

Use of alkaline mine waste as treatment for acid drainage

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Abstract

The environmental impact of industrial drainages on South Africa affects surface- and groundwater 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. There is an industrial area, with two mines and a fertilizer industry, allocated between the town and Kruger National park. In this study, several options have been researched to improve the environmental impact of that area and to reduce the risk of environmental damage to Kruger National park.

The main aim of this experimental study was to investigate the possibility of treating the extremely acidic drainage produced in this area with the alkaline rocks (mainly carbonatite) disposed in the waste rock dumps and tailings of the mines. Thus, the quality of their water would be improved and, at the same time, the volume of the waste rock dump and/or tailings material within the mine facilities will be reduced.

The experiments showed a clear improvement of the acidic water with the carbonatite from dump: pH increased from 1.4 to 4.3; total dissolved solids (TDS), electrical conductivity (EC) and salinity (Sal) decreased up to 68%, sulfate dropped 28%, total iron decreased 99.6%. The experiments with tailing material showed similar results; TDS, EC and Sal decreased between 51 and 65% and total iron was 96% removed. The main difference between the treatment with dump and with tailing is about the sulphate; the tailing removed up to 53.4% of sulfate, which is 30% more than the removal produced by waste rock dump.

This is the first study about using carbonatite as a water treatment. The results obtained from the batch experiments encourage a deep study about the use of this mine waste in a future treatment plant.

Key words: Acid drainage, batch experiment, carbonatite, tailing, Water treatment, Kruger National Park.

Introduction

The Phalaborwa Industrial Complex (PIC) is allocated in the central Lowveld of Limpopo province. It includes two mines and a fertilizer industry. Due to its proximity to the Kruger National Park (KNP), the area is especially sensitive to the environmental impact that PIC may cause to the surrounding area, with the ground- and surface water the main concern. There are numerous watercourses on PIC; northern courses drain into Loole Creek (seasonal tributary of Selati River), Eastern course drain to Tshutshi Spruit (seasonal tributary of Olifants River), and southern watercourses drain directly into the Selati River and Olifants River. Both rivers also catch groundwater which flows radially from PIC, mainly in the south and east sectors. According to Department of Environmental Affairs “Olifants river is negatively impacted by poor quality of water as a result of mining activities at Phalaborwa” “from the Selati Confluence to Downstream border in the Kruger National Park” (DEA 2009).

Climatology is also an important environmental factor to be considered, since it directly and indirectly influence the quality of the water. Temperature, precipitation and evaporation affect the physicochemical characteristics of the surface water stored in the dams within the PIC and, therefore

the characteristics of the water that infiltrates into the aquifers. These parameters may affect a water treatment system and should also be considered during its design.

The area experiences subtropical conditions, with dry winters and wet summers. The temperature is warm to hot; in summer the daily temperatures range from 18 to 30° C while in winter it ranges from 10 to 23 °C. The average rainfall is 480mm per annum, but it varies from 250 to 700mm. The number of rain days is about 65 days per annum. January use to be the rainiest month and most of the rainfalls occurs in the form of heavy showers accompanied by electrical storms. The average evaporation is 2074 mm per annum. The wind blows at medium speed at about 1.1 - 3.5 m/s, predominantly from south-southeast. The area is under calm conditions 29% of the time. (DEA 2009).

The aim of this study is to approach an affordable solution for the fertilizer industry, whose process water lies in several dams allocated within the facility. This is at the expense of climatic condition that may decrease its volume and increase the concentration of pollutants by evaporation during climatic water deficit periods, or contrary wise during water excess periods. Treating this water up to the quality level that can be re-used for the plant process, employees, irrigation, etc. would be the best option from an economic and environmental point of view. Conventional water treatment was not an affordable option in the past due to the extremely high cost necessary to treat water of these specific characteristics. Therefore, the present study focuses in searching an affordable pre-treatment that increases the quality of the water up to level that can be successfully treated by a conventional industrial water treatment system.

The water is extremely acidic and hence needs large amounts of alkaline material to achieve the desired neutral stage. Within the PIC area there are large volume of carbonatite piled in the waste rock dumps and tailings of the mines facilities. Several experiments have been performed to test the carbonatite as reagent that could be used to increase the quality of the water up to desired level. Due the proximity of this material and its waste-character, it is the material of choice for this experiment. The success of the results could make a significant improvement in the environmental impact of the PIC to the surrounding area and an important decrease of the environmental risk that PIC represents for KNP. The success of the present research could entail a drastic decrease of the volume of dumps and/or tailings of the mines as well as decreasing the risk of spillages to ground- and surface water bodies.

