CHAPTER 1: INTRODUCTION

1.1 BACKGROUND

1.1.1 Water demand

Due to the limited annual rainfall, South Africa is considered a semi arid country. For that reason, water has been identified as the country's most limiting natural resource. Due to both the rapidly growing population and its upliftment, the total water demand for agriculture, domestic use, industrialisation and mining has increased rapidly. Estimates of the current patterns of use and anticipated future uses of South Africa's water resources, based on existing patterns of water exploitation, indicate that the demands for water in each sector of the economy will increase. It is estimated that this increase will amount to 111% for the mining industry by the year 2030 (Basson *et al*. 1997). Water demand in several regions of the country has already exceeded the available supplies. These demands are being met by progressively larger water transfers from those catchments where demands have not exceeded supplies and "excess" water is still available (Ashton & Haasbroek, 2000). Consequently the water allocation priorities must be aligned with national development objectives and hence should place greater emphasis on ensuring that scarce water resources are used in such a way that maximum long-term benefits for the country as a whole can be derived (Basson *et al.* 1997; Muller, 2000; Ashton & Haasbroek, 2000). Improved water management in the mining industry could be achieved by pollution prevention, e.g contamination of clean water with pollutants caused by mining operations should at all times be avoided (Pulles, 2006). This can be achieved by preventing the transport of the generated contaminants to the water resource.

Water management efforts should not only be directed at source level, but should focus equally strongly on the re-use of industrial effluent waters. For this reason the treatment and re-use of industrial and mining effluents has become not only a priority but a necessity. The re-use of industrial effluent waters may furthermore have economical benefits. Jovanovic *et al*. (1998, 2002) investigated the use of partially treated mine water for irrigation. Greben *et al.* (2003) showed that treated mine water from a nickel and copper mine in Botswana could potentially be used for the irrigation of citrus crops. It can be envisaged that this form of agriculture will result in additional job creation and consequently in some degree of poverty alleviation, showing that treated mine water, used for irrigation as opposed to non treated mine water, which is stored in decommissioned mines, can benefit the country and its people.

1.1.2 Origin of AMD

The scarcity of water is exacerbated by pollution of the surface- and ground- water resources due to industrial activities such as mining. By its very nature and scale, mining has a marked and visual impact on the environment. Mining is implicated as a significant contributor to water pollution, the prime reason being, that most of the geological formations that are mined contain pyrites which oxidize to form sulphuric acid when exposed to air and water. Due to the weathering of pyrite, sulphate as soluble ferrous irons are released. Metal sulphides other than pyrite will also release soluble ions, such as zinc, copper, lead, nickel and cadmium. The combination of auto-oxidation and microbial sulphur and iron oxidation produces large volumes of sulphuric acid, which is highly corrosive and when discharged into river systems can cause major environmental problems, one of them being the high toxicity level towards aquatic biota. This polluted, often acidic and sulphate rich water is referred to as Acid Mine Drainage (AMD). Sulphate needs to be removed from mining effluents to avoid salination of surface water. The removal of sulphate also reduces the risk of scaling as well as the possibility of biocorrosion of pipes and mining equipment. The present recommended sulphate discharge concentration imposed by the Department of Water Affairs and Forestry (DWAF) is at a concentration lower than 500 mg/ℓ (South African water quality guidelines).

1.1.3 Environmental impact due to coal mining activities in South Africa

While a mine is operational, the act of mining, i.e. sinking of shafts or open pits and the excavation of ore, can have a significant impact on the natural water environment, as mining activities inevitably disrupt pre-existing hydrological pathways (Younger & Wolkersdorfer, 2004). In excess of 200 Mℓ/day of mining effluent is discharged annually into the water bodies of the Gauteng region, which approximately accounts to sulphate loads of 73 000 tonnes/annum, while this contribution is estimated to be 12 000 tonnes/annum in Mpumalanga. Mine water in the Upper Olifants River Catchment in Mpumalanga (upstream of Loskop Dam) is at times discharged, resulting in local acidification and regional salination of surface water resources. Although mine water in the Olifants River Catchment currently amounts to only 4.6% of the total water usage, it contributes 78.4% of the sulphate load. Mine water in the catchment of the Witbank Dam and Middelburg Dam is rich in calcium, magnesium and sulphate and is acidic. When the pH is below 5.5, water can be toxic to plant and fish life and corrosive to pipelines and equipment.

