Feasibility of the scale-up of a semi-passive biological sulfate reduction process treating high sulfate mine-influenced water

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Abstract

Acid mine drainage (AMD) is widely spread across South Africa's mining landscape including several remote locations. Mintek's cloSURE® technology is a low-cost, low-maintenance, technology designed for treatment of small point sources in these remote locations.

The aim of Mintek's cloSURE® technology is to treat AMD and produce irrigation quality water for reuse in irrigated agriculture. The process employs biological sulfate reduction in the first stage, to remove sulfate, increase pH and remove metals. This is followed by biological oxidation of sulfide for sulfur recovery in the second stage.

This paper investigates the feasibility of scaling up the two-stage integrated process and identifies potential areas of improvement that could be incorporated for commercial scale plants. Laboratory-scale testwork was conducted in 1 m columns, and the pilot-scale testwork involved 5m³ reactors. Both systems were packed with an organic material mix comprising of woodchips, hay and cow manure. A mine water sample with a sulfate concentration of 3900 mg/L and low pH was supplemented a source of liquid organic carbon to maintain performance of the sulfate reducing reactors. The performance and chemistry of both testwork phases was measured by tracking the sulfate reduction rates, pH levels, sulfide concentrations and metals concentration in the treated water. This data was compared to understand the effect of scale-up on performance.

The results showed reduction of sulfate by more than 90% in both testwork phases. The pH of the treated water was above 7.1, and metals were within the required ranges for water fit for reuse in irrigation, based on the South African Water Quality Guidelines for Irrigation.

In an attempt to develop and scale-up a sustainable process for the treatment of high sulfate mine waters in a South African context, this paper discusses several challenges related to operation and scale up such as organic substrate provision at scale; feed interruptions; feed chemistry variations and H_2S safety at scale.

Keywords: Biological sulfate reduction, semi passive treatment, sulfide oxidation

Introduction

South Africa has a severe and persistent challenge from mines post closure and legacy mine sites; that of large volumes of mining-influenced water being discharged to the environment. South Africa's coal deposits and gold reserves are associated with pyrite which, when exposed to oxygen and groundwater during excavation of mines, produces mining influenced water with elevated sulfate concentrations, from 1 000 mg/L to 10 000 mg/L depending on the local geohydrology. Concentrations of metals are low, resulting in limited scope for recovery of value from the water, except for the water itself.

This highly mineralised water severely affects fresh water resources that are essential for irrigation of South Africa's important agricultural areas, and that are relied upon by local communities for drinking, household activities and livestock watering.

While prevention of mining-influenced water is the ideal solution, there are already large volumes of mine water discharging from closed and rehabilitated coal mines (Grobbelaar et al. 2004). There are several

reverse osmosis plants for treatment of water from coal mining areas, owned and operated by the mining houses, however there is a need for low cost, sustainable solutions for point sources of mine water discharge for rehabilitated mines post closure.

One potential solution for treatment of acidic, sulfate-laden mine water is biological sulfate reduction, which employs a complex consortium of microbes, in the presence of a source of organic carbon, to reduce sulfate to sulfide and produce alkalinity (Equation 1). The sulfide in turn reacts with iron and other metals to produce a stable metal sulfide precipitate (Equation 2).

$$2\ CH_2O + SO_4^{2-} \rightarrow 2\ HCO_3^- + H_2S \qquad [1]$$
$$H_2S + Me^{2+} \rightarrow MeS + 2H^+ \qquad [2]$$

Due to the high levels of sulfate in the feed water and the low concentrations of metals, excess sulfide remains in the treated water, and further oxidation of the sulfide is required to prevent sulfate re-formation or escape of hydrogen sulfide gas.

Sulfide is partially oxidised to sulfur under conditions where the stoichiometric ratio of sulfide to oxygen is greater than 2:1 (Buisman et al. 1990; van Hille and Mooruth 2011):

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \qquad [4]$$

Mintek has developed a biological process, cloSURE®, for treatment of acidic mine waters with elevated sulfate concentrations. It is a low-cost, low-maintenance technology designed for treatment of small point sources of discharge. The aim of the technology is to treat acidic mine water and produce irrigation quality water for reuse in irrigated agriculture (du Preez 2022). The process employs biological sulfate reduction in the first stage, to remove sulfate, increase pH and remove metals. This is followed by biological oxidation of sulfide in a floating biofilm for sulfur recovery, in the second stage.

This paper investigates the feasibility of scaling up this process and identifies potential areas of improvement that could be incorporated for commercial scale plants.

