



Metal removal from mine water using integrated passive treatment system at Witkrantz discharge point in the Ermelo Coalfields, Mpumalanga[©]

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Abstract

Passive treatment technology has been used successfully worldwide for treatment of contaminated mine water, but its applicability in South Africa is limited. To help understand its applicability in the South Africa's context, a pilot plant consisting of integrated anaerobic and aerobic units, was operated in Carolina, Mpumalanga. The main objective was to raise pH levels and remove the contaminants. An overall removal rate of at least 90% was achieved for contaminants such as Fe, Al, Zn, Ni. Overall sulphate was removed up to 30%, with no Mn removal. Deterioration of treated water was due to sludge clogging and depletion of treatment materials. Future investigations will focus on characterisation of organic and alkaline substrates.

Keywords: AMD, SRB, Passive treatment, Contaminants, Anaerobic and Aerobic Units

Introduction

Passive treatments uses natural, chemical and biological processes and requires regular but low maintenance, it is relatively low in capital and operational cost, and can provide long-term water management and treatment based on potential for lower overall costs (Hedin et al., 1994; Younger et al., 2002; Wolkersdorfer, 2008). This technology offers justification of raising pH, lowering acidity, reducing toxic metal concentration, sulphate concentration and salinity. Passive treatment is used as a long-term sustainable solution in many parts of the world and it has been globally success-

ful in United State of America, United Kingdom, Germany and France (Hedin and Nairn, 1992; Kleinmann and Hedin, 1993; Hedin et al., 1994; Wolkersdorfer, 2008). However, in South Africa there are still knowledge gaps in terms of passive treatment applications for remediation of AMD. Witkrantz discharge point has high volume of water with an estimated average flow rate of 30 L/min (fig. 1a) and an oxidation pond was constructed as water controlled dam to reduce Fe concentration (fig. 1b). Over 76 samples were collected and characterised showing low pH of 3 to 3.5, elevated metals and sulfate concentrations.



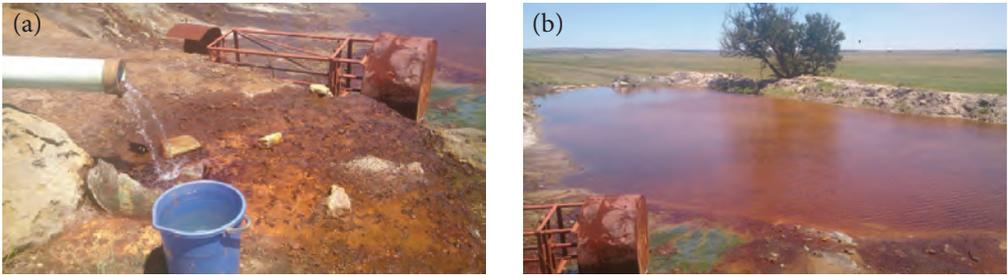


Figure 1 (a) AMD discharging from Witkrantz coal mine (b) AMD pond adjacent to the Witkrantz discharge (Photographs by Obed Novhe).

A pilot passive treatment plant was constructed to treat 1440 L of contaminated mine water discharging from abandoned Witkrantz coal mine and operated for 15 months (Novhe et al., 2016). The treated water was discharged to the nearby stream and eventually to Boesmanspruit dam. The study area is located on the farm Witkrantz 53 IT, portion 11 in Mpumalanga Province approximately ± 60 km from the town of Ermelo. The area forms part of Ermelo Coalfield and all seams occur within Vryheid Formation of Ecca Group, Karoo Supergroup. The purpose of this study is to determine the overall metal removal rates from integrated passive treatment system at Witkrantz discharge.

Methodology

Experimental design

The system consisted of two Reducing and Alkalinity Producing System (RAPS), an oxidation pond and cascading trench. As indicated by Novhe et al., (2016), the RAPS consisted of 1.5 t limestone (85% of CaCO_3) at the bottom of 1000 L tank, 0.3 t of organic substrates (cow and chicken manure, sewage sludge and powdered limestone) above the limestone and for vertical flow of water a layer of 0.3 m was maintained. Slightly steep and shallow cascading trench consisted coarse limestone was also constructed for further Fe removal.

Water sampling and analysis

Water samples were collected in pre-cleaned and pre-contaminated 100mL and 200mL polyethylene bottles. For anions and cations, filters of $0.45\mu\text{m}$ were used to remove particulates from suspension. Samples for major

and trace cations were preserved using the 2M of Nitric Acid (HNO_3) and kept at a temperature of below 6°C prior chemical analysis. ICP-MS and IC technique was used to analyse the samples. On-site parameters such as pH, temperature, dissolved oxygen, redox and electrical conductivity were conducted with the aid of WTW 3430 Digital Multimeter. Hach DR 1900 meter was used to measure alkalinity, aluminium, manganese and iron concentrations. Bucket and stopwatch method was used to measure the flow rate.

