Development of a pilot-scale semi-passive system for the bioremediation of ARD

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Abstract

Acid rock drainage from diffuse sources such as waste rock dumps, tailings impoundments and discard coal dumps represents a significant environmental risk to South Africa, particularly with respect to sulphate salinity. Passive or semi-passive remediation options may be more practical, sustainable and affordable in many cases. Where sulphate salinity is a concern, biological sulphate reduction (BSR) plays a key role. Widespread application of BSR has been constrained by the cost of the electron donor, process kinetics and management of the sulphide product. The system developed addresses the challenge of biomass retention by employing submerged carbon microfibers to provide a large surface area for microbial attachment. Electron donor for the sulphate reduction and sulphide oxidation is provided by the anaerobic degradation of complex organic carbon sources (eg grass, algae, manure) in a separate hydrolysis reactor. Finally, sulphide management is achieved through the partial oxidation of aqueous sulphide to elemental sulphur, which is recovered as a value-adding product. Extensive laboratory-scale tests have demonstrated proof of concept, achieving sulphate reduction efficiencies of over 90% at a feed concentration of 1 g/l. Efficient biomass retention resulted in volumetric sulphate reduction rates over 50% higher than in corresponding stirred tank reactors. In excess of 70% of the sulphur in the feed (as sulphate) was recovered as elemental sulphur in the harvested biofilm. Process optimisation, at laboratory scale, suggested a 2 day hydraulic residence time (HRT), with biofilm harvesting every 4-5 HRTs. A pilot scale system consisting of three 2000 l reactors has been installed at a colliery in South Africa, to initially treat 1000 l/day. Sulphate reducing inoculum was prepared in a series of 210 l and 1000 l containers. A number of technical and logistical challenges have been overcome, leading to successful re-inoculation and demonstration of proof of concept at pilot scale.

Key words: Semi-passive process, sulphate reduction, sulphide oxidation, minewater remediation

Introduction

The contamination of surface and groundwater by acid mine drainage (AMD) and acid rock drainage (ARD) and the consequences for the environment, agriculture and human health are serious concerns in the regions of South Africa impacted by mining activities. The longer-term impact of mining activities, particularly coal mining, is predicted to be worse in South Africa than other countries as a result of a unique combination of climate, geography, scale of deposits and population distribution (McCarthy, 2011).

Acid drainage is generated via the oxidation of sulphide minerals, typically pyrite, when exposed to oxygen and water (Johnson and Hallberg, 2005; McCarthy, 2011). In South Africa, mine water can be divided into two broad categories. The first, AMD, originates from the rebound of groundwater through abandoned mine workings, once dewatering has ceased and is characterised by large volumes of heavily impacted water. The volume and composition of the AMD precludes the application of biological treatment options in most cases. The second type, referred to as acid rock drainage (ARD) in this paper, originates from diffuse sources, such as waste rock dumps, tailings impoundments, coal discard heaps and unworked pits. These sites are more numerous, are likely to affect a greater area

and can persist for decades. Acid rock drainage, from diffuse sources as well as end-of-pipe sources, is more amenable to biological treatment.

A variety of technologies have been developed for the treatment of AMD and ARD. The established methods are based on oxidation, neutralisation, precipitation and sedimentation. The most appropriate treatment is dependent upon the volume of the effluent, concentration type of contaminants and the pH of the water (Gazea *et al*., 1996). Acid drainage treatment technologies can be divided into two broad categories, active and passive treatment systems.

Active treatment typically involves the installation of agitated reactors or similar units, which require constant energy input. Furthermore, the addition of alkaline chemicals and reagents to treat the acidic effluent can become costly, given that the drainage may persist for several decades, or longer, at decommissioned mine sites (Gazea *et al*., 1996). The energy intensity and extensive use of lime mean the long-term sustainability of many active treatment technologies is questionable, both from an economic and environmental perspective.

Passive systems depend on processes that are kinetically slower than those involved in active systems and thus require longer hydraulic retention times (HRTs) and larger areas to achieve similar results. Passive treatment options include anoxic limestone drains, permeable reactive barriers, natural and constructed wetlands and engineered biological treatment systems.

