Long-Term Remediation of Acid Mine Drainage from Abandoned Coal Mine Using Integrated (Anaerobic and Aerobic) Passive Treatment System, in South Africa: A Pilot Study

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Abstract

Acid mine drainage from abandoned mines is primarily responsible for degradation of scarce water resources in South Africa. Owing to the nature of previous legislations, the South African government has inherited environmental liabilities of most of the abandoned mine sites, and hence there is a need to develop long-term sustainable remediation solutions. To contribute towards development of sustainable mine water management solutions in South Africa, a pilot passive treatment plant consisting of integrated anaerobic and aerobic units has been constructed to treat 1440 liters of acid mine drainage per day from an abandoned underground coal mine. During the first six months of operation, the pilot plant has successfully neutralized the water and substantially removed contaminants, such as Fe, Al, Co, Zn, Ni, As, Pb, V, but with limited SO_4 reduction (only 30% removal rate was achieved). Thereafter, there has been a decrease in treated water quality with time, and this was largely due to clogging and/or depletion in the treatment materials. The study demonstrated that passive treatment can be used as a long-term remediation of polluted mine water from abandoned mine sites in South Africa. The results of this pilot-scale test will be used to design an optimised full-scale plant, and also assist in an optimized design of additional pilot plants in other abandoned mining areas.

Key words: Acid mine drainage, Passive treatment, Anaerobic and Aerobic units

Introduction

Many of the abandoned mines in South Africa generate contaminated mine drainage, and over the years this has led to a deterioration in the water quality in many surface streams and ground water, as reported by a number of researchers (Naicker et al. 2003; McCarthy 2011; Yibas et al. 2013). Owing to the nature of previous legislation, the South African government has inherited environmental liabilities of most of the abandoned mine sites, and hence there is an urgent need to develop long-term sustainable remediation/management strategies (Swart 2003). Passive treatment is a technology of choice for long term remediation of polluted mine water in many parts of the world such as the United States, United Kingdom and Germany, due to the following benefits over active treatment(Hedin et al. 1994; Kleinmann & Hedin 1993; Younger 2000; Wolkersdorfer 2008):

- usually low operational cost; can be very efficient in metals removal;
- can reduce or eliminate the use of hazardous chemicals;
- potential to recover valuable products that can offset the cost of maintenance; and
- acceptance by social communities since the systems employed are more natural and aesthetic in their appearance and may support plants and wildlife

However, the application/adoption of passive treatment in the South African is limited and not well understood. Hence, there is a need to explore the potential application of these systems for a long-term remediation of acid mine drainage. Research in South Africa has been mainly on lab/bench-scale, using artificial mine water and only focusing on the development of passive anaerobic sulphate reduction technology. To contribute towards development of sustainable mine water management solutions in South Africa, a pilot passive treatment plant consisting of integrated anaerobic and aerobic

units has been constructed to treat 1440 litres of acid mine drainage per day from an abandoned underground coal mine.

Study area

The pilot plant is situated near Carolina in the Mpumalanga Province on the farm Witkranz 53 IT, portion 11. Geologically, the area forms part of the Ermelo coalfield, situated south of Carolina. All the coal seams occur within the Vryheid Formation of the Ecca Group, Karoo Supergroup. Sandstones with subordinate shales represent the bulk of the Vryheid Formation (Bell & Jermy 2002). There is very little information about the mining history of the area. However, an old mine plan obtained from a local mining company shows mining activities in a portion of land to the east of the main discharge point, using both underground and open-cast methods (Figure 1). In terms of hydrology, the site is situated in the Komati–Crocodile catchment area. The acid mine water discharges into the Boesmanspruit, which flows in a northwest direction into the Boesmanspruit dam. The pilot plant was constructed adjacent to the discharge point (Figure 1).

Figure 1 Old underground mine plan adjacent to the Witkranz discharge point.

Methods

Field observation and sampling were conducted to characterise the acidic mine water discharge. The hydrogeochemical parameters are summarised in Table 1. On-site measurements/analyses in respect of parameters such flow rate, pH, electrical conductivity (EC), and elemental concentrations were conducted. Water samples were also analysed by means of ICP-MS and IC and the element concentrations were compared with the South African domestic water quality standards. Both discharges are generally characterised by a low pH, with concentrations elevated by as much as two and even three orders of magnitude than the acceptable limit of Fe, Al, Mn and sulfate and slightly elevated arsenic (As).

