

# Evidences of Effective Treatment of Alkaline Mine Drainage with BaCO<sub>3</sub>

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## ABSTRACT

An experimental lab scale reactor that treats alkaline mine drainage has been developed based on hydrogeochemical characteristics of most of the South African coal mines leachates, which generally have high concentrations of sulfates, TDS (total dissolve solid), salinity and heavy metals (mainly Fe<sup>3+</sup> and Al<sup>3+</sup>).

The experiment development was based on the DAS system (disperse alkaline substrate). In this case, barium carbonate (BaCO<sub>3</sub>) was used as alkaline reactive, fixed to a non-toxic inert matrix (wood chips). The experiment was carried out with 3 different proportions of wood:BaCO<sub>3</sub> (w/w); 1:2, 1:3 and 1:4 with a residence time of 24 hours. SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> contained in AMD precipitate as BaSO<sub>4</sub> and CaCO<sub>3</sub>, respectively, according to (1) thermodynamic modelling by PHREEQC, (2) geochemical and (3) mineralogical characterization. The pH increased up to 9-10, which allowed the removal of divalent metals. Reactors were maintained for 6 months and the results that were acquired from all of them demonstrated their reactivity, without saturation or clogging in any of the columns, towards the total removal of nitrates (100%), 93% of sulfates, 50% hardness (Ca<sup>2+</sup>, Mg<sup>2+</sup> and Na<sup>2+</sup>), as well as 68-93% of metal removal (Fe<sup>3+</sup>, Al<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Mn<sup>2+</sup>, in moderate concentrations). Therefore, parameters such as salinity, TDS and conductivity decreased throughout the experiment. Water volume treated was approx. 764 L during 26 weeks in the lab scale reactors and the physicochemical parameters of the water after treatment are within the allowable limits for drinking water, according to SANS 241 class 1 for Drinking Water (South African national standard, 2006; 2011).

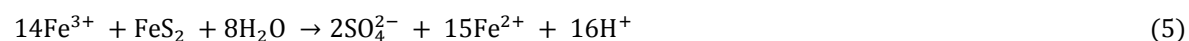
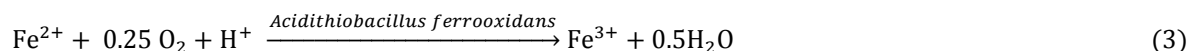
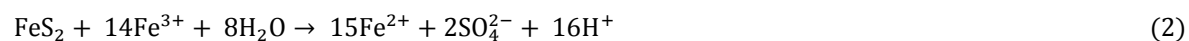
## INTRODUCTION

### *Coal mine drainage*

South Africa has 95% of Africa's known coal reserves and the 9<sup>th</sup> biggest recoverable coal reserves (61 000 Mt) in the world where 27 400 Mt were proven coal reserves in 2012 (Energy Information Administration, 2014).

These coal deposits have about 4% of pyrite (Snyman & Botha, 1993; van Dyk, 2006) which is the cause for the coal mine drainage to contain sulphur. However the typical acidity produced by the oxidation of pyrite (equations 1 and 2) and by the subsequent oxidation and precipitation of Fe (equation 3 to 5) is neutralized by the CO<sub>3</sub><sup>2-</sup> released from the calcite (CaCO<sub>3</sub>) and dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) that is contained in South African's coal; about 6.7% and 10.1% respectively (van Dyk, 2006). Therefore, coal mines in South Africa can generate acid, neutral or alkaline mine drainage (AMD) (Kirby, Dennis & Kahler, 2009). When pyrite and other sulfide minerals associated with coal deposits are exposed to water and oxygen, several chemical and biochemical reactions take place. These reactions can be seen in the Singer & Stumm (1970).

Oxidation of pyrite can be produced by oxygen (eq. 1) or ferric iron (eq. 2) in the presence of water. Further oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> occurs when sufficient oxygen is dissolved in the water or when water is exposed to atmospheric oxygen (eq. 3). This reaction is also accelerated by the presence of oxidizing bacteria such as *Acidithiobacillus ferrooxidans*. Ferric iron can either precipitate as Fe(OH)<sub>3</sub>, (eq. 4) or it can react directly with pyrite to produce more ferrous iron and acidity as shown by eq. 5. The presence of alkaline compounds such as calcite and dolomite decreases the acidity of the AMD by consuming protons (H<sup>+</sup>) and releasing bicarbonate anion (HCO<sub>3</sub><sup>-</sup>) as shows the eq. 6 and 7 (Pokrovsky, Golubev & Schott, 2005).