The reagents used in this study come from the dump and tailing and contains the mined and processed carbonatites and foskorite rocks from the Palabora Complex (PC). PC is an intercontinental plug that was emplaced at 2060 Ma into granite basement of the Archean Kaapvaal craton (Wu et al. 2011). This complex is mainly formed by carbonatite, foskorite, syenite and pyroxenite (Giebel, Gauert & Costin 2016) been carbonatite the most interesting rock in this study due to its high concentration of carbonates (mainly calcite), which has high acid consumption potential. The PC has the unique carbonatites in the world that hosts minable Cu ore. Carbonatites with low concentration of Cu (among other metals) are deposited in the waste rock (WR) dumps while those with high concentrations are crushed, milled and the Cu-rich fraction is separated from the host rock, mostly carbonatite, which is then deposited on the tailings (Roux et al. 1989).

Methodology

Two sets of solid samples (mainly carbonatite) were collected from a WR dump and a tailing. A portion of each sample (100 g) was grinded to powder size. Water samples from the dam, which collects drainage produced by the fertilizer industry (FI) have been treated with carbonatite from the dump and tailing in six different experiments:

- Experiment D1(Dump 1): five falcon tubes were filled with 40 mL of subsamples from FI and 1 g of carbonatite from dump (ratio 1:40 w/v) and placed in a rotor at 30 rpm (Figure 1 left). Each subsample was removed after 2, 4, 6, 12 and 24 hours from the rotor, respectively. Physicochemical parameters (pH, EC, T and TDS) were measured from each subsample. Then they were centrifuged at 3000 rpm for 20 min at 5°C to separate the solid products from the solution. The supernatant of each subsample was collected with a sterile syringe and filtrated with 0.45 µm syringe filter of cellulose acetate. Sulphate and total iron were analysed

with spectrophotometer HACH DR 3900. The supernatant extracted from each subsample was acidified and stored till its analysis by ICP.

- Experiment D2 (Dump 2): The methodology was the same than in experiment D1. Only the amount of carbonatite was increased up to 2g (ratio 2:40 w/v).
- Experiment D3 (Dump 3): The methodology was the same than in experiment D1. Only the amount of carbonatite was increased up to 3g (ratio 3:40 w/v).
- Experiment D4 (Dump 4): 250 mL flask was filled with 200mL wastewater from the fertilizer industry and 20 g of carbonatite from the dump (ratio 4:40 w/v). The flask was agitated horizontally at 160 rpm for 24 hours in a shaking incubator (Figure 1 right). pH, EC, T and TDS were measured directly from the flask after 2, 4, 6, 12 and 24 hours of agitation. At the end of the experiment the solution was centrifuged, filtrated and analysed as described above (experiment D1).
- Experiment T1 (Tailing 1): five subsamples were filled with 40 mL of wastewater from the fertilizer industry and 1 g of carbonatite from the tailing (ratio 1:40 w/v). The methodology was the same than in experiment D1 and the contact time for each subsample was 2, 4, 6, 12 and 24h, respectively.
- Experiment T3 (Tailing 3): The experiment T1 was repeated with 3 g of tailing (ratio 3:40 w/v). The same protocol was repeated.



Figure 1 Pictures of batch experiments with 50 mL falcon tubes in the rotor (left) and 250 mL flask in the shaking incubator (right).

Analytical procedures.

The physicochemical parameters of the FI sample (previous treatment) were analysed on site, also each subsample was analysed immediately at the end of each designated time. This was to avoid any possible change on the hydro-geochemical characteristics of each subsample due to gas leakage or any further reaction, i.e. precipitation, which may occur over time. The following parameters were measured by YSI ProDSS multi-parameter; temperature, pH, electrical conductivity (EC) and total dissolved solids (TDS). Each subsample was then filtered with teflon filters 0.45 μm (cellulose acetate). The spectrophotometer Hach DR 3900 Benchtop was used to determine the concentration of sulfates and iron; the analyses were performed as described in USEPA Sulfaver 4 Method 8051 (equivalent to USEPA375) and USEPA Ferover Method 8008, respectively. After filtration, pH, EC and TDS of the samples from the experiment D1 were measured again. The aim of this double check was to elucidate possible benefices of including a filtration system in the possible upscaling of the water treatment system. The sample from FI and the subsamples from each experiment were stored at 4 °C for further ICP-OES analyses.

