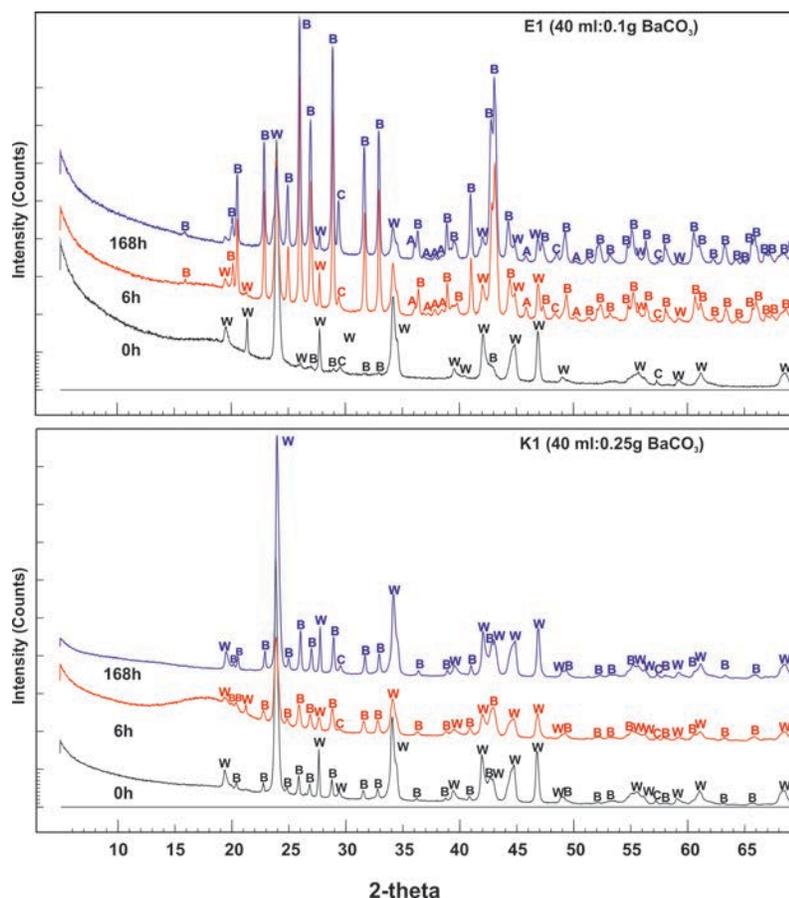
Figure 3 Difractograms of E1 and K1 at 0, 6 and 168 h. W: witherite, B: barite, C: calcite and A: aragonite