Therefore the alkalinity of the coal mine drainage depends, among others, on the ratio between acidic and alkaline minerals of each specific coal deposit and surroundings.

### *Case study*

The case study was done on the alkaline drainage generated by a coal mine situated at (25°42'23.2"S, 29°59'32.7"E), that is mining the coal from the north eastern coalfield of the Karoo basin, located in Mpumalanga province. The AMD generated is collected in the evaporation dam located SW within the facility area (25°42'20.4"S 29°59'28.4"E). This AMD has a pH of 7.45 and, in contrast, the electrical conductivity (EC), salinity (Sal) and total dissolved solids (TDS) are fairly high (2090 µS/cm, 980 mg/L and 100mg/L, respectively). The AMD has high concentrations of sulfates and nitrates (1 253 mg/L and 3 032 mg/L respectively) as well as dissolved Ca and Mg (262.41 mg/L and 132.60 mg/L respectively).

### *State of the art AMD treatments*

Many passive and semi-passive treatments have been developed over the past three decades to remediate AMD, such as aerobic and anaerobic wetlands, Anoxic Limestone Drains (ALD), limestone sands, beds, ponds and open channels, diversion wells, reducing and alkalinity producing systems (RAPS), ReRAPS, water-powered devices, windmills, sodium carbonate briquettes, sodium hydroxide, hydrated lime and quick lime ( e.g. Watzlaf et al., 2004). Recently, a new system has been developed with the aim to solve the clogging problem caused by the Al<sup>3+</sup> and Fe<sup>3+</sup> precipitation that has been documented in many of these systems (Robbins et al., 1996; Cravotta and Trahan, 1999; Watzlaf et al., 2000; 2002; Rees et al., 2001; Ziemkiewicz et al., 2003; Rose et al., 2004). This new system called Dispersed Alkaline Substrate (DAS) consists of an inert matrix of wood chips, which provide high permeability and reduce clogging problems, mixed with a fine-grained alkaline material such as limestone sand (Rotting et al., 2008).

The reactor system that the authors have developed on a laboratory scale is based on a modified DAS system. The modification includes the substitution of limestone (CaCO<sub>3</sub>) with barium carbonate (BaCO<sub>3</sub>) powder. This system, called B-DAS, has been designed with the aim to improve the removal of sulfates by precipitating it as BaSO<sub>4</sub> as well as improving the salinity (see reactions below). The aim is extended to find a system that is able to remediate not only acid mine drainage but neutral and alkaline mine drainages as well. BaCO<sub>3</sub> easily dissolves at a pH above 4 which makes it ideal to treat these drainages. The AMD used in this study has a pH of 7.45 which undergoes the dissolution process as follow; BaCO<sub>3</sub> is dissolved (eq. 8). Dissolved sulfates can precipitate as barium sulfates (eq. 9). The pH is increased to 10 by consuming protons and releasing hydroxide anion (eq. 8) and bicarbonate anion (eq. 10). The high pH and the presence of bicarbonate anions promote metal precipitation as carbonates (e.g. Ca and Mg):



## METHODOLOGY

### *Column experiment*

Three down-flow columns were constructed from PVC pipes (10 cm inner diameter, height 50 cm) and equipped with four additional lateral sampling ports. Each port had a small perforated pipe in the column matrix to promote homogeneous samplings and allow homogeneous flow within the columns by increasing the area of sampling while, avoiding, as far as possible, preferential flow.

Each column contained a layer of quartz gravel (particle size about 5-8 mm) at the bottom (2.5 cm). This layer was covered with a 40 cm reactive material layer, which consisted of BaCO<sub>3</sub> and wood shaving mixture. Each column had different ratios of wood: BaCO<sub>3</sub> (w/w); these were columns (A) 1:2 (260g:520g), (B) 1:3 (240g:720g) and (C) 1:4 (220g:960g).

During the six months of the experiment the down-flow reactors, with supernatant open to the atmosphere, were fed with the AMD, as input water from the top using a peristaltic pump and flowed down gravitationally. The outflow was collected in a container that also functioned as an aeration and sedimentation tank. The flow rate was 1.09 mL / min with a residence time of 24 hours for each B-DAS columns. The porosity of the systems was 70% (volumetrically calculated).

### *Sampling*

During the first week of the columns running, samples were taken daily from the outlet of each column (A, B and C) and after that sampling was done weekly for the next six. Another set of samples were taken monthly from the four sampling ports of each column, to evaluate the spatial evolution of each column during the experiment.