Biological treatment has the potential to be more cost effective and sustainable than the physical and chemical processes mentioned above. The biological treatment of ARD is centred on the activity of sulphate-reducing bacteria (SRB), which are able to reduce sulphate to sulphide, coupled to the oxidation of an electron donor, typically an organic carbon molecule. The sulphate is reduced to sulphide, coupled to the simultaneous generation of alkalinity, predominantly as bicarbonate (HCO_3^-). From an ARD treatment perspective the alkalinity acts to neutralise the acidity while the sulphide is available for the precipitation of metals as metal sulphides (Johnson and Hallberg, 2005).

A number of active commercial processes, based on biological sulphate reduction, have been developed (Janssen *et al*, 1995; Rose, 2013), but their widespread application has been constrained by three factors. These are the cost of the electron donor, the relatively slow growth of sulphate reducers and the associated kinetic constraints and the management of the sulphide product. The disadvantages of conventional active and passive biological systems has led to the development of semi-passive or managed passive systems and South African researchers have played a leading role in this. The Integrated Managed Passive (IMPI) process was developed by Pulles Howard and de Lange with the aim of achieving high rates of sulphate reduction over a sustained period, utilising lignocellulosic material as the source of electron donor. The hydrolysis of lignocellulose was identified as the rate limiting step and long-term reactor studies allowed the characterisation of five distinct phases of sulphate reduction in passive systems (Molwantwa *et al*, 2010).

A demonstration scale IMPI system, designed to treat 200 m^3 of minewater, was constructed at the Middelburg mine in Mpumalanga. The system contained a novel sulphide oxidation reactor, the linear flow channel reactor (LFCR) which made use of a floating sulphur biofilm to achieve partial oxidation of sulphide. The system was affected by a number of construction and operational issues, as well as challenges with the LFCR and performance did not meet expectations. A detailed study into the LFCR was conducted at the University of Cape Town, leading to further optimisation in design and operating parameters (van Hille and Mooruth, 2013).

A parallel research project, investigating options for biomass retention to enhance sulphate reduction performance and low hydraulic residence times (van Hille *et al*, 2015) demonstrated that carbon microfibres provided an ideal support matrix for the attachment of SRB. The reactor was sealed with an air-tight lid, but sufficient oxygen entered the reactor to support the formation of a floating sulphur biofilm at the air-liquid interface. This suggested that the sulphate reduction and sulphide oxidation reactions could occur simultaneously within a single reactor. The detailed hydrodynamic study performed on the LFCR (Mooruth, 2013) showed no turbulent mixing within the reactor and confirmed the existence of a microaerobic zone within the floating biofilm, while the majority of the bulk liquid remained anaerobic.

Previous research at UCT investigating the anaerobic digestion of microalgal species showed that the digestate produced during fed-batch operation retained significant (2-4 g/l) soluble COD and that this was primarily composed of acetate and propionate, potential electron donors for SRB. The digestate was used as the base for an SRB feed medium and the results showed similar or improved sulphate reduction performance in CSTRs when compared to parallel reactors fed on lactate-based Postgate medium (van Hille *et al,* 2015).

The data from the various research programmes led to the conceptual design of an integrated semi-passive process for ARD treatment consisting of an LFCR, containing carbon microfibers, which could support simultaneous sulphate reduction and partial sulphide oxidation, with the recovery of a value adding elemental sulphur product. Effluent from a biogas digester or similar anaerobic reactor could be used as the electron donor and carbon source. This paper provides a summary of the proof of concept of the combined channel reactor, the study to determine optimal HRT and describes the process of scale-up to a pilot scale system at the New Vaal Colliery.

