The use of passive treatment systems to remediate AMD from abandoned coal mines, eMalahleni, South Africa – column experiments ©

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Abstract

In contributing towards mine water treatment solutions in South Africa, an experiment on Dispersed alkaline substrate (DAS) and reducing and alkalinity producing system (RAPS) systems was performed in the laboratory. The main aim of the study was to investigate the effectiveness of DAS and RAPS in treating AMD. Both treatment systems were able to raise the pH from an average of 3 to 8. Contaminants such as Fe, Al, and Zn were removed below detection limit. The column experiments remediated acid water successfully for 21 weeks after which the DAS system clogged while RAPS was continuing to treat AMD successfully.

Keywords: Passive treatment technologies, DAS, RAPS

Introduction

Owing to the nature of previous legislation in South Africa (SA), mines were abandoned without rehabilitation as the main focus at the time was on production and profit with little or no regard to the environment (Manders 2009). Many of abandoned coal mines generate contaminated mine water and, over the years, disposal, discharge, and seepage of such polluted water have resulted in the degradation of the water quality of streams and underground water (McCarthy 2011).

Passive treatment technologies are progressively gaining favor as a choice for long-term remediation of polluted mine water in many parts of the world owing to their association with low costs of implementing, operation, monitoring and maintenance (Hedin et al. 1994; Watzlaf et al. 2004), since they rely on natural ameliorative processes to remove contaminants in water (Hedin et al. 1994). Passive treatment systems utilise naturally available energy sources such as topographical slope, microbial energy, photosynthesis and chemical energy to operate successfully over its design life (PIRAMID Consortium 2003).

DAS and RAPS were investigated in treating mine water from an abandoned coal mine in eMalahleni, RAPS, a combination of anoxic limestone drain and a compost wetland, is one of the traditional passive treatment options for net-acidic mine water treatment (Riefler et al. 2008; Kepler &McCleary 1994) and DAS is a passive system introduced in Spain by Rötting et al. (2008) with the intention of solving the clogging problems associated with most of the passive treatments. Rötting et al. (2008) described DAS as a system composed of coarse matrix (e.g. wood shavings) for high permeability mixed with a fine-grained alkaline material (e.g. calcite) to provides a bulk reactive surface area, for reaction with mine water before it is coated (Rötting et al. 2008; Macias et al. 2012). DAS basically include neutralisation of mine water where metals precipitate out as oxyhydroxides while RAPS presents anaerobic/reducing conditions where metals precipitate out as metal sulfide before neutralisation process. Some of the differences between DAS and

RAPS treatment systems are listed in Tab. 1, which might be advantages and disadvantages associated with the two systems.

Materials and methods

Feedstock

AMD treated for this study was collected from a discharge collecting point of an abandoned mine situated about 25km South East of eMalahleni. A 25L polyethylene 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. Tests for pH, redox (pE), EC, TDS and dissolved oxygen (DO) were performed in the field, as they are, likely to change with time, using pH and EC meter, also called multi-meter. The multimeter 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. AMD samples were collected weekly following WRC 2000 procedure. Water samples were collected using 100 mL polyethylene bottles that were rinsed at least three times using the water to be sampled. The samples were filtered using a 0.45 µm filter membrane for elemental (major-, minor- and trace-element) and anion analyses. Elemental analysis samples were also acidified using 3M nitric acid (HNO3) for preservation purposes. Immediately upon collection, samples were placed in a cooler (at 4 °C) for transportation and storage. Chemical analyses were carried out using inductively coupled plasma mass spectrometry (ICP-MS) and

ion chromatography (IC). X-Ray diffraction (XRD) and X-Ray fluorescence (XRF) analysis were used for the reactive material (limestone) for mineral and elements (traces and major) identification and concentrations before and after use respectively.

Experimental setup

Experimental design consisted of two passive treatment systems, DAS and RAPS. DAS system (Fig. 1) was comprised of three columns with the first column containing a mixture of 25 % (v/v) limestone and 75 % (v/v) wood shavings for neutralization processes. The second column was comprised of manure to create anaerobic conditions and the third column was made to collect the treated water before exposure to oxygen. A constant upward flow movement of 0.15 L/min mine water was maintained in the system while also maintaining residence time of 24 hours. RAPS system (Fig. 2) consisted of three columns, first and second columns were containing a layer of 30% (v/v) manure underlain by 50% (v/v) limestone. The downward flow movement of 1.2 L/min mine water was maintained in the system with a contact time of 24 hours.

