Passive Treatment Technologies for the Treatment of AMD From Abandoned Coal Mines, eMalahleni, South Africa-Column Experiments

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Abstract

Acid mine drainage (AMD) production from abandoned coal mines is a world-wide environmental problem. Characteristics of AMD includes low pH (<4), high sulfate (SO_4) concentrations, high acidity levels and potentially hazardous metals such as Al, Fe and Mn. Passive treatment technologies for AMD remediation can function in remote areas with low costs of operation, monitoring and maintenance and therefore are practical for setting up on abandoned mine sites. Even though such systems have been used to treat acid mine water efficiently, limitations such as coating and clogging as a result of Al^{3+} and Fe^{3+} oxyhydroxide precipitates have been reported.

For solving the clogging problems associated with most of the passive treatments, dispersed alkaline substrate (DAS) was introduced in Spain by Rotting, et al. A DAS is a system composed of coarse matrix mixed with a fine grained alkaline material. The main aim of the study was to investigate the effectiveness of the DAS system in treating AMD from an abandoned coal mine of eMalahleni, South Africa and compare it with the traditional reducing and alkalinity producing system (RAPS).

The column experiments remediated acid water successfully for 21 weeks after which the DAS system clogged while RAPS was continuing to treat AMD successfully. For assessment of the treatment systems water parameters such as pH, Redox, total dissolved solids (TDS), concentrations of metals and metalloids were analysed weekly. Both treatment systems were able to raise the pH from an average of 3 to 8. Contaminants such as Fe, Al, and Zn were completely removed. Mn concentrations were reduced but were still above the South African water quality standards.

Keywords: Passive treatment technologies; Acid mine drainage; Dispersed alkaline substrate; Reducing and alkalinity producing system

Introduction

Acid mine drainage (AMD) from old and abandoned coal mines is a world-wide environmental disaster. In South Africa, the state is legally responsible for rehabilitation of such environmental complications since most of such mines operated before implementation of any legislation such as Minerals and Petroleum Resources Development Act (MPRDA), No.28 of 2002, which puts emphasis on sustainable development and environmental protection [1].

AMD is produced when sulfide minerals such as Pyrite (FeS_2) undergo oxidation in the presence of water and oxygen forming sulfates and Ferrous Iron (Fe^{2+}) (Equation 1) [2-4].

$$2FeS_2(s)+7O_2(g)+2H_2O(l)=2Fe_2+(aq)+4SO_4^{2-}(aq)+4H+(aq) \quad (1)$$
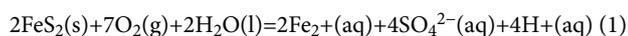
Characteristics of AMD include low pH (<4), High electrical conductivity (EC) and total dissolved solids (TDS), high sulphate (SO_4) concentrations and high acidity levels leaching potentially toxic metals such as aluminium (Al), iron (Fe), and manganese (Mn) in streams/rivers threatening the limited water resources of South Africa. An example is comprehended in the study done in the Loskop Dam Nature reserve, downstream of Olifants River Catchment in Mpumalanga where AMD from abandoned coal mines was linked to the death of fish and crocodiles in the dam [5-8].

Passive treatment technologies of AMD are more practical for setting up on abandoned mine sites since some removal of acid and toxic metals will benefit the receiving environment and due to the association with low cost of implementing, operation and maintenance [9-11]. Such conventional treatments have been tried and tested in many parts of the world with their performance and effectiveness in acid water remediation differing in longevity and success from one place to another.

Reducing and alkalinity producing system (RAPS) which is the combination of anoxic limestone drains and a compost wetlands is one of the traditional passive treatment options for net-acidic mine water treatment [12,13]. Dispersed alkaline substrate (DAS) is a passive system introduced in Spain by Rotting et al. with the intention of solving the clogging problems associated with most of the passive treatments [14]. DAS is a system composed of coarse matrix (e.g. wood shavings) mixed with a fine grained alkaline material (e.g. limestone). The woodchips/wood shavings are supposed to provide high permeability while the limestone provides a bulk reactive surface area, where it will dissolve and react with AMD before it is coated [14,15].

Aims and Objectives

The general aim of the research was to contribute towards mine water treatment solutions in SA by investigating different passive treatment systems in remediating AMD from coal mines. The study investigated a DAS system in treating AMD from an abandoned coal mine in eMalahleni, Mpumalanga Province and compared it with RAPS which have been investigated and implemented in many parts of the world.