Methods

Microbial cultures

The sulphate reducing bacteria (SRB) mixed microbial community was obtained from the Department of Microbiology, Biochemistry and Biotechnology at Rhodes University, originally from the anaerobic compartment of a facultative pond at the Grahamstown sewage treatment works, and has been maintained on modified Postagate B medium at UCT since 1999 (van Hille and Mooruth, 2013). The sulphide oxidising bacteria (SOB) culture was obtained from previous studies (van Hille and Mooruth, 2013) on sulphide oxidation conducted within the Centre.

Linear flow channel reactors (LFCRs)

The channel reactor provided a flow-through system with no turbulent mixing. It was constructed from Perspex (11 mm thickness) and had internal dimensions of 250 mm (l) x 10 mm (w) x 15 mm (h). The front wall of the reactor was fitted with nine sample ports, allowing sampling in a horizontal and vertical direction. The reactor was fitted with three ports in the left wall and three at equivalent heights in the right wall. Effluent flowed from the top outlet port, maintaining a liquid height in the reactor of 85 mm, giving a working volume of 2.125 l. A plastic strip (10 mm wide) holding carbon microfibers (AMT Composites, Cape Town) was suspended between the middle ports. The strip had bundles of microfibers (90 mm long) protruding from each side. A heat exchanger (4 mm ID) was fitted between the lower ports and facilitated temperature control by pumping warm or cold water through it. Feed was pumped in continuously from the uppermost port and effluent flowed from the equivalent port on the far side.

The pilot scale channel reactors were constructed of Plexiglass (15 mm thickness) with dimensions of 3 050 mm (l) x 1 350 mm (w) x 750 mm (h). At a working liquid height of 500 mm the volume was just over 2 000 l. The front wall of the reactor was fitted with 15 sampling points. The left and right side walls contained a single port (30 mm diameter) for fresh feed and effluent outflow. The reactor contained three parallel beams, manufactured from two pieces of aluminium angle between which the carbon fibres were held. The fibres extended approximately 200 mm from each side of the beam. The sulphur harvesting screen was constructed of aluminium square tubing which created a frame that held the same plastic mesh as shown in the laboratory scale reactor. The constructed pilot scale LFCR, fitted with the carbon fibre beams and harvesting screen and loaded into the support stand at the New Vaal site is shown in Figure 1.

Analytical methods

All pH testing was done on a Cyberscan 2500 micro pH meter. The meter was calibrated daily using standard (pH of 4.0 and 7.0) buffer solutions. Aqueous sulphide was quantified using the colorimetric DMPD method (APHA, 2005).

Figure 1 *Image illustrating the pilot scale LFCR reactor on site, prior to inoculation*

For the laboratory-scale experiments anions (sulphate, chloride, phosphate and nitrate) were measured using a Dionex ICS-1600 system. The system was equipped with an AS22 anion column, a 10 µl injection loop and a conductivity detector with suppression. Mobile phase (22 mM NaOH) was pumped through at a rate of 1.5 ml/min. Anion standards (20, 40, 60, 80 and 100 mg/l) were prepared using sodium salts. Dissolved sulphate concentrations at the pilot site were measured using the barium sulphate method (APHA, 2005).

A full volatile fatty acids (VFAs) analysis was conducted to quantify the concentration of lactic, acetic, propionic, iso-butyric, butyric, iso-valeric and valeric acids. The concentration of each VFA was determined using HPLC on a Waters Breeze 2 HPLC system equipped with a Bio-Rad Organics Acids ROA column and a UV (210 nm wavelength) detector (van Hille and Mooruth, 2013).

Proof of concept study

To test proof of concept the small LFCR was inoculated with a mixture of the SRB and SOB cultures and fed with modified Postgate B medium (1 000 mg/l SO_4^{2-}) at a rate equivalent to a 4 day HRT. The temperature was controlled at 30˚C. Samples (2 ml) were removed daily from the middle (FM) and lower (FB) sample ports in the first and third (BM and BB) rows, as well as from the effluent port. The pH and sulphide concentration were measured immediately, after which the remainder of the sample was prepared for chromatographic analysis (VFAs and anions). Biofilm formation was observed visually and once a thick, stable biofilm had been formed it was periodically harvested by physically breaking it apart so that the fragments sank onto the submerged screen. The sulphur product was recovered by removing the screen.