Finally, the columns were drained and column C was cut with an angle grinder to have access to the precipitates formed on the wood shavings (see left of figure 4). Three samples of precipitates were collected at the top, middle and bottom of the column for further analysis.

### *Analytical techniques*

#### Water analysis

Source water was collected from the evaporation dam in 25L carboys, transported to the laboratory and stored at 4°C. pH, EC, Sal, TDS, redox potential (ORP) and temperature (T) was measured on site. These physicochemical parameters were also analysed from the columns weekly and monthly. The measures were done with the ExStix®II multi-probe and ExStix®II ORP probe. ORP measures were corrected to the Eh standard hydrogen electrode (SHE). Samples were analysed by ICP at the Institute for Groundwater Studies at UFS, filtered and acidified to pH < 2 with HNO<sub>3</sub> 2% (v/v), to compare influent and effluent chemistry of the columns. Sulfate (SO<sub>4</sub><sup>2-</sup>), Fe<sup>2+</sup> and Fe<sup>Total</sup> concentrations were analysed by a HACH spectrophotometer (model DR/900 colorimeter) according to the colorimetric methods described in the HACH Procedures Manual (Method Sulfate 608, Method Ferrous iron 255 and FerroVer 265, respectively).

### Geochemical modeling

The precipitation of newly formed solid phases by the BaCO<sub>3</sub> was confirmed by using a thermodynamic model (PHREEQC) as well as by characterizing the final solid products. These saturated mineral phases in the system were estimated, assuming that the initial solution in contact with an alkaline material (in our case BaCO<sub>3</sub>) reaches equilibrium with that material. The PHREEQC-2 geochemical speciation model (Parkhurst & Appelo, 2005) in conjunction with the MINTEQA thermodynamic database (Allison et al., 1991) was used to determine the aqueous speciation of solutions and saturation indices (SI) of solid phases that could control the concentration of dissolved species in the simulation  $SI = \log(IAP/KS)$  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 regards to a solid phase.

### Mineralogical characterization

The Panalytical Empyrean x-ray diffractometer (XRD) was used under the following conditions: slit fixed at 10mm, Cu / K $\alpha$  monochromatic radiation, 40mA and 45 kV. Samples were run at a speed of 2 $^\circ\theta$  /min (5-70 $^\circ$ ) to analyse the precipitates formed. Interpretation of data was done by the Highscore program. Samples were milled previously to a particle size less than 10 micron. Due to the small quantity of sample, a zero-background wafer sample holder was used.

The scanning electron microscope Jeol GSM 6610 equipped with energy dispersive system (SEM-EDS) was used for the analysis, along with Astimex 53 Minerals Mount MINM25-53 standards. The accelerating voltage of the beam during analysis was 20.0 kV with a spot size of 50 and working distance of 10 mm. Sample preparation for this method involves a strip of double-sided carbon tape attached to a glass section. The samples were coated with a thin layer of carbon ( $\pm$  15-100nm) to prevent charging.