1.1.4 Approaches for the treatment of AMD

Because of the variety of mine waters encountered in nature and because of the familiarity of the mining sector with the physical and chemical processes, necessary to separate metals and water, there is a wide range of conventional treatment methods for mine waters (Younger *et al*. 2002). Mine waters can be treated *chemically* applying lime and limestone neutralization technologies, however the residual sulphate in the form of gypsum ($CaSO_4$) is dependent on the solubility of gypsum, which is about 1500 mg/ℓ as sulphate (SO_4). For removal of sulphate to below this concentration, the *biological* sulphate reduction technology can be applied. In order to achieve biological sulphate reduction, anaerobic conditions, favoured by the SRB and the presence of suitable carbon and energy sources, have to be adhered to. Successful sulphate reduction is typically associated with a pH increase due to the production of sulphide and alkalinity. Therefore, the biological sulphate reduction technology is particularly beneficial to industries experiencing AMD problems, as it results in removal of sulphate, in an increase in the pH of the treated water and often in metal removal. The latter occurs as a result of the formation of sulphides, followed by metal precipitation as metal-sulphides. To avoid incurring high additional treatment costs, the idea of an integrated treatment system was conceived, in which initially the high sulphate load is treated chemically with limestone until the sulphate concentration is reduced to approximately 1500 mg/ℓ. The remaining sulphate concentration can then be treated biologically, with the advantage that less carbon and energy source is required than in the case of a full biological treatment at sulphate concentrations of e.g. 2500 mg/ℓ (Maree *et al.* 2004)

1.1.5 Biological sulphate removal technology

In the presence of sulphate, the SRB utilize organic products as the carbon and energy source, providing electrons, while sulphate is used as the terminal electron acceptor with hydrogen sulphide (H_2S), CO_2, H_2O or HCO_3^- and in some cases acetic acid as the end products (Greben *et al*. 2002). When sugars are used as carbon sources, intermediate products, such as volatile fatty acids (VFA's), e.g., butyrate and propionic acid, as well as ethanol are formed. In a well functioning bioreactor, these products will be subjected to acetogenesis, performed by the acetogenic bacteria (AB), to produce acetic acid. Good results for sulphate removal have recently been obtained using ethanol (De Smul *et al*. 1997, Greben *et al*. 2000a), sucrose (Maree *et al*. 1986; Greben *et al*. 2000b) as well as methanol, both at thermophilic (Weijma *et al*. 1999) and at ambient temperatures (Tsukamoto & Miller, 1999).

1.1.6 Bio-waste Products

Inexpensive but complex carbon sources such as saw dust and sewage sludge (Butlin *et al.* 1949, 1960; Knivett, 1960; Sadana & Morey, 1962; Tuttle *et al.* 1969; Conradie & Grütz, 1973) have also been evaluated. Although good sulphate removal was obtained using these different carbon sources, long retention times of 5-10 days were required. Maree and Strydom (1985) treated mine water with pulp mill effluent and sewage as energy sources.

Recently, the use of other easily available organic waste, in the form of cow manure, grasses, hay, corn stalks etc. has come to the forefront. The study of Coetser *et al.* (2000) evaluated several complex as well as simpler carbon sources for potential use in passive biological removal treatment systems to treat AMD. They found that Kikuyu grass cuttings, silage and hay, together with propionic-butyric- and lactic acids were the preferred carbon sources to give the most effective sulphate reduction, while in their investigation, acetic acid, pyruvate and ethanol did not result in effective sulphate reduction. Studies, executed by Dill *et al.* (2001) showed that when using hay as the carbon and energy source, a 99% SO_4 removal efficiency was obtained, while this was 97.8% when using Kikuyu grass.

