Salinity, Sanitation and Sustainability:
A Study in Environmental Biotechnology and
Integrated Wastewater Beneficiation in South Africa

Volume 4

# THE RHODES BioSURE PROCESS®

## Part 1: Biodesalination of Mine Drainage Wastewaters

Report to the Water Research Commission

by

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# FOREWORD

The work presented in this series covers a decade of concerted research into critical sustainability issues in the water-scarce Southern African situation. The provision of safe and adequate drinking water and sanitation services to all our people remains a challenge. Pervasive salination from a range of mining, industrial and agricultural activities threatens the quality of our water resources. Simultaneously, the complex ecological needs of the aquatic environment are being understood with ever-increasing clarity.

Significant progress has been made in meeting some of these challenges. In the years since the democratic elections of 1994, millions of previously unserviced South Africans have been supplied with safe drinking water and sanitation services. The problem of increasing salinity of our water resources, with its direct economic impacts and future threat to sustainability, is being addressed at policy and implementation levels, for example by reduction-at-source measures. The ecological needs of the aquatic environment have been recognised by the provision in our water law of a prioritised ecological reserve, to be managed by the catchment management agencies being formed.

Such promising developments notwithstanding, ultimately sustainable resolution of these issues depends crucially also on acquiring appropriate and affordable technologies that provide physical solutions to our water-related challenges. It is in this context that the research described in this series deserves special commendation for the highly innovative biotechnological linkage developed between the treatment of saline wastewaters on one hand and domestic sewage and sludges on the other.

In the novel approach followed, salinity and sanitation issues are each viewed essentially as a resource base (rather than simply as “waste problems”) in a suite of integrated process schemes which can be variously manipulated to deliver products of treated water, recovered nutrients and metals, and algal biomass. The paradigm is consequently changed from one of “managing problems” to one of “engineering opportunities”, with the potential of offering a major contribution towards the management of water and sanitation in the RSA. Some applications have already been taken to full scale implementation, for example in the accelerated digestion of sewage sludge. Significantly, the achievements of this research add weight to biotechnology as “the” technology of the 21st century.

So, as we approach the World Summit on Sustainable Development, we can reflect on the provisions of Agenda 21 adopted after the Earth Summit some 10 years ago, and note that in this time we have ourselves in various ways “done something” about our own situation. And we can therefore point with a justifiable sense of pride and achievement to the body of work presented here as being “Made in South Africa”, at a time when social, environmental, political and economic calls are being made to all of Africa to stand up in the continental and global communities of nations.

My deep thanks and appreciation go to the Water Research Commission for the foresight in funding this work, and, in particular, to Prof Peter Rose and his research team at Rhodes University, for the vision, purposefulness, innovation and application with which this work has been conceived and executed.

Ronnie Kasrils

Minister of Water Affairs and Forestry
Pretoria
31 July 2002

# EDITOR’S NOTE

In 1990 the Water Research Commission, under the (then) Executive Director Dr Piet Odendaal, appointed the Environmental Biotechnology Group at Rhodes University, led by Prof Peter Rose, to carry out a one-year feasibility study to evaluate the potential of a biotechnological approach to the linked treatment and management of saline and sanitation wastewaters with recovery of useful components such as nutrient bio-products.

In the intervening years, this seminal project has resulted in a rich research programme, managed initially by Dr Oliver Hart, subsequently by Zola Ngcakani, and latterly (since 1997) by myself. The progression of the research programme is reflected in this series of reports. Report 1 critically reviews the main arguments considered in the sustainability discourse and their relation to salinity and sanitation, and presents an overview of the work covered in the individual Reports 2 – 12, each of which deals with specific aspects of the research programme. The reports are also to be issued on CD.

The research period concerned spans approximately the decade between the Rio Earth Summit in 1992 and the imminent World Summit for Sustainable Development in Johannesburg. During this time, international concern has been expressed about the limited extent to which the sustainability objectives formulated at Rio, as captured for example in Agenda 21, have been followed through to implementation.

By contrast, it is a noteworthy achievement of this research programme that the “sustainable biotechnology” originally conceptualised by the researchers has in fact, by dint of rigorous research development, experimentation and testing, been translated into a suite of practicable processes for delivering treated water as well as value-adding organic and inorganic co-products. In some applications, full-scale plants are already being installed, fulfilling the cycle of research → development → implementation.

It is probably fair to say that the full potential of the original work initiated twelve years ago, with its various applications as they have been developed since then, could at inception only have been dimly foreseen – which, with hindsight, underscores the clarity, breadth and depth of the originators’ vision.

It has been a pleasure and a privilege to be involved with this work as Research Manager, and now as Editor of this series. I am confident that you, the reader, will find the contents both informative and as stimulating as I have.

*Greg Steenveld*
Water Research Commission
Pretoria
31 July 2002

# PREFACE

This report is one of a series of twelve Water Research Commission studies undertaken by the Environmental Biotechnology Group at Rhodes University, on biotechnology and integration in the management of saline and sanitation wastewater systems. Environmental problems in these areas are reckoned to be responsible for six of the seven priority pollution issues undermining the sustainable development project in Southern Africa. While both salinity and sanitation have separately been the subject of quite extensive investigation, relatively little has been reported on the potential linkage of these systems in meeting sustainable development objectives.

At the time these studies commenced, in 1990, focus on the operationalisation of the sustainability idea had identified 'integrated waste resource management' as a key requirement for progress towards 'closed systems' production. Here human activities, and the associated technological environment, would be detached as far as possible from the bio-physical environment related to natural systems. Waste recovery, recycle and reuse had emerged as major strategies for achieving the radical shift to new technologies which would enable societies to live off nature's income, rather than consuming its capital. Waste beneficiation (a term still more common in the traditional resources sector, and referring to operations that add value by transforming raw material into finished products), was seen as a means of placing treatment operations on an economic footing, with value added in the form of products and services accrued in the waste management operation.

To meet the time-scale of the sustainability agenda, the breakthroughs in technology required would have to be initiated now to guarantee their availability in the next 2 to 4 decades. This led to widespread use of technology-push approaches in sustainable technologies research.

The principal aim of this programme was thus to investigate the potential of environmental biotechnology for the development of technological enablement in the linkage of saline and sanitation wastewater management. This involved initial studies in the biology of organic saline wastewater impoundments and an evaluation of the recovery of nutrient values in these wastes in the form of high-value bio-products produced by halophilic micro-organisms. Integrated Algal Ponding Systems were investigated as a 'core technology' in delivering these objectives.

A critical path research methodology was used to identify technological constraints in the organic saline wastewater treatment operation and served to prioritise the research inputs required to underpin bioprocess development. Studies in the microbial ecology and environmental biotechnology of these systems provided the basis for bio-process innovation, and the subsequent development of treatment processes to full-scale engineered applications.

This series includes an introductory volume which provides an overview of the twelve-year programme to date. The reports are listed inside the front cover, and each study in the series is identified by a 'racing flamingo' number, which also appears on the outside cover. This relates to the appearance of a large flock of flamingoes, which took up residence on tannery wastewater ponds following the installation of the *Spirulina*-based Integrated Algal Ponding System developed in the initial studies in this series. The development of the 'Salinity, Sanitation and Sustainability' programme is outlined below in Figure P1, and shows studies in the integrated algal ponding of saline, and domestic and industrial wastewaters, leading to the Rhodes BioSURE Process®, which provides linkage in the treatment of sulphate saline wastewaters and sewage sludge disposal.

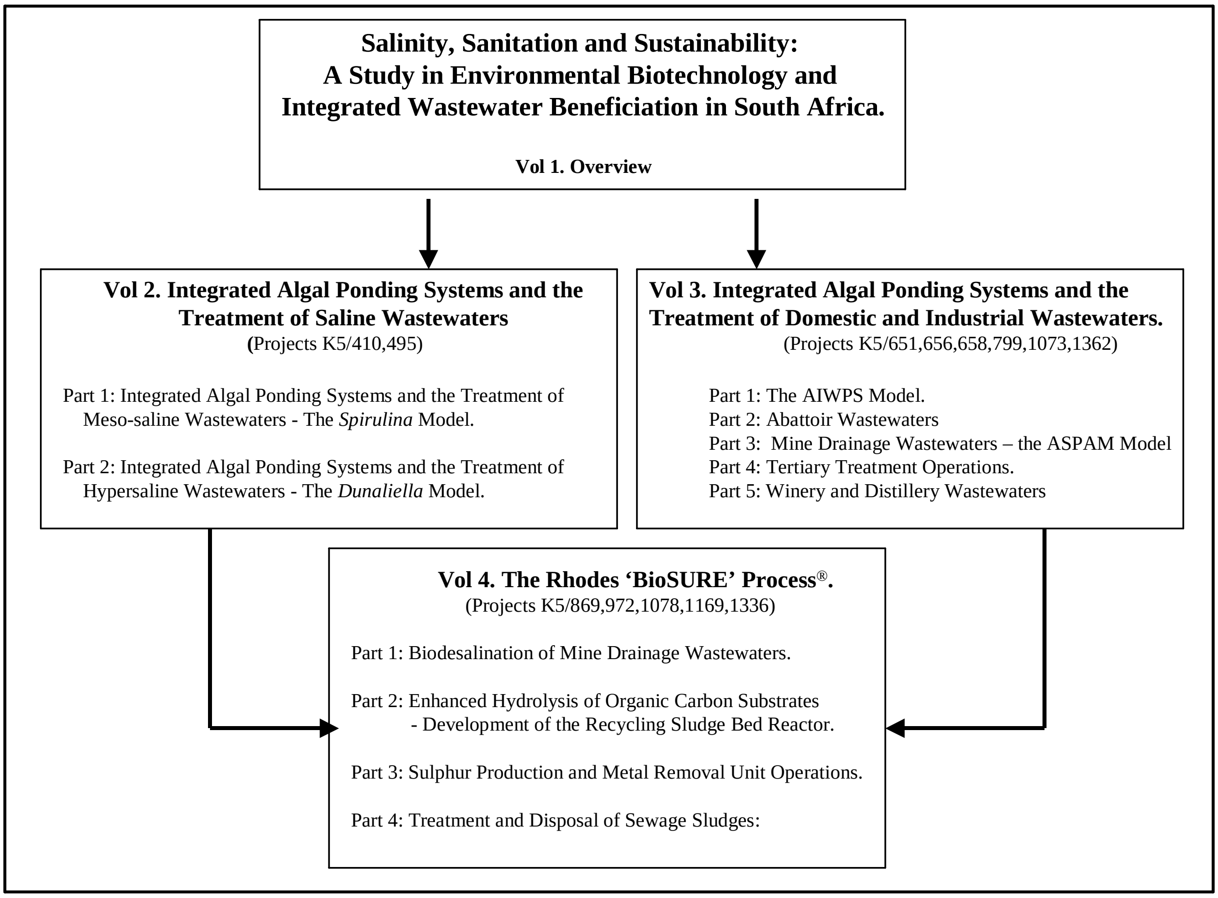

**Figure P1.** Research projects undertaken as components of the Water Research Commission study 'Salinity, Sanitation and Sustainability'.

A large number of people have assisted generously in many ways in the development of these studies, and are thanked under Acknowledgments. The support of former Water Research Commission Executive Director, Dr Piet Odendaal, is noted in particular. His vision of research needs in water resource sustainability, in the period leading to the Rio Earth Summit in 1992, not only contributed to this study, but also initiated early contributions to sustainable development research in water and sanitation service provision to developing communities. His inputs, together with Research Managers Dr Oliver Hart, Mr Zola Ngcakani, and Mr Greg Steenveld, have made substantial contributions to the development of the ideas investigated in these studies. The contribution and enthusiasm of my post-graduate research students is beyond measure.

*Peter Rose*
Environmental Biotechnology Group
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Grahamstown

# CONTENTS

# EXECUTIVE SUMMARY

## 1. BACKGROUND

The strategic significance of pollution in the deteriorating quality of the national water resource, and its long-term impacts on environmental sustainability and sustainable development have been widely noted (Walmsley *et al*., 1999). Issues broadly related to salinity and sanitation have been identified as among the highest priority pollution concerns throughout the Southern African Region (DEAT, 1999; 2000). The problems of a creeping salinisation of the public water system has been the subject of growing attention in South Africa over a period of many years (Commission of Enquiry into Water Matters, 1970; Stander, 1987; DWAF, 1989; DEAT, 1999, 2000), and the contribution of mine drainage wastewaters, especially in the salinisation of the Vaal River system, has been highlighted in numerous Water Research Commission (WRC) studies (Heynike, 1981, 1987; Schutte, 1983; Funke, 1990; Du Plessis, 1990; Pulles *et al*., 1995; Scott, 1995). Environmental problems associated with large-scale mine dewatering operations have become increasingly apparent (Pulles *et al*., 1995).

