

Neutralization of Acid Drainage and Concentration of Rare Earth Elements Using Carbonatites – Results from a Bench Scale Experiment

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Abstract

Remediation of acid mine and industrial drainages has high costs involved due to the infrastructure, consumables and disposal of the waste produced by current water treatments. This study provides the first insight into a novel neutralization process using rare earth-bearing carbonatite from a waste rock dump that generates a marketable by-product, capable to defray the water treatment cost.

Mineralogical and geochemical analysis of the carbonatite, performed before and after the treatment, showed REE-enrichment in a specific section of the water treatment prototype, while the hydrochemical analysis of the water revealed effective neutralization and removal of pollutants.

Introduction

The environmental impact of acid drainages in South Africa affects ground- and surface water in a country already stricken by the extreme scarcity of water resources. Ba-Phalaborwa municipality of Limpopo province is a clear example of this environmental impact. The Phalaborwa Industrial Complex (PIC) hosts manufacturing plants and mines, whose activities are closely monitored due to their proximity to the Kruger National Park (KNP) and human settlements (DEA 2009). The waste rock dumps (WRD) of this complex are composed mainly of carbonatite-material, with high concentrations of rare earth elements (REE) (Gómez-Arias et al. 2016).

Therefore, this alkaline material becomes an attractive solution to not only neutralize the acid drainage, but also to enrich them in REE. In fact, the REE from both the carbonatite and the drainage could be concentrated while treating the acid water (Gómez-Arias et al. 2016). A bench scale water treatment

was used to chemically and mineralogically characterize the removal of pollutants from the acid drainage, as well as the concentration the REE within the matrix of the reactor. The successful outcome is exciting since a) a reduction of the waste rocks deposited within the mining facility can be achieved, b) a reduction of the volume of acid water retained from the manufacturing plant can be achieved while improving the water quality and c) additional value will be generated from the wastes generated by the companies by yielding a marketable concentrated-rare-earth-product.

Methodology

Experiment set up

The bench-scale water treatment set-up consisted of two reactors made of PVC pipes (10 cm inner diameter, height 50 cm) connected in series, as well as two decanters. Each reactor had four sampling ports and an outlet port connected with perforated pipes inside



the reactors. The decanters were placed after each reactor to allow suspended solids to settle and to hold small particles that may be released from the reactors.

Each reactor contained a layer of quartz gravel (particle size: $\approx 5\text{--}8$ mm) at the bottom (2.5 cm) covering the outlet port. This layer was used as a drain and was covered with 40 cm of reactive material, which is a mixture of wood shavings and powdered alkaline material. Carbonatite powder collected from a WRD was used for the first reactor (reactor A) and BaCO_3 (Protea Chemicals Company, SA) was used in the second reactor (reactor B) as the alkaline material.

Acid water from manufacturing plant (50L) was collected from PIC's dam and pumped to the top of reactor A with a peristaltic pump. The water flowed gravitationally through the mixture and it was collected from the bottom of the reactor in a container that acted as a decanter (decanter A). Then the water was pumped to the top of reactor B and it was finally collected in decanter B. The flow rate was 1.1 mL/min with a residence time of 24 hours per reactor.

Hydrochemical characterization

Samples were collected daily for 30 days from each sampling-port as well as from the outlets, the inlet and both decanters. The physicochemical parameters of the samples were analysed immediately to avoid the dissolution effects of the CO_2 (g) and O_2 (g). Parameters such as dissolved oxygen (DO), temperature (T), pH, electrical conductivity (EC) and to-

tal dissolved solids (TDS) were measured in all samples with an ExStix®II multi-probe, while oxidation-reduction potential (ORP) was measured with an ExStix®II ORP (Pt and Ag/AgCl electrodes) probe. Then each sample was filtered with Teflon filters $0.45\ \mu\text{m}$ and acidified with 10% HNO_3 . Total Element Concentration (TEC) was analysed by ICP-OES Teledyne Leeman-Prodigy XP, minor elements with ICP-MS PerkinElmer-Nex-Ion2000 and major anions (PO_4^{3-} , SO_4^{2-} and NO_3^-) with HPLC Shimadzu-Prominace.

Geochemical characterization

At the completion of the experiment, both reactors were drained, opened and 3 samples were collected at the top, middle and bottom of each reactor. The samples were freeze dried overnight and prepared for mineralogical and geochemical characterization. The mineralogical characterization of the final products was performed by X-ray diffraction (XRD, powder method) using a methodology described in Gomez-Arias et al. (2016).

Results and discussion

The hydrochemical characterization showed an improvement in the water quality after treatment. In order to facilitate a full and coherent interpretation of the results, the discussion of each step on the system will be done individually.