However these mineral phases could be masking other sub-idiomorphic or amorphous crystals, mainly in the K interactions, where the metal concentrations were high. This was corroborated by SEM-EDS analyses, where Fe^{3+}, Al^{3+} and Mn^{2+} were detected in the precipitates (Figure 4). The thermodynamic simulation with PHREEQC also supported this hypothesis by predicting the precipitation of Fe^{3+} and Al^{3+} as oxy-hydroxysulfate, poorly crystallized according to XRD analyses. This acted as a sink for trace elements and contributed to reaching the requirements for drinking water. The minerals phases of Mn^{2+} and Zn^{2+} were not predicted to be saturated by PHREEQC, however both metals were 100% removed from the AMDs. This again demonstrated that there are several discrepancies between the theoretical thermodynamic fundaments and the real geochemical data acquired throughout the experiment. Finally, the improvement of the quality of the AMDs used in the four interactions has been so effective that the final concentration of the sulfates was within the limit allowable for drinking water (South African National Standard 241, 2006; 2011).
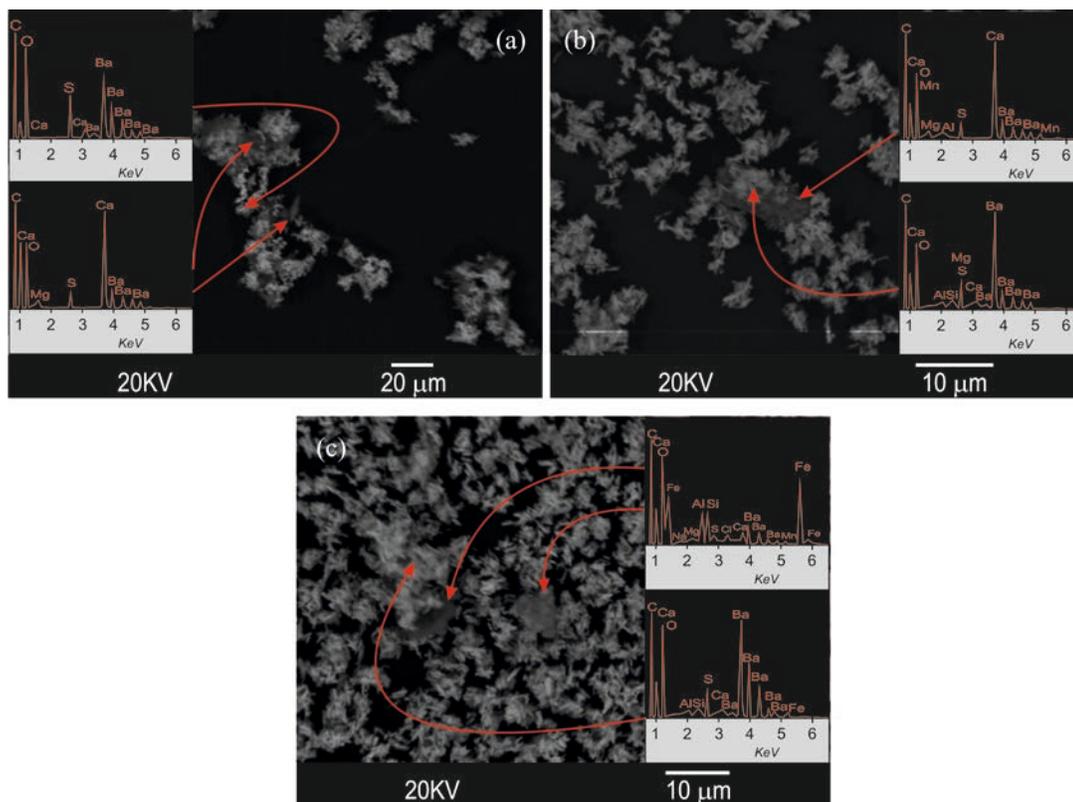
Figure 4 SEM-EDS images of minerals phase neoformed poorly crystallized

CONCLUSIONS

Batch experiments were conducted with the aim to study the behaviour and optimize the use of $BaCO_3$ in AMD remediation. Four interactions were carried out with two different AMDs and four different ratios (w/w) $BaCO_3$: AMD (1:400 and 1:57 with AMDE (alkaline) and 1:160 and 1:80 with AMDK (acid)). Each interaction was composed of 15 sub-samples, each of them with different contact time between AMD and $BaCO_3$ (from 0 to 168 h). All the samples achieved a steady state between 6 and 24 h. However the low solubility of the $BaCO_3$ at high pH slowed down the dissolution in E interactions, where the pH reached up 9.98 and the dissolution continued after 168 h. Nevertheless, E1 interaction reached a sulfates removal of 86% between 6 and 24 h. The sulfates and Ca removal were the most meaningful results in E interactions. Moreover, the total metal removal in K interactions was the determining factor for the improvement of the water quality. According to these results, the ratio used in the E1 interaction can be considered as the optimum to be used in systems with a residence time of 24 hours.

XRD and SEM-EDS analyses corroborated the sulfates and metals evolution over time by the identification of crystalline and amorphous mineral phases. The modelling also predicted the precipitation of mineral phases such as barite, calcite and Fe/Al oxy-hydroxides. However there were discrepancies between the predictions and the data acquired from the experiments, such as the removal of Zn and Mn that probably were precipitated as carbonates. Therefore the $BaCO_3$ dissolution varies according to the pH and the composition of the AMD. However, at the end of each experiment the water was within the South African National Standard for drinking water.

ACKNOWLEDGEMENTS

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