Methods

The laboratory-scale setup consisted of a 1 m biological sulfate reduction column with an operating volume of 13 L, continuously operated at 10 d hydraulic retention time and a sulfide oxidation tank with an operating volume of 14 L and a depth of 20 cm (Fig. 1). The cloSURE® pilot plant consistent of a 4500 L sulfate reduction reactor, continuously operated at a retention time of 9 d for a period of 500 d, and integrated with a sulfide oxidation tank after 142 days (Fig. 1), which consisted of five channels in series, resulting in a total operating length of 18 m, a depth of 0.6 m and a volume of 4000 L, and was operated continuously with a target HRT of 6 days. A greenhouse was constructed over the tank to protect the biofilm from wind and rain.

In both studies, the sulfate reducing reactor was packed with polypropylene biofilter media to immobilise the microorganisms, and was inoculated using treated effluent from Mintek's previous pilot plant (Neale 2018), which included the complex consortium of microbes for degradation of the organic substrates and reduction of sulfate. Abattoir effluent was mixed with the mine water feed to provide a source of organic carbon and nutrients.

The feed water for both the laboratory- and pilot-scale testwork was obtained from a local coal mining operation. The feed was acidic ($\approx$ pH3) with elevated sulfate concentrations (between 3000 mg/L and 4500 mg/L), but was neutralised using lime for the laboratory-scale testwork (Tab. 1).

Time series data was collected and analysed during the laboratory and the pilot studies, including sulfate and sulfide concentrations, pH levels, redox potential and metals concentrations. To understand the how the systems behaved when scaling up, four key indicators were considered for comparison at steady state, namely, sulfate reduction rates, whether effluent parameters met South Africa Target Water Quality Guidelines (DWAF 1996), sulfide removal and biosulfur production.
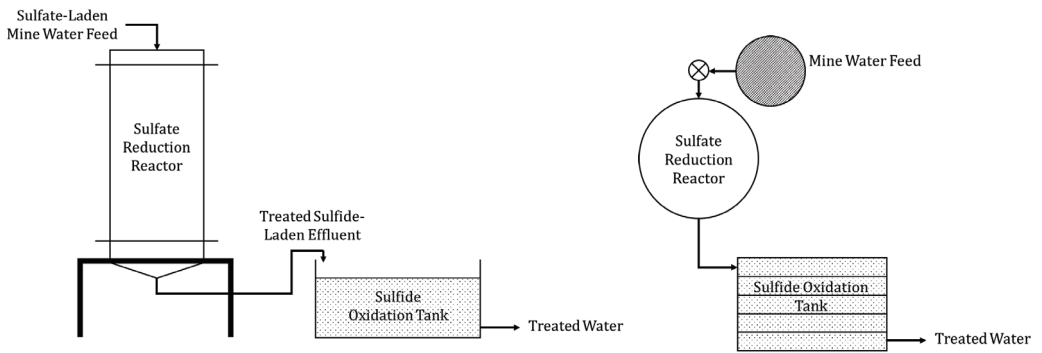
Figure 1 Schematic of the integrated cloSURE® process (left) and pilot plant layout (right)

Results and Discussion

Laboratory- and Pilot-Scale Time Series Data

The laboratory-scale sulfate reducing reactor reached steady state after 14 weeks (98 days) (Fig 2 right), likely due to the temperature being maintained at 30 °C for the duration of the test run. An average sulfate reduction rate of 389.9 g/m³/d was achieved during steady state. Between 55% and 96% sulfide was removed in the sulfide oxidation tank, however towards the end of the test run the sulfate concentrations were elevated suggesting that sulfide oxidised to sulfate instead of sulfur (Fig. 2 left). A thick sulfur biofilm was established in the sulfide oxidation tank, at a rate of 22.42 g/m²/d, which consisted of 53% total sulfur, 4.23% calcium, 2.18% magnesium and 0.22% manganese.

The pilot-scale sulfate reducing reactor achieved steady state after more than 250 days. Between Days 286 and 384, an average sulfate reduction rate of 219 mg/m³/d was achieved, up to an average of 366 mg/m³/d between Days 384 and 476, when feed sulfate concentrations were elevated (5900 mg/L) (Fig. 3 left). The maximum reduction rate was 504 mg/m³/d. Typical values for passive treatment processes range between 28 mg/m³/d and 76 mg/m³/d (Pulles 2009). cloSURE® is not strictly passive as it is intended for treatment of elevated sulfate levels and therefore requires addition of an organic carbon source on a regular basis, which enables the higher sulfate reduction rates.