Removal rates or loads

Concentration difference between two sampling points was calculated using a formula developed by (Wieder 1993) to determine the removal rates. The average load removal (ΔL , L/d) was determined by subtracting effluent loads from influent loads, dividing by influent load and multiplying by 100%.

$$\Delta L\% = (L_{\text{inf}} - L_{\text{eff}})/L_{\text{inf}} * 100\% \quad (\text{eq. 1})$$

Where: $\Delta L\%$ is the average load removal expressed in %, L_{inf} is the influent load expressed in L/d and L_{eff} is the effluent load expressed in L/d. Results were analysed and presented in multiple variables scatterplots using Statistica software.

Results

Table 1 summarises water quality of the influent and effluents from the anaerobic and oxidizing units, as mean and standard deviation (SD). The contaminants (Fe, Al, Zn, Ni and SO_4) removal rates are presented against pH and time in Fig 2, 3, 4 and 5 for RAPS1, RAP2, Oxidation Pond and Cascading Trench, respectively.



Table 1. Water quality of the influent and effluents from the anaerobic and oxidizing units.

Parameter	Influent		RAPS1		RAPS2		Oxidation Pond		Cascading Trench	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
pH values	3.3	0.3	6.2	0.6	6.2	0.6	6.4	0.8	7.1	0.7
Ec (mS/cm)	2.1	0.1	2.1	0.1	2.1	0.1	1.8	1.0	1.9	0.9
Fe (mg/L)	225.7	53.6	181.8	43.1	181.8	43.1	80.1	64.9	15.7	27.1
Mn(mg/L)	29.9	8.7	32.5	4.9	32.5	4.9	31.3	9.0	28.0	12.1
Al (mg/L)	28.2	6.8	2.1	5.8	2.1	5.8	0.4	1.0	0.1	0.2
Ni (mg/L)	2.1	1.3	1.1	1.2	1.1	1.2	0.5	0.8	0.0	0.1
Zn(mg/L)	3.0	4.3	0.4	0.6	0.4	0.6	0.2	0.4	0.1	0.2
SO ₄ (mg/L)	1098.4	177.8	1041.2	251.4	1041.2	251.4	971.5	237.3	971.5	237.3

The role of alkalinity on pH

Many authors reported cases of successfully treating AMD using bioreactors (Gusek et al. 1999; Reisinger et al. 2000; Reisman et al. 2003; Kuyucak et al. 2006). Bioreactors are responsible for generating alkalinity and raising pH levels using SRB. The role of alkalinity is to neutralise acidity in the AMD by dissolution. As reported by Novhe et al., (2016), RAPS 1 and 2 consisted at least 85% of CaCO₃ and 0.3 t of organic substrates which included chicken and cow manure, and powdered limestone. This enabled rapid generation of alkalinity, especially in the first few months. From November 2014 to April 2015, alkalinity averaged at 150 mg/L to 230 mg/L in RAPS 1 and 2 respectively. This increased the pH from the influent of 3.5 to 6 (RAPS 1) and 6.5 (RAPS2) (fig 2 & 3). Further alkalinity generation was observed in the cascading trench averaged at 300 mg/L. Consequently, pH was recorded to be 7.5 at the effluent (fig 5). Alkalinity decreased with time throughout the system. A sudden decrease in alkalinity could be due to clogging and depletion of materials. However, alkalinity maintained its integrity at 100 mg/L despite exhaustion of materials from May to August 2015.

Overall metal removal rates

There was substantial removal of contaminants > 90% throughout the system except for Mn. This could be due alkalinity generation from SRB and limestone dissolution which increased pH near neutral. Targeted contaminants includes: Fe, Al, Mn, Zn, Ni, Cd, Pd, Co, Cu and As. (Sheoran et al. 2010) reported that Fe forms iron sulphides and carbonates when pH is near neutral and in reducing

conditions, and at pH ≥ 3.5 iron oxihydroxides are formed (Gilbert et al. 2005). ICP-MS and IC results showed a decrease of Fe concentration from ≈ 300 mg/L (inlet) to 0 mg/L (effluent) over time. Removal of Fe ranged from 15% to 70% from RAPS 1 and RAPS 2 respectively (fig 3 & 4). The low removal rate of 15% in RAPS 1 could be attributed to slow rate of H₂S generation from microbial activities. Over time, Fe was further removed at 80% and 100% in the oxidation pond and the cascading trench respectively (fig 4 & 5). Generation of alkalinity by SRB reduced the concentration of metals and therefore precipitating them as metal sulphide.