Hydraulic residence time study

The effect of HRT on the performance of the system was investigated by changing the feed rate to the reactor. Prior to the start of the study, stable performance was established at a 4 day HRT. The biofilm was harvested on day 0, when monitoring of the experiment began. The reactor was fed with modified Postgate B medium at a flow rate of 0.53 l/d and sampled daily, as described above. Effluent from the reactor was collected in a sealed bottle over varying time intervals and the volume quantified to confirm the HRT. A portion of the collected effluent was treated for chromatographic analysis, while the rest was used to measure pH and redox potential.

After approximately 3 HRTs the biofilm was collapsed, by physically breaking it up and allowing the fragments to sink and settle on the screen. The biofilm reformed within 24 hours and after another 3 HRTs the biofilm was collapsed again and the sulphur harvested by removing the screen and transferring the solids to a glass petri dish for drying and further analysis. Following harvesting, the feed rate was increased to achieve the next HRT and the process was repeated, terminating at an HRT

of 0.5 d. The one exception to the procedure described above occurred after the first biofilm collapse in the 4 d HRT study, where the biofilm was allowed to persist for just over 7 HRTs to determine whether the biofilm would collapse, unassisted, under the mass of accumulated sulphur.

Inoculum scale-up and pilot plant inoculation

The microbial inoculum, containing the sulphate reducing and sulphide oxidising consortia, was scaled-up in order to inoculate the 2 000 l pilot scale reactors. Inoculum build-up was started at laboratory scale in a series of 10 and 15 l glass containers, maintained in batch mode on an acetate based medium with an initial sulphate concentration of 3 500 mg/l. Stock cultures from these reactors were blended into four 25 l plastic drum, transported to the mine site and used to inoculate four 210 l drums containing raw mine water. Each 210 l drum was supplemented with 500 g of sodium acetate and 100 g of yeast extract. More recently, a 1000 l tank was inoculated so that over 1 800 l of active inoculum can be maintained.

The first of the 2 000 l channel reactors was filled with raw minewater from the active pit, diluted to a sulphate concentration of 2 000 mg/l and inoculated with 380 l of SRB inoculum on 3 November 2015. During December 2015 ingress of clean water into the pit reduced the suphate concentration to below 250 mg/l, negatively affecting the reactor and inoculum cultures. Subsequently, sodium sulphate from the mine's freeze crystallisation plant was used to supplement the raw feed. The channel reactor was reinoculated at the beginning of May 2016, with 1 200 l of active SRB inoculum.

Results and discussion

The results from the proof of concept and optimisation of HRT studies have been described in greater detail elsewhere (van Hille *et al*., under review) and will be summarised here to provide context for the scale-up to pilot scale.

The reactor was inoculated with an active SRB culture and the initial sulphide concentration was approximately 250 mg/l. This decreased rapidly during the first hours following inoculation as a result of unimpeded oxygen mass transfer across the liquid surface, resulting in the sulphide oxidation at the surface. However, within 24 hours a thin, but complete biofilm was observed over the entire surface. The biofilm provides a barrier that slows down oxygen mass transfer and creates the necessary redox microenvironment to support partial oxidation of sulphide to elemental sulphur.

Once the biofilm had formed the aqueous sulphide concentration in the bulk liquid began to increase steadily, from around 80 mg/l to over 230 mg/l by day 10. This indicated effective sulphate reduction, which was confirmed by the residual sulphate data that showed between 85% and 95% sulphate reduction efficiency. No significant sulphide was measured in the effluent from the reactor, suggesting that sulphide oxidation within the biofilm was complete. The rate of sulphide oxidation was significantly higher than that achieved in an actively aerated abiotic system (van Hille and Mooruth, 2013), confirming the activity of the sulphide oxidising microbes.

Harvesting the biofilm resulted in a rapid and significant decrease in the sulphide concentration in the bulk liquid, again a consequence of removing the barrier to oxygen mass transfer and the sulphide concentration only increased again once the biofilm had reformed. Sulphate reduction rates were not affected at all, indicating that all oxygen entering the reactor was consumed at the surface and the bulk of the reactor liquid remained anaerobic (confirmed by redox potential data).