It had been assumed since the early 1900s that when the gold mines on the Witwatersrand finally closed, and dewatering operations ceased, the mines would fill over a period of time to a subsurface water table, and that this would signal the end of the mine water pollution problem. Scott (1995) in a seminal study of the East and Central Rand Basins has shown, however, that not only will filling occur faster than anticipated (around 10 years), but that large volumes (> 70 $ML.day^{-1}$) of highly polluted mine drainage wastewater may be expected to decant continuously at the surface, and flow into the public water system. Including the Mpumulanga coal fields, this may add up to hundreds of ML of acid mine drainage (AMD) entering the Vaal River system daily. Younger *et al*., (1997) have found that flush waters of extremely poor quality flow for around four times the fill time of a mine, following closure, and thereafter may continue for long periods of time through many decades to centuries.

Walmsley (1995) has noted that the Mine Remediation Bond system, which insures regulation-compliant mine closure, was never intended to handle a regional problem of this magnitude and time-scale, and it is clear that over time the burden and costs of remediation will likely revert to the community at large. This predicted long-term mine water remediation problem which will need to be addressed raises critical issues in both environmental and social sustainability and has focused considerable interest in the technologies available to deal with the nature and dimension of the problem.

Physico-chemical process have been extensively investigated in the treatment of these wastewaters (Pulles, *et al*., 1995). While chemical precipitation and membrane-based desalination processes may be highly engineered and function efficiently, they tend to be expensive and require ongoing costly operational controls. The disposal of reject brines also presents a problem on which little real progress has been made over the years (Buckley *et al*., 1987).

Biological approaches to AMD treatment have thus been the subject of increasing interest, particularly as a source of sustainable solutions for dealing with the problem. The biological approach targets one or more of the following objectives:

☐ Removal of contaminating heavy metals;
☐ Neutralisation of acidity;
☐ The reduction of sulphate salts to the sulphide form;
☐ Oxidation of sulphide and its removal from the system as elemental sulphur;
☐ Polishing of the treated stream to remove residuals of metals, sulphides, organics and possible microbial contaminants, prior to its final discharge into the environment.

However, the cost of the carbon source (mainly ethanol and hydrogen gas have been used), and the size of the reactors needed to treat large volume flows, have been factors constraining widespread implementation of biological process developments (Rose *et al.*, 1998).

This report describes the development of the Rhodes BioSURE Process® which resulted from studies undertaken in the Environmental Biotechnology Group (EBG) at Rhodes University on the use of waste organic carbon as electron donor sources for sulphate reduction in low-cost bioreactor applications. This development targeted the establishment of a functional linkage in mine water treatment and organic waste disposal in order to provide an ‘integrated waste resource management’ approach to the mine drainage problem, which in turn may advance progress towards ‘closed system’ production objectives. Where the use of a widely available waste organic carbon source such as sewage sludge (which carries its own disposal costs), could be used as the electron donor source for sulphate reduction, the sustainability advantages of the co-disposal treatment process over the time frames anticipated would be particularly favourable.

## 2. ENHANCED HYDROLYSIS OF ORGANIC CARBON WASTES

Previous studies in the microbial ecology of tannery waste stabilisation ponds (WRC Project K5/495), undertaken by the EBG in the early 1990s, had shown an unexpected enhanced degradation of particulate COD (CODp) in sulphate reducing environments (Dunn, 1998). Reciprocal sulphate reduction and sulphide oxidation reactions in the pond water column was observed to be associated with high rates of hydrolysis and organic solids removal, and these findings were incorporated into the development of an Integrated Algal Ponding Systems (IAPS) approach to the management of tannery wastewaters. A full-scale ponding system was then retrofitted with the construction of an IAPS at Mossop-Western Leathers Co. in Wellington (Rose *et al.*, 2002a). In addition to enhanced solids degradation in the biosulphidogenic environment, heavy metal removal as sulphide precipitates and the neutralisation of the AMD stream had also been observed in the tannery IAPS.

Oswald (1995) had observed that the earthwork pond provides a bioreactor at least an order of magnitude cheaper than steel-reinforced concrete structures. Based on the results noted above, a study was undertaken to investigate the use of ponds in AMD treatment. During this investigation it became apparent that not only had the use of integrated ponding systems in AMD treatment received scant previous attention, but that the biosulphidogenic hydrolysis of complex organic carbon sources could play a crucial role in the provision of electron donor sources for sulphate reduction from a potentially wide range of organic wastes. However, little was known about the mechanisms involved in the enhanced hydrolysis effects observed.

These studies on ponding systems in AMD treatment were undertaken in WRC Project 656 (Appendix 1), and resulted in the development of the novel ASPAM Process. The results have been described in Report 6 in the 'Salinity, Sanitation and Sustainability' series (Appendix 1).

## 3. WRC PROJECTS K5/869 AND K5/972

In addition to a clear need to subject the enhanced hydrolysis observations to more rigorous investigation, which followed from the studies outlined above, it was also identified that while the pond held many advantages as a bioreactor, it did not necessarily provide the only or the most versatile reactor system for all applications in AMD treatment.

The task of further developing a sustainable sulphate reduction technology based on complex organic carbon electron donor sources, and low-cost bioractor structures, was taken up in WRC Projects K5/869, 'Biological sulphate desalination and heavy metal precipitation in industrial and mining effluents using the IAPS'; and Project K5/972 'Process development and system optimisation of the integrated algal trench reactor process for sulphate biodesalination and heavy metal precipitation in mining and industrial effluents'. In these projects provision was made to undertake both fundamental and applied studies concurrently and, in addition to investigating the mechanisms of enhanced hydrolysis, the development of the Recycling Sludge Bed Reactor (RSBR) was initiated based on observations in tannery ponding systems.

These studies commenced in 1997 against the background of the now notorious environmental incident at Grootvlei Mine, in Springs. Here, due to degradation of the Blesbokspruit Ramsar wetland site, the mine dewatering permit was withdrawn, and with the shutdown of pumping operations innundation of the mine threatened. Resumption of pumping was dependant on the construction of a high density sludge (HDS) lime treatment plant, and permit renewal was linked, by a Cabinet decision, to the conduct of a desalination technology evaluation exercise. Suppliers were to be invited to submit proposals, undertake pilot studies to be completed by 1 September, 1997, and be ready to supply, construct and commission a full-scale plant before 1 December, 1999 (Van Wyk and Munnik, 1997). Other issues that were to be investigated included the control of impacts on the wetland, the disposal of desalination brines and sale of potable water.

The EBG was invited to participate in the desalination technology evaluation exercise, and a decision was made to undertake the scale-up of the RSBR configuration then under development. In addition to continuing studies in Grahamstown, a pilot plant was to be constructed to operate on-site at the Grootvlei

Mine. The project would concentrate on biological AMD treatment using only sewage sludge as the electron donor source. The East Rand Watercare Company (ERWAT) agreed to participate and primary sewage sludge (PSS) was to be provided from their nearby Ancor Works.

The following combined research objectives were identified for the WRC Projects K5/869 and K5/972:

1. To expand studies undertaken in elucidating the reaction mechanism involved in the phenomenon of biosulphidogenic enhanced hydrolysis of complex carbon substrates;
2. To evaluate reactor design options in which the enhanced hydrolysis reaction may be applied in the treatment of AMD;
3. To undertake scale-up development of the AMD biodesalination process using complex carbon substrates as the electron donor source for sulphate reducing bacteria (SRB)-driven sulphate reduction;
4. To undertake process evaluation at pilot-scale treating an authentic AMD stream;
5. To establish the technical feasibility of a linkage between AMD treatment and PSS co-disposal, and to demonstrate a basis for technological and environmental sustainability in the long-term management of these waste streams.

This report describes the development in what became known as the Rhodes BioSURE Process®. In addition to bioreactor development it details the 18 month piloting study including plant construction, process optimisation and monitoring. While this phase of the study concentrated on the sulphate reduction stage of the desalination exercise, the detailed metal precipitation and sulphide oxidation unit operations were to be investigated as subsequent research projects. This work was handled in Project K5/1078, and these findings will be detailed in Report 11 of the series. Process modeling and aqueous chemistry studies were to be undertaken in collaboration with Prof Geoff Hansford and Dr Alison Lewis at the UCT Chemical Engineering Department, and Prof Dick Loewenthal at the UCT Civil Engineering Department. These results are reported separately in Ristow *et al*. (2002).

The more fundamental investigation of the sulphidogenic enhanced hydrolysis reaction mechanisms are detailed in Part 2 of this report ‘Enhanced hydrolysis of organic carbon substrates - Development of the Recycling Sludge Bed Reactor’ (Appendix 1).

## 4. THE RECYCLING SLUDGE BED REACTOR

It had been noted in tannery ponds, systems in which solids accumulation is a notorious problem, that reciprocal interaction between the water column and the sediment, and establishment of well-defined sulphide gradients, seemed to play an important role in the biodegradation of CODp (Dunn, 1998). Particlulates not subjected to this recycling effect become compacted into sediments which were sulphate mass transfer limited, and remained largely undegraded.

Observations of enhanced hydrolysis of particulate organic carbon in biosulphidogenic environments were subjected to more detailed study by Patricia Molepane (MSc, 2000), who investigated the use of sewage sludge as a carbon source in sulphate reduction (Report 6 in the ‘Salinity, Sanitation and Sustainability’ series). Kevin Whittington-Jones (PhD, 2000) constructed a laboratory-scale RSBR in an attempt to model the events observed in the tannery ponds (Figure 1a), and to investigate the reaction mechanisms involved (Figure 1b).

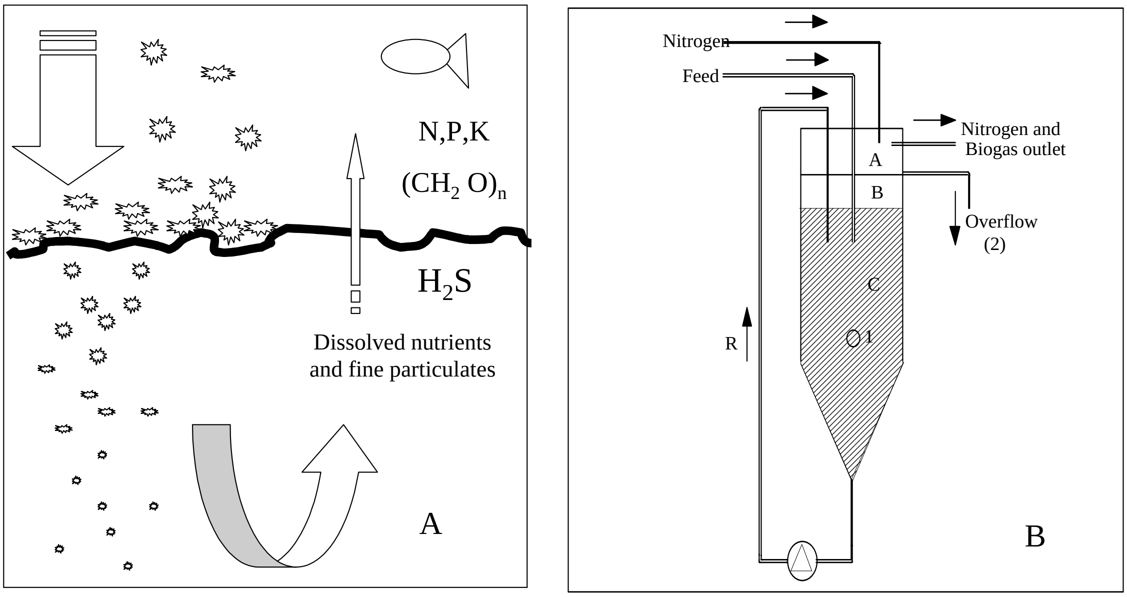

**Figure 1.** The breakdown and solubilisation of particulate organic matter in sulphidogenic settlement and sedimenting processes observed in natural systems (A). This was simulated in a 2L prototype study (B) of the Recycling Sludge Bed Reactor. The degrading sludge is returned via line R to blend with the incoming feed.