1.2 STUDY OBJECTIVES

The objective of the study was to find an appropriate and cost effective treatment method for AMD using alternative and possible cheaper carbon and energy sources for the biological sulphate removal process. The potential use of a bio-waste product is attractive to the biological sulphate removal technology, as the challenge is to develop technologies that economically produce simple sugars and/or fatty acids from complex polymers such as cellulose/lignin. This approach emphasizes the utilisation of a bio-waste product, such as grass cuttings, rather than its treatment thus shifting the process from reducing the potential for pollution to productive utilisation.

It is hypothesized that anaerobic cellulose degrading microorganisms originating from rumen fluid can produce energy sources in the form of VFA and other intermediates for SRB in the biological sulphate removal process, when contacted with grass cuttings.

1.3 RESEARCH QUESTIONS

1.3.1 Cellulose degradation, VFA production, sustainable sulphate reduction

To achieve the set objectives, the main research questions are focussed on the fermentation of grass-cellulose and on the use of these fermentation products as substrates in the biological sulphate removal. Can it be proven that the proposed technology is feasible to obtain a sustained removal of sulphate from mine water? With the aim to answer this hypothesis, the following research questions were stipulated.

- Can VFA be produced from cellulose in grass cuttings, using naturally occurring micro organisms and can biological sulphate removal be obtained using the formed fermentation products?
- Will a larger amount of grass cuttings (and thus an increased cellulose concentration) affect the VFA concentration and the sulphate reduction rate?
- When using the same amount of grass cuttings, which fermentation products are generated using 1) SRB for fermentation and 2) utilising rumen as the inoculum and in what concentrations will they be present? Can the generated VFA be used for sulphate removal?
- What are the VFA production and sulphate reduction rates when utilising rumen microbes as the inoculum in reactors containing grass cuttings in combination with 1) sulphate, 2) no sulphate and 3) tryptone?
- What is the sulphate removal rate using a two and three stage reactor system containing rumen organisms to produce the carbon and energy source for the biological sulphate removal through fermentation of cellulose in grass cuttings, when feeding 1) artifical feed water and 2) pretreated mine effluent?
- Can a process description of the reactor be developed using mass balances based on the operational results of the combined fermentation and sulphate removal reactor.
- How does the sulphate removal technology described compare to other processes in the market place

The study portrayed in this thesis aimed to find a technology to treat AMD using biowaste products to allow the treated water to, be re-used in the coal processing plant, be used for irrigation or be re-charged to rivers from where some of it originated.

1.4 REFERENCES

Ashton, P.J. and Haasbroek, B. (2000). Hydropolitics in the Developing World – *A Southern African Perspective,* Chapter 14. Anthony Turton and Roland Henwood (Ed.): 187-205. AWIRU, Pretoria, 2002, 269 pp.

Basson, M.S., Van Niekerk, P.H. and Van Rooyen, J.A. (1997). Overview of water resources availability and utilisation in South Africa. *DWAF Report P RSA/00/0197. Pretoria: Department of Water Affairs and Forestry and BKS.*

Butlin, K.R., Adams, M.E. and Thomas, M. (1949). The isolation and cultivation of SRB. *Proc. Soc. Appl. Bact.* **2:** 39-42.

Butlin, K.R. (1960). Microbial sulphide production from sulphate enriched sewage sludge. *J. Appl. Bacteriol*. **23:** 158-165.

Coetser, S.E., Cloete, T.E. and Zdyb, L. (2000). Biological sulphate reduction in artificial acid mine drainage using different carbon sources. *Proceeding Y2K Millennium Meeting, Grahamstown 23-28 January, 2000*: 606.

