EXECUTIVE SUMMARY

Water is increasingly being recognised as an important strategic resource and the sustainability of water resources is becoming the focus of more attention. South Africa has been classified as a water-stressed country. A 1999 report by the Department of Water Affairs and Forestry (DWAF) predicted that the demand for potable water would exceed the supply by 2020. The provision of services to previously disadvantaged communities and the potential for large scale contamination of water resources mean that this may occur sooner than expected. The threat of acid rock drainage (ARD) to South Africa's water resources, particularly in the gold and coal mining regions was identified over 20 years ago, but the response to the threat has in general been inadequate. Acid rock drainage originates from the oxidation of sulphide minerals that are exposed to oxygen and water. This typically occurs as a consequence of mining or mining-related activities. The process may occur through chemical weathering, but is substantially accelerated by the action of autotrophic iron and sulphur oxidising microbes. Acid rock drainage is a long term issue, with discharges from contaminated sites predicted to persist for decades to centuries. The management of ARD discharges needs to be considered accordingly. A number of treatment technologies have been developed for the remediation of ARD. The most widely used methods are active, chemical processes that involve oxidation of metal ions to their least soluble state, neutralisation of the acidity, precipitation of metal oxides or hydroxides and solid liquid separation by sedimentation. The end product from such systems is a metal sludge and a water stream that is near neutral pH, with very low concentrations of most soluble metals. However, the sulphate load in the partially treated water is still unacceptably high, typically in the region of 2 000 to 3 000 mg/L. The sulphate concentration is governed by the solubility of gypsum ($CaSO_4$), which forms as a consequence of pH neutralisation with lime or limestone. A number of physical and chemical technologies, such as reverse osmosis and ion exchange, are available to reduce the sulphate load and have been successfully implemented in places. These technologies are costly, particularly in terms of operating costs and are not economically viable as long terms options, unless substantial value recovery from by-products can be integrated into the system. Biological systems offer a potentially effective alternative to active physical and chemical processes, with lower operating costs and enhanced sustainability. These systems are based on the action of sulphate reducing bacteria (SRB), which reduce sulphate to bisulphide (HS^-) with the generation of bicarbonate alkalinity as a by-product. The primary operating cost associated with these systems is the provision of the electron donor/carbon source. Most commercial systems use ethanol, methanol or volatile fatty acids (VFAs). Recent research has focussed on the utilisation of complex or waste carbon sources, such as sewage sludge and lignocellulosic material. These need to be converted by associated microorganisms to produce the VFAs required by the SRB, which reduces process kinetics. They are more amenable to passive systems, where the retention times within the system are substantially higher.

The integrated managed passive (IMPI) process was developed by Pulles Howard and De Lange in association with Rhodes University. It is a semi-passive process, requiring minimal maintenance. The process incorporates a series of degrading packed bed reactors (DPBRs) to reduce the sulphate and sulphide oxidation reactors to convert the sulphide to elemental sulphur. The DPBRs are packed with discrete layers of manure, straw and wood chips that degrade over time to sustain the sulphate reduction. The sulphide oxidation is facilitated by a floating biofilm that incorporates sulphide oxidising microorganisms. The biofilm acts as a barrier to oxygen mass transfer and creates a redox and pH environment conducive to the partial oxidation of sulphide to elemental sulphur, the desired product. This technology has been implemented at a demonstration scale at BHP Billiton's Middelburg coal mine. The operation of the demonstration plant has been compromised by a number of design and technical issues. The work described in this report was commissioned to provide fundamental information that could be used to enhance process efficiency.

Two units of the IMPI process were simulated at the Department of Chemical Engineering at the University of Cape Town. Two DPBR columns were transported from the Golder Associates Research Laboratories (GARL) in Midrand and set up as saturated upflow systems. Three linear flow channel reactors (LFCRs) were designed and purpose built using similar dimensions to the pilot reactors at GARL. The LFCRs were designed to support a significantly enhanced sampling regime, with 15 sample ports, spread across three levels, in the front wall. The reactors could be sealed and the headspace gas flushed at a controlled rate, allowing the quantification of sulphide lost to the air. Several analytical techniques were developed and optimised to facilitate the measurement of a range of sulphur species, including polysulphides, and allow a complete sulphur mass balance to be closed. Two abiotic control experiments were run, where the sulphide containing solution was pumped into the LFCRs in the absence of microorganisms. In the first case the pH was not controlled and ranged between pH 11.5 and pH 11.9. The solution remained clear and no sulphur was observed to form.

The overall sulphide conversion was 24.7%, with the majority forming thiosulphate and polysulphides. Less than 5% of the converted sulphide reported as sulphate. The second abiotic control was run with the pH of the sulphide feed controlled at pH 7. During the operation of the reactor the pH fluctuated between pH 7.1 and pH 7.8 as a result of chemical reactions. The solution had a distinctive yellow-green colour and colloidal sulphur particles were visible for a short period. A total of 33.8% of the sulphide was converted, with no sulphate detected.