With an increase of pH near neutral, Al was able to precipitate as Al(OH)₃, i.e. gibbsite and removed at 93% and 100% in RAPS 1 and 2 respectively (fig 2 & 3). There was a sudden decrease in Al removal rate in RAPS 1; however, the other units maintained the removal rate of 100%. Zn, and Ni were removed below detection limit (fig 2 & 3). Their removal in the system was due to microbial sulphate reduction (as metal sulphides) and co-precipitation with Fe and Al (oxy)hydroxides, (Gilbert et al., 2005). There was a sudden drop in April 2015 from RAPS1, however, the other units continued to remove contaminants (Zn, Ni and Al) at 100%. Other metals such Cd, Pb, Co, Cu and metalloid As showed similar trends and were also removed below detection limit. The non-removal of Mn was probably due to the presence of Fe in the oxidation pond and cascading trench. (Thomas and Romanek, 2002) documented that a high pH is required for Mn to precipitate and Fe must have been completely removed in the system. (Strumm and Morgan, 1996) revealed that in



AMD the oxidation of Mn is slow; however it can be stimulated by bacteria and catalysis by surfaces.

Effects of sulfate reduction on metal removal

The overall removal of sulphate in the system was 30% (fig 2 & 3). Sulfate reduction in this system was mainly due to microbial activities in RAPS 1 and 2 (anaerobic units). According to Sheoran et al. (2010) processes responsible for removing metals include adsorption, co-precipitation, biosorption and filtration. The success of this is determined by a reliable carbon source and a conducive environment for SO₄ reduction for microbial activity. Carbon source reduce sulphate to hydrogen sulphide which reacts with dissolved metals to form metal sulphide. In addition, materials should have enough pores to promote permeability. Locally, available treatment materials are preferred as they are readily available and

inexpensive. The 30% sulphate reduction recorded in the first few months decreased with time as treatment materials get depleted and the system experienced clogging.

Conclusions

Generation of alkalinity by both SRB and limestone dissolution increased the median pH throughout the system from as low as 3 to an average of 7.5. The overall metal removal rate in the system was greater than 90% excluding Mn. The performance for this pilot plant has been adequate in generating alkalinity and removing contaminants such as Fe, Al, As, Zn, Cd, Co, Pb, Ni at 100% and below detection limit. Furthermore, there was substantial SO₄ removal rate of 30%. However, Mn was not removed as a pH of at least 9 and high oxidation rate are required. Microbial sulfate reduction which releases hydrogen sulphide contributed to removal of metals.

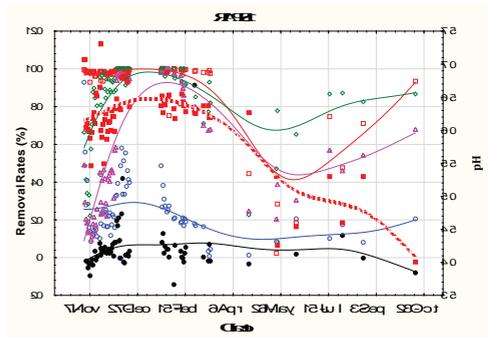


Figure 2 Contaminants removal rates against pH in the RAPS1.

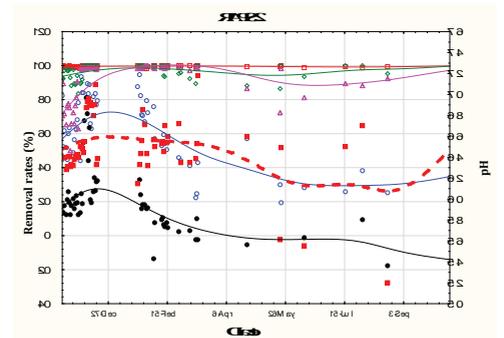


Figure 3 Contaminants removal rates against pH in the RAPS2.

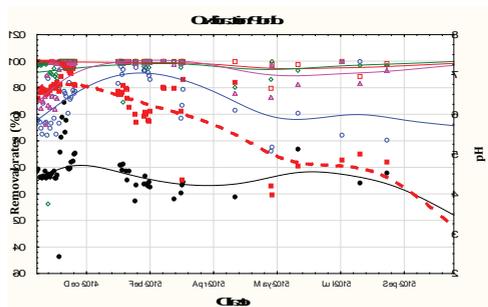


Figure 4 Contaminants removal rates against pH in the oxidation pond.