Conradie, P.J.A. and Grütz, P.W.E. (1973). The treatment of acid mine waste in a mixture with raw sewage sludge in an anaerobic digester. *Report to the Chamber of mines(File no W6/534/3)*. National Institute for Water Research, Pretoria

De Smul, A., Dries, J., Goethals, L., Grootaerd, H. and Verstraete. W. (1997) High rate of microbial sulphate reduction in a mesophile ethanol fed expanded-granular-sludge-blanket reactor. *Appl. Microbiol. Biotechnol.* **48:** 297-303

Dill, S., Cloete, T.E., Coetser, L. and Zdyb, L. (2001). Determination of the suitability of alternative carbon sources for sulphate reduction in the passive treatment of mine water. *WRC Report*: 802/1/01.

Greben, H.A., Maree, J.P. and Mnqanqeni, S. (2000a). The comparison between sucrose, ethanol and methanol as carbon and energy source for biological sulphate reduction. *Water Sci.Technol*. **41**(12): 247-253.

Greben, H.A., Maree, J.P., Singmin, Y. and Mnqanqeni, S. (2000b). Biological sulphate removal from acid mine effluent using ethanol as carbon and energy source. *Water Sci.Technol*. **42**(3-4)**:** 339-344.

Greben, H.A., Bologo, H. and Maree, J.P. (2002). The effect of different parameters on the biological volumetric and specific sulphate removal rates. *Water SA*. *Special Edition,* WISA Biennial Conference 2002, pp: 33-37

Jovanovic, N.Z., Barnard, R.O., Rethman, N.F.G and Annandale, J.G. (1998). Crops can be irrigated with lime-treated acid mine drainage. *Water SA.* **24** (2):113-123.

Jovanovic, N.Z., Annandale, J.G., Claassens, A.S., Lorentz, S.A.,Tanner P.D., Aiken, M.E. and Hodgson, F.D.I. (2002) Commercial production of crops irrigated with gypsiferous mine water. *Water SA.* **28** (4): 413-423

Knivett, V.A. (1960). The microbiological production of Vitamin B_{12} and sulphate from sewage. *Prog. Indust. Microbiol.* **2:** 27-32.

Maree, J.P. and Strydom, W.F. (1985). Biological sulphate removal from a packed bed reactor. *Wat Res*. **19:** 1101-1106.

Maree, J.P., Gerber, A., Strydom, W.F. (1986). A biological process for sulphate removal from industrial effluent. *Water SA*. **12:** 139-144.

Maree, J.P., Greben, H.A. and de Beer, M. (2004). Treatment of acid and sulphate-rich effluents in an integrated biological/chemical process. *Water SA*. 30**(2)**: 183-189

Muller, M. (2000). Transforming water law to achieve South Africa's development vision: A case study in international law. In *Proceedings of the Second World Water Forum.* The Hague, 17-22 March

Pulles. W. (2006). Management options for Mine Water Drainage in South Africa. In *proceedings* of Mine Water Draianage (South African Perspective). Randfontein 19-20 October, 2006

Sadana, J.C. and Morey, A.V. (1962). Microbiological production of sulphide from Gypsum. *J. Sci. Industr. Res.*, **21**: 124-127.

Tsukamoto, T.K. and Miller, G.C. (1999). Methanol as a carbon source for microbiological treatment of acid mine drainage. *Wat.Res.* **33:** 1365-1370.

Tuttle, J.H., Dugan, P.R., MacMillan, C.B. and Randles, C.I. (1969). Microbial dissimilatory sulphur cycle in acid mine water. *J.Bacteriol.,* **97:** 594-602

Weijma, J., Hulshoff Pol, L.W. Stams, A.J.M., and Lettinga, G. (1999). Thermophilic sulphate reduction and Methanogenesis with Methanol in a high rate Anaerobic reactor. *Biotechnol. Bioeng.* **67**: 354-363.

Younger, P.L., Banwart, S.A. and Hedin, R.S. (2002). Mine Water. Hydrology, Pollution, Remediation. Kluwer Academic Publishers. Dordrecht, Boston, London pp 442

Younger, P.L and Wolkersdorfer, C. (2004). Mining impact on the fresh water environment: technical and managerial guidelines for catchment scale management. *Mine water and the environment.* 23: S2-S80