The reactor was fed a mixture of PSS (as a convenient source of particulate organic carbon), and synthetic AMD as the sulphate source. The headspace was sparged with nitrogen gas to maintain anaerobic conditions. Gradients of increasing sulphide concentration, alkalinity and sludge density were found to be associated with a reduction in particle size, and an increase in the soluble or filtered COD (CODf) fraction. On recycle to blend with the incoming stream the larger remaining settleable particulate solids returned to the bed, while the solubilised fraction (including volatile fatty acids) passed out of the reactor. A multi-stage configuration of the RSBR (Figure 2) was used to investigate the use of the solubilised sewage sludge fraction for driving sulphate reduction.

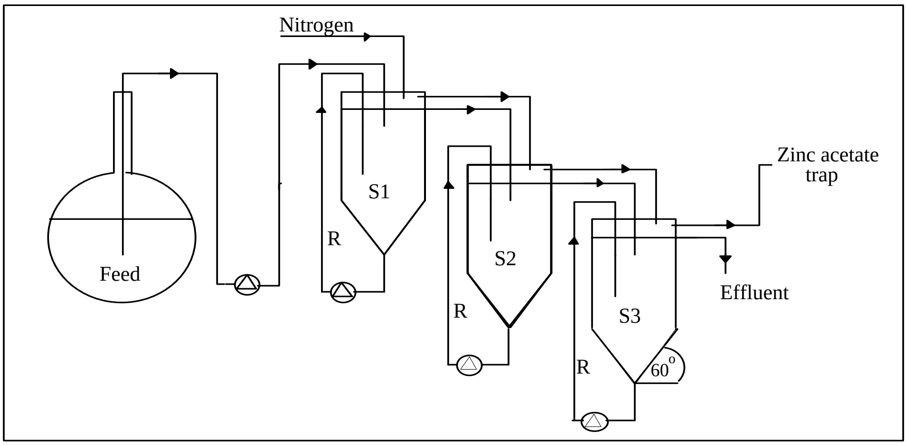

**Figure 2.** The multi-stage Recycling Sludge Bed Reactor used to investigate the solubilisation of primary sewage sludge and its utilisation as an electron donor source in sulphate reduction activity.

The 2L RSBR was scaled up as a 10L perspex bench-scale unit, and then through 1 $m^3$ to a 23 $m^3$ reactor which was used in the Grootvlei pilot plant study (Figure 3).

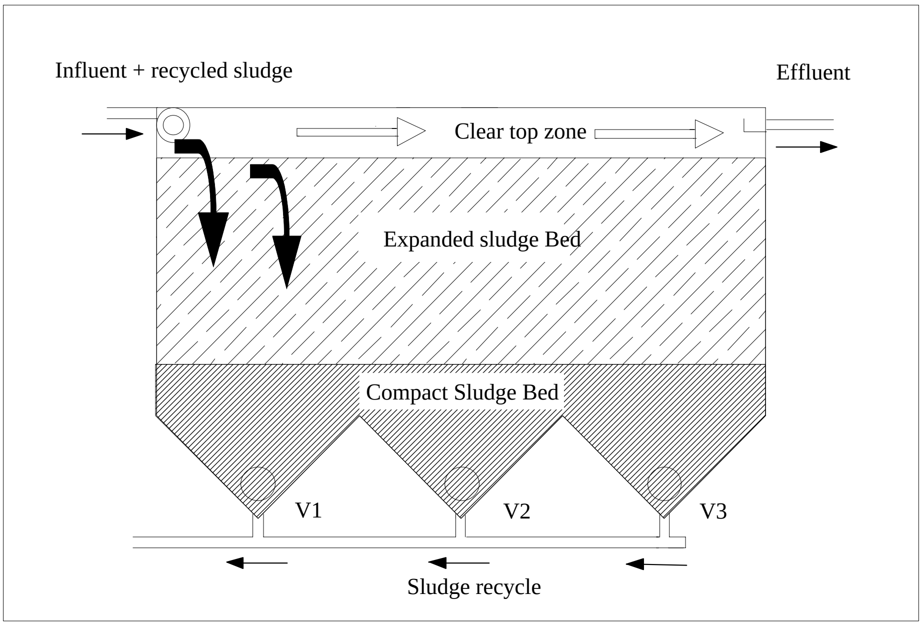

**Figure 3.** The pilot-scale Recycling Sludge Bed Reactor used to investigate the solubilisation of primary sewage sludge and its utilisation as an electron donor source in sulphate reduction activity.

Results from the laboratory-scale RSBR study confirmed that a complex carbon source such as PSS could be used to drive biological sulphate reduction and that the hydrolysis of PSS was enhanced in a recycling biodulphidogenic environment. It was shown in this study that on the basis of total sulphate reduction achieved a minimum of 52% of the particulate carbon entering the RSBR had to have been solubilised to its readily available form. This value exceeded all previous published values by approximately 20%, and demonstrated the efficacy of the recycling sludge bed concept.

A descriptive model was developed to explain the phenomenon of enhanced hydrolysis in the RSBR. It was proposed that sulphide has a direct effect on the physical integrity of the sludge flocs, and during the recycling events, large flocs are fractured. This promotes the release of soluble hydrolysis products and sulphide from the floc, primarily volatile fatty acids (VFA) and reducing sugars. The smaller flocs are recycled to the inlet of the reactor where they come into contact with fresh substrate, and refloculate in the upper settling zone of the RSBR. During reflocculation, fresh substrate, sulphate, bacteria and associated hydrolytic enzymes are incorporated into the centre of the flocs. These then settle into the base of the reactor and as hydrolysis proceeds, the products of the process stimulate further hydrolysis.

Subsequent work by Jennifer Molwantwa (MSc, 2002) confirmed that the maximum percentage solubilisation of PSS was significantly greater under sulphidogenic (63%) than equivalent methanogenic conditions (31%). This suggests that a certain organic fraction that would be considered recalcitrant under methanogenic conditions is susceptible to microbial degradation under sulphidogenic conditions. The rates of hydrolysis were investigated using highly selective metabolic inhibitors, and it was shown that the rate of hydrolysis, measured as the rate of reducing sugar production, was three times greater under sulphidogenic than methanogenic conditions.

The enzymology of the enhanced solubilisation process has also been investigated and Whiteley *et al*. (2002 a,b,c,d) have reported increased activity in certain enzymes in the sulphidogenic environment.

## 5. THE RHODES BioSURE PROCESS® - CONFIGURATION

A dual-stage sulphate reduction operation was thus conceptualised on the basis of the above findings and the 10 L and 1 $m^3$ RSBR studies undertaken at the EBG Experimental Field Station in Grahamstown led to the development of what became known as the Rhodes BioSURE Process®. This process which involves the separate optimisation of the hydrolysis and sulphate reduction reactions (Figure 4) includes the following individual unit operations:

1. The influent AMD stream is mixed with alkaline sulphide-rich effluent from the sulphate reducing reactor R2. A metal sulphide precipitate strips the major fraction of the heavy metal load in the influent stream before it passes to the RSBR (R1);

2. The electron donor and carbon source (PSS was used in these studies), is added to the stream following metal precipitation, and before it enters R1. In this unit the initial sulphate reduction and enhanced hydrolysis reactions are optimised, solids are drawn down into the reactor bed, and sludge is continuously settled and recycled to blend with the incoming AMD feed (see Figure 3). The solubilised product passes to R2, and residual particulate carbon settles to the sludge bed to be cycled once again;

3. Sulphate reduction is optimised in R2. An Anaerobic Baffle Reactor (ABR) was used in this study and provides a low-cost quasi-passive reactor configuration where the consumption by SRB of the different hydrolysis products may be self-optimised, and with the establishment of adapted microbial consortia in each compartment;

4. The sulphide stream passes to a Sulphide Oxidising Bioreactor (SOB) where the now reduced sulphates are removed as elemental sulphur, thereby achieving the partial biodesalination of the AMD stream;

5. Following treatment the neutralised stream passes finally to a polishing unit where residual sulphides may be oxidised, remaining metals adsorbed, and the final stream disinfected prior to final discharge of the treated water. A High Rate Algal Pond (HRAP) was used in this study.

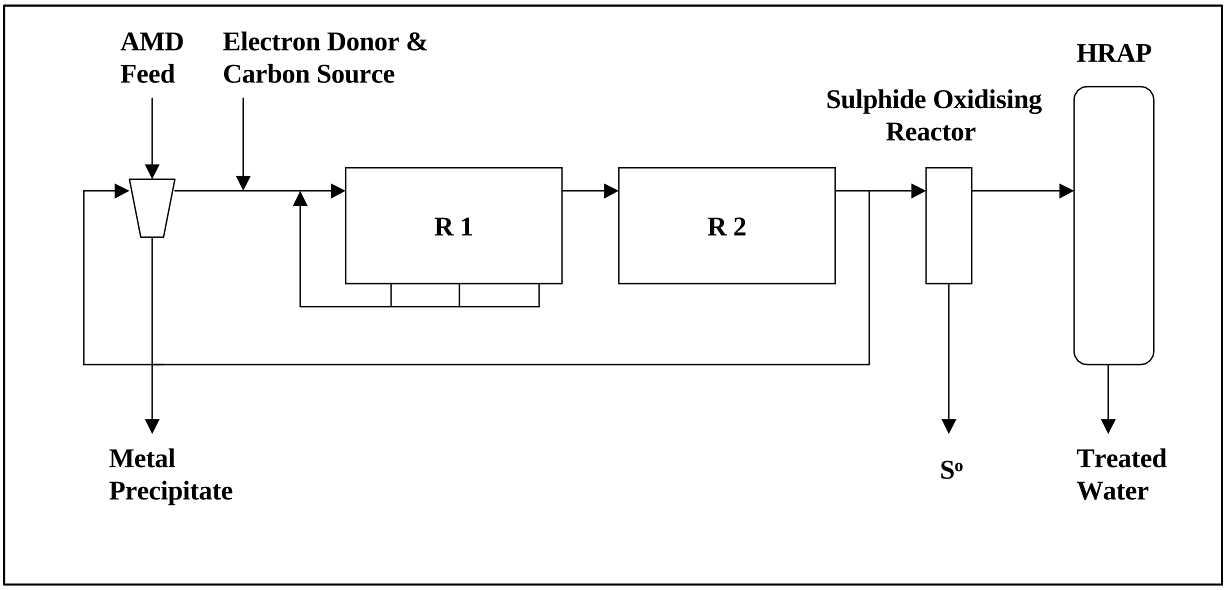

**Figure 4.** Process flow diagram of the Rhodes BioSURE Process® applied to the treatment of acid mine drainage wastewater. R1 = Recycling Sludge Bed Reactor; R2 = Anaerobic Baffle Reactor; R3=Sulphide Oxidising Bioreactor (SOB); HRAP = High Rate Algal Pond; PSS = primary sewage sludge. A side stream of sulphidic wastewater is blended with incoming minewater to precipitate contaminating heavy metals. The carbon source is added to the metal-free stream which passes to R1 where hydrolysis of particulates and some sulphate reduction occurs. The dissolved organic stream passes to R2 where it is used as feedstock in the final sulphate reduction step. The treated water is then discharged via a Sulphide Oxidation Reactor producing elemental sulphur, and finally through an HRAP polishing step.

## 6. THE BioSURE PROCESS® PILOT PLANT

The decision was made to design and construct the pilot plant for the Grootvlei study on the basis of a 20 fold scale-up of the 1 m$^3$ RSBR and ABR studies. Both the RSBR and the ABR were constructed from 6 m steel shipping containers (initial volume 30.4 m$^3$ prior to modification). These were fitted with sedimenting valleys for sludge collection, and to facilitate recycle as required (Figure 3). Following modification the liquid volumes of the RSBR and ABR were 23 m$^3$ and 25 m$^3$ respectively.

The plant (Figure 4) was constructed and hydraulically tested in Grahamstown, and then transported to site at Grootvlei Mine in Springs. The sulphate saline feed was drawn from the mine's High Density Sludge (HDS) lime treatment plant and thus the constituent metal removal and neutralisation reactions were optimised separately.

Following initialisation the plant was operated for a 12 month period until the end of March 1999. The piloting programme was undertaken by Chris Corbett (MSc, 2001).

**Figure 4**.Headgear at the No.3 shaft Grootvlei Mine with the Rhodes BioSURE Process® pilot plant in the foreground.

The reaction mechanism of the two components of the RSBR system was subjected to detailed investigation and the results are detailed in Part 2 of this report; 'Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa, Volume 4. The Rhodes BioSURE Process®. Part 2: Enhanced Hydrolysis of Organic Carbon Substrates - Development of the Recycling Sludge Bed Reactor' (Whittington-Jones *et al.*, 2002).