The selection of a suitable passive treatment system was done with the aid of the periodic table for passive treatment developed by Gusek (Gusek 2009; Gusek 2013) and the flow chart, as adopted from Hedin et al. (1994). Based on the chemistry of the seepage and the site characteristics, the selected passive treatment system consists of two cells of vertical flow ponds or a Reducing Alkalinity Producing System (RAPS), which combines the mechanisms of anaerobic treatment wetlands and anoxic limestone drains, as developed by Kepler and McCleary (1994), a settling pond and an open/ cascading limestone bed for Fe removal. Figures 2 and 3 show a layout of pilot passive treatment system in Carolina.

The RAPS and oxidation units were constructed in a 1 000 L (height = 1 160 mm, length = 1 200 mm and width = 1 000 mm) plastic containers (Figure 2). About 1.5 t of limestone (with at least 85% $CaCO_3$) was placed at the bottom of the tank, forming a layer 0.5 m deep. Directly above the limestone

layer, about 0.3 t of organic substrate (consisting of manure, cow manure, chicken manure and powdered limestone) was placed to form a layer about 0.2 m deep. A layer about 0.3 m deep of water was maintained above the organic substrate layer, to encourage vertical flow. The RAPS units were followed by a settling/oxidation pond to collect treated or partially treated waters. This pond allows iron and other precipitates to settle and is useful in providing a more constant flow rate into a down-gradient treatment system. The settling pond was sized to allow a primary retention time of 8 hours. The last unit in the system was a cascading limestone trench for the oxidation and removal of Fe under oxidising conditions (Figure 3). Since dissolved oxygen decreases with depth, this shallow cascading trench helped to increase rate of oxidation.

Acid mine water was piped directly from the source and the flow rate was controlled by means of gate valve to the initial RAPS unit. A flow rate of 1L/min was used as the primary flow rate, which provided the optimal residence time of 8 hours for each RAPS unit. The influence of residence time on the neutralisation rate and removal of metals was examined by varying the inflow rate, which is inversely proportional to residence time. The construction of the pilot plant started on 27 October 2014, and it has been operational from 1 November 2014. On-site analyses of water quality parameters including, pH, redox, electrical conductivity, dissolved oxygen and temperature were done using a WTW multi 3430 meter. Alkalinity was also analysed in the field by means Hach DR 900 spectrophotometer. In addition, flow rate was measured by means of the bucket and stopwatch method. Water samples were collected using 100ml plastic bottles. The samples were filtered using 0.45 µm filters. For trace and major metals and metalloids, samples were preserved by acidification using 3M nitric acid (HNO_3). Analyses were done by means of ICP-MS and IC analytical techniques. Precipitates that had formed in the treatment units (RAPS1, RAPS2 and oxidation pond) were collected after 12 months of operation from the tops and bottoms of the units, and analysed for mineralogical compositions using XRD and SEM.

Table 1 *Analytical data for acid mine drainage sources in the study area.*

	Carolina/ discharge	DWAF guideline
Flow (L/min)	34	
pH	3.06	6-9*
EC (mS/m)	254	
Dissolved oxygen (mg/L)	5.20	
Redox (mV)	350	
Calculated acidity	967.77	
Na (mg/L)	8.16	
Mg (mg/L)	61.25	
Al (mg/L)	40.62	0 - 0.15*
K (mg/L)	7.54	
Ca (mg/L)	170.16	
V (mg/L)	0.01	
Cr (mg/L)	0.01	
Fe (mg/L)	331.56	0 - 0.1*
Mn (mg/L)	20.3	0 - 0.05*
Co (mg/L)	1.65	
Ni (mg/L)	1.67	
Cu (mg/L)	<0.02	
Zn (mg/L)	2.26	0 - 3.0*
As (mg/L)	0.06	0 - 0.01*
Cd (mg/L)	0.01	
U (mg/L)	0.01	
SO_4^{2-}(mg/L)	2524.77	0 - 200*

