Low-Cost Biological Treatment of Metal- and Sulphate-Contaminated Mine Waters

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Abstract This paper describes the development of a passive biological sulphate reduction (BSR) process. Laboratory-scale test work was performed on a mine-impacted water from a South African coal mine. The substrate mix comprised wood chips, wood shavings, hay, lucerne and cow manure. Over 90 % sulphate removal was achieved, the pH level was raised to above 7, and metals were precipitated. Operating parameters were optimised to increase process kinetics.
The results were used to design a pilot plant which will be operated at the coal mine, treating several hundred litres of water per day.

Keywords passive treatment, biological sulphate reduction, mine waters, pilot plant

Introduction

The threat to the South African environment from acid mine drainage and mine-impacted waters is well documented (NSTF/SAASTA 2011; Turton 2013). Effluents from the gold- and coal-mining industries can severely impact upon the quality of water supplies, and affect all major industries across the value chain. These acidic and metal-contaminated waters are typically treated by lime neutralisation, which removes the metals and increases the pH levels, but the discharge sulphate level remains high (Lorax Environmental 2003). Biological treatment using sulphate-reducing bacteria offers an alternative to conventional technologies for the localised treatment of effluents from the mining and metallurgical industries. The process has several advantages: both sulphate and metals are reduced to low levels, and less solid waste is produced compared to chemical precipitation. Passive processes have relatively low capital costs, and operating costs can be substantially reduced by using inexpensive carbon and energy sources. Numerous BSR plants have operated worldwide, focused primarily on increasing the pH levels and precipitating the metals (Watzlaf *et al.* 2004; Doshi 2006; Jamil and Clarke 2013). In South Africa, however, stringent regulations enforce lower sulphate discharge limits of 200600 mg/L (Arnold *et al.*, 2016), for which BSR is ideally suited.

The main objectives of the test work programme were to:

- Identify a suitable low-cost substrate and electron donor to be used in the process.
- Determine the maximum extent of sulphate removal during passive biological treatment of the mine water.
- Evaluate the effect of key operating parameters on the rate and extent of sulphate reduction, including temperature, pH level, sulphate loading, metal concentrations and hydraulic residence time (HRT).

Methods

Water Samples

Two water samples from a South African coal mine, located near eMalahleni (formerly Witbank) in Mpumalanga Province, South Africa, were utilised in the test work programme. The water samples contained trace quantities of several base metals, over 3000 mg/L of sulphate, and appreciable quantities of magnesium, calcium and manganese. The alkalinity of the water sample was 516 mg/L, and the pH level was 7.26.

Equipment

The test work was conducted in a series of three water-jacketed columns, each 1 m tall and 0.3 m wide, giving an internal volume of just over 70 L, as shown in fig. 1 and fig. 2. Each column was supported on a stand, which housed a conical section with a single outlet. A perforated plate, placed between the column and the conical section, acted as a support for the substrate.

***Figure** 1 Multi-stage column system*

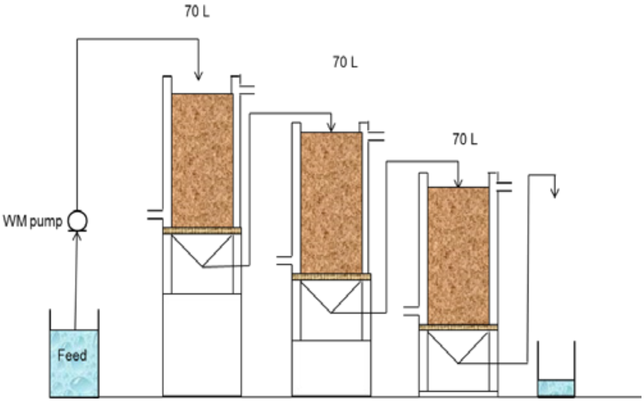

***Figure 2** Schematic diagram of the three-stage column setup*

The water jackets of the columns were connected to a heating and chilling unit, which was fitted with a pump that circulated water through the jackets. Measurement of the temperature in the columns was used to control the flow rate of water through the water jackets, allowing the column temperatures to be maintained at 20 °C, eliminating temperature fluctuations caused by daily and seasonal variations in the ambient condition.