A series of experimental runs was performed in which feed from the DPBR columns was used. This effluent contained organisms capable of oxidising sulphide and forming the floating biofilm. The results from these studies illustrated the relationship between organic carbon flux, biofilm formation and efficient partial sulphide oxidation to elemental sulphur. During the first experimental run a discrete biofilm did not form, despite the presence of microorganisms in the liquid phase. The reactor achieved a sulphide conversion of approximately 70%, but the vast majority was fully oxidised back to sulphate. Colloidal sulphur particles were observed below the air-liquid interface. Less than 5% of the converted sulphide exited the reactor as colloidal sulphur, implying that it was an intermediate and the majority was further oxidised to sulphate. High performance liquid chromatography (HPLC) analysis of the DPBR effluent showed that almost no organic carbon (<5 mg/L acetate and no sugars) was leaving the columns. Extracellular polymeric substances (EPS) form an important structural component of biofilms, but are not excreted by cells under carbon limiting conditions. This finding explains the lack of biofilm formation and highlights the need for sufficient organic carbon flux through the system. The high sulphate concentration in the DPBR effluent also suggested that the columns were not reducing sulphate particularly efficiently. The second reactor run resulted in the formation of a biofilm, but this did not extent across the entire surface of the reactor. The sulphide oxidation efficiency increased to over 90%, with the majority being converted to sulphur. Less than 10% of the consumed sulphide was fully oxidised to sulphate. However, a significant portion (30%) of the sulphur remained as colloidal particles suspended in the liquid and was lost in the effluent. While a discrete biofilm was observed it did not progress through the stages observed in previous studies and was uniformly “brittle” and “flaky”. Scanning electron microscopy, with electron dispersive x-ray analysis (SEM-EDX), showed the presence of discrete sulphur globules, embedded in a matrix consisting of some organic matter, but substantial chemical precipitates. These data again alluded to a limitation in organic carbon, which was confirmed by HPLC analysis of the DPBR overflow.

In order to address the issue of organic carbon subsequent experimental runs were performed with organic supplementation, in the form of 20 g of acetate added to the LFCR on start-up. In this case a complete biofilm was formed and stable operation was achieved after three days. The reactor performed well for the duration of the experiment, with a sulphide conversion efficiency of 82%. Of the converted sulphide 93% was partially oxidised to elemental sulphur, with 98.7% of the sulphur reporting to the biofilm. Although the biofilm did not pass through a distinct “sticky” phase and remained relatively brittle, the structural integrity was significantly improved.

One of the primary aims of this study was the determination of parameters describing the sulphide oxidation kinetics. A detailed hydrodynamic study, performed as part of the WRC solicited project (K5/1834) showed significant inhomogeneity within the reactor, meaning that plug flow could not be assumed, as had been the case for previous work. The complexity of the fluid flow meant that simple kinetic models could not be used.

As a first approximation, in order to determine the rate order of the reaction, each of the 15 sampling ports was modelled as a batch reactor. This allowed the determination of rate constants for sulphide disappearance in the bulk fluid, from which the rates could be estimated. For the abiotic controls these were estimated at 0.005 mmoles/day and 0.31 mmoles/day for the uncontrolled and pH controlled systems respectively. For the biological system where a complete biofilm was formed this increased to 1.61 mmoles/day. The LFCR data highlighted the importance of organic carbon flux through the integrated system. Analysis of the effluent from the DPBR reactors showed that very little organic carbon present. This was despite the supplementation of the DPBR feed with 1.5 g/L molasses. The molasses feed concentration was increased to 2.5 g/L in an attempt to increase the organic carbon supply to the LFCRs. This had a positive effect for the first week, with the sulphate reduction efficiency of the DPBRs increasing. However, after a week the pH in the DPBRs dropped significantly and sulphate reduction activity was dramatically reduced. The feed was stopped and the columns re-inoculated with an active SRB culture, after which the molasses supplementation was reduced back to 1.5 g/L. A series of batch tests (1 L) was performed to determine the sulphate reduction efficiency when molasses was the sole carbon source. The reactors were loaded with 2 g/L sulphate and 1.5 g/L molasses and inoculated with increasing volumes (20, 50 and 100 mL) of DPBR effluent. A positive control was run under similar conditions, but inoculated with 10 mL of active SRB sludge. The three reactors inoculated with the DPBR effluent rapidly (24 hours) converted the

molasses to VFAs, resulting in a pH decrease to below pH 5. This inhibited sulphate reduction and no sulphide was produced for the duration of the experiment, despite sulphide supplementation (to 50 mg/L) after 24 hours to increase pH and reduce the redox potential. In contrast, the reactor inoculated with SRB sludge maintained the pH around pH 7 and produced sulphide at a linear rate for the first two days. This was followed by a 12 hour period of limited activity, followed by another 48 hours where sulphide was produced at a constant, but slightly lower rate. The data suggest that there are two carbon sources in the molasses that are sequentially metabolised. The sulphide concentration in the reactor reached a maximum of 250 mg/L (36% sulphate reduction) after 111 hours. This value is similar to the highest sulphide concentration detected in the DPBR effluent when the feed was supplemented with 1.5 g/L molasses. This suggests that the molasses, which is added to “kickstart” the utilisation of the lignocellulosic material, is responsible for supporting the majority of the sulphate reduction in the DPBRs. The rapid conversion of molasses to VFAs in the batch tests inoculated with DPBR overflow further suggests that the molasses supplementation has selected for a population that preferentially metabolises molasses. In conclusion, the work presented in this report has demonstrated that efficient sulphide oxidation is possible in the LFCRs, provided the organic carbon and sulphide concentrations in the feed solution are sufficient and stable. Sufficient organic carbon is required to sustain a stable biofilm, which is necessary to prevent the sulphide from being fully oxidised back to sulphate. The oxygen mass transfer into the system is independent of the sulphide concentration in the influent, so large fluctuations in the feed sulphide concentration (as observed from the DPBR columns) can result in the sulphide to oxygen stoichiometry becoming favourable for oxidation beyond sulphur, to thiosulphate or sulphate. Therefore, while the data indicate that the process could be effective there is currently insufficient data on the stability of the DPBR effluent, in terms of sulphide and organic carbon concentrations, to conclude that performance will be consistent.