Results

The quality of the water that is in contact with the carbonatite from the dump and the tailing improved over time. The pH increased from 1.4 to 2.3, 4.1, 4.2, 4.3, 3.0 and 3.1 after 24 hours of contact time in experiments D1, D2, D3, D4, T1 and T3, respectively, while EC and TDS decreased between 23 and 65 %. The best removal rate of EC and TDS were obtained in the experiment D2 and D3 with an average of 60 and 65 %, respectively. However the experiment D1 shows similar improvement after filtration on both parameters, increasing more than twice of the initial removal rate, probably due to the removal of suspended solids whose size were bigger than 0.45 µm. The drop of values from parameters such as TDS and EC, obtained from filtered solution, suggested that a filtration system could be an alternative as a post-treatment. According to the HACH analysis the concentration of sulphate, decreased between 14.4 and 53.4% in all the experiments (the maximum removal was achieved on experiment T3) with the exception of experiment D2, in which sulphate concentration increased slightly (Table 1). The majority of the sulphate was removed within 2 to 4 hours of contact time. The removal of iron oscillated between 96.3 and 99.6% in all the experiments and the majority of the removal was again within 2 to 4 hours of contact time (Figure 2).

Table 1 pH and removal of EC, TDS, Sulfates and Iron measured immediately after 24 hours of contact time.

Parameters	D1	D1 filtered	D2	D3	D4	T1	T3
pH	2.3	2.4	4.1	4.2	4.3	3	3.1
Removal (%)							
EC	23	56.1	60.1	59.5	25.4	56	51
TDS	25.7	58.9	65	64.4	33.6	48.9	59.5
Sulfates	14.4		-2.5	21.2	28	18.6	53.4
Fe total	96.3		99.5	99.6	96.3	99.5	96.4