After approximately seven days the biofilm was thick and had a characteristic white to yellow colour, indicative of elemental sulphur (Figure 2a). Physical disruption of the biofilm caused the fragments to sink and these were collected on the submerged harvesting screen (Figure 2b). The final product was a mixture of elemental sulphur and organic material (Figure 2c).

The reactor was operated for just under 100 days, through a series of biofilm development and harvest cycles and demonstrated consistently effective sulphate reduction (>80%) and removal of the sulphide product. The pH remained stable (pH 7.5-7.8) and loss of sulphide as H_2S gas was insignificant. The experiment demonstrated that effective sulphate reduction and partial sulphide oxidation was possible within a single reactor unit and that the sulphur product could be easily harvested.

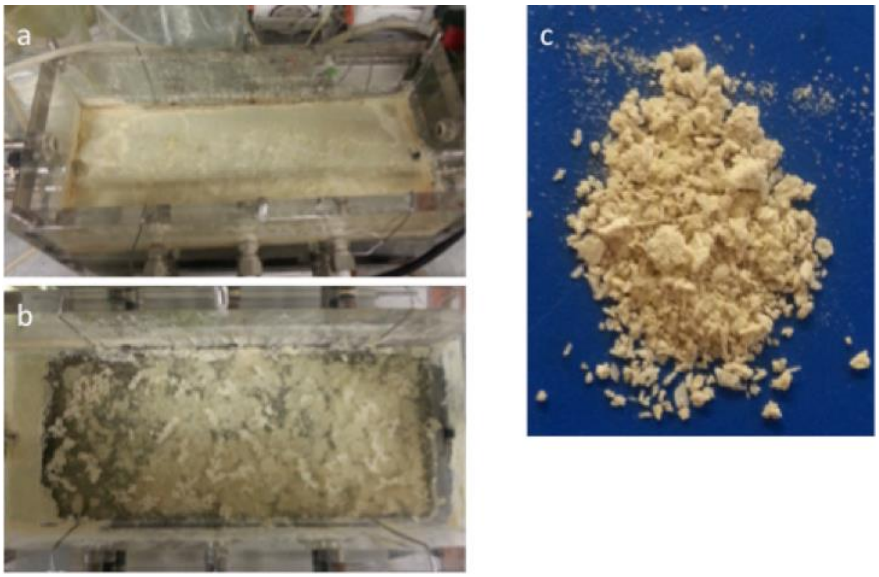

Figure 2 *Photographs showing (a) complete biofilm prior to collapse, (b) the biofilm following collapse onto the submerged screen and (c) the dried sulphur product*

The next phase of the research was aimed at determining the optimal hydraulic retention time. The sulphate reduction and sulphide oxidation reactions occur in spatially distinct regions of the reactor. The sulphate reduction occurs in the bulk volume, while the sulphide oxidation is essentially confined to the air-liquid interface, so is surface area rather than volume dependent. For the system to be effective, the rate of sulphate reduction cannot significantly exceed the rate of sulphide oxidation.

The aqueous sulphide data (Figure 3) showed a similar trend to that observed during the proof of concept study, with a steady increase in sulphide concentration followed by a raid decrease immediately after collapse or harvesting of the biofilm.