Reactor A:

An averaged increase of pH from 1.4 to 3.53, was achieved in reactor A (Fig. 2). At the be-

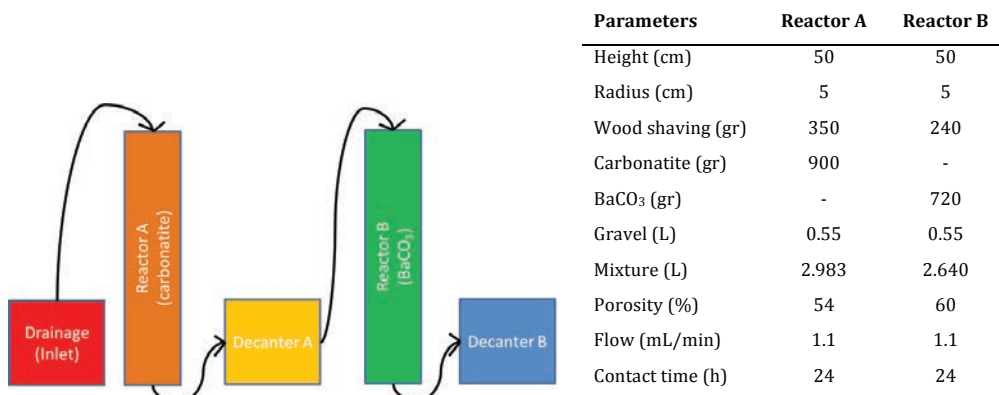


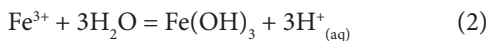
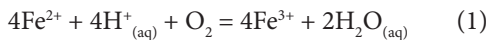
Figure 1 Bench-scale water treatment scheme (left) and specifications (right)



gining of the experiment the pH increased up to 4.48, however the efficiency decreased over time, due to the consumption of CaCO_3 present in the carbonatite and/or the passivation of the system, probably due to the precipitation of gypsum and Fe- oxyhydroxysulfates, as it was previously described by Soler et al. 2008.

An average decrease in EC and TDS of 56.1%, was measured (Fig. 2), mainly due to the removal of sulfate and phosphate. At the beginning of the experiment both parameters decreased about 73%, but their decreasing rate declined between 40 and 66.7% thereafter, which was probably related to the passivation of the calcite, as mentioned above.

DO decreased from the top to the bottom of the reactor and it decreased over time up to 85% (Fig. 2). This correlates with the ORP measurements that showed an evolution of the redox conditions, which alter from an oxidizing to a reducing environment. This was partially due to the precipitation of Fe, which is an oxygen consuming reaction (Eq 1 - 2), but probably enhanced by the usage of wood shavings in the reactive material, which could serve as a carbon source for sulfate reducing bacteria (SRB), known precursor of the reducing environment (Caraballo et al. 2011).



The concentration of sulfate decreased by 46.5%, on average, which means that more than 4000 mg of sulfate was precipitated as neoformed minerals per litre of water treated (Fig. 2). The sulfate removal observed in this experiment is higher than previous batch experiments where the same water was treated with a carbonatite sample (Gómez-Arias et al. 2016). This might be due to the possible presence of SRB, previously described.

On average, the concentration of phosphate decreased by 66.6% (Fig. 2). As described by Liu et al. (2012), the presence of calcite and the increase of pH are directly related to the precipitation of phosphate. However, Liu et al. (2012) also described the influence of the ratio / at low pH; with ratios of between 1.5-3 phosphate, removal will be enhanced, while higher ratios will inhibit phosphate removal. The ratio of the drainage was 4 before treatment, but as sulfate was removed through the reactor, this ratio kept oscillating. This could explain the oscillation of the phosphate concentration, not only in reactor A, but along the entire water treatment system.

The analyses by ICP-OES showed high concentrations of trivalent (523.7 mg/L of Al, 165.0 mg/L of Fe and 7.7 mg/L of Cr) and divalent metals (1102.8 mg/L of Mg, 774.53 mg/L of Ca, 21.9 mg/L of Cu, 43.4 mg/L of Mn, 0.94 mg/L of U, among others) in the inlet. The neutralization process produced by the disso-