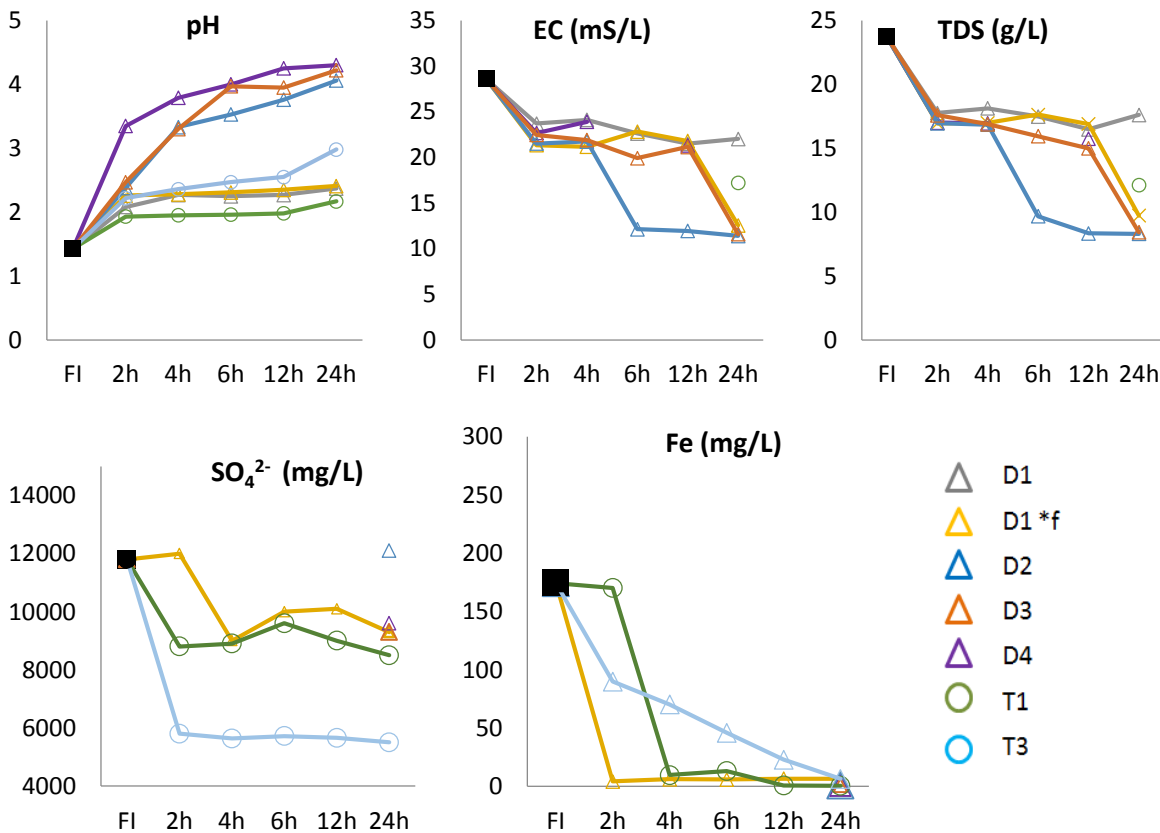


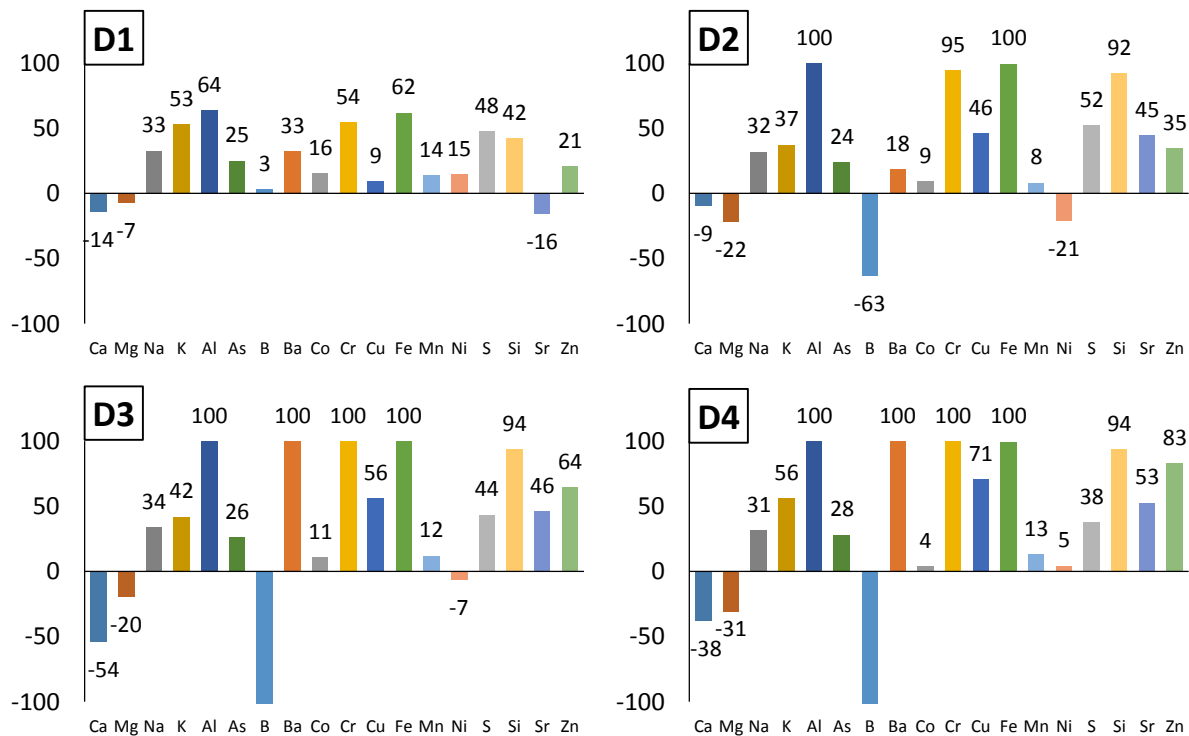
Figure 2 Temporal evolution of pH (top-left), EC (top-middle), TDS (top-right), sulfates (bottom-left) and total iron (bottom-right) for each experiment; D1 (grey), D1 filtered (yellow), D2 (dark blue), D3 (orange), D4 (purple), T1 (green) and T3 (Clear Blue)

ICP-MS results

According to the ICP analyses, the concentration of most of the cations and anions present in the water decreased in all the experiments performed with carbonite and tailing (figure 3); Na, K, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, SO_4^{2-} , Si and Zn. However the concentration of Ca increased in all the experiments, probably due to the dilution of $CaCO_3$ present in the carbonatites. Mg also increased, but only in the experiments with dump material; the experiments with tailing show removal of about 20%. Sr, B and Ni did not follow a clear pattern; the concentration of Sr decreased by about 50% during the experiments D2, D3 and D4, but increased between 4 and 36% in the rest. B increased about 80% throughout the experiments D2, D3, D4 and T3, but decreased 3 and 7% in experiments D1 and T1, respectively. The concentration of Ni increased in experiments D2 and D3 (21 and 7%, respectively). The differences on the removal ratio of Sr, B and Ni were probably related to the presence of those elements in the reactive material used, which might be dissolved by the acidic water.