## RESULTS AND DISCUSSION

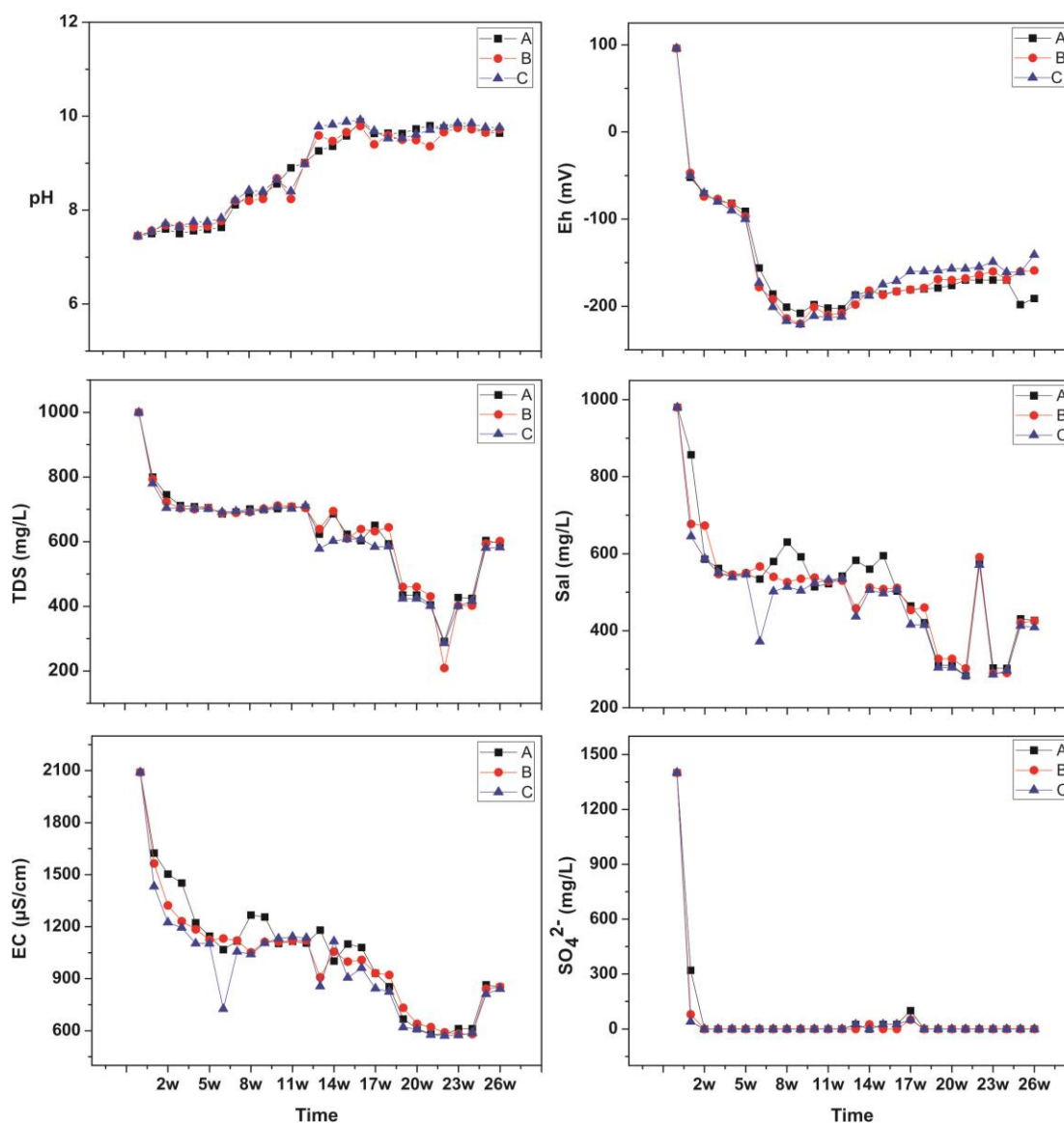
### *Water analysis*

#### Temporal evolution

Figure 1 indicates that the data of the three columns are similar; the pH increased from 7.5 to 9.8 and the rest of the parameters (TDS, Sal, Cond, Eh, sulfates and iron) decreased from the first sampling performed after 24 hours. Fe<sup>2+</sup> and Fe<sup>Total</sup> concentrations were always below detection limit (BDL). The sulfate concentration decreased from 1400 mg/L to BDL after one week. However Sal, TDS and Cond reached the lowest values after four months (from 980 mg/L, 1000 mg/L and 2090  $\mu$ S/cm to 283 mg/L, 209 mg/L and 576  $\mu$ S/cm, respectively). The Eh decreased from 296 to 150 mV within the first 24 hours and continued to decrease for two month to -21 mV, thereafter stabilized at about  $-35 \pm 15$  mV.

The ICP analysis (Table 1) shows that the concentration of the Ba in the water increased in the first sampling, this is probably because the BaCO<sub>3</sub> powder that is not attached to the wood shavings is released into the water, however the Ba concentration decreased and stabilized around 0.7 mg/L thereafter. Most of the compounds started to decrease within 24 hours such as Ca, Mg, Cl, NO<sub>3</sub>, SO<sub>4</sub>

and Zn; from 262.4, 132.6, 9.2, 3032, 1253, 0.007 mg/L to 36.8, 97.8, 4.1, 1766, 147 and 0.003 mg/L, respectively (calculated as the average of the three columns). The rest of the compounds, such as Na, K, Al, Fe and Mn clearly started to be removed from the second sampling (5<sup>th</sup> week) from 4.9, 5.9, 0.044, 0.057 and 0.03 mg/L to 3.1, 5.3, 0.03, 0.008 and 0.002 mg/L, respectively (calculated as the average of the three columns). At the end of the experiment all the compounds were within the limits allowable for drinking water according to SANS 241 (South African national standard 2006; 2011), except for the Mg that exceed the limit by 15mg/L. The final removal of each compound is shown in Table 2. The similar evolution of the three columns, allowed for the spatial evolution analysis to be performed in column B and the geochemical characterization of the precipitates in column C.