Results

Feedstock characterization

Mine water

Tab. 2 provides an initial chemical composition of the mine water in question. It can be noted that the mine water is characterized by low pH (2.7), and high concentration of SO_4^{-2} (1006.4 mg/L), metals

Table 1 Some of the differences between DAS and RAPS

DAS	RAPS
Comprises of fine particle sizes of alkaline material that provide a large reactive surface area and dissolves before being coated by precipitates	Gravel particles of limestone tend to lose reactivity or permeability due to precipitates formation on the surface of the limestone grains or on pore spaces of the system
No reducing organic matter, the system only uses alkaline material that is meant to add alkalinity and raise pH in the system, precipitating metals as metal hydroxides	Introduces anaerobic conditions which consume dissolved oxygen and reduces sulfate and metal concentration, where metals precipitate out as metal sulfides and neutralise the water by adding alkalinity by limestone dissolution.
Lack of sulfate reduction	Have been described to reduce sulfate concentration by increasing sulfide production
Efficient treatment of mine water expected as the system is expected to efficiently use the alkaline material	Coating and armoring of the limestone grains might result in passivation of the material
High Fe(III) and AI concentrations can be treated	inflowing Fe(III) and Al concentrations can cause passivation





Figure 1 DAS setup

Figure 2 RAPS setup

Table 2 Some of average water results mine water and the target water quality range (DWAF Standards)

Parameter	рН	EC	CI	SO ₄	Ca	Al	As	Co	Fe	Mn	Ni	Zn
Concentration	2.7	2.7	0.9	1006.4	49.7	109.7	0.007	0.8	132.1	7.3	0.9	2.4
DWAF guideline	6-9*			0 - 200*		0 - 0.15*	0 - 0.01*		0 - 0.1*	0 - 0.05*		0 - 3.0*
All concentrations expressed as mg/L except for pH and EC (mS/cm)												

Table 3 Summary of water quality results

Sample	Alkalinity	Redox	Concentrations as mg/L												
ID		as CaCO ₃	cm)	(mV)	SO4	AI	As	Cd	Co	Fe	Ca	Mn	Ni	U	Zn
		(IIIg/L)			DWAF Guideline (domestic use, human consumptio					sumption)					
					0 - 200	0 - 0.15	0 - 0.01	0 - 0.005		0 - 0.1	32	0-0.05			0 - 3.0
										Analysed					
AMD	2.7	0	2.7	476	1006.4	109.7	0.007	0.01	0.8	132.1	49.7	7.3	0.9	0.01	2.4
DAS A	7.9	407.8	2	153	1083.8	<0.1	< 0.001	< 0.003	0.4	3	478.2	2.3	0.8	< 0.001	<0.03
DAS B	8.1	334	2.2	144	1279	<0.1	< 0.001	< 0.003	0.3	1	507.8	3.5	0.5	< 0.001	<0.03
DAS C	8	218.8	2.3	287	1050.2	<0.1	< 0.001	< 0.003	1.4	15	495.2	4	0.3	< 0.001	<0.03
RAPS A	7.9	243.2	2.2	145	1195.4	<0.1	< 0.001	< 0.003	0.2	2	411.9	3.3	0.3	< 0.001	0.1
RAPS B	8.3	206.7	1.9	132	959	<0.1	< 0.001	< 0.003	0.3	3	339.9	3.3	0.2	< 0.001	0.1
RAPS C	8.1	241.9	2	140	1071.2	<0.1	<0.001	<0.003	0.2	19	377.6	4.8	0.2	<0.001	0.1

and metalloids such as Fe (132.1 mg/L), Al (109.9 mg/L), and Mn (7.3 mg/L), exceeding industrial water standards limits as set by the South African Department of Water Affairs (DWAF, 1996). Minor to trace concentrations of Co, Ni, and Zn were also noticed in the mine water.

Reactive material

X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) analysis were used for the limestone characterization for mineral and elements (traces and major) identification and concentrations before and after use respectively.

Passive treatment results

Tab. 3 summarize water quality of acidic mine water and treated water from DAS and RAPS systems.

Fig. 3 shows the change in pH of the AMD and the treated water from DAS and RAPS systems over time (weeks). An increase in the pH of the water throughout the treatment systems was observed to an average of 8 in both systems. Substantial alkalinity, as CaCO₂, was generated in the systems from 0 mg/L in the acid mine water to an average of 320.2 mg/L DAS system and 230.6 mg/L in RAPS system. Fig. 4 shows an increase in the Ca²⁺ concentration that was witnessed in the DAS (493 mg/L) and RAPS (376 mg/L) passive systems compared with mine water Ca²⁺ concentration of 49 mg/L. Average of 478.2 mg/L Ca²⁺ concentration was detected in DAS A, 507.8 mg/L was analyzed in DAS B and 495.2 mg/L was detected in the RAPS C after exposure to oxygen. An increase in pH, alkalinity and Ca2+ concentrations were expected as the limestone reacts with the acid water.