By ensuring that the main aim is met the following specific objectives were looked at:

- Reaching neutral pH (6~9)
- Lower concentrations of metals, e.g. Fe<1 mg/L, Al<0.15 mg/L and Mn<1 mg/L
- Lower sulfate levels (<200 mg/L)

Materials and Methods

Feedstock

AMD treated for this study was collected from a discharge collecting point of an abandoned mine situated about 25 Km South East of eMalahleni. A 25 L container was used to carry the acid water from the site to the laboratory. The container was rinsed many times (about 5 times) before filling it with the AMD. This acid water is characterized by pH levels that are approximately 2.7, EC values that are extremely high (~1672 mS/m), high sulfate levels and high concentrations of metals (Fe, Al and Mn) exceeding industrial water standards as set by DWAF (Table 1).

Parameters	Average Douglas discharge	Target water quality range (DWAF)-Industrial standards
pH	3	6~9
EC (µS/m)	1672	70
Al (mg/L)	115	0.15
Fe (mg/L)	180	0.1
SO_4^{2-} (mg/L)	6091	200
Mg (mg/L)	20	30
Mn (mg/L)	5	0.05

Table 1: Average water results AMD and the target water quality range (DWAF Standards).

Cow manure that was used comprised pH of approximately 6.8, EC was about 280 mS/cm and moisture content was measured to be 68.9%. Limestone used in both treatment systems contained about 93% of calcium carbonate in the form of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). The particle sizes of the limestone used in the DAS system were <0.106 mm while the limestone used in the RAPS system were >7 mm.

Experimental setup

Two passive treatments, i.e. DAS and RAPS, were staged in the laboratory for the passive treatment of AMD.

DAS: Acid water was pumped with a peristaltic pump at a constant flow rate in an upward flow movement into the first column containing a mixture of 25% (v/v) limestone and 75% (v/v) wood shavings. The residence time in the treatment system was set to 24 hours so that there can be enough effluent for sampling resulting in the acid water being treated to be in contact with the material in one column for 12 hours.

RAPS: Acid water was pumped with a peristaltic pump through a tube at a constant flow rate into the first column containing a layer of manure underlain by limestone. Manure substrate occupied 30% (v/v) of the column, while the limestone occupied 50% (v/v). In a downward movement, the treated water from the first column flows into the second column which is the same material contained in the first column. The residence time of 24 hours was set for the acid water to be treated in the passive system with 12 hour contact time of the treated water in each column.

Analytical methods

XRD and XRF analysis were used for the reactive material (limestone) for mineral and elements (traces and major) identification and concentrations before and after use respectively. Tests for water pH, redox (pE), EC, TDS and dissolved oxygen (DO) were done in the laboratory to evaluate the quality of the treated water using pH and EC meter, also called multi-meter. The multi-meter was calibrated every time before use. For the conductivity probe, EC solution was used for calibration and pH calibration solutions, 4.0, 7.0 and 10.0, were used for the pH probe.

The water samples were collected weekly following WRC 2000 procedure and submitted for the IC and ICP-MS (inductively coupled mass spectrometry) analysis to identify concentrations of metals and metalloids. Alkalinity and acidity tests were also conducted to check whether the water is acidic or alkaline.

Geochemical method

PHREEQC was used to evaluate the behavior of the selected treatment methods in order to predict its efficiency in treating acid mine water [16]. PHREEQC uses a solubility method to detect thermodynamically probable solid phases using the Activity and Mass-action equation (Equation 2), where SI is saturation index, IAP is ion activity product and KS is solid solubility product.

SI=Log IAP/KS (2)

Results and Discussion

pH

Increment of the pH was achieved by both passive treatment systems (Figure 1) to be within the water quality standard of 6~9 as set by DWAF [17]. The average pH value of the treated water from both DAS and RAPS system increased to 8. For the DAS system, this pH value obtained was higher compared to the DAS treatment systems that were since introduced and tested by Caraballo et al. that indicated an average pH of 6.4 [18,19]. RAPS system also showed a higher average pH compared to the RAPS pilot systems by Nairn & Mercer and Matthies et al. which presented a pH of 6 and 5 respectively [20,21].
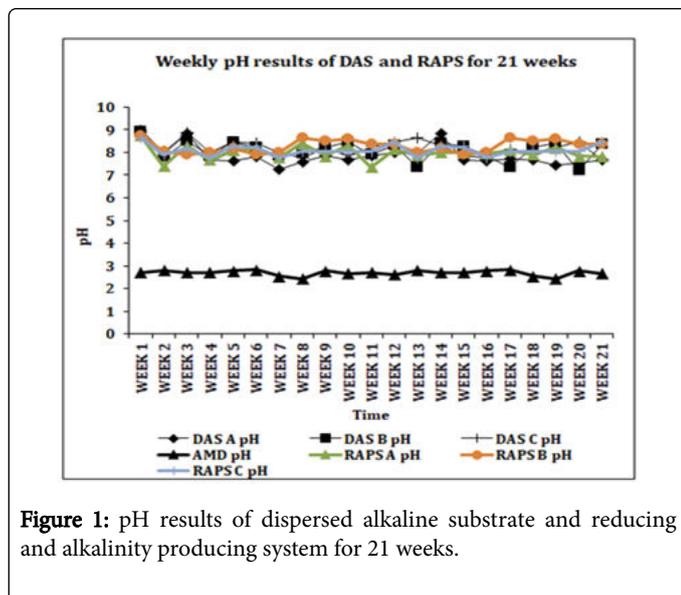
Figure 1: pH results of dispersed alkaline substrate and reducing and alkalinity producing system for 21 weeks.