After a period of 230 days for biofilm establishment in the sulfide oxidation tank, from day 370 of the pilot study, effluent sulfide concentrations were low and the floating biofilm began to thicken, indicating the sulfide was partially oxidised to biosulfur (Fig. 3). Excess sulfate not removed the sulfate reducing reactors, was reduced in the oxidation tank, resulting in additional sulfide production. When accounting for the additional sulfide produced, a maximum of 72% sulfide was removed with an average of 31% during the piloting period. Biofilm production amounted to 3.42 g/m2/d consisting of 60% total sulfur, 21% calcium, 0.70% iron and 0.60% magnesium.

Table 2 Metal concentrations in the feed as sampled at the end of each study. Note that As, Be, Ca, Mo, Pb, and Si were below threshold detection levels and are not included here

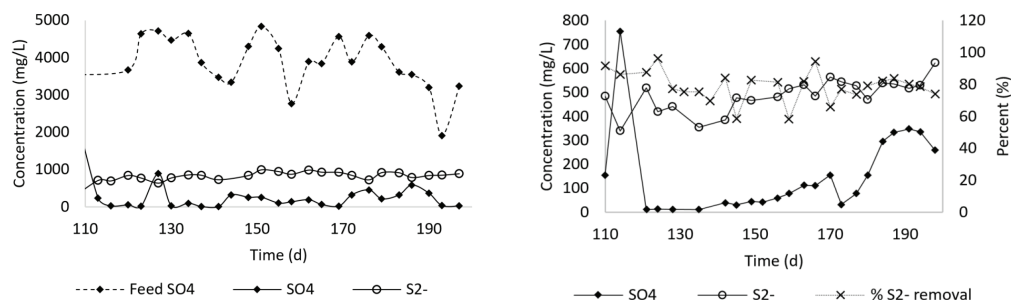|	Cl	F	Na	Ca	Mg	Al	Co	Cu	Fe	Li	Mn	Ni	V	Zn
								mg/L						
Laboratory	13.2	0.23	38	674	325	0.02	0.80	<0.02	0.03	0.25	47	0.54	<0.025	1.08
Pilot	39	0.40	123	458	249	38	0.03	0.01	327	0.35	1.08	0.36	<0.025	1.33

Figure 2 Time series data of the sulfate reduction (left) and sulfide oxidation step (right) in the laboratory-scale integrated process, showing sulfate (SO4) and total sulfide (S2-) concentrations during steady state

Laboratory- and Pilot-Scale Comparative Performance Data

Given the high sulfate reduction rates in both the laboratory- and pilot-scale processes, sulfate concentrations in the effluent were low, with 95% and 84% removal of sulfate (Tab. 3). Alkalinity was produced due to microbial metabolism of the organic carbon source, increasing the pH of the effluent to neutral in both studies. In the laboratory-scale testwork, all metals were below the Target Water Quality Requirements, and in the pilot-scale study, all metals concentrations were within the target requirements (Tab. 4), except for manganese (94% removal). These results suggest the treated water from both studies meet the targets for irrigation quality water. Sulfide concentrations were low in the laboratory-scale treated water (55–66% removal), with

more biosulfur product formed. The pilot-scale sulfide oxide oxidation results show that that tank did perform as efficiently at scale, likely due to the depth of the tank preventing contact of sulfide-laden water with the biofilm or oxidation zone.

Scalability

Both the laboratory- and pilot-scale sulfate reduction processes achieved high rates of sulfate reduction, 390 g/m³/d and 219–366 g/m³/d, respectively, depending on feed sulfate concentrations. The slight improvement in performance of the laboratory-scale reactors is likely due to tighter control over operation of a smaller-scale process, including increased accuracy in feed make-up and measured feed and effluent volumes. Overall, the results for effluent parameters were similar and
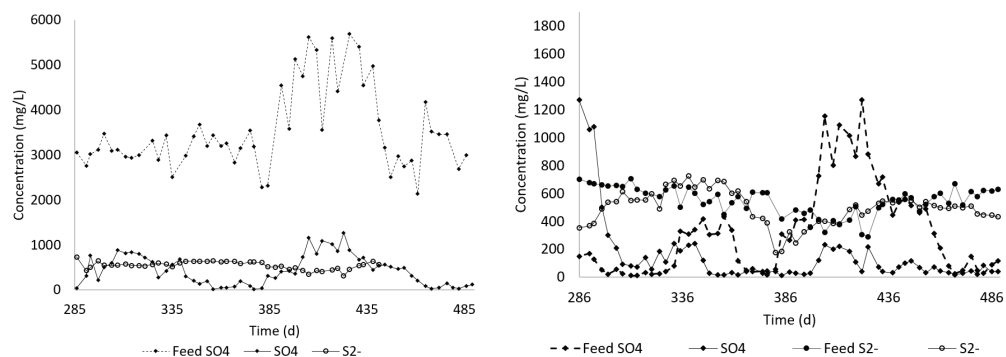