Figure 3 pH of inflow and outflow water in the passive treatment system



Figure 4 Ca²⁺ concentration of inflow and outflow water in the passive treatment system

	Total Fe (mg/L)	Fe ferrous (mg/L)	Fe ferric (mg/L)	DO (mg/L) @19.80c
AMD	132.1	0	132.1	7.94
DAS A	3	2	1	7.66
DAS B	1	0	1	7.86
DAS C	15	2	13	7.85
RAPS A	2	0	2	7.19
RAPS B	3	0	3	7.40
RAPS C	19	3	16	7.48

Table 4 Average values of forms of iron and dissolved oxygen after 21 weeks



Figure 5 Piper diagram of the hydro-chemical regime of passively treated acid mine water

Referring to Fig. 5 below, treated water is classified in having high concentrations of $Ca^{2+} + Mg^{2+}$ and HCO^{3-} ions. According to the diagram, mine water had 0% concentration of $CO_3^{2-} + HCO_3$, 100% concentration of SO42- + Cl- ions. This contaminated water contained about 0.7% of $Ca^{2+} + Mg^{2+}$ ions and 93% concentration of $Na^{2+} + K^+$ ions. The treated water for DAS and RAPS systems showed an addition in the concentration of $CO_3^{2-} + HCO^{3-}$ and $Ca^{2+} + Mg^{2+}$ ions. There was a reduction of SO_4^{2-} ions in the treated effluents of both DAS and RAPS.

Metal and metalloids removal

There was substantial contaminants removal in both treatment systems (>95 %) except for Mn and SO₄²⁻. This was primarily due to limestone dissolution which increased the pH near neutral. ICP-MS and IC results revealed that the average concentration of total Fe in acid water was measured at 132.1 mg/L. This concentration was 1321-fold higher than the required limit, as per the domestic water use standard and according to the spectrophotometer, this was all in Fe²⁺ ion form. Referring to Tab.4, DAS A reduced 97.7% of the total Fe concentration, and the remaining 2.3% was comprised of 67% of Fe³⁺ and 33% of Fe2+ ions. DAS B further reduced 99% of the total Fe concentration which was in the Fe²⁺ ion form. DAS C showed an increase of 11.4% in the total Fe concentration which was made up of 87% Fe2+ ions and 13% was Fe³⁺ ions. RAPS A managed to reduce 98.5% of total Fe concentration from the initial 132.1 mg/L in the AMD and the remaining 1.5% was all in Fe²⁺ form. RAPS B increased the concentration of the Fe from RAPS A by 0.8% which was all Fe²⁺. A Further 14.4% increment of Fe concentration after exposure to oxygen in RAPS C was analyzed and detected to be 84% Fe3+ and 16% Fe2+.

Average Al concentration of the inlet was 110 mg/L. As presented in Fig. 6 and 7, while the neutral pH level was reached, both systems managed to reduce the Al concentration. White precipitates were observed at the inlet



Figure 6 Al concentrations and pH levels of dispersed alkaline substrate for 21 weeks



Figure 7 Al concentrations and pH levels of reducing and alkalinity producing system for 21 weeks

point of the both DAS and RAPS columns and this could be associated with precipitation of Al as Al(OH) such as gibbsite mineral. DAS A had an average of 0.05 mg/L, DAS B showed an average of 0.02 mg/L and DAS C showed an average concentration of 0.02 mg/L in 21 weeks of operation. Similar to DAS, RAPS system also managed to reduce the Al concentration of AMD as seen in Figure 35. RAPS A had an average of 0.04 mg/L, RAPS B gave an average of 0.02 mg/L and RAPS C gave an average concentration of 0.03 mg/L. There was minimal Mn reduction by the two passive treatment systems even though the concentrations were still high above the water quality range of the domestic water standard. Average concentrations of Mn for RAPS A, B and C were found to be 3.3 mg/L, 3.3 mg/L and 4.8 mg/L for 21 days of running the experiment. According to the study by Thomas & Romanek 2002, Mn needs a very high pH, greater than 8, and high oxidising conditions to precipitate out. Average SO₄²⁻ concentration for AMD was

analysed to be 1006 mg/L after 21 weeks. No SO_4^{2-} concentrations were achieved by both systems. The same trend of not being able to decrease the sulfate concentration was also experienced in the study done by Nairn & Mercer (2000), instate, the concentration was increased by the treatment system.