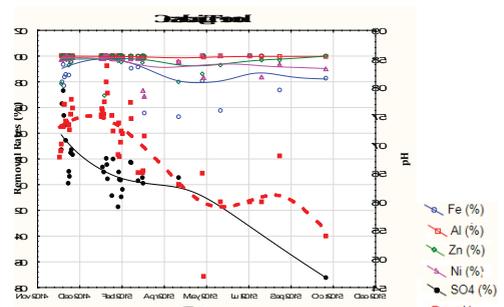


Figure 5 Contaminants removal rates against pH in the Cascading Trench.



For instance, the gradual decrease in Fe concentration from anaerobic units was due to microbial sulfate reduction which releases hydrogen sulphide and it further precipitates as hydroxides from oxidation pond and cascading trench. Depletion of treatment materials and clogging due to sludge (built-up) contributed to removal rate of metals being constant.

Recommendations

It is of paramount importance to select suitable organic materials to adsorb metals and encourage optimum microbial SRB. To prevent clogging and armouring from Al and Fe hydroxides, accumulated precipitates need to be flushed. Because Mn oxidation is slower than Fe oxidation, it is recommended that Fe must be removed completely before treating Mn. To select the most suitable treatment materials for mine water, local available organic and alkaline substrates need to be characterised.

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References

- Gilbert O, Pablo de J, Cortiina, JL, Ayora, C (2005) Municipal compost-based mixture for acid mine drainage bioremediation: metal retention mechanism. *Applied Geochemistry*, 20(9), pp.1648–1657.
- Gusek JJ, Wildeman TR, Miller A (1999) Design, construction and operation of a 1,200 gpm passive bioreactor for metal mine drainage. In: *Phytoremediation and innovative strategies for specialized remedial applications*, Battelle Press, Columbus, OH, pp.217–223.
- Hedin RS, Nairn RW (1992) Designing and sizing passive mine drainage treatment systems - Online. Available at: <http://wvmdtaskforce.com/proceedings/92/92HED/92HED.HTM>.
- Hedin RS, Nairn RW, Kleinmann RLP (1994) Information Circular 9389: Passive treatment of coal mine drainage, pp.1–44.
- Kleinmann P, Hedin RS (1993) Treat mine water using passive methods. *Pollution Engineering*, 25(August), pp.20–23.
- Kuyucak N, Chabot F, Martschuk J (2006) Successful implementation and operation of a passive treatment system in an extremely cold climate. In *Proc. of the 7th Int. Conf. on acid Rock Drainage (ICARD)*. St. Louis, MO, In: R.I. Barnhisel (Ed), American Society of Mining and Reclamation (ASMR), Lexington, KY, pp. 3132–3138.
- Novhe NO, Yibas B, Coetzee H, Atanasova M, Netshitungulwana R, Modiba M, Mashalane T (2016) 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. *Mining Meets Water -Conflicts and Solutions*, (1), pp.668–675.
- Reisinger RW, Gusek JJ, Richmond TC (2000) Pilot-scale passive treatment test of contaminated waters at the historic Ferris-Haggarty mine, Wyoming. In: *Proc. of the 5th Int. Conf. on Acid Rock Drainage (ICARD)*, Denver, CO, pp. 1071–1077.
- Reisman DJ, Gusek JJ, Bishop M (2003) A pre-treatability study to provide data for construction of a demonstration bioreactor. In: *The Proc. of the 10th Int. Conf. on Tailings and Mine Waste*, Vail, CO, pp. 305–315.
- Sheoran AS, Sheoran V, Choudhary RP (2010) Bioremediation of acid-rock drainage by sulphate-reducing prokaryotes: A review. *Minerals Engineering*, 23(14), pp.1073–1100, doi:10.1016/j.mineng.2010.07.001.
- Strumm W, Morgan, JJ (1996) *Aquatic chemistry, chemical equilibria and rates in natural waters* 3rd edn., Wiley, New York.
- Thomas RC, Romanek CS (2002) Passive treatment of low pH, ferric iron-dominated acid rock drainage in a vertical flow wetland II: Metal removal, American society of mining and reclamation, Lexington KY, pp.752–775.
- Wieder RK (1993) Ion input/output budget for five wetlands constructed for acid coal mine drainage treatment. *Water, Air and Soil Pollution*, 71, pp.231–270.
- Wolkersdorfer C (2008) *Water Management at Abandoned Flooded Underground Mines*, Heidelberg: Springer.
- Younger PL, Banwart SA, Hedin RS (2002) *Mine Water- Hydrology, Pollution, Remediation*. Dordrecht: Kluwer.