All of the columns were packed with a mixture of the following quantities of organic substrates (measured by volume), which were mixed together and blended before being loaded into the columns:

- 20 % cow manure
- 20 % hay
- 20 % wood shavings and saw dust
- 40 % wood chips

A layer of silica pebbles was spread over the top of the distribution plate, to prevent blockages of the holes in the distribution plate caused by fines migrating downwards.

Inoculation, Start-up and Operation

The cow manure that formed 20 % of the substrate was the main source of sulphate reducing bacteria (SRB) and cellulose degraders. In addition, a 10 L quantity of product liquor from an existing BSR process was added to the substrate mixture during its blending, in order to supplement the inoculum with an active culture and reduce the start-up time.

The blended substrate mixture was firmly hand-packed into the columns. The columns were slowly filled by pumping mine water into the bottom of the column. In this way, air bubbles in the substrate were forced out as the water level slowly rose through the column.

The mine water feed was stored in a 10 L tank, from where it was pumped to the top of the first-stage column. The feed flow rate was adjusted to target a particular HRT. The water percolated in a downward-flowing flooded mode through the substrate bed, and exited through a flexible tube attached to the bottom of the column. The flexible tube was routed up the outside of the column to near the top edge. A T-piece was fitted to the top of the tube to assist with fluid level adjustment inside the column, and to direct the flow to the next column. The product from the third-stage column was collected over a 24-hour period, and the volume was measured and logged daily.

Daily measurements were made of the pH levels, redox potentials (vs Ag|AgCl), electrical conductivity and sulphate concentrations in each column. Routine sulphate concentrations were measured using the barium chloride gravimetric method (Jeffery *et al.* 1989). Once steady-state operation was achieved, liquor samples were collected from each column and submitted for metal analysis by inductively coupled plasma optical emission spectrometry (ICP-OES), sulphate determination using liquid ion chromatography (IC), sodium and potassium analysis by atomic absorption spectroscopy (AAS), while ammonium and phosphate were measured by colorimetric techniques.

Process Chemistry

The simplified process chemistry of the biological sulphate reduction process is as follows:

$$SO_4^{2-} + 2CH_2O\ (aq) + H^+ \rightarrow H_2S + 2HCO_3^- \qquad (1)$$

$$H_2S + Me^{2+} \rightarrow MeS + 2H^+ \qquad (2)$$

Results

The HRT in each column was initially set at 7 days. At the outset, cow manure was the preferred substrate, but it was found to have a clay-like structure, which was not porous enough to allow good contact between the fluid and the substrate. When the cow manure was mixed with lucerne straw, the performance of the columns improved. It was determined that regular addition of the faster-reacting components of the substrate (cow manure and lucerne straw) was required to maintain the performance levels. In the latter stages of the test, "kraal" manure and lucerne pellets were evaluated as an alternative to cow manure. ("Kraal" is the Afrikaans word describing an enclosure for cattle or other livestock. Kraal manure consists of organic material comprised of the residues of plants that are digested by cattle and then composted.) The results reported here are for the last 200 days of the test work programme, where the objective was to reduce the HRT by regular addition of substrate (kraal manure and lucerne). On day 315, 10 L of substrate was removed from the first-stage column and replaced with 5 L of kraal manure and 5 L of lucerne pellets. Thereafter, regular substrate replenishment was undertaken, as summarised in tab. 1, which also shows the impact that this had on the extent of sulphate reduction achieved in the first-stage column.

Table 1 *Schedule for the addition of fast-reacting substrate*

Day	Kraal manure added (L)	Lucerne pellets added (L)	First-stage sulphate reduction (%)
315	5	5	45.6
350, 364, 378	1	0	68.5, 54.2, 55.8
388, 395, 406	1	1	59.1, 49.3, 46.7
417, 431, 438	1	1	72.7, 96.1, 96.5
446, 452, 461	1	1	92.8, 95.9, 92.7
474	1	1	95.1

On day 465, the mine water feed to the plant changed slightly, as the original sample was depleted. The new feed was similar to the first one, with almost exactly the same sulphate concentration.