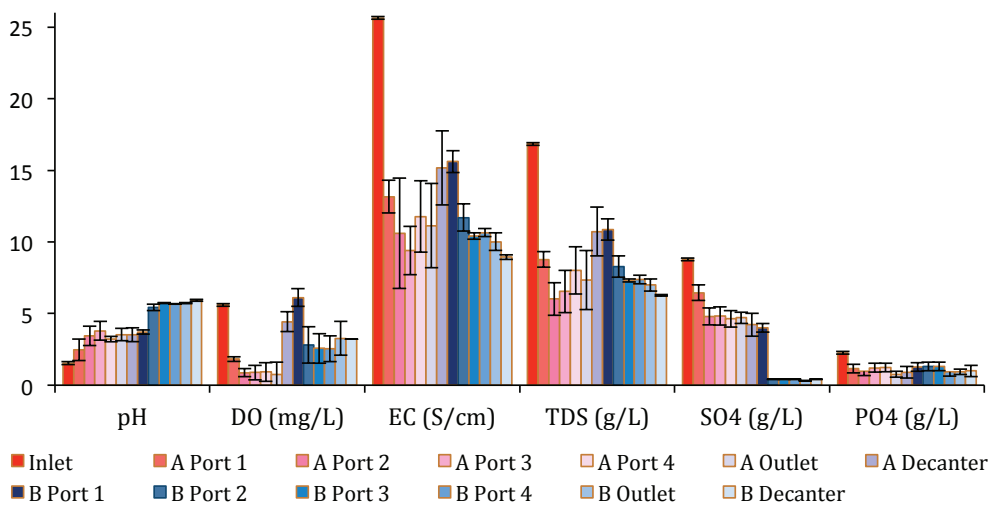


Figure 2 Evolution of physicochemical parameters throughout the entire water treatment, showing the average of each section (columns) and their standard deviations (lines).



lution of the calcite promoted the precipitation of Al (92.0%), Fe (81.2%), Cr (90.4%), Cu (68.8%), Pb (61.4%) and U (63.7%), among others. However, there was an increase in the concentrations of Ca and Mg, due to the dissolution of the carbonatite, which contained these elements in the form of carbonates (Gómez-Arias et al. 2017). While their concentrations increased from port 1, it was in port 2 where the maximum concentration was achieved (1515.1 mg/L of Mg and 1575 mg/L of Ca), decreasing thereafter.

The ICP-MS analysis detected high concentrations of REE (Fig. 3), especially light lanthanides (Ce>La>Nd>Y>Gd>Sm>Pr>Dy>Sc>Er>Eu>Yb>Ho>Lu>Tm), with a sum of 419.1 µg/L in the water used as inlet. The concentration of REE in solution increased at the first port (up to 1236.12 µg/L, in total), due to the dissolution of the carbonatite that hosts high concentrations of REE (Gómez-Arias, et al. 2017). Thereafter, REE decreased drastically in port 2, and from port 3 to the outlet most REE were below detection limit (4.5 µg/L), except for Sc and Y (8.4 and 5.2 µg/L, respectively).

Decanter A

The characteristics of the water that reached the decanter from reactor A changed over

time. The small turbulence produced by the water dropping from reactor A to the decanter promoted the introduction of oxygen in water. This enhanced the precipitation of Iron oxy-hydroxides (Taylor et al. 1984; Banks et al. 1997) as it was shown by the decrease in Fe concentration between the inlet and the outlet of the decanter (from 41.8 to 6.7 mg/L, on average), as well as the acidification of the water due to the Hydroxyl-group consumption (Eq. 1-2). Some particles released from reactor A were probably re-dissolved within decanter A due to this acidification (pH decreased from 4.03 to 3.05). This process probably contributed to the increase of EC, TDS, SO_4^{2-} and PO_4^{3-} (14534 to 17760 mS/cm, 10.048 to 12.405 g/L 4.7 to 6.4 g/L and 0.74 to 1.27 g/L, respectively). However, all the elements analysed by ICP decreased; Al, Cu, Fe, Pb and U were removed by more than 80%, while the rest were removed between 12 and 51%.

Reactor B

The dissolution of the BaCO_3 produced an increase in the pH (eq. 3 to 5) (Gómez-Arias et al., 2015) from 3 to 5.78, on average. The maximum pH achieved at the outlet of column B was 6.08. The TDS and EC decreased between 44 and 47% (from 12.42 to 6.99 g/L