The pH increase was primarily due to the calcite dissolution (Equation 3 and 4), releasing Ca^{2+} into the solution resulting in generation of alkalinity in the systems to be increased from 0 mg/L in the acid mine water to an average of 462 mg/L as $CaCO_3$ in the DAS system and 272 mg/L as $CaCO_3$ in the RAPS system.

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + CO_2 \quad (3)$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3 \quad (4)$$
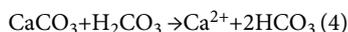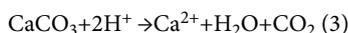
The increase in the Ca^{2+} concentration was witnessed in the DAS (~493 mg/L) and RAPS (~376 mg/L) systems compared with the AMD Ca^{2+} concentration which was very low with an average of ~49 mg/L (Figure 2). This was however expected with the pH increment and alkalinity increase, as the limestone reacted with the acidic water.
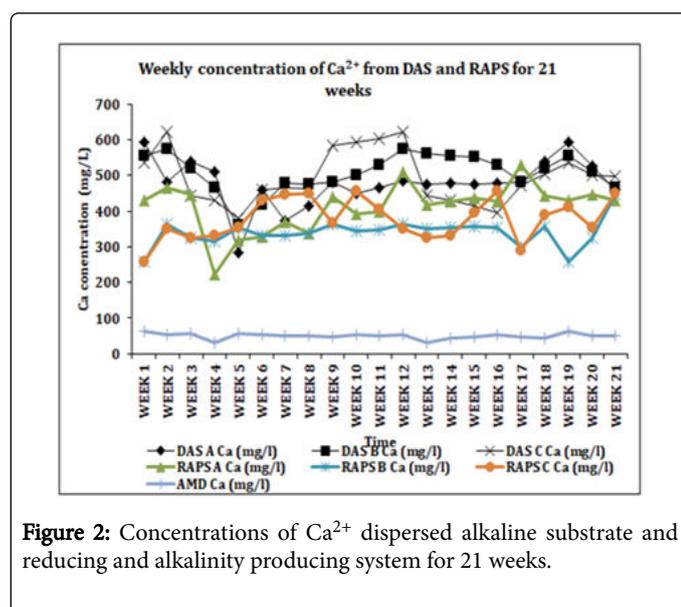
Figure 2: Concentrations of Ca^{2+} dispersed alkaline substrate and reducing and alkalinity producing system for 21 weeks.