The routine measurements of the pH levels, redox potentials, conductivities, sulphate concentrations, sulphate removal levels and sulphate reduction rates are shown in fig. 3.

The pH levels ranged between 7.0 and 7.5, and the redox potentials remained below around 320 mV (vs Ag|AgCl), even after the HRT in each stage was reduced from 7 to 4 days.

Each addition of fresh substrate resulted in an immediate increase in the conductivity of the solution, indicating the release of ions from the substrate. By day 406, after several substrate replenishments, the conductivity in Column 1 increased from 5 to about 7 mS/cm,

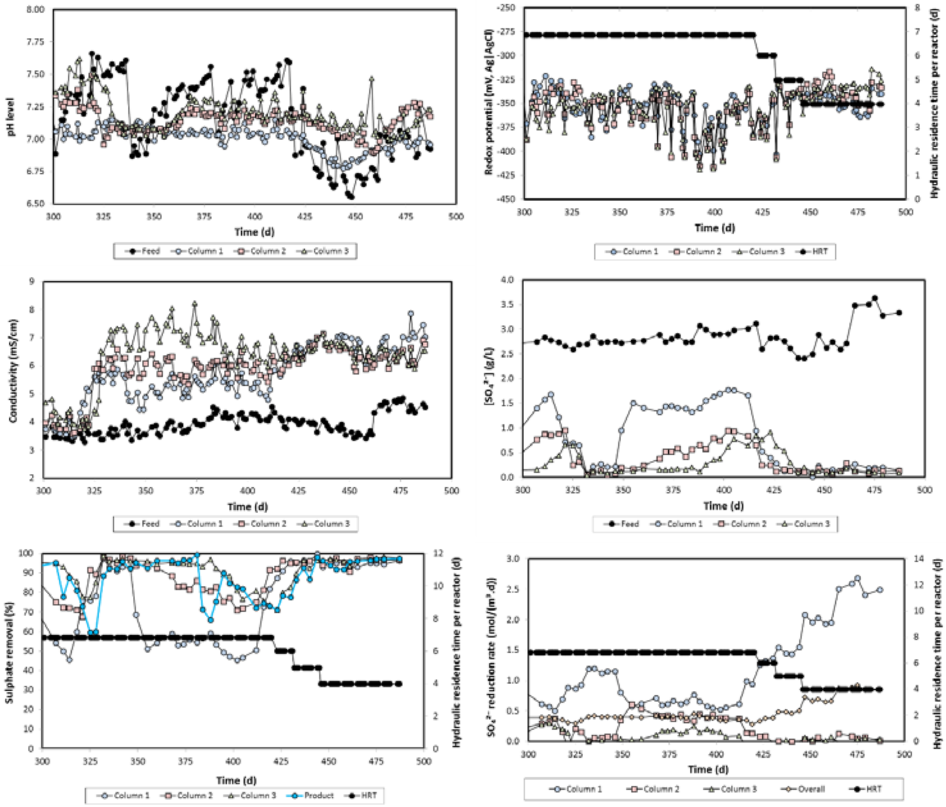

Figure 3 *Performance of the biological sulphate removal reactor system*

and the sulphate concentration decreased to around 500 mg/L. Towards the end of the run, the performance improved further, with the concentration in the final effluent being maintained below 150 mg/L, even after the single-stage HRT was reduced to 4 days.

With routine substrate replenishment, the sulphate removal level in Column 1 increased from around 50 % on day 412 to over 95 % by day 430. This made it possible to reduce the HRT in each column from 7 to 4 days. Even after this was done, the sulphate removal level remained above 95 %. It is anticipated that further reductions in the HRT will be possible, allowing the sulphate removal load to be spread over the three columns. Further optimisation of the quantity and frequency of the addition of fresh substrate will also be investigated. Towards the end of the experiment, the volumetric rate of sulphate reduction in Column 1 increased to over 2.5 mol/(m^3.d) as the HRT was reduced to 4 days. The overall sulphate reduction rate increased to around 0.9 mol/(m^3.d) by day 465, with very little contribution from Columns 2 and 3.