*Department of Water Affairs limit for Human consumption

Figure 2 *Carolina pilot passive treatment RAPS and oxidation units*

Figure 3 *Carolina pilot passive treatment cascading trench*

Results and Discussions

Alkalinity generation

The system added substantial alkalinity during the first six months of operation (Figure 4). Consequently, there was an increase in the pH of the water from the source throughout the treatment plant. The pH from the inlet ranged from 2.5 to 3 and it increased to an average 6.5 (from RAPS 1 to 2, respectively). This conforms to what is expected for alkalinity generation, which averages at 120 mg/L and 230 mg/L (as $CaCO_3$) for both RAPS 1 and RAPS 2, respectively. The alkalinity generation of the two RAPS units is attributed to bicarbonates released from microbial SO_4 reduction and the dissolution of limestone. However, after six months there was a decrease in alkalinity addition over time, which was attributed to clogging and depletion of the treatment materials. Clogging is associated with precipitate build-up when the pH increases and the formation of algae on top of the treatment units. After 15 months of operation the average pH in the RAPS units was 4.5 and 6, for RAPS1 and RAPS2 respectively. This also conforms to alkalinity, with average values of 40 and 80 mg/L (as $CaCO_3$), for RAPS 1 and RAPS2 respectively.

The pH in the oxidation pond remained above 6.5 during the initial 60 days. After this period, up to the present date, the pH has dropped to below 5 in the oxidation ponds. This is likely to have been caused by the hydrolysis of iron and manganese. The reactions of Fe and Mn under oxidation conditions are known to add to the proton acidity, and hence this led to a decrease in the pH of the oxidation pond over time. Another possible cause for the decrease in the pH and alkalinity may be

ascribed to the oxidation of metal sulfides that have precipitated in the pond. The likely reactions in this regard are similar to the reactions responsible for the generation of AMD.
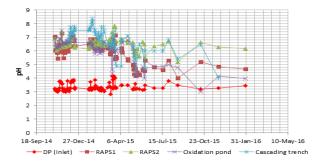

Figure 4 pH of inflow and outflow water in the passive treatment system

Metals removal

Figure 5 shows the concentration of iron in the inflow and outflow water of different units in the pilot passive treatment system. There was a gradual decrease in the concentration of iron throughout the passive treatment units. The average Fe in the inlet (source) is 250 mg/L, and the concentration decreased to an average of 150 mg/L and 100 mg/L in the RAPS 1 and RAPS 2, respectively. The decrease of Fe in these anaerobic units is attributed to microbial sulfate reduction process, which releases hydrogen sulfide. The hydrogen sulfide then reacts with Fe and precipitates as iron sulfide. Iron removal rates in the RAPS units increase with time during the initial stages of operation, and this could be attributed to an increase in the community of sulfate reducing bacteria. Iron was further decreased in the oxidation pond and cascading trench, resulting in a concentration as low as 10 mg/L and to below detection limit, respectively. The decrease of iron in these units is associated with oxidation, where iron precipitates as hydroxides. Cascading trenches show the highest rate of iron removal, which is attributed to a high rate of oxidation in the trench. The average Fe removal in the passive treatment system was at least 95% during the first six months. After six months there was a decrease in the removal rate of Fe, mainly due to clogging/armouring and depletion in the treatment materials. Armouring and clogging in the RAPS units relates to the precipitates built up in the organic substrate and the limestone bed.
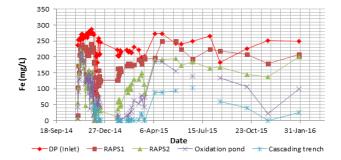

Figure 5 Fe concentrations of inflow and outflow water in the system

Figure 6 and 7 show the concentration of Al, Zn, Ni, and Co in the inflow and outflow water of different units in the pilot passive treatment system. Al concentration of the inlet (the source) averages 30 mg/L, which is way above the required limit, as per the domestic water use standard. Figure 6 shows that Al decreased to below zero in the system from the RAPS 1. This is attributed to the increase in the pH to above 6 and, hence, Al is likely to precipitate at this pH. White precipitates were observed on top of RAPS 2, and this could be associated with a hydroxide of aluminium, such as gibbsite. Metals such as Zn, Ni and Co are removed in a similar manner in anaerobic and aerobic units. These metals are initially removed as sulfides in the RAPS units owing to microbial sulfate reducing and the residual or remaining dissolved metals co-precipitating with hydroxides of iron. The hydroxides of Fe are known to be excellent sorbents of trace metals, such as Co, Ni, and Zn and, subsequently, can control their mobility, fate and transport in the environment.
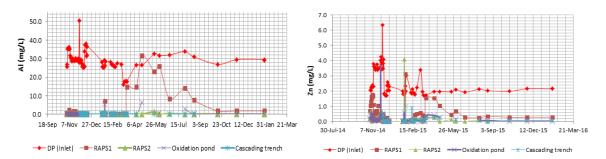
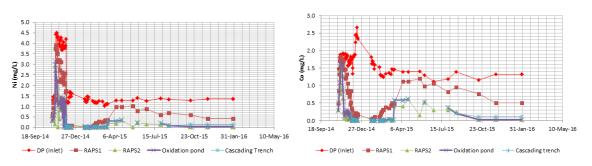*Figure 6 Al and Zn concentrations of inflow and outflow water in the system*