**Figure 1** physicochemical parameters (pH, sulfates, Sal, TDS, Cond and Eh) of the water samples collected from the outlet of the three columns (A, B and C) over time

**Table 1** ICP water analysis of the main chemical compounds at the inlet and outlet of the columns A, B and C (As, Cu, Cd, Ni, Pb and Cr were always below detection limit (BDL))

	NO <sub>3</sub>	Ca	SO <sub>4</sub>	Mn	Na	Fe	Al	Zn	Mg	K	Cl	Ba
<b>INLET</b>	<b>3032</b>	<b>262.4</b>	<b>1253</b>	<b>0.03</b>	<b>4.9</b>	<b>0.057</b>	<b>0.044</b>	<b>0.007</b>	<b>132.6</b>	<b>5.9</b>	<b>9.2</b>	<b>0.11</b>
<b>Day 1</b>												
<b>Sept A</b>	1784	45.6	233.3	0.065	6.9	0.071	0.044	0.004	89.7	23.6	4.3	92.79
<b>Sept B</b>	1843	27.1	133.5	0.034	5.2	0.009	0.027	0.003	112.9	32.7	4.1	76.37
<b>Sept C</b>	1670	37.8	74.4	0.042	7.2	0.027	0.041	0.003	90.9	12.8	4	77.07
<b>Month 2</b>												
<b>Oct A</b>	1685	11.2	240	0.002	2.9	0.008	0.029	0.006	132.3	4.6	5.9	0.95
<b>Oct B</b>	1701	9.7	218.2	0.002	3.2	0.011	0.029	0.004	137.8	5.2	5.6	1.36
<b>Oct C</b>	1715	10.6	253.1	0.003	3.1	0.004	0.031	0.004	133.2	6.1	5.4	1.45
<b>Month 4</b>												
<b>Dec A</b>	2.8	5.3	116	0.002	1.4	0.024	0.006	0.002	118.2	6.7	9.6	0.67
<b>Dec B</b>	1	5.3	71.9	0.001	1.8	BDL	0.002	0.004	141.8	3.7	6.3	0.80
<b>Dec C</b>	1.1	4.8	68.6	0.001	1.2	BDL	0.005	0.003	118	4	6.4	0.73
<b>Month 6</b>												
<b>Feb A</b>	0.3	4.7	78.8	0.002	BDL	0.006	0.008	0.002	111.1	4.8	6.6	0.75
<b>Feb B</b>	0.3	5	88.6	0.001	1.2	0.006	0.007	0.003	120	4.9	7.5	0.73
<b>Feb C</b>	0.3	5	96.6	0.003	BDL	0.055	0.009	0.003	113.2	11.8	14.8	0.74

**Table 2** percentage removal of the main compounds in the three columns at the end of the experiment

Removal %	NO <sub>3</sub>	Ca	SO <sub>4</sub>	Mn	Na	Fe	Al	Zn	Mg
<b>Column A</b>	99.99	98.2	93.7	94.2	100.0	89.3	82.0	73.1	16.2
<b>Column B</b>	99.99	98.1	92.9	95.6	74.3	89.4	84.6	65.9	9.5
<b>Column C</b>	99.99	98.1	92.3	89.0	100.0	92.2	78.8	65.8	14.6
<b>AVERAGE</b>	99.99	98.1	93.0	92.9	91.4	90.3	81.8	68.3	13.4

Spatial evolution

Two sets of samples from the four sampling ports, named from top to bottom: one, two, three and four, were collected from column B and analysed. The residence time of the AMD in the column was 24 h, therefore the contact time with the reactive material of the samples from each port was approximately 6, 12, 18 and 24 h, respectively. The results (Figure 2) show that the removal of every compound analysed occurred mainly at port one. The composition of the water at port two, three and four had no significant differences. Therefore, the fast dissolution of the BaCO<sub>3</sub> in contact with the AMD is displayed. This is also demonstrated by the analysis of precipitates.