# 7 CONCLUSIONS

A number of conclusions may be drawn from the studies which have resulted in the development of the Rhodes BioSURE Process®.

1. Initial observations of enhanced hydrolysis of complex organic carbon substrates in biosulphidogenic environments have been followed up, and the broad effects confirmed in laboratory and pilot-scale studies. A descriptive model has been developed explaining the phenomenon in terms of reaction configuration and enzymatic effects. The establishment of dynamic sulphate reducing populations and sulphide gradients has been shown to enhance the activity of specific hydrolytic enzymes responsible for the breakdown and solubilisation of complex organic substrates such as PSS. Computer modeling of the RSBR operation has been undertaken;

2. The sulphidogenic hydrolysis reaction has been used in the conceptualisation and development of the Rhodes BioSURE Process® as a multi-stage operation in which complex organic carbon waste may be hydrolysed as an electron donor source. Sulphate reduction utilising the VFA intermediates produced is optimised in a separate unit operation with sulphide and alkalinity generated used to precipitate heavy metals and neutralise AMD streams. A biodesalination of the stream may be effected where the influent sulphate is removed as elemental sulphur. The core operations of solubilisation and sulphate reduction have been reported here and other units of the overall process will be detailed in separate reports in this series;

3. Reactor design, scale-up, pilot plant construction and operation and monitoring of the process treating AMD on-site at a gold mine over the period of a year has been reported;

4. The principles of the BioSURE Process® design were demonstrated in the pilot study with PSS solubilisation and COD mobilisation to VFA intermediates being the primary events taking place in the RSBR, and sulphate reduction and VFA consumption taking place in the second stage (R2) operation;

5. Enhanced hydrolysis of PSS in the RSBR was demonstrated with solubilisation values > 98% recorded here. Sludge accumulation in the RSBR was hence extremely slow and the reactor was not desludged during the study period;

6. A COD:$SO_4$ ratio of 2:1 was shown to provide an effective feed blend to the process where PSS is the electron donor source;

7. Notwithstanding a number of shock loads and a variable feed composition over the course of the study period, the system maintained a ~75% sulphate removal using PSS as the electron donor source;

8. It was demonstrated that rigorously maintained anaerobic conditions are necessary in the reactor headspace to prevent the re-oxidation of sulphide to elemental sulphur and sulphate. It was shown in nitrogen headspace sparging studies that the performance efficiency values recorded over the study period should be adjusted upwards by around 8-10%. Stable operation of the process with this adjustment demonstrated sulphate removal in the range of 80-85%;

9. It was shown, in addition to the above, that an increase in hydraulic residence time in the ABR would serve to increase sulphate reduction rates due to improved utilisation of VFA, and producing a potential sulphate removal ~90%. This indicates that while the ABR offers advantages of a low-cost reactor environment, it may not be the most efficient, and that other reactor configurations should be considered where more efficient throughput is required;

10. Using the HRAP in the final polishing operation, a microbiologically acceptable final effluent can be produced and infectious elements in the PSS feed effectively removed from the system.

## 8 RECOMMENDATIONS

A number of recommendations were made on the basis of the studies reported here:

1. Fundamental studies in the descriptive and quantitative modeling of the process should be continued in order to develop suitable kinetic criteria for the design of large-scale BioSURE Process® systems;

2. Follow-up studies on metal removal and sulphur recovery unit operations should be undertaken;

3. The observations of efficient PSS solubilisation should be followed up and possible application of the BioSURE Process® should be investigated in a sludge disposal application;

4. Application of the BioSURE Process® in the solubilisation of other organic wastes should be investigated.

## 9 RESEARCH PRODUCTS

A number of research products were generated during the course of the studies associated with the development of the BioSURE Process® including 7 PhD and 8 MSc theses, 7 patents, 1 paper, 2 reports, 11 international and 19 local conference presentations.

# 10 FOLLOW-UP ACTIONS

The initial observations of sulphidogenic enhanced hydrolysis, where complex organic carbon substrates were utilised as the electron donor source, led to the development of the RSBR and the sulphate reducing unit operations of the Rhodes BioSURE Process®. However, to effect a complete biodesalination function the final removal of the sulphate and metal loads from the wastewater stream is required. The development of the sulphide oxidation and sulphur and metal removal unit operations were tackled in a number of follow-up WRC projects. Follow-up actions have also included process development and modeling studies and applications of the principles of the BioSURE Process® in a number of areas.

## 10.1 Metal Removal

Studies reported in the ASPAM development had shown the feasibility of metal sulphide precipitation by recirculation of mixtures of the sulphidic organic stream from the sulphate reduction step with alkalised waters from the HRAP units. Follow-up studies on the processes involved in these reactions, and their potential application in process development were undertaken in collaboration with Prof Dick Loewenthal, Civil Engineering Department, UCT. These results will be the subject of a separate report.

The relationship of algal/sulphide metal precipitation reactions has also been the subject of studies by Prof John Duncan in the Department of Biochemistry, Microbiology and Biotechnology at Rhodes University. These will also be the subject of separate WRC reports.

## 10.2 Sulphide Oxidation and Sulphur Recovery

Final removal of sulphur species from the AMD wastewater requires the linearisation of the biological sulphur cycle and this may be effected by the oxidation to elemental sulphur of the sulphide produced in the RSBR. Development of a biologically-founded process for sulphur formation was investigated and based on the preliminary description of floating sulphur biofilms observed during studies on the microbial ecology of tannery ponding systems. This approach to biological sulphur formation was developed into a sulphide oxidising floating sulphur biofilm reactor (Appendix 3).

These studies were undertaken in WRC Projects K5/1078 and K5/1336 and will be detailed in Report 11 of the series, ‘Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa’. Volume 4. The Rhodes BioSURE Process®. Part 3: Sulphur Production and Metal Removal Unit Operations.

## 10.3 Modeling of the BioSURE Process®

Where the initial stages of BioSURE Process® development were founded in studies of microbial ecology, environmental biotechnology and bioprocess development, the reliable engineering of scale-up requires a quantitative basis for process modeling. Modeling studies were undertaken in collaboration with Prof Geoff Hansford and Dr Alison Lewis of UCT Chemical Engineering Department, and their students Neil Ristow and Anthony Knoble. Both AQUASIM and ASPEN approaches were undertaken in the modeling of the RSBR, and the results of these studies will be reported separately.

### 10.4 The Enzymology of Enhanced Hydrolysis

Studies on the mechanisms of enhanced hydrolysis of PSS, undertaken by Molepane (2000) and Whittington-Jones (2002), had shown the involvement of an interaction between sulphide gradients and enhanced enzyme activity. The studies became the subject of a follow-up study in the Environmental Enzymology Group, headed by Prof Chris Whiteley, in the Department of Biochemistry, Microbiology and Biotechnology at Rhodes University. Work by Drs Francois van Jaarsveld and Bret Pletschke has provided a theoretical model for the enzymology of enhanced hydrolysis. This work will be reported in WRC Project K5/1170.

### 10.5 Extension of BioSURE Process® Applications

Where the core insight of the BioSURE Process® involves the enhanced hydrolysis of complex carbon substrates to sustain active sulphate reduction, it became apparent that the reactions involved might be usefully related in other application areas. Full-scale commercial application of the Rhodes BioSURE Process® has become an important objective, and industrial partnerships to undertake this procedure have been established. The development of the Rhodes BioSURE Process® and the RSBR has been the subject of a number of patents (Appendix 2).

1. Follow-up studies in partnership with ERWAT have been undertaken applying the BioSURE Process® to sewage sludge solubilisation and disposal (WRC Project K5/1169).

2. The use of the enhanced hydrolysis reaction has been investigated in the mobilisation of lignocellulosic wastes to be used as electron donor sources in passive minewater treatment systems. The development of this approach is the subject of a Department of Arts, Culture, Science and Technology (DACST) Innovation Fund Project headed up by Pulles, Howard and De Lange Inc.

3. A study has been undertaken with ESKOM support to investigate the use of the BioSURE Process® mobilisation of maize wastes as electron donor sources in active systems treating coal mine wastewaters.

The above studies will also be the subject of independent reports.

# ACKNOWLEDGMENTS

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# ABBREVIATIONS

| | |
|---|---|
| ABR | Anaerobic Baffle Reactor |
| AFP | Advanced Facultative Pond |
| AMD | Acid Mine Drainage |
| ASPAM | Algal Sulphate Reducing Ponding Process for Acidic Metal Wastewater Treatment |
| BT | Blend Tank |
| COD | Chemical Oxygen Demand |
| $COD_f$ | Filtered COD |
| $COD_p$ | Particulate COD |
| $COD_t$ | Total COD |
| DACST | Department of Arts Culture Science and Technology |
| DEAT | Department of Environment and Tourism |
| DWAF | Department of Water Affairs and Forestry |
| EBG | Environmental Biotechnology Group |
| ERWAT | East Rand Water Care Company |
| FP | Facultative Pond |
| HDS | High Density Sludge |
| HRAP | High Rate Algal Pond |
| HRT | Hydraulic Retention Time |
| IAPS | Integrated Algal Ponding Systems |
| PFP | Primary Facultative Pond |
| PSS | Primary Sewage Sludge |
| RSBR | Recycling Sludge Bed Reactor |
| SHT | Sludge Holding Tank |
| SOB | Sulphide Oxidising Bioreactor |
| SRB | Sulphate Reducing Bacteria |
| SRT | Sludge Retention Time |
| SS | Single-Stage |
| TDS | Total Dissolved Solids |
| UCT | University of Cape Town |
| UD | Upflow Digester |
| UN | United Nations |
| VFA | Volatile Fatty Acids |
| WRC | Water Research Commission |
| WSP | Waste Stabilisation Pond |

# NOTATION

A wide range of terms has been used over the years by different authors to describe various configurations of ponding systems used in wastewater treatment and in algal biotechnology applications. This has created a certain confusion in the literature, and to avoid possible further confusion the following usage has been followed in this study:

1. The term Advanced Integrated Wastewater Ponding System (AIWPS) refers to a specific trade-marked process application design. This ownership of name has been respected and care has been taken throughout not to use the term in a generic sense to cover the many forms of integrated ponding systems involving the use of algal photosynthesis. The term Algal Integrated Ponding Systems (AIPS), and Integrated Algal High Rate Oxidation Ponding Process (IAHROP), which was used in this sense in the earlier part of this study to describe the hybrid algal ponding systems, the development of which was under consideration in this programme, has been changed to Integrated Algal Ponding Systems (IAPS) to avoid confusion;

2. The IAPS is used here to refer generically to combinations of ponding system unit operations involving an algal component in their operation;

3. The term High Rate Algal Pond (HRAP) has been used here and replaces High Rate Oxidation Pond (HROP) used in some literature references, as it is not necessarily inclusive of the algal component;

4. The terms algae or micro-algae are used for convenience in the more traditional sense, broadly covering both the eucaryotic algae as well as the cyanobacteria.

# 1 SALINITY, SANITATION AND MINE DRAINAGE WASTEWATERS

## 1.1 INTRODUCTION

The problem of a creeping salinisation of the public water system has been the subject of growing attention in South Africa over a period of many years (Commission of Enquiry into Water Matters, 1970; Stander, 1987; DWAF, 1989; DEAT, 1999, 2000), and the contribution of mine drainage wastewaters, especially in the salinisation of the Vaal River system, has been reported in numerous Water Research Commission (WRC) studies (Heynike, 1981, 1987; Schutte, 1983; Funke, 1990; Du Plessis, 1990; Pulles *et al*., 1995; Scott, 1995).

While slimes dams, rock heaps and sand dumps from gold mines, and also coal mines, have all contributed to the salinity problem, the major fraction of total dissolved solids (TDS) reaching the Vaal River has come from the dewatering of gold mine underground workings (Funke, 1990). Pyrite and arsenopyrites may constitute up to 9% of gold bearing ore bodies in the Witwatersrand (Funke, 1990), and the biological and physico-chemical processes giving rise to its oxidation, with acid formation and heavy metal solubilisation, have been well described (Kuenen and Roberstson, 1992; Robb, 1994; Johnson, 1995). The long-term implications of acid mine drainage (AMD) formation have been noted by Younger, *et al*. (1997), and flows of highly polluting waters may continue after mine closure for many decades to centuries.