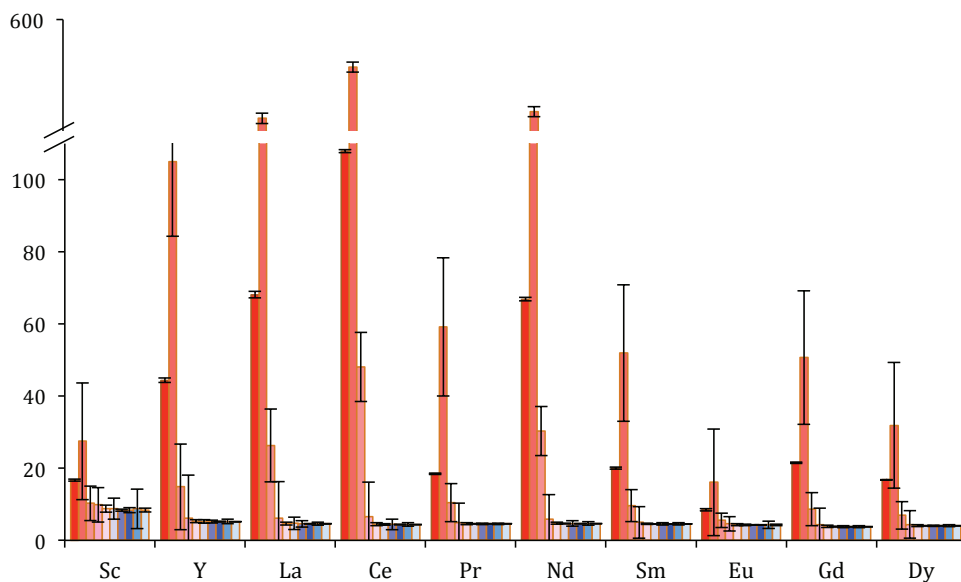
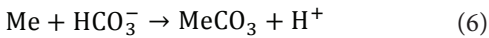
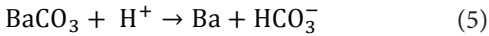
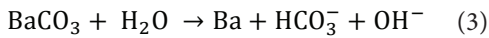


Figure 3 Evolution of main REE, including Y and Sc, throughout the entire water treatment, showing the average of each section (columns) and their standard deviations (lines) colour coded as figure 2.



and from 17740 to 1000 mS/cm, on average). The dissolved sulfate was precipitated as barite (BaSO_4) decreasing the concentration of it in solution down to 0.67 g/L (eq. 4). While Ca and Mg were mainly precipitated as Ca-MgCO_3 (eq. 6), dropping their concentration in solution from 0.86 to 0.03 g/L of Ca and from 1.24 to 0.48 g/L of Mg. At the outlet of column B, the concentration of the other metals analysed were below 0.001 g/L, except for Ba that oscillated between 0.9 and 3.2. At the inlet of Reactor B the concentration of U was already depleted to 0.02 mg/L, which was completely depleted in the top section of the reactor, since no trace of U was detected from port 2 downwards.



Decanter B

The main function of decanter B was the settling of suspended solids that could come from reactor B, as well as to promote the stabilization of the water characteristics. The pH increased slightly to 5.94, while the TDS and EC decreased by approximately 4%.

The comparison between the characteristics of the water before treatment (inlet) and at the end of the treatment (Decanter B) demonstrates the improvement on the water quality achieved throughout the water treatment system (Fig. 2); pH increased from 1.5 to 5.94, while TDS, EC, sulfate and phosphate decreased from 16.8 g/L, 25.63 mS/cm, 7.3 g/L and 2.3 g/L to 6.28 g/L, 8.94 mS/cm, 0.4 g/L and 1 g/L, respectively. All the metals analysed were removed by more than 95%, including Al (99.8%), Cr (94.4%), Cu (97.5%), Fe (98.9%), Mn (99.3%), Pb (95.9%) and Se (99.9%). Only Ca removal was slightly lower (92.6%) and Mg was removed by 56.6%. There were no REE nor U detected at the end of the treatment.

XRD results

The mineralogy characterization by XRD analysis to the starting alkaline material (carbonatite) used in reactor A, showed calcite

(CaCO_3) as the principal compound, followed by dolomite (Ca-MgCO_3) and apatite (REE-bearing $\text{Ca}_5(\text{PO}_4)_3$). However, the matrix of carbonatite used for water treatment showed lower concentration of calcite after treatment. This was expected since the dissolution of the calcite by the acid drainage is well documented and commonly used as remediation of acid mine drainages (AMD) (e.g. Caraballo 2015). The main neoformed mineral phases at the top and middle sections of reactor A were gypsum, hydrotalcite and anhydrite. According to literature (Birjega et al., 2005 and Baumer et al., 1996), those neoformed minerals can accommodate REE in their structure. In contrast, the bottom showed calcite as predominant mineralogy. Consequently, scarce neoformed minerals were detected in this section of reactor A.

The analysis of the witherite (barium carbonate) used as the reagent in reactor B, showed the following neoformed minerals: barite (BaSO_4), brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which act as a sink for divalent elements. The dissolution of witherite during the water treatment was demonstrated by the decrease in its concentration. However, the total consumption of this reagent was not achieved at the end of the experiment.

Conclusions

This study has demonstrated: a) that the bench scale successfully remediated acid water with high concentration of salts and metals, b) that commercial calcite, commonly used in any DAS system can be replaced by carbonatite (mining by-product) which will decrease costs dramatically, c) that the high concentrations of REE, commonly found in acid water from mines and industries, can be precipitated within the carbonatite matrix, and finally d) that REE-bearing minerals of the carbonatite can be dissolved by acid water to re-precipitate together with acid-water-REE. Further studies need to be performed in order to characterize the REE-enriched material and its feasibility as a marketable product.

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