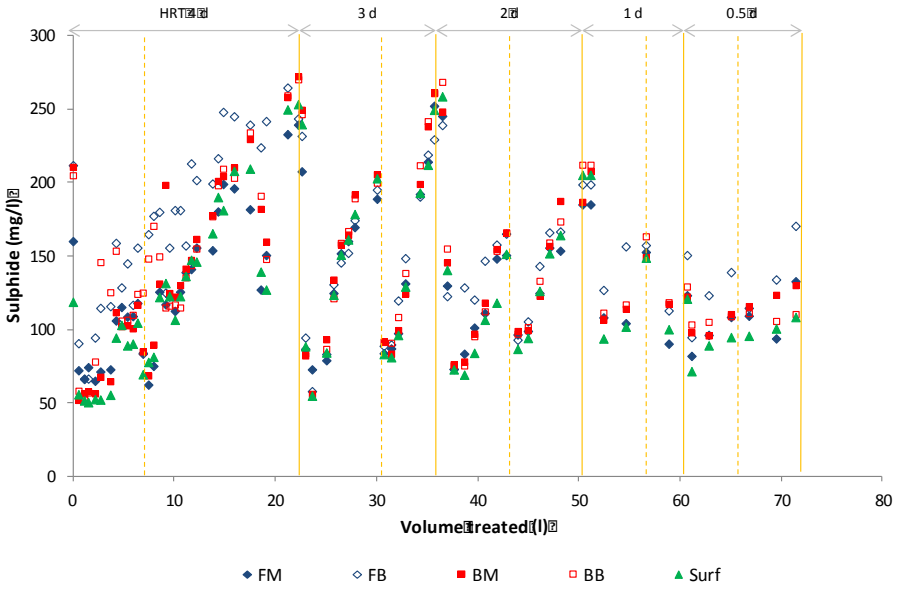

Figure 3 *Aqueous sulphide concentration at different points in the reactor as a function of HRT. Dashed vertical lines indicate biofilm collapse, while complete vertical lines indicate biofilm harvesting*

The data are presented as a function of volume treated, rather than time, to prevent compression of the data points at the low HRTs. The maximum sulphide concentration attained decreased with decreasing HRT, suggesting that sulphate reduction efficiency may decrease at low HRT. Concentrations in excess of 200 mg/l were achieved at HRTs between 4 and 2 days.

The sulphate reduction data (Figure 4) were consistent with the sulphide data. Initially, while the SRB were colonising the carbon fibres, the sulphate reduction efficiency was around 50%, but this increased significantly after about 30 days. Almost complete sulphate reduction (>95%) was achieved at a 3 and 2 day HRT. While the residual sulphate concentration did increase at the lower HRTs, it remained above 70% at an HRT of 12 hours. This equates to a volumetric sulphate reduction rate of 62.5 mg/l.h, which is significantly higher than the maximum observed in a conventional CSTR (39 mg/l.h) and similar to that achieved in a hybrid system using membrane filtration to achieve biomass retention.

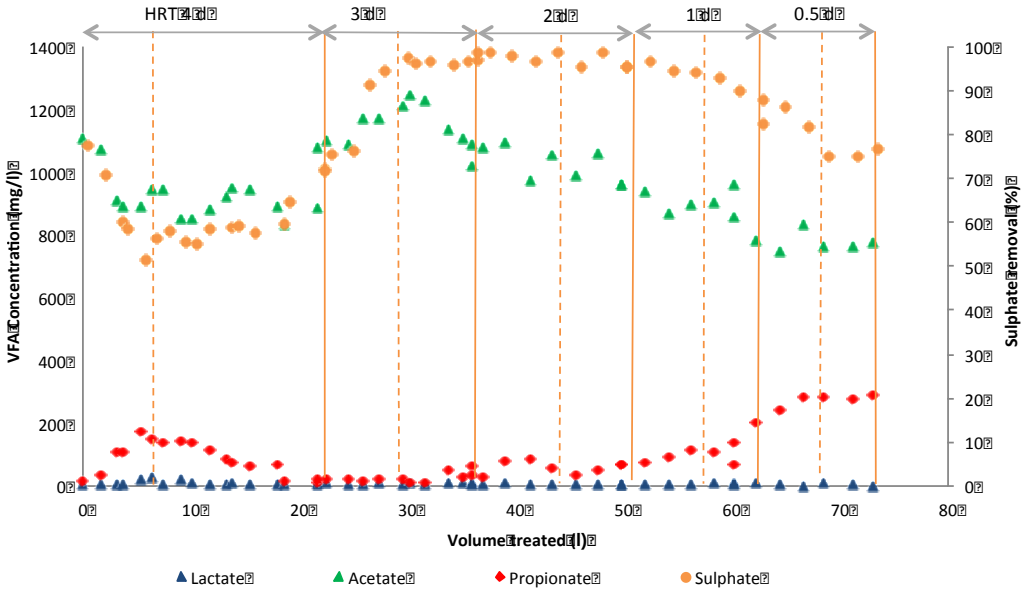

Figure 4 *Mean sulphate reduction efficiency and residual VFA concentrations measured during the HRT optimisation study*