Up to the 1950s, each of the Witwatersrand mines was responsible for its own dewatering. But as some were abandoned or closed, more and more pumping was left to the remaining mines, especially on the East and Central Rand Basins (Scott, 1995). By 1991 dewatering of the East Rand Basin was largely managed from the Sallies and Grootvlei Mines, and the Central Rand from the ERPM and Durban-Roodepoort Deep Mines. Historical evidence for substantial recharge of the underground system of workings from surface waters, including the Blesbokspruit and Florida Lake, meant that good water was being drawn into the system to be pumped out as bad (Scott, 1995).

The realisation that the final state of the mine water problem would ultimately have to be addressed at some stage following mine closure was noted as early as 1903 (Scott, 1995). It was an underlying assumption by many that when workings finally ceased, and the pumping stopped, this would signal the end of the mine water pollution problem. Mine flooding would cause water levels to rise to a sub-surface water table, and thereafter not only would further AMD production cease but, due to density stratification, existing low-grade waters would remain trapped in the lower void areas. Some, such as Dolan (1961), took the view that when water filling of the mines did actually become a problem it would be solved given the intrinsic ingenuity found in this country!

Scott (1995), however, investigated the flooding of the Central and East Rand gold mines and showed that not only would flooding on final closure be more rapid than formerly thought (around a decade on average), but that a stable steady head would not be established at a sub-surface level as originally thought. Instead, he predicted that due to hydraulic gradients mine waters would continue to rise and finally decant at the surface. In the case of the East Rand this would most probably occur at South East Shaft on the Central Rand, and No. 3 Shaft at Nigel. The total anticipated final discharge of mine water for the two systems could exceed 70 $ML.day^{-1}$ (Scott, 1995).

While the final quality of the discharged water is difficult to define, Scott (1995) has suggested it will be poor, and that the Kimberley Reef Basin, with a higher pyrite content than Main Reef ore, should be used as the indicator of the maximum level of degradation to be expected. Younger *et al*. (1997) have investigated AMD production in British mines, and reports ongoing AMD production following flushing may last anywhere from many decades to several centuries. The flushing phase, which has been estimated by Younger (2000) to last around four times the fill time, may be expected to bring to the surface water of extremely poor quality. Steep thermal gradients within the South African gold mines may ensure vertical mixing and thus a continued production of polluted waters. Furthermore the recharge of the dolomites, lying above the gold bearing deposits on the East Rand, with acid contaminated waters, has raised fears of karst formation, and the development over time of a sinkhole problem similar to that encountered in the Carltonville area (Scott, 1995).

The anticipated discharge of large volumes of highly polluted waters to the Vaal River system, over a possibly extended period of time (decades to centuries), has raised concerns relating to the treatment of this stream, and specifically to the long-term sustainability of the technologies applied. Among the options Scott (1995) has considered are allowing the water to decant at the surface, and then treating this where and when it happens. Alternatively continuation of pumping operations would hold the water level at 550 m below datum, to prevent its entering the dolomitic strata on the East Rand. This water would then be treated in a controlled manner at one site, and could be used to supplement scarce water resources. This would be an important consideration given the anticipated increase in water demand over the next 30 years of 220% for urban and domestic users, and 112% for the mining and industry sectors (DEAT, 1999). The National State of the Environment Report expects total abstractions will then amount to 58% of mean annual runoff, well beyond the 40% cut-off commonly used to indicate conditions of severe water stress (UN, 1997).

In either event, whether pumped or allowed to decant at the final hydraulic horizon, it is evident some form of remediation will be required. The mine Rehabilitation Bond system, which makes financial provision for mine closure, was never intended to handle a problem of this magnitude or time scale. Given the long-term nature of the problem, and the low levels of Rehabilitation Bonds (Walmsley, 1995), it is apparent that the ultimate responsibility and the final costs of treatment will become a charge likely to fall to the community at large.

## 1.2 GROOTVLEI MINE - A CASE STUDY

The dolomitic strata above the East Rand Basin are intersected by Grootvlei Mine on both sides of the Blesbokspruit. Pumping to maintain mine workings has increased from around 24 ML.day$^{-1}$ in the late 1980s (Funke, 1990) up to 136 ML.day$^{-1}$ by the mid-1990s, in order to prevent flooding of its underground workings. With an increasing burden of pumping falling on this mine the quality of the water has also deteriorated with pH values between 4.6 and 6.7; TDS 2455 - 3671 mg.L$^{-1}$; sulphate 1379 - 2293 mg. L$^{-1}$; iron 158 - 386 mg.L$^{-1}$ and temperatures up to 27 °C (Grootvlei Mine, 1997).

As a result of these levels of discharge, water levels have risen in the Blesbokspruit, a recognised Wetland of International Significance under the Ramsar Convention, and also large deposits of iron oxide have appeared downstream of the discharge outlet. A study of the system (Walmsley, 1995), undertaken to investigate the environmental and economic impacts of continued high volume dewatering, reported the following:

- The heavy metal and salt loadings, and the predicted elevated winter temperatures, would likely have a significant impact on benthic fauna, amphibians and fish. This would manifest as a reduction in the populations of these fauna, and would also affect the overall productivity of the wetland;

- Prey reduction for piscivorus species would have serious impacts on 75% of the bird species, with the loss of rare species such as the Little Bittern and the Yellow Billed Stork. In contrast higher salt loading would encourage increased numbers of the Greater Flamingo. The wetland's use by a large number of ducks had already been discontinued;

- Further loss of bird species would impair the wetland's recreational value;

- Substantial impacts on downstream agriculture were likely with long-term salinisation of lands currently under irrigation. In poorer drained soils this would likely manifest in the following 5-6 years;

- The landscape and the vegetation of the wetland would not be significantly affected.

In contrast, the effects of stopping the dewatering pumping operations, and the immediate consequent mine closure, would have a number of impacts including:

- The foreclosure of any future mining activities, particularly in the Kimberley Reef Basin with substantial remaining reserves;

- Loss of employment due to retrenchments of 4266 jobs;

- A serious depression of the East Rand economy;

☐ Costs to the mine owners, the State, and indirect costs to the economy, would amount to R422 million.year$^{-1}$ at 1995 costs.

In early 1996, and following a failure to reach agreement on the terms of the Mine's permit to pump water to the Blesbokspruit, the Minister of Water Affairs and Forestry ordered shutdown of the dewatering pumps. After two weeks, and the threatened flooding of the No 3 Shaft pump station, the order was rescinded following an agreement by the mine to construct a High Density Sludge (HDS) lime treatment plant to remove metals and neutralise the mine water before its discharge to the Blesbokspruit. Among a number of further recommendations considered by Cabinet in February 1997, was that it be an obligatory requirement of the permit to discharge to the Blesbokspruit that the mine undertake a desalination technology evaluation exercise to determine 'best available technology' to deal with the salinity problem. Suppliers were to be invited to submit proposals, undertake pilot studies to be completed by 1 September, 1997, and be ready to supply, construct and commission a full-scale plant before 1 December, 1999 (Van Wyk and Munnik, 1997). Other issues that were to be investigated included the control of impacts on the wetland, the disposal of desalination brines and sale of potable water. It was noted that Rand Water (the regional water utility), and the East Rand Watercare Company (ERWAT) (the major utility treating industrial and domestic wastewaters on the East Rand), were to be approached as potential operators of the desalination plant.

## 1.3 THE RHODES ENVIRONMENTAL BIOTECHNOLOGY GROUP

At this time the Environmental Biotechnology Group (EBG) at Rhodes University was commencing a pilot study of a novel sulphate saline wastewater treatment system which became known as the Rhodes BioSURE Process®. This study, which was to be located at the Bickley Sewage Works at Nigel, near Springs on the East Rand, was to evaluate previous findings at scale-up which had shown that an enhanced hydrolysis of complex organic carbon wastes in sulphidogenic environments could be successfully used as electron donor sources to support high rates of sulphate reduction. In addition to sewage sludge, tannery wastes from the Seton Leathers tannery in Nigel were also to be investigated.

This process development exercise followed studies in saline biotechnology which commenced at Rhodes University in the mid 1980s, and had become the subject of the Water Research Commission (WRC) programme 'Salinity, Sanitation and Sustainability' commencing in 1990 (Rose, 2002a). These studies had focused initially on IAPS for treating tannery wastewaters containing high levels of organic material, sulphate and heavy metal contamination. Results in these Integrated Algal Ponding Systems (IAPS) studies led to an investigation of ponding systems for the treatment of large AMD flows and development and patenting of the Algal Sulphate Reducing Ponding Process for Treating Acid and Metal-containing Wastewaters - (ASPAM) (Rose *et al.*, 2002b). These developments are noted below and described in detail in Report 6 'Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa. Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters. Part 3: Mine Drainage Wastewaters - The ASPAM Model' (Rose *et al*., 2002b).

## 1.4 TREATMENT OF SULPHATE SALINE WASTEWATERS

The AMD problem and sulphate salinisation of mine drainage has been the subject of considerable research focus by the mining industry over a period of many years (Pulles *et al*., 1995), and both physico-chemical and biological process have been investigated in the treatment of these wastewaters. While chemical precipitation and membrane-based desalination processes may be highly engineered and efficient, they tend to be expensive and require skilled and costly operational controls. The disposal of reject brines also presents a problem on which little real progress has been made. Buckley *et al*., (1987), have noted that the lack of provision of adequate methods for brine disposal has rendered the authorities responsible for pollution control powerless to enforce the desalination of saline effluents, despite legislation available to do so.

Biological approaches to AMD treatment have been the subject of increasing interest, and have been extensively reviewed by Kuenen & Robertson (1992); Gadd & White (1993); Barton (1995) and Johnson (1995). Most process developments have focussed of the role of the Sulphate Reducing Bacteria (SRB) in sulphate reduction, the associated precipitation of metal sulphides, and acid neutralisation reactions. However, the biological production of sulphide also presents the opportunity for its oxidation and removal as elemental sulphur under controlled conditions (Scheeren, *et al*., 1993). The biodesalination of sulphate wastewaters thus produces a 'clean' and useful end product, and avoids the brine concentrate dilemma. However, the cost of the carbon source (mainly ethanol and hydrogen gas have been used), and the size of the reactors needed to treat large volume flows, have been largely responsible for constraining commercialisation of these process developments (Rose *et al*., 1998).

The studies outlined in this report on the development of biological processes in the treatment of AMD were undertaken against the background of the unfolding minewater problems described above. Studies in the microbial ecology of tannery wastewater stabilisation ponds (WSP), undertaken by the EBG in WRC Project K5/495, had produced unexpected research findings relating to the enhanced hydrolysis of complex organic carbon compounds in biosulphidogenic environments (Rose *et al*., 1998). While the treatment of sulphate saline tannery wastewaters using IAPS had been the principal focus of this investigation, it was shown that these organic wastes may be used as carbon and electron donor sources by microbial consortia including SRB populations. These findings contributed, not only to an understanding of the performance of natural sulphidogenic systems, but also provided the stimulus to investigate bioprocess applications in the treatment of sulphate saline wastewaters, on which the studies reported here are based.

### 1.4.1 Integrated Algal Ponding Systems

The EBG had commenced the WRC-sponsored study 'Salinity, Sanitation and Sustainability' in 1990, on the research and development of an integrated approach to the management of salinity and sanitation problems utilising algal ponding systems

(WRC Project K5/495 'A Biotechnological Approach to the Removal of Organics from Saline Effluents'). The study of the microbial ecology of these systems had been undertaken as a component part of an exercise to develop the application of IAPS to tannery effluent treatment (Rose *et al*., 1996; 2000a; Dunn, 1998). The study, at Mossop-Western Leathers tannery in Wellington (Western Cape Province), and at the Leather Industries Research Institute (LIRI) in Grahamstown, resulted in the development and construction of a pilot, and then a full-scale, IAPS system on-site at the tannery (Figure 1.1). Technical-scale IAPS had also been constructed by the EBG for the treatment of domestic wastewaters (WRC Project K5/ 651), abattoir wastewaters (WRC Project K5/658), and winery and distillery wastewaters (WRC Project K5/1073). Project details are noted in Appendix 3.

**Figure 1.1**. The Waste Stabilisation Pond evaporative disposal system treating tannery wastewaters at the Mossop-Western Leathers Co. Wellington. This installation was retrofitted to include the IAPS design.

The IAPS development in Wellington involved the retrofitting of the WSP and included the establishment of a Primary Facultative Pond (PFP), and a 2500 m$^2$ High Rate Algal Pond (HRAP), sustaining the production of micro-algal biomass, principally *Spirulina* sp. The harvesting of the *Spirulina* biomass has been subsequently commercialised for aquaculture rations production, and this development is described in Rose *et al*., (2002a).