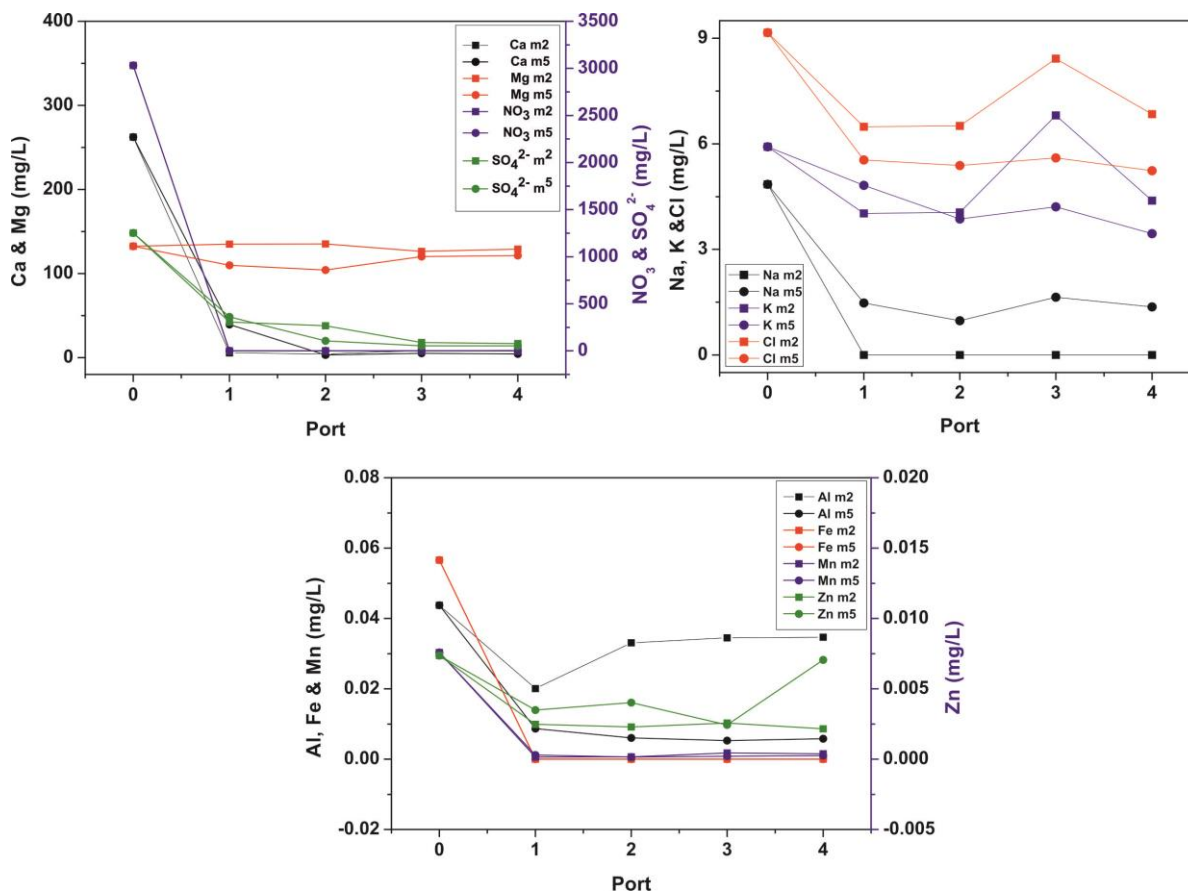


Figure 2 Spatial evolution of the main chemical compounds of the water throughout column C, from top (inlet) to bottom (port 4)

### Geochemical modelling

The simulation was based on the physicochemical characteristics of the AMD used as the solution in this experiment. Witherite was assumed as equilibrium phase 0, since total dissolution was expected. The predicted precipitates were barite ( $\text{BaSO}_4$ ; SI~3.49), calcite ( $\text{CaCO}_3$ ; SI~1.25), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ; SI~2.50),  $\text{Fe}(\text{OH})_{3(a)}$  (SI~1.75), hausmannite ( $\text{Mn}_3\text{O}_4$ ; SI~15.34) and pyrolusite ( $\text{MnO}_2$ ; SI~9.85). However, due the low concentration of Fe and Mn, those precipitates could be masked in the XRD analysis.