Figure 7 Ni, and Co concentrations of inflow and outflow water in the system

Sulfate reduction

Figure 8 shows sulfate reduction with time in the treatment plant. The SO_4 level in the inlet averages 1 500 mg/L which slightly decreases in the RAPS units to an average of 1 000 mg/L. There has been substantial SO_4 reduction in the anaerobic units, especially RAPS2 during the first six months of system operation, and this has been attributed to microbial processes. The average removal of sulfate in the system was only 22%. After six months, SO_4 reduction has been decreasing with time and this is attributed to clogging and depletion of the treatment materials. Sulfate reduction is important in the system for more effective secondary alkalinity addition and the removal of metals.
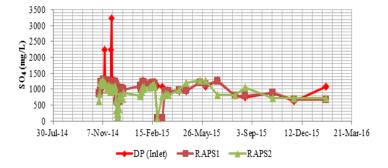

Figure 8 SO₄ concentrations of inflow and outflow water in the system

Mineralogical composition of precipitates

Mineralogical compositions of the precipitates were analysed by means of XRD and SEM, (figures 9, 10, and 11). The top layer of RAPS 1 principally consists of goethite (FeOOH) (84.8%), followed by jarosite [$KFe_3(SO_4)_2(OH)_6$] (8.3 wt%) and hematite (3.32 wt%), whereas the bottom layer consists of palygorskite $(Mg,Al)_2Si_4O_{10}(OH).4(H_2O)$ (47.7 wt%), gypsum ($CaSO_4.2H_2O$) (23.15 wt %), jarosite (10.96 wt %), sulfur (7.91 wt%), calcite (6.37 wt %), dolomite (2 wt %) and quartz (3.6 wt %) (Figure 9). It should be noted that palygorskite, calcite, dolomite and quartz are not secondary minerals, since there are weathered from the limestone used in the system. The presence of high concentrations of iron hydroxide minerals on the top layer of RAPS1 is indicative of a high rate of oxidation. The presence

of jarosite is indicative of a low pH on top of RAPS1, which is an inlet of the system. However, since this is vertical flow system, the pH increases downwards — hence the formation of gypsum at the bottom of the unit.

The top layer of RAPS2 principally consists of amorphous contents (100 wt %) or poorly crystalline materials that do not contribute to diffraction peaks (figure 10). Based on field observations, the top layer of RAPS2 consisted of white to orange slurry-like precipitates. The white could be attributed to Al oxy-hydroxides and orange could be indicative of Fe oxy-hydroxides. Gypsum (68.9 wt %) is predominant at the bottom of the RAPS2 unit, where the pH is higher. Figure 11 shows a well-developed gypsum crystal at the bottom of RAPS2. Goethite is the dominant mineral species in the oxidation pond, especially in the top layer, and this is again attributed to high rate of oxidation in the pond (figure 10).
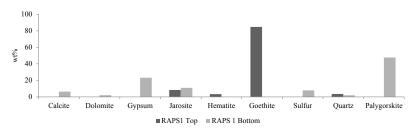

Figure 9 Mineral composition of precipitates formed in the RAPS 1 top and bottom layers
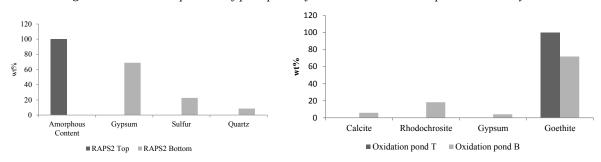