Figure 3 Time series data of the sulfate reduction (left) and sulfide oxidation step (right) in the pilot-scale cloSURE® process, showing sulfate (SO4) and total sulfide (S2-) concentrations during steady state

Table 3 Comparison of averaged effluent data between laboratory- and pilot-scale systems and the Target Water Quality Requirements (TWQR)

	SO_4 mg/L	S^{2-} mg/L	pH	Alkalinity mgCaCO$_3$/L
Laboratory	177	69	7.19	2470
Pilot	38	460	7.59	3050
TWQR	–		6.6–8.5	–

the metals concentrations were below the Target Water Quality Requirements for all parameters and elements, except manganese in the pilot study.

The sulfide oxidation results indicate that the pilot oxidation tank did not perform as efficiently as the laboratory-scale tank, indicating that further design modifications may be required to improve the recovery of biosulfur.

Challenges for scale up

Organic substrate provision at scale

Elevated sulfate concentrations in mine water feed requires the addition of a suitable source of organic carbon, which would increase operating and transport costs of a field-scale plant. A plant treating 1 ML/d mine water, removing 3 g/L sulfate requires 1250 L ethanol, or 15000 L abattoir waste, per day. The concentration of organic carbon in the feedstock will determine the volumes required, which has implications for storage, transport, handling and storage time on site, all of which increase capital and operating costs. Based on the authors' experience in South Africa, this factor is the primary reason sulfate reduction has not been feasible in treating mine water with elevated sulfate concentrations. However, waste materials and blended organic feedstocks provide an opportunity to solve these challenges.

Packed bed materials could include low value materials or waste products, including woodchips or plastic waste to reduce capital costs.

Feed Interruptions

Experience from both laboratory testwork and piloting showed that operating parameters and flows need to be kept constant during start-up. Once steady state is achieved, flow rates can be ramped up slowly to target flows and retention times. Feed interruptions during start-up resulted in poor performance, however once steady state was achieved, stoppages or low flows did not have a detrimental effect on the process.

Feed Chemistry Variations

The mine water feed was neutralised with lime in both the laboratory-and pilot-scale studies, however, towards the end of the piloting work, the feed was no longer neutralised but remained at pH 3.39, with no detrimental effect on the process. During the summer months, the mine water feed had high sulfate concentrations, up to 6000 mg/L coupled with high iron concentrations up to 1600 mg/L, which resulted in elevated sulfate reduction rates and sulfide generation with removal of 99.99% of the iron; this did not have an effect on the effluent quality. These results demonstrate the robustness of the

Table 4 Comparison of metals concentrations between laboratory- and pilot-scale systems and the Target Water Quality Requirements (TWQR)

	Cl	F	Na	Ca	Mg	Al	Co	Cu	Fe	Li	Mn	Ni	V	Zn
								mg/L						
Laboratory	-	0.4	38	210	376	0.35	<0.01	0.11	0.18	0.735	0.017	<0.025	<0.025	0.12
Pilot	-	0.4	70	264	193	0.1	<0.01	<0.01	1.02	0.09	0.07	0.025	<0.025	0.52
TWQR	100	2	-	-	-	5	0.05	0.2	5	2.5	0.02	0.1	1	100

process when the mine water feed chemistry is highly variable.

H$_2$S Gas Safety

The sulfate reducing reactor has the potential to release hydrogen sulfide gas with implications for plant operator safety. The reactors were designed with a down-flow configuration to prevent loss of sulfide for downstream sulfur production and escape of H$_2$S. A well-established biofilm in the sulfide oxidation tank prevents escape of gas and converts available sulfide to a sulfur product. There is still potential risk of localised H$_2$S exposure during biofilm harvesting and a mechanical solution is recommended at minimise risk of exposure to plant operators.

Conclusions

The sulfate reduction step showed similar performance at laboratory- and pilot-scale, with high rates of sulfate reduction and sulfide generation. Metals precipitated as expected and final effluent quality from both studies produced water which met the Target Water Quality Requirements for irrigation. The sulfide oxidation step achieved good performance at laboratory-scale producing increased mass of sulfur product than at pilot-scale, as well as increased removal of sulfide. During scale-up, the design of the oxidation tank should be modified to ensure optimal contact of sulfide-laden water with the biofilm or sulfide oxidation zone.

The results confirm that the biological process is scalable, with the correct oxidation tank design for optimal removal of sulfide and production of biosulfur. Start-up of both the sulfate reducing reactor and oxidation tank requires ongoing monitoring and maintenance, but once the process achieves steady state it is robust, tolerating variable feed flows and interruptions as well as variable feed water chemistry.

Acknowledgements

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