As can be seen in the graphics below, 1 gram of carbonatite (ratio w (g): v (mL) 1:40) was not enough to achieve the maximum quality that the water can achieve through these treatments. When the amount of reactive material was increased (i.e. experiment D2, ratio 2:40), there was a clear improvement of the quality of the water. However, according to the results, the ratio 3:40 (experiments D3 and T3) was considered as the optimum ratio since there was a clear improvement with respect to the ratio 2:40, but there was no clear improvement of the experiment with ratio 4:40 (experiment D4) with respect to 3:40.

In experiments D3 and T3 (both 3g of reagent) most of the elements (Na, Al, As, Ba, Cr, Fe, Mn and Si) had the same ratio of removal (about 34, 100, 27, 100, 100, 99, 14 and 93 % on average, respectively, with a standard deviation of 0.9). However the dump material is more effective in the removal of Cu, Sr and Zn, but the increase of Ca was lower in all the experiments with dump material than in those with the same ratio reagent/water of tailing. It increased the concentration of Mg, B and Ni, probably because these elements were present in the carbonatite. Therefore the removal induced by the tailing material was better for those elements, as well as for Co and specially sulphate.



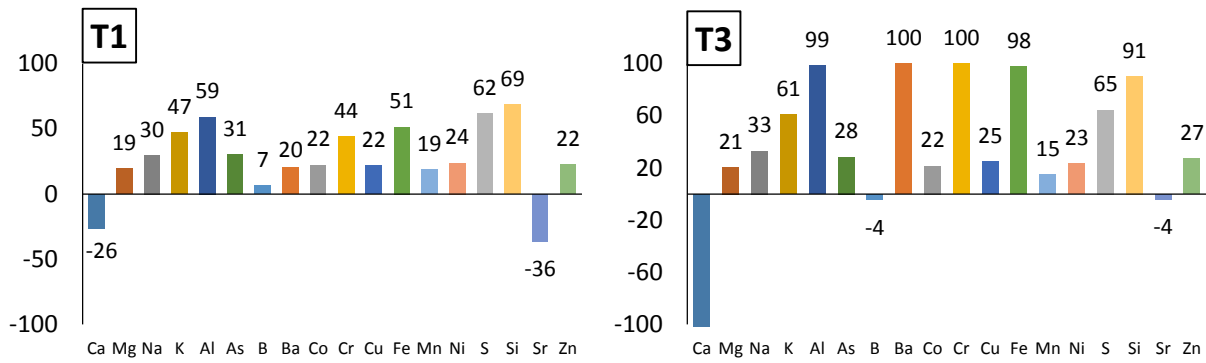


Figure 3 Percentage of removal (positive) and increasing (negative) of all the elements analysed in the samples (Cd, Mo and Pb were always below detection limit) after 24 hours of contact time.

Conclusions

According to the results, the quality of the water improved with carbonatite from both dump and tailing material. The improvement can be observed within two hours, but they keep improving over time and reached the highest quality at 24 hours. The lowest percentages of removal were obtained in experiments with ratio 1:40 (in both cases dump and tailing). The experiment with ratio 2:40 got a higher removal and the experiments with ratios 3:40 and 4:40 gave the best results. Therefore the ratio 3:40 would be the recommended ratio since it was the most efficient. By comparing the experiments D1 with T1 and D3 with T3, it can be concluded that the tailing produced better removal rates than the dump material, especially for sulphate.

For all these reasons, a treatment of FI water with carbonatite from the tailing with a ratio w/v of 3:40 would be recommended and further research will be performed to optimize a possible water treatment system with this material as main reagent in a 3:40 ratio. This water treatment would improve the characteristics of the water from the FI. At the same time it will reduce the volume of tailing from the mine. Therefore, the environmental impact on Palabora Industrial Complex and thus Kruger National Park would be reduced considerably.

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