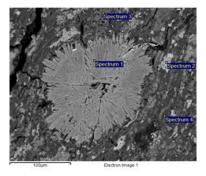*Figure 10 Mineral composition of precipitates formed in the RAPS 1 top and bottom layers*

Figure 11 SEM image for the RAPS2 unit bottom layer, showing a well-developed gypsum crystal

Conclusions

The pilot passive treatment system at Carolina demonstrated that passive treatment is a potential long-term suistanable remediation measure for polluted mine water from abandoned mine sites in South Africa. The geochemical mechanism of passive treatment of polluted mine water is a complex process, comprising of a number of reactions that occur under different redox conditions. Hence, to achieve optimum long-term remediation of polluted mine water in South African abandoned mine sites; an integrated passive treatment approach is envisaged. Some of the lessons learnt and recommendations for future design of appropriate passive treatment systems are as follows:

- During the first six months of operation, the Carolina pilot plant successfully neutralised the water and substantially removed contaminants such as Fe, Al, Co, Zn, Ni, As, Pb, V, but achieved limited SO_4 reduction (only a 30% removal rate was achieved). Thereafter, there was a deterioration in treated water quality over time, largely due to clogging and/or depletion of the treatment materials. Periodic flushing of the system is envisaged. In addition, the system should be optimised for SO_4 removal. SO_4 reduction is mainly attributed to microbial activities, and hence conditions necessary for optimum reduction should be considered. Such conditions include, use of appropriate organic substrate, pH, redox, flow rate/contact time.
- There was minimal or no removal of Mn in the system and this may be attributed to the presence of Fe in the oxidation pond and cascading trench, which tend to compete for oxygen consumption. A Mn removal bed is envisaged in this regard.
- Mineralogy and bulk geochemical analyses undertaken showed a clear variation in the geochemistry of the precipitates formed in the passive treatment units. This conforms to the quality of the inflow and outflow water in the system. Metals such a Fe, Zn, Cu precipites as sulphides in the anaerobic units and as oxides or hydroxides in the aerobic units. Accumulation of these mineral/metal species in the passive treatment units present an opportunity to recover valuable products that can offset remediation costs.

Acknowledgements

References

Bell, F.G. & Jermy, C.A., 2002. A geomechanical survey of some different facies in relation to stability at a mine in the Eastern Transvaal Coalfield, South Africa. Engineering Geology, 64(1), pp.19–39.

Gusek, J.J., 2009. A Periodic Table of Passive Treatment for Mining Influenced Water. 2009 National Meeting of the American Society of Mining and Reclamation, pp.550–562.

Gusek, J.J., 2013. A Periodic Table of Passive Treatment for Mining Influenced Water. International Mine Water Association Symposium, 1, pp.575–580.

Hedin, R.S., Nairn, R.W. & Kleinmann, R.L.P., 1994. Information Circular 9389 : Passive treatment of coal mine drainage. , pp.1–44.

Kepler, Douglous A and McCleary, E.C., 1994. Successive Alkalinity Producing Systerm for the treatment of Acid Mine Drainage. , pp.195–204.

Kleinmann, P. & Hedin, R.S., 1993. Treat Mine Water Using Passive Methods. Pollution Engineering, 25(August), pp.20–23.

McCarthy, T.S., 2011. The impact of acid mine drainage in South Africa. South African Journal of Science, 107(5/6), pp.1–7.

Naicker, K., Cukrowska, E. & McCarthy, T.S., 2003. Acid mine drainage arising from gold mining activity in Johannesburg, South Africa and environs. Environmental Pollution, 122(1), pp.29–40.

Swart, E., 2003. The South African legislative framework for mine closure. Journal of The South African Institute of Mining and Metallurgy, 103(8), pp.489–492.

Wolkersdorfer, C., 2008. Water Management at Abandoned Flooded Underground Mines, Springer.

Yibas, B., Netshitungulwana, R., Novhe, N.O., Mengistu, H., Sakala, E., Thomas, A., & Nyambeze, O., 2013. " Reliable Mine Water Technology " IMWA 2013 A holistic approach towards best management practices of mine pollution impacts using a catchment area strategy , South Africa. In pp. 117–122.

Younger, P.L., 2000. The adoption and adaptation of passive treatment technologies for mine waters in the United Kingdom. Mine Water and the Environment, 19(2), pp.84–97.