Metals: Fe, Al and Mn

The ICP-MS results revealed that the total Fe was reduced from an average of 136 mg/L in the AMD to 1 mg/L in DAS and 3 mg/L in RAPS but increasing again after exposure to oxygen in both the treatment systems. The concentration of total Fe in AMD according to the spectrophotometer used, was all Fe^{2+}. The Pourbaix diagrams (Figure 3), was also used to predict the different ions of iron at different values of the pH and pE. The decrease in the pE values were also observed during the respective experimental runs, which is due to the buffering effect of $Fe(OH)_3$, as complimented by the PHREEQC simulation on Figure 4. It is also observed from the same figure that pE (pE=Eh/0.059 V), decreases as the pH is being increased by neutralization reaction.
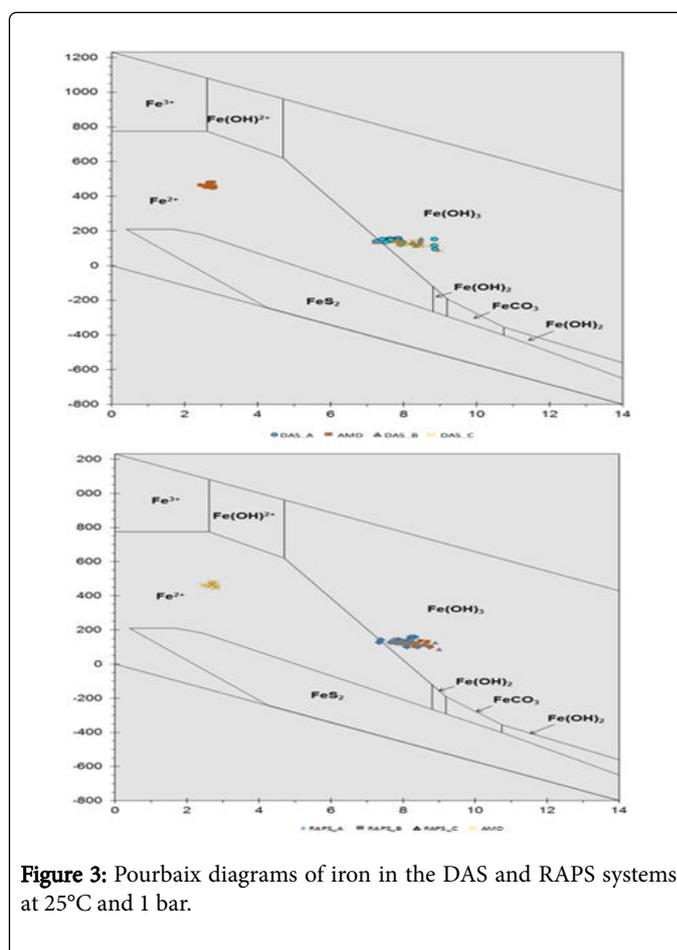
Figure 3: Pourbaix diagrams of iron in the DAS and RAPS systems at 25°C and 1 bar.

According to the ICP-MS results Al was also decreased in the passive systems from an average of 110 mg/L in AMD to 0 mg/L in the DAS and RAPS passive systems (Figure 5). The removal of Al was an objective met, to reduce the Al concentration to the acceptable water quality standard of <1.5 mg/L as set by DWAF [17]. The pH increase led to the insolubility of the Al concentrations as Al hydrolysis occurs resulting in low concentration levels.
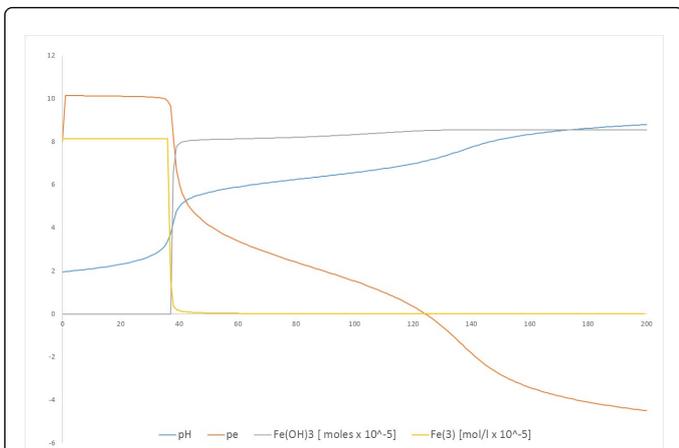
Figure 4: PHREEQC simulation results showing an increase in pH and a decrease in Eh when the AMD solution reacts with calcite.

Mn concentrations were reduced by the two passive treatment systems even though the concentrations were still above the water quality range of the domestic water standards according to DWAF [17]. Mn was reduced from an average of 7 mg/L to 3.2 mg/L in the DAS and 3.7 mg/L in the RAPS. According to the study by Thomas & Romanek, Mn needs a very high pH of greater than 8 to precipitate out [22]. PHREEQC simulations suggested that the decrease in Mn concentration in the treated water was likely precipitated out as $MnCO_3$.