An observation was made during this study of the near complete solubilisation of the particulate organic solids entering the PFP. This was particularly significant given the previous tendency of these ponding systems to fill over time with the build-up of undigested solids sediments. Further investigation showed the establishment of a sulphuretum-type behaviour in the PFP providing a complete sulphur cycle with both sulphate reducing and sulphide oxidizing environments, below and above an oxypause at about 0.5 m (Figure 1.2). The complete reduction of sulphate entering the anaerobic compartment (~1500 mg.L$^{-1}$), and the removal of equivalent COD values indicated high rates of SRB activity (Dunn, 1998).

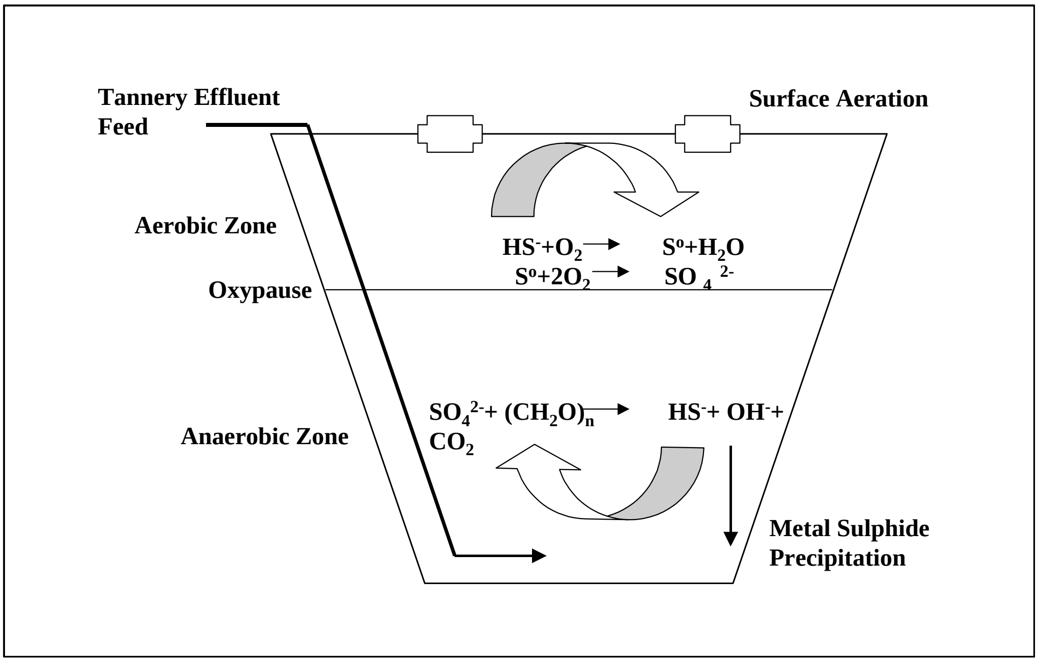

**Figure 1.2.** A cross sectional illustration of the sulphuretum-type behaviour of the Facultative Pond treating tannery wastewaters at the Mossop Western Leathers Tannery in Wellington, RSA. A full sulphur cycle from complete sulphate reduction to nearly complete sulphide oxidation in the upper aerobic compartment is sustained by the complex organic carbon waste stream.

Contaminating heavy metals were precipitated as metal sulphides in the PFP, and the residual sulphides were largely reoxidised in the upper aerobic compartment. The role of biosulphidogenic activity in the enhanced hydrolysis and solubilisation of complex organic carbon substrates became the subject of a follow-up investigation, and a basic input into the development of the Rhodes BioSURE Process® described below. These studies also led directly to the investigation of a ponding systems approach to AMD treatment.

### 1.4.2 ASPAM Process in AMD Treatment

Although it has been known that WSP support SRB activity (Pescod, 1996), and that sulphate reduction processes may be associated with severe odour production in ponding systems, the use of IAPS in the treatment of high sulphate saline AMD streams has not been previously reported (Rose *et al*., 1998).

However, the potential use of these systems in AMD treatment, particularly for large volume flows, may be supported by a number of observations:

❑ The linkage between the treatment of large volumes of wastewaters, and mass algal production, has been firmly established as a mature and widely utilised operational technology. Both WSP and integrated system applications have developed (Oswald, 1988a; Mara *et al*., 1996);

❑ The earthwork pond provides a reactor at least an order of magnitude less costly to construct than steel-reinforced concrete vessels (Oswald 1995);

❑ Renewable algal biomass as a potential carbon and electron donor source for SRB activity may be reliably produced in large amounts (up to 50 tons.ha$^{-1}$.yr$^{-1}$), in separately optimised HRAP systems (Oswald 1988b);

❑ The ability of algal biomass to alkalise acidic wastewaters, and to adsorb and sequester heavy metals, and thereby reduce metal concentrations to residuals in the ppb range, has been demonstrated and commercialised (Wilde & Benneman 1993).

Against the background of a growing awareness of the extent of the AMD problem to be managed in both coal and gold mines in South Africa, a 3 year WRC-sponsored study (Project K5/656) was undertaken by the EBG in 1995, to evaluate the feasible development of IAPS in AMD treatment. The Wellington studies had indicated the potential value in linking co-disposal of complex organic waste streams with AMD treatment, and that an enhanced hydrolysis of complex organic carbon could provide cost-effective substrates for SRB-based remediation systems. Utilisation rates comparable to those reported for refined carbon substrates such as ethanol and lactate could be considered (Rose *et al*., 1998).

The study on an IAPS-based application in AMD treatment commenced in 1995, and following an investigation of the unit operations involved at both laboratory- and pilot-plant scale, the project resulted in the development of the ASPAM process (Rose *et al*., 2002b).

The development of the ASPAM system led directly to the conceptualisation of the Rhodes BioSURE Process®, and will be described in some detail (Figure 1.3). The system consists of the following unit operations:

### 1. Advanced Facultative Pond

At (1) a portion of the treated water flows into the Advanced Facultative Pond (AFP) together with the carbon source which may include a range of organic wastes. Recirculation of algal-laden waters from HRAP 2 is used to maintain an oxygenated layer on the surface of the AFP and thus control sulphide gas release.

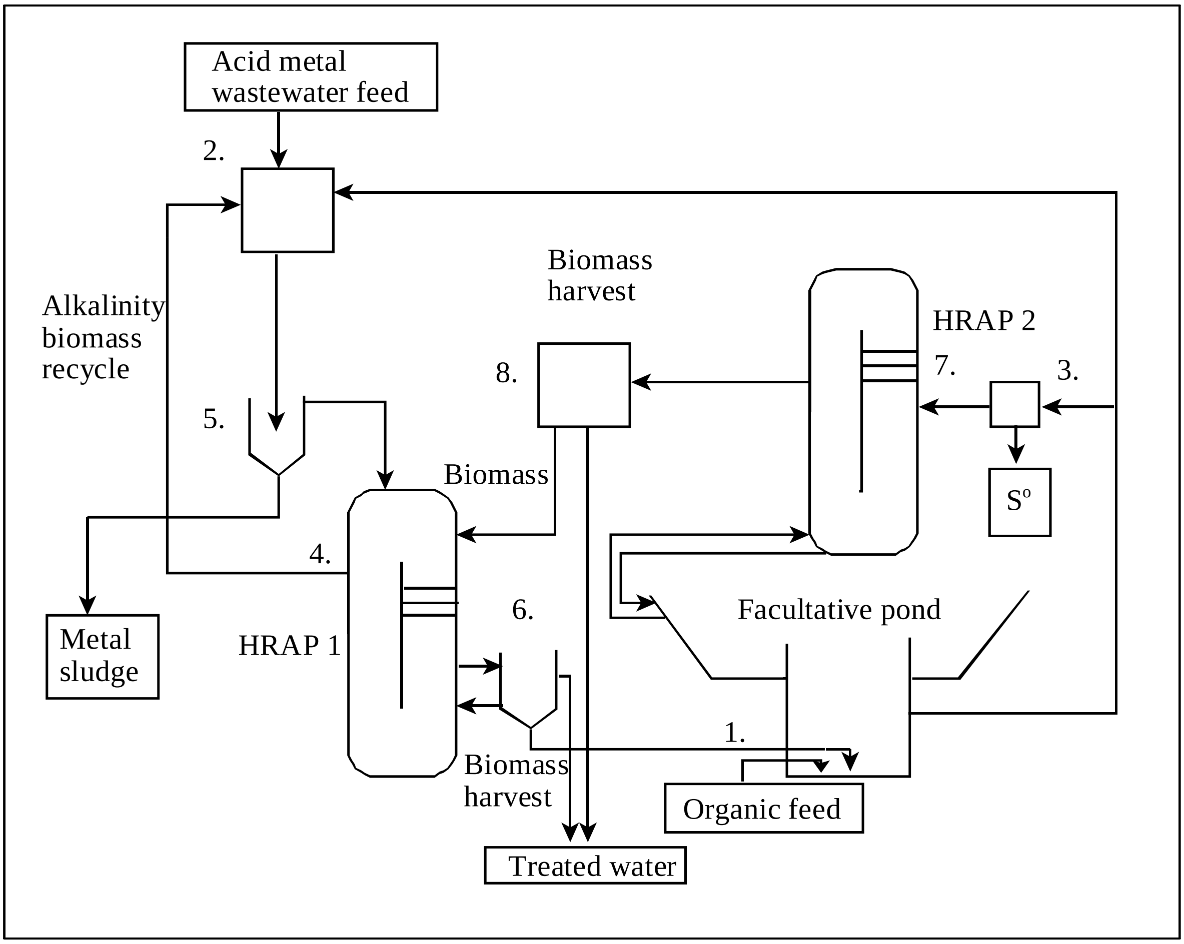

**Figure 1.3**. Flow diagram of the individual unit operations of the Integrated Algal Sulphate Reducing Ponding Process for Acid Metal Wastewater Treatment (ASPAM). Organic feed enters at 1= Facultative Pond with anaerobic upflow digester compartment; Feed water enters at 2 = Inlet and metal precipitation unit; Sulphide is recycled to metal precipitation unit from 3 = sulphide recycle and sulphur recovery unit; Alkalinity and algal biomass generated in High Rate Algal Pond (HRAP)1 recirculated via 4; 5 = Metal sludge settler; 6 = Algal biomass settler; 7 = High Rate Algal Pond (HRAP)2 for capping the Facultative Pond and seeding HRAP 1 with fresh biomass; 8 = Algal biomass harvester.

The AFP described by Oswald (1998 a&b), provides for the inclusion of one or more Upflow Digesters (UD) in the base of the pond, enabling optimum anaerobic digestion function. Tannery pond studies in Wellington, South Africa, had shown that sulphidogenic anaerobic digestion will perform efficiently utilising tannery waste as an electron donor source. High rates of sulphate reduction were observed to be associated with an accelerated hydrolysis and solubilisation of particulate organic matter fed to the system. An associated precipitation of heavy metals was also observed in this unit with low residual metal levels in the effluent (Dunn, 1998).

The maintenance of an aerobic compartment above the anaerobic layer was shown in the tannery IAPS not only to provide for odour control, with the scrubbing of released gasses, but also to ensure that the sulphur cycle was completed above the oxypause, with a nearly full oxidation of sulphide back to sulphate (Rose *et al.*, 1996).

Objectives identified for the current study included an evaluation of the performance of a sulphate reducing anaerobic pit in the AFP, operating as an Upflow Digester (UD), and also the performance of a number of organic carbon sources, other than tannery waste, as electron donors for sulphate reduction.

## 2. Metal Precipitation Operation

Sulphide-rich waters pass from (1) to the metal precipitation unit operation (2) where, in mixing with the influent AMD stream, a combination of metal complex formation reactions would occur. Effective precipitation of heavy metals in the sulphidogenic tannery wastewater AFP had been reported by Boshoff (1998) and Dunn (1998), and the relative advantages of metal precipitation as the sulphide compared to metal hydroxide forms has been widely noted (Peters and Ku, 1985; Singh, 1992 and Hammack *et al*., 1994). Dunn (1998) had reported preliminary observations on both the *ex situ* precipitation of metals utilising the sulphide-rich AFP liquors in the tannery IAPS, and also their removal in the presence of algae in the HRAP. Both systems demonstrated strong alkalising properties with the influent pH elevated to values between 9 and 10, at the end of the ponding cascade.