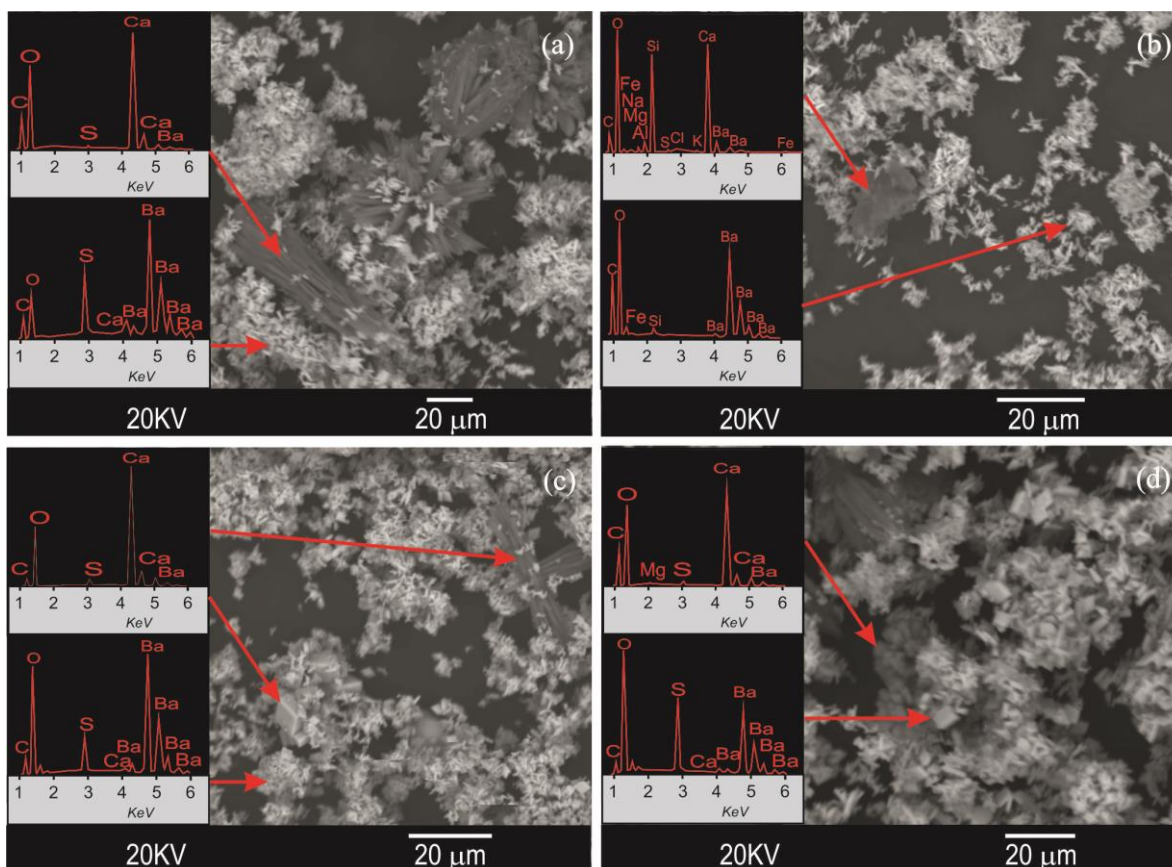
### Mineralogical characterization

According to the SEM-EDS analysis of the bottom sample, the composition of most of the crystals were mainly Ba (79 - 95%), O (4 - 21%) and some of them also had trace amounts of sulfur (0.5 - 4%) in the form of clear needles smaller than 5 $\mu\text{m}$ . The XRD analyses determined that those crystals were 95.1% witherite ( $\text{BaCO}_3$ ) and 4.9% barite ( $\text{BaSO}_4$ ) (red diffractogram in Figure 4). In the middle