No sulfate reduction was observed in both the treatment systems. In fact, an increase in sulfate average concentrations was observed in all the samples. The same trend of not being able to decrease the sulfate concentration was also experienced in the study done by Nairn & Mercer [20]. This may be due to various reasons such as that the organic substrate in both the treatment systems does not contain any sulfate reducing bacteria (SRB) which are important microorganisms in reducing sulfates to sulfites. Measures of analyzing the organic substrate for biological activities were not conducted and therefore it is not known whether sulfate reducing bacteria were present or not.
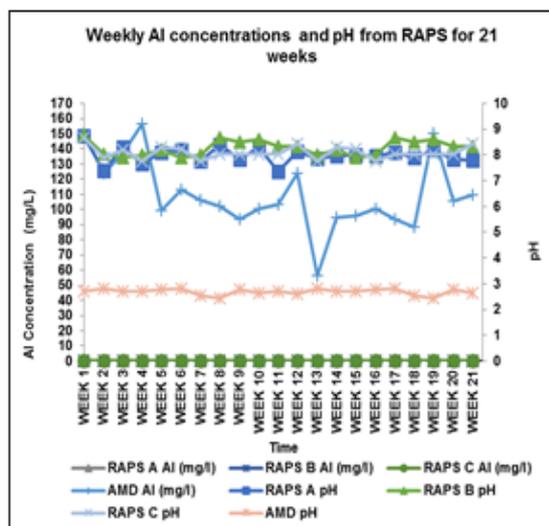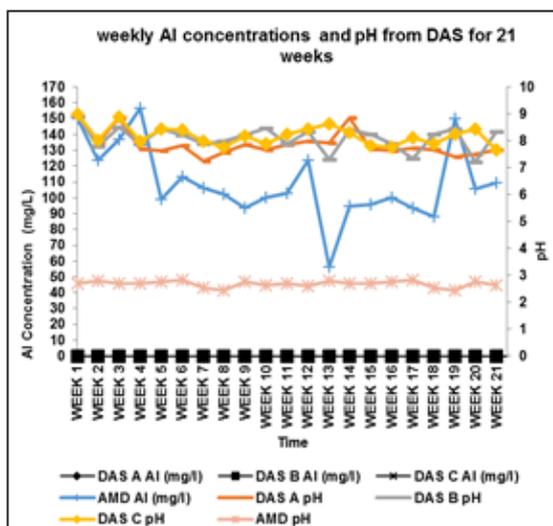
Figure 5: Al concentrations and pH levels of DAS and RAPS for 21 week.

Conclusions

The laboratory scale experimental work was done to compare the effectiveness of the DAS system in treating AMD from an abandoned coal mine in eMalahleni, Mpumalanga Province, with the traditional RAPS which have been investigated and implemented in many parts of the world for net-acidic mine water treatment. DAS was introduced in Spain by Rotting, et al. to address the problem of choking that is associated with most reported passive treatments [14]. From the experiment, the DAS system with the setup explained in this study blocked after 21 weeks of operation while the traditional treatment system that was being compared with, RAPS, was still able to treat acid water efficiently without any signs of clogging.

Before DAS system choked, both technologies (DAS and RAPS) were able to take most contaminants to the accepted water quality standards of South Africa as set by DWAF [17]. Most of such contaminants are mentioned below:

- pH was raised from an average of 3 in AMD to 8, which is neutral conditions in the two systems solely from limestone dissolution.
- Acidity was completely removed and alkalinity was generated from 0 mg/L in the AMD to an average of 462 in the DAS and 272 in the RAPS system.
- Low redox potential which concluded the presence of reducing conditions in the systems and therefore oxidation process is slowed down or stopped completely in the system.
- High concentrations of contaminants such as Fe and Al were completely removed from an average of 132 mg/L and 110 mg/L respectively.
- Mn concentrations were also reduced but remained above the water quality standards due to the maximum pH of 8 in both DAS and RAPS. The decrease was from an average of 7 mg/L to 3.2 mg/L in the DAS and 3.7 mg/L in RAPS.

Some of the contaminants that were equal or increased by the two systems are mentioned below:

- Increase in Ca^{2+} concentration was observed from an average of 49 mg/L in the AMD to 376 mg/L and 493 mg/L in the RAPS and DAS systems respectively.
- Average sulfate concentrations increased in all instances.

It is concluded that treatment of AMD by passive treatment systems is possible looking at the discussion above. Such technologies are mostly short term solutions depending on the design and materials used. From the experiment, the DAS system with the setup explained in this study blocked after 21 weeks of operation while the traditional treatment system that was being compared with, RAPS, was still able to treat acid water efficiently without any signs of clogging. In the columns containing the DAS system in the laboratory, observation of an orange-yellow precipitate was made which started at the bottom where the treated water enters the column, running upwards, clogging the system to a point where the water was not able to pass through the column.

More research on different designs, setups and materials to use for acid mine drainage is still needed to address:

- The issue of longevity as a result of coating and clogging from Al^{3+} and Fe^{3+} oxy-hydroxide precipitates resulting in the passivation of the alkaline substrate leading to failure of the system.
- Material that can increase the pH to accommodate Mn removal to the accepted water quality standards.
- Material that would allow for SO_4^{2-} reduction.

Acknowledgment

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