The objective of this component of the study was to investigate the feasibility of utilising both the micro-algal and sulphidic AFP streams in a metal precipitation unit operation, providing primary treatment of the influent AMD stream. Following the formation of a metal complex precipitate, and the removal of the major portion of the metal contaminants from the influent stream, the metal residuals would be stripped and the effluent finally polished during the subsequent stages of HRAP operation.

The stripping of sulphide gas from the pond liquors, and its use directly for metal removal in the precipitation unit, is an added option, but has not been further considered in the study reported here.

## 3. High Rate Algal Pond 1

Following the removal of metal sludges, the partly neutralised AMD passes to HRAP 1 (4). Here photosynthetically-driven alkalisation would be optimised and final metal removal effected by micro-algal biosorption.

The observations of the alkalising and metal binding properties of micro-algae in the tannery IAPS had been investigated by Boshoff (1998) and Dunn (1998). These had indicated the need for the inclusion of HRAP 1, following preliminary metal removal and prior to the stream entering the AFP. The relatively high pH minima of the bio-sulphidogenic system in the AFP makes the neutralisation of the acid stream essential to the operation of this unit. Neutralisation may be handled by both feeding HRAP 1 liquors forward to the precipitation unit, and through *in situ* alkalisation in the raceway itself. Physiological stress in this unit may be expected to depress micro-algal growth rates. In this regard it would be important to maintain biomass against washout by replacement with algae recovered from HRAP 2 (8), prior to discharge of the final treated stream.

4. High Rate Algal Pond 2

At (7) a portion of the AFP surface water circulates through HRAP 2 where a high concentration of algal biomass is maintained. This is used for recirculation and capping of the surface of the AFP to contain sulphide release, and for constant biomass replenishment to HRAP 1, in which a stress reduction of growth rates would be anticipated.

The performance of the biomass recycling and pond capping operation has been investigated in the tannery IAPS (Rose *et al.*, 2002a) and the Grahamstown AIWPS studies (Rose *et al.*, 2002b).

Issues which needed to be clarified in this study included an evaluation of the potential toxicity of sulphide production in the AFP on the micro-algal biomass circulated from HRAP 2. The Wellington study had shown that the HRAP following the AFP in that system had been able to handle a limited level of sulphide throughput (Dunn, 1998), but this had not been quantified.

5. Treated Water

At (6) the main flow of treated water exits the system from HRAP 1. This follows harvesting of the algal biomass, and together with a portion of treated water the biomass passes into the AFP where the organic carbon feed requirement is supplemented.

The use of algal biomass as a carbon source for sulphate reduction in AMD treatment was studied by Boshoff (1998). Photosynthetic production within the system would not only contribute to the organic carbon requirement, but in small installations might provide an independence from external carbon sources.

6. Sulphur Recovery and Biodesalination

A portion of the total sulphur load entering the system would be removed with the metal sulphide sludge. Where a more complete sulphate removal is required a biodesalination of the AMD may be achieved by passing the reduced AFP waters through a sulphur recovery unit (3). Here elemental sulphur ($S^o$) will be a final by-product of the process. Sulphide oxidation and sulphur recovery is the subject of separate WRC Projects K5/1078 and K5/1336 (Appendix 1).

## 1.5 PROJECTS K5/869 AND K5/972

During the development of the ASPAM system further studies were undertaken investigating the phenomenon of enhanced hydrolysis in biosulphidogenic environments (Rose *et al.*, 2002b). The effective use of a number of complex carbon substrates was demonstrated in the treatment of both tannery and AMD sulphate saline effluents, and the feasibility of an extensive low-cost approach to treating large AMD volume flows had been demonstrated. This appeared to offer the possibility of a sustainable alternative to highly engineered systems, using costly electron donor sources, especially where treatment would be needed over very long periods of time. Scale-up development of these findings, in the treatment of AMD, was incorporated into two follow-up WRC projects to be undertaken by the EBG:

2. Project K5/869: 'Biological sulphate desalination and heavy metal precipitation in industrial and mining effluents using the Integrated Algal Ponding System';

3. Project K5/972: 'Process development and system optimisation of the Integrated Algal Trench Reactor Process for sulphate biodesalination and heavy metal precipitation in mining and industrial effluents'.

These projects were planned to undertake further process development of the ASPAM system, and a scale-up pilot plant process evaluation exercise was proposed for construction at the Bickley Sewage Works in the Nigel area. Tannery effluent and AMD, in addition to sewage sludge were available close to site. A more fundamental study of the biosulphidogenic enhanced hydrolysis phenomenon was also to be undertaken, continuing studies already underway in Project K5/656, and with the objective of underpinning the process development exercise to be undertaken.

These studies commenced in 1997, and focused initially on the development of reactor designs in which the enhanced hydrolysis reactions might be optimised. This took place against the background of the Grootvlei incident, and later that year the EBG was invited to participate in the desalination technology evaluation exercise noted earlier. At this time it was decided to shift the focus of the Project 869/972 study to Grootvlei Mine, and to concentrate on AMD treatment using only sewage sludge as the electron donor source. The participation of ERWAT was agreed, and PSS was to be provided from their Ancor Works nearby.

The above developments influenced the decision to refocus the research objectives outlined in the original research proposal, and it was agreed that the fundamental and process development studies, involved in Projects 869 and 972, would be handled together. While this phase of the study concentrated on the sulphate reduction stage of the desalination exercise, the metal precipitation and sulphide oxidation unit operations were to be undertaken as subsequent research projects. This work will be reported separately in Project K5/1078.

## 1.6 RESEARCH OBJECTIVES

The following revised research objectives were identified:

1. To expand studies undertaken in elucidating the reaction mechanism involved in the phenomenon of biosulphidogenic enhanced hydrolysis of complex carbon substrates;

2. To evaluate reactor design options in which the enhanced hydrolysis reaction may be applied in the treatment of AMD;

3. To undertake scale-up development of the AMD biodesalination process using complex carbon substrates as the electron donor source for SRB-driven sulphate reduction;

4. To undertake process evaluation at pilot-scale treating an authentic AMD stream;

5. To establish the technical feasibility of a linkage between AMD treatment and PSS co-disposal, and to demonstrate a basis for technological and environmental sustainability in the long-term management of these waste streams.

# 2 DEVELOPMENT OF THE RHODES BioSURE PROCESS®

While empirical observations of sulphate reduction efficiencies achieved in the Wellington tannery IAPS and the ASPAM studies were encouraging, it was evident from the outset that the mechanism underlying the observations of enhanced biosulphidogenic solubilisation of complex organic substrates was poorly understood. Further development of the process would depend in large measure on an improved understanding of the fundamental mechanisms involved. This insight underpinned the WRC decision to pursue a two-pronged approach in follow-up investigations. The technology scale-up evaluation programme would run together with a more fundamental investigation of the biological and physico-chemical processes underlying the phenomenon of biosulphidogenic enhanced hydrolysis.

These studies resulted in the development of what subsequently became known as the Rhodes BioSURE Process®. The process development studies are described in this report (Part 1) and the details of the enhanced hydrolysis studies are covered in Part 2.

## 2.1 ENHANCED HYDROLYSIS

It had been noted in the tannery pond study (Dunn, 1998), in both the retrofitted PFP and the shallower evaporation ponds (Figure 1.1), that reciprocal settling and upwelling of particulate organic carbon COD fractions (CODp) served to counteract mass transfer limitations between the water column and the sediment. This movement of CODp through sulphide gradients, established in these systems, seemed to play an important role in their breakdown into smaller sized fractions and ultimately in their biodegradation. Particlulates not subjected to this passage became compacted into sediments which were sulphate mass transfer limited, and remained largely undegraded. This would lead to sludge build-up, a notorious problem in these systems. These findings are described in Figure 2.1a.

The observations of enhanced hydrolysis of CODp in the recycling biosulphidogenic pond environment were subjected to more detailed study by Jennifer Molepane (MSc, 2000) and Kevin Whittington-Jones (PhD, 2000). The Recycling Sludge Bed Reactor (RSBR) was conceptualised as a laboratory system in which the events observed in the ponds might be modeled and subjected to more rigorous investigation (Figure 2.1b).

In these studies the reactor was fed a mixture of primary sewage sludge (PSS) (as a convenient source of particulate organic carbon), and synthetic AMD as the sulphate source. The headspace was sparged with nitrogen gas to maintain anaerobic conditions. High rates of sulphate reduction were observed in the sludge bed, and Whittington-Jones (2000) was able to demonstrate a clear particle size reduction in the RSBR. Gradients of increasing sulphide concentration, alkalinity and sludge

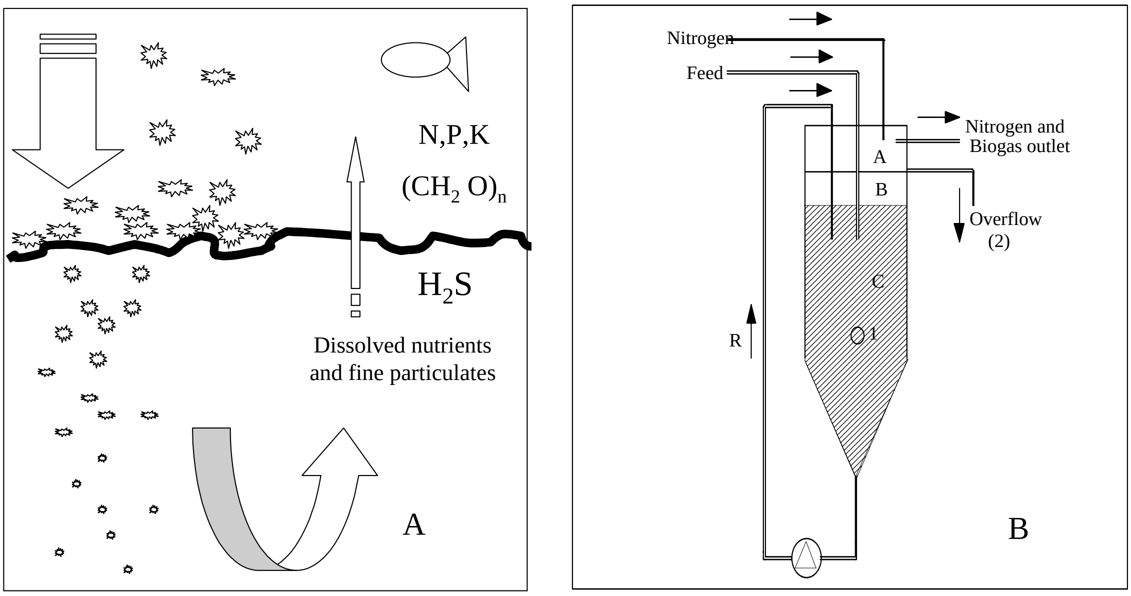

**Figure 2.1.** The breakdown and solubilisation of particulate organic matter in sulphidogenic settlement and sedimenting processes observed in natural systems (A). This was simulated in a 1L prototype study (B) of the Recycling Sludge Bed Reactor. The degrading sludge is returned via line R to blend with the incoming feed.

density were associated with a reduction in particle size, and an increase in the filtered COD fraction (CODf). On recycle to blend with the incoming stream the larger remaining settleable particulate solids returned to the recycling bed, while the solubilised fraction passed out of the reactor.

This seemed to correspond to Dunn's (1998) observations in the WSP sediment/water column. Where SRB largely use small organic molecules, such as volatile fatty acids (VFA) and alcohols as electron donors, it was assumed that the now solublilised fraction of CODf would become available in this way to sustain the high rates of sulphate reduction observed in the anaerobic compartment of the pond water column.

This hypothesis was tested in a multi-stage configuration of the RSBR (Figure 2.2). Studies in this unit showed increasing enzyme activity to be associated with the increasing sulphide gradient within the bed. It also largely confirmed the proposition that the recycling bed was responsible for the movement of particles through a gradient of changing sulphate, sulphide, alkalinity and enzyme activity levels. These factors were in some way responsible for the enhanced hydrolysis of particulates which had been observed. This view was further strengthened by the results of a series of *in vitro* studies which are described in detail in Part 2 of this report series (Whittington-Jones *et al*., 2002). Where hydrolysis occurred mainly in the first unit, its consumption in sulphate reduction was completed in the second stage and it was shown that a minimum of 52% CODp entering the RSBR must have been solubilised to its readily available form. This value exceeded previously published values by about 20%. These studies suggest that optimisation of the enhanced hydrolysis and sulphate reduction reactions would be best effected in separate unit operations.