On day 486, water samples were removed from the columns and chemically analysed. The results are summarised in tab. 2.

Table 2 *Measured chemical compositions in the biological sulphate reduction plant on day 486*

Element/ compound	Feed (mg/L)	Column 1 (mg/L)	Column 2 (mg/L)	Column 3 (mg/L)
SO^{2}	3340	140	130	90
S^{2}	9	802	360	200
NH	5	709	858	697
Be	<0.02	<0.02	<0.02	<0.02
HCO	106	7802	7676	7260
Na	258	195	209	241
Mg	537	514	447	399
Al	4.7	3.7	3.0	2.2
Si	5.2	23	27	29
PO^{3}	<0.01	<0.01	0.1	0.1
Cl	<0.01	0.35	0.34	0.34
K	172	456	531	548
Ca	587	475	544	400
Cr	0.07	0.09	0.18	0.33
Mn	36	2.0	3.4	2.5
Fe	0.49	1.16	0.95	1.56
Co	0.06	<0.02	<0.02	<0.02
Ni	0.07	0.09	0.06	0.16
Cu	<0.02	0.03	0.04	0.02
Zn	<0.02	0.02	0.02	0.02
As, Mo, Ag, Cd	<0.02	<0.02	<0.02	<0.02
Pb	<0.02	0.1	<0.02	<0.02
Alkalinity	87	6395	6292	5951
pH level	6.93	6.97	7.20	7.23

The sulphate concentration in the final effluent was 90 mg/L, indicating a sulphate removal level of over 97 %. The residual sulphide, ammonium, bicarbonate, sodium, magnesium, potassium and calcium concentrations were relatively high, and manganese was not completely removed. In a separate experiment (data not shown), it has been shown that sulphide and manganese can be removed using a two-stage process comprising an oxidation pond and a pebble-bed pond. Significant reductions in the ammonium, bicarbonate, phosphate and calcium levels, and minor reductions in the magnesium and potassium levels, can also be achieved.

The fitness for use of the treated effluent produced (after the polishing process to remove residual metals) is currently being evaluated. Use of the water for crop irrigation (for both food and energy crops) is being considered.

Pilot Plant Design and Construction

A pilot plant will be installed at a South African coal mine in Mpumalanga Province, South Africa. Although the treatment process is intended to be "passive", safety is a paramount requirement, requiring some "active" aspects to be incorporated into the design. The pilot plant was designed conservatively, with a HRT per stage of 6 days, at a feed rate of 245 L/d, giving a plant comprising three reactors with an active volume of around 7 m^3 each.

To ensure safe operation of the pilot plant, a gas scrubber was incorporated into the design to capture and eliminate any gaseous hydrogen sulphide (H_2S) emissions from the BSR reactors. To assist in the capture of the H_2S emissions, closed vessels with a vent were specified in the design.

Manufacturing of the BSR plant has been completed (fig. 4), and the plant will be installed at the mine site shortly. An inoculum for the pilot plant has been prepared at Mintek. A total of around 4000 L is available, which will be transported to the site once the plant has been installed. The support materials and substrate have been blended, and will be transported to the mine site in 1 m^3 bulk bags.

Figure 4 *Biological sulphate reduction pilot plant, showing the reactors (left) and the gas scrubber (right)*

Conclusions

The passive BSR process is a low-cost, low-maintenance niche technology, envisaged to find application in the coal- and gold-mining industries. It is aimed at treating relatively low volumes of mine waters emanating from existing processes, and especially after mine closure, to produce effluents with sulphate concentrations that are within the limits specified by regulations for discharge or re-use.

The results described here have demonstrated very high sulphate removal levels. A pilot plant has been designed and will be operated at a local coal mine site to demonstrate the process. Further work will be conducted to optimise the process parameters and to polish the effluent from the biological process, and attention will also be given to the treatment and disposal of the spent substrate materials.

Acknowledgements

This paper is published with the permission of Mintek. The work reported in this publication was conducted within the framework of the ACQUEAU-labelled project called MIWARE (Mine water as a resource). Mintek's contribution to the project is funded jointly by Mintek and the South African Department of Science and Technology (DST), overseen by the Water Research Commission (WRC).

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