At the 1 day HRT sulphide was detected in the reactor effluent and this concentration increased at the 12 hour HRT, indicating that sulphide oxidation became rate limiting. In addition, the volatile fatty acid data suggested a shift in microbial metabolism at HRTs below 1 day. While lactate utilisation remained complete, significant concentrations of propionate were detected in the effluent. Propionate is indicative of lactate fermentation, rather than oxidation, confirming a shift in microbial community structure. This phenomenon was observed previously in CSTRs (Oyekola *et al*., 2012) and was attributed to a combination of the decrease in sulphide concentration, to levels which no longer inhibit lactate fermenters, and increase in available lactate as sulphate reduction efficiency decreased.

The performance data suggest that a 2 day HRT is optimum for achieving a high volumetric sulphate reduction and sulphide oxidation rate. Gravimetric analysis of the harvested biofilm, used to complete the sulphur mass balance, confirmed the highest sulphur recovery efficiency was achieved at a 2 day HRT.

Inoculum scale-up and pilot plant inoculation

The three 2 000 l channel reactors have been set up on site at the New Vaal Colliery outside Vereeniging. Each reactor has been placed on a purpose built steel stand, which provides additional structural support to prevent bulging of the walls of the Perspex reactors. The height of the stands has been staggered to facilitate gravity flow between the reactors when connected in series.

The first reactor was inoculated with around 380 l of SRB inoculum on the 2nd of November 2015. The original intention was to use sufficient inoculum to achieve an initial sulphide concentration of around 150 mg/l, to provide enough sulphide to form a complete biofilm across the surface of the reactor. However, due to a limited volume of inoculum being available the initial sulphide concentration was only 67 mg/l. After 24 hours a thin sulphur film had formed on the surface on the reactor, with the aqueous sulphide concentration being reduced to below 10 mg/l at all points sampled.

These data confirmed the presence of an active sulphide oxidising community. The reactor was sampled again on the 10th of November and the aqueous sulphide concentrations remained low. The sulphate concentration had decreased from approximately 2 000 mg/l to just over 1 700 mg/l. While this showed some sulphate reduction activity, the rate (1.56 mg/l/h) was significantly lower than equivalent rates achieved in the laboratory reactors.

Following the challenges resulting from the significant improvement in pit water quality additional SRB inoculum was grown up. This allowed the channel to be reinoculated with a greater volume of active culture and resulted in a higher initial sulphide concentration (180 mg/l). Sampling after 48 hours revealed a complete biofilm over the entire reactor surface, the expected stratification in residual sulphide (70-80 mg/l near the surface and 160-180 mg/l near the bottom) and an average residual sulphate concentration of 1 400 mg/l. This represented a sulphate reduction rate of 12.5 mg/l/h.

Conclusions

The research conducted to date has demonstrated the feasibility of a novel reactor configuration that simultaneously facilitates high rates of sulphate reduction and sulphide oxidation in a low cost unit, suitable for passive or semi-passive operation. The efficient retention of the SRB on the carbon microfibres supports the high sulphate reduction rates, while the sulphur product can be easily recovered by collapsing the biofilm onto a removable screen.

The successful demonstration of the reactor at laboratory scale has prompted the evaluation of the technology at pilot scale, with three 2 000 l units installed at the New Vaal Colliery. The first reactor was inoculated in November 2015. A number of challenges, particularly relating to water quality, have been experienced on site, but these have been overcome and the system was re-inoculated at the beginning of May 2016, with very encouraging results.

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