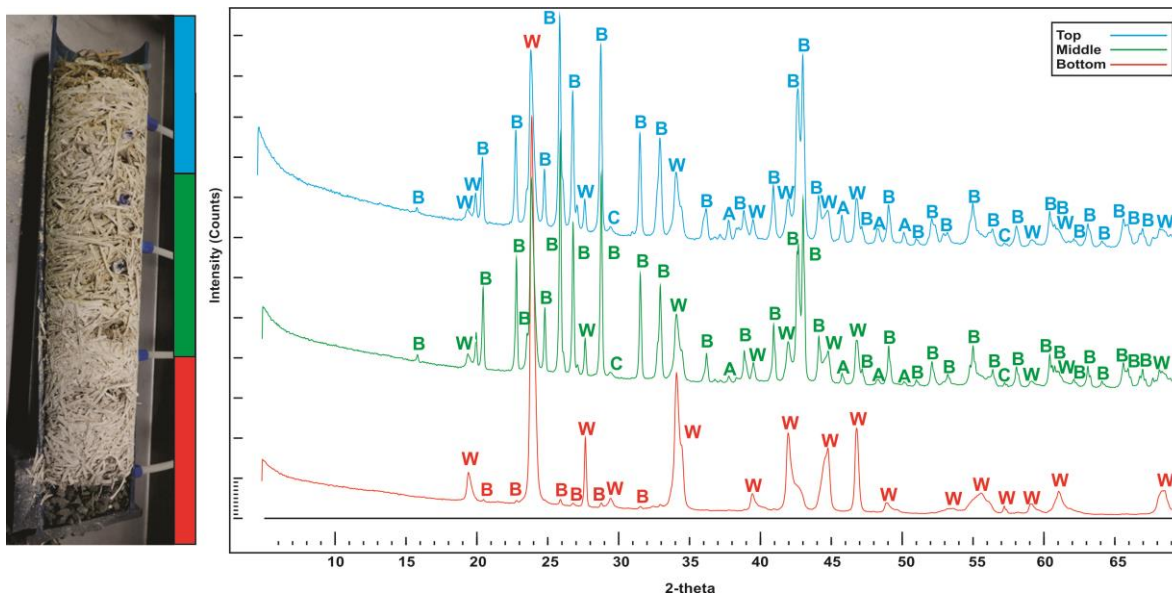


sample the concentration of witherite was lower (24.4%); the precipitation of barite increased (56.4%); the precipitation of Ca detected in SEM analysis (Figure 3c & d) was confirmed by the XRD analysis where calcite and aragonite were detected (6.4 and 12.8% respectively). However, the precipitation of Mg and K detected by SEM were masked in the XRD analysis, mainly due to the high concentration of barite (green diffractogram in Figure 4). In the top sample the concentration of witherite (Figure 3b) and barite were slightly lower (23.4 and 46.7%, respectively), but calcite and aragonite concentrations were higher (7.6 and 22.3%, respectively) (Figure 3a). In this section of the column precipitates with Al, Fe, Mg, Na, Si, Cl and K were also found (Figure 3b).

According to the analyses, the AMD dissolves the  $BaCO_3$  in the top of the column and releases  $Ba^{2+}$  and  $HCO_3^-$ , both precipitate mainly as  $BaSO_4$  and  $CaCO_3$ . Thereafter, the AMD was already remediated and did not continue to react with the  $BaCO_3$  in the column. This is confirmed by the neoformed minerals found at the top and the middle, whereas the bottom sample still had reactive  $BaCO_3$  and no neoformed mineral phase was found. Furthermore, in the picture of Figure 4 it can be observed that the bottom of the column is still white due the  $BaCO_3$  that remained on it.



**Figure 3** SEM images of (a) top sample: fibrous aggregates of  $CaCO_3$ , acicular  $BaSO_4$ , (b) amorphous precipitation and  $BaCO_3$ ; (c) middle sample: fibrous and rhombohedral crystals of  $CaCO_3$  and acicular  $BaSO_4$  (d) globular  $CaCO_3$  and orthorhombic  $BaSO_4$ .



**Figure 4** XRD diffractograms of the three samples: bottom (red), middle (green) and top (blue) of column c (left picture). W: witherite, B: barite, C: calcite and A: aragonite

## CONCLUSIONS

764 L of alkaline coal mine drainage from the site was treated by the B-DAS (Barium carbonate - disperse alkaline substrate) system in lab scale reactors. The aim to remove the high cations and anions concentration as well as the Sal and TDS from this drainage was achieved. According to the water analysis and the mineralogical characterization, the B-DAS system has demonstrated the capacity to remove 93% of sulfates through the precipitation of barite ( $\text{BaSO}_4$ ); 98% of Ca by precipitation of calcite and aragonite ( $\text{CaCO}_3$ ); remove Mn, Na, Fe, Al, Zn, Mg (93, 91, 90, 82, 68 and 13%, respectively). K and Si were also found in the neoformed precipitates.  $\text{NO}_3^-$  was also removed (99.9%) from the AMD, but the absence of N in the precipitates and the extremely reductive condition in the reactor (Eh about -35 mV) could have promoted the denitrification process. The EC, Sal and TDS decreased about 50 – 70%.

According to the XRD analysis, after 6 months, column C had about 22 % of the  $\text{BaCO}_3$  at the top and 95 % at the bottom of the column. Therefore, the reactive capacity of the  $\text{BaCO}_3$  could be extended. Neoformed crystals were found in the top and middle samples, but not in the bottom sample, indicating that the dissolution of the  $\text{BaCO}_3$  and the consequent precipitations took place in less than six hours (estimated residence time of the water in the top section of the column), demonstrating the effective treatment and the capacity of this system.

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