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Conclusions

It can be concluded that from the experiments, the DAS system with the setup explained in this study blocked after 21 weeks of operation while the traditional treatment system, RAPS, was still able to treat acid water efficiently without any signs of clogging. Generation of alkalinity led to pH increase from an average of 3 in contaminated mine water to 8, which is neutral conditions in the two systems solely from limestone dissolution. High concentrations of contaminants such as Fe, Al, and Zn were completely removed to below ICP-MS detection limit except Mn. There was no SO42- reduction in both systems which 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 sulfate to sulfide.

Acknowledgements

The authors would like to thank the Council for Geoscience for funding the project and all colleagues who participated in the project.

References

- Bell, F.G. et al., 2001. Environmental impacts associated with an abandoned mine in the Witbank Coalfield, South Africa. International Journal of Coal Geology, 45(2–3), pp.195–216. Available at: http://www.sciencedirect.com/science/ article/pii/S0166516200000331 Accessed 15 March 2015.
- Caraballo, M.A. et al., 2011. Hydrochemical performance and mineralogical evolution of a dispersed alkaline substrate (DAS) remediating the highly polluted acid mine drainage in the full-scale passive treatment of Mina Esperanza (SW Spain). American Mineralogist, 96(8–9), pp.1270–1277.
- Caraballo, M.A. et al., 2007. Treatment of high metal concentration AMD using Dispersed Alkaline Substrate (DAS), a novel passive treatment system. Geochimica et Cosmochimica Acta, 71(15S), p.A143-.
- Colvin, C. Et al., 2011. Coal and Water Futures in South Africa: The case for protecting headwaters in the Enkangala grasslands. WWF Report, pp.1–82.
- Department of Water Affairs and Forestry (1996) South African Water Quality Guidelines (second edition), Volume 1: Domestic Use.
- Hedin, R.S., Nairn, R.W. & Kleinmann, R.L.P., 1994. Information Circular 9389 : Passive treatment of coal mine drainage. , pp.1–44.
- Hedin, R.S., Watzlaf, G.R. & Nairn, R.W., 1994. Passive Treatment of Acid-Mine Drainage with Limestone. Journal of Environmental Quality, 23(6), pp.1338–1345.
- Lai, J., 2013. Impact of anthropogenic pollution on selected biota in Loskop Dam. Submitted in partial fulfillment of the requirement of the degree Master of Science In the Department of Genetics, Faculty of Natural and Agricultural Science University of Pre. The University of Pretoria.
- Manders, P., 2009. Acid Mine Drainage in South Africa. Briefing Note 2009/02, CSIR, (August), pp.1–2.
- Matthies, R., Jarvis, A.P. & Aplin, A.C., 2009. Performance Evaluation of Two Reducing and Alkalinity Producing Systems for Coal Mine Drainage Remediation After 4 Years of Operation., (October), pp.531–538.
- Mccarthy, T.S., 2011. The impact of acid mine drainage in South Africa. South African Journal of Science, 107(5/6), pp.1–7.

- Munnik, V. 2010. The social and environmental consequences of coal mining in South Africa. p.24.
- Nairn, R.W. & Mercer, M.N. 2000. Alkalinity generation and metals retention in a successive alkalinity producing system. Mine Water and the Environment, 19(2), pp.124–133.
- PIRAMID Consortium. 2003. Engineering guidelines for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters, Available at: http://www.sciencedirect. com/science/article/B6VFB-4TTM32K-1/2/f64 aaedd08d767f3972295ee34233383 Accessed 21 April 2015.
- Rapson, L.A. 2004. The development of a riskbased computer database to prioritise the environmental rehabilitation of defunct and aban-

doned collieries in the Witbank area of South Africa.

- Riefler, R.G. et al. 2008. Role of sulfur-reducing bacteria in a wetland system treating acid mine drainage. Science of the Total Environment, 394(2–3), pp.222–229.
- Rötting, T.S. et al. 2008. Field application of calcite Dispersed Alkaline Substrate (calcite-DAS) for passive treatment of acid mine drainage with high Al and metal concentrations. Applied Geochemistry, 23(6), pp.1660–1674.
- Thomas, R.C. & Romanek, C.S. 2002. Passive treatment of low-pH , ferric iron-dominated acid rock drainage in a vertical flow wetland ii : metal., pp.752–775.
- Watzlaf, G.R. et al., 2004. The Passive Treatment of Coal Mine Drainage. , pp.1–72.