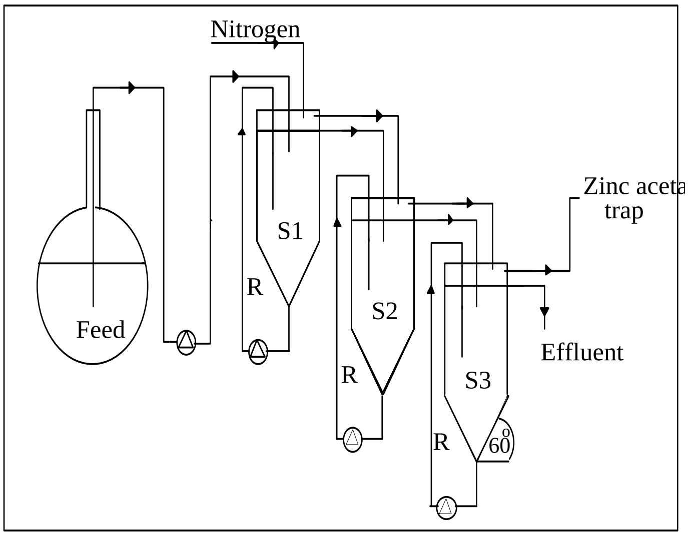

**Figure 2.2.** The 3-stage Recycling Sludge Bed Reactor used to investigate the solubilisation of primary sewage sludge and its subsequent use as an electron donor source in sulphate reduction activity.

## 2.2 The Recycling Sludge Bed Reactor

Development of AMD biodesalination, and the use of complex carbon compounds as low-cost electron donor sources, had been investigated and reported by Boshoff (1999) and Molepane (2000), and pilot studies had been scaled from 1L, through 10L bench units, to a 1 $m^3$ pilot plant using PSS and tannery effluents. A standard UD design had been used for these units, which had been located at the EBG Experimental Field Station in Grahamstown, and on-site at Seton Leathers tannery in Nigel (Rose *et al.*, 2000b).

On the basis of the above findings work then commenced on the scale-up of the 2L RSBR in order to investigate optimisation of the hydrolysis reactions. This commenced with the construction of a 10 L perspex bench-scale unit and was configured on the basis of the three vessel reactor design described above. The three recycling reactor functions were incorporated into a single vessel as shown in Figure 2.3. Provision was made for sludge concentration and collection in three sedimentation valleys, and its recycle to blend with the influent stream. The residual settleable CODp would fall to a second passage through the sludge bed. The solubilised organic fraction would pass out of the reactor to be utilised for further sulphate reduction in a second stage unit operation.

A mixture of PSS and synthetic AMD was fed to the system and the resulting sludge bed differentiated into an expanded upper, and a more compacted dense lower form. The design for the RSBR was then scaled-up with the construction and operation of a 1 $m^3$ unit.

The above studies showed that the hydraulic retention time (HRT) of the RSBR might be manipulated in such a way that the hydrolysis event would mainly occur in this unit, and that the effluent, while showing a 95% to 98% reduction in settleable solids, would contain primarily un-utilised hydrolysis products. This finding suggested the use of a dual stage process, in which sulphate reduction, commencing in the first stage hydrolysis process, would be completed in a second stage, and the two operations could be separately optimised.

While it seemed that any suitable reactor could be used in the second stage of the operation, the Anaerobic Baffle Reactor (ABR) configuration was used as it offered advantages of quasi-passive operation. However, sludge recycling was found to be necessary and draining valleys were fitted to the base of each chamber of the ABR to provide for this function (Figure 2.3).

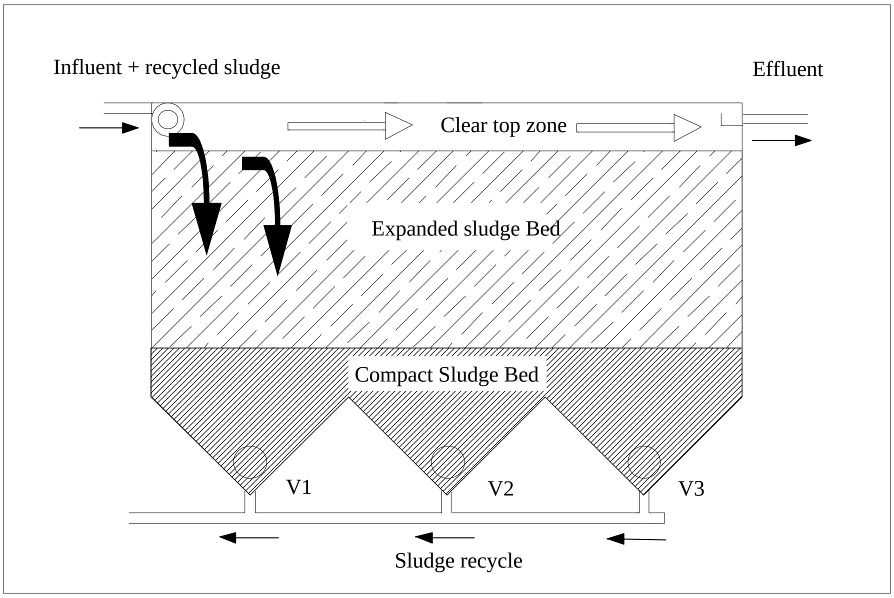

**Figure 2.3.** The Recycling Sludge Bed Reactor showing the segregation of settled sludge, the recycle of the sludge bed to blend with the incoming flow, and the supernatant liquid carrying the solubilised product to the second stage in the BioSURE Process®.

## 2.3 BIOSURE PROCESS® CONFIGURATION

A dual-stage sulphate reduction operation was thus conceptualised on the basis of the 10L and the 1 $m^3$ RSBR studies undertaken at the EBG Experimental Field Station in Grahamstown. The process flow diagram is shown in Figure 2.4 and involves the following individual operations:

1. The influent AMD stream is mixed with alkaline sulphide-rich effluent from the ABR (R2 ). A metal sulphide precipitate strips the major fraction of the heavy metal load in the influent stream before it passes to the RSBR (R1);

2. The electron donor and carbon source (PSS in these studies), is added to the stream following metal precipitation, and before it enters R1. In this unit the initial sulphate reduction and enhanced hydrolysis reactions are optimised, solids are drawn down into the reactor bed, and sludge is continuously settled and recycled to blend the with the incoming metal-stripped AMD feed. The solubilised product passes to R2;

3. Sulphate reduction is optimised in R 2. The ABR provides a quasi-passive reactor configuration where the consumption by SRB of the different hydrolysis products may be self-optimised with the establishment of different physiological groups in each compartment. Microbial population studies would be needed to demonstrate this point;

4. The sulphide stream passes to a Sulphide Oxidising Bioreactor (SOB) where the now reduced sulphates are removed as elemental sulphur, thereby achieving the partial biodesalination of the AMD stream;

5. Following treatment, the neutralised stream passes finally to a polishing unit (an HRAP was used in this study), where residual sulphides may be oxidised, remaining metals adsorbed, and the stream disinfected prior to final discharge of the treated water.

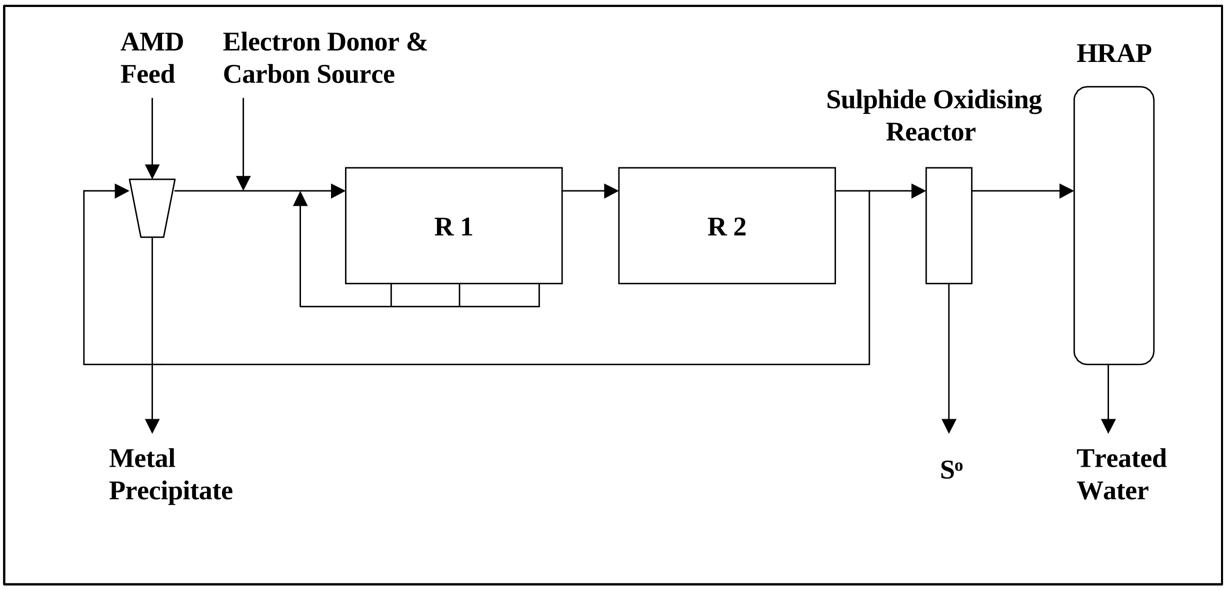

**Figure 2.4.** Process flow diagram of the Rhodes BioSURE Process® applied to the treatment of acid mine drainage wastewater. R1 = Recycling Sludge Bed Reactor; R2 = baffle reactor; HRAP = High Rate Algal Pond; PSS = primary sewage sludge. A side stream of sulphidic wastewater is blended with incoming minewater to precipitate contaminating heavy metals. The carbon source is added to the metal-free stream which passes to R1 where hydrolysis of particulates and some sulphate reduction occurs. The dissolved organic stream passes to R2 where it is used as feedstock in the final sulphate reduction step. The treated water is then discharged via a Sulphide Oxidation Reactor producing elemental sulphur, and finally through an HRAP polishing step.

# 3 PILOTING THE BioSURE PROCESS®: DESIGN, CONSTRUCTION AND OPERATION

Towards the end of 1997, while the work described above was still ongoing and pilot studies were being planned in Nigel for the following year, the EBG was invited to participate in the Grootvlei desalination technology evaluation exercise. The time-frame for the completion of the first phase of this undertaking had been shifted into 1998, and a decision was made to proceed directly to the design and construction of the Rhodes BioSURE® Pilot Plant, to enable participation in this exercise.

This stage of scale-up was undertaken while both laboratory and small-scale piloting studies continued at the EBG Experimental Field Station in Grahamstown. Supporting studies underpinning an understanding of fundamental aspects of the process also continued concurrently, and are outlined in Part 2 of this report (Whittington-Jones *et al*., 2002).

## 3.1 DESIGN

The decision was made to design and construct the pilot plant on the basis of a 10-20 fold scale-up of the 1 $m^3$ RSBR and ABR studies. Given the provisional nature of experience with the new system, the design and construction of the pilot plant was likely to be an iterative process involving both research and engineering inputs. The decision was thus made to construct the pilot plant in Grahamstown, using locally available materials, pumps, fittings etc., and then to transport it to site following preliminary hydraulic testing. These requirements influenced both the choice of materials used, and final design of the system (Figure 3.1).

Both the RSBR and the ABR were to be constructed from 6 m steel shipping containers (volume 30.4 $m^3$ prior to modification). These were adapted as illustrated in Figure 3.2, to provide sedimenting valleys for sludge collection, and to facilitate recycle as required. Following modification, the liquid volume of the RSBR and ABR were 23 $m^3$ and 25 $m^3$ respectively.

The RSBR was divided into three contiguous sections of equal size, with the lower 1m of each section forming a separate sludge collection valley. The valleys were constructed by welding 10 mm mild steel plates into the base of the container at 45° angles. A slotted sludge withdrawal pipe was fitted transversely across the base of each valley and connected to the reactor feed line. The RSBR effluent was collected over a crown weir from where flow was by gravity to the ABR. Sampling ports were inserted into the roof of the reactor enabling sampling at 0.2, 0.75 and 1.7 m below the liquid surface. Two inspection manholes with bolted steel covers were fitted to the reactor roof.

The ABR was similarly configured for sludge recovery and recycle, and baffles inserted to provide for the tortuous flow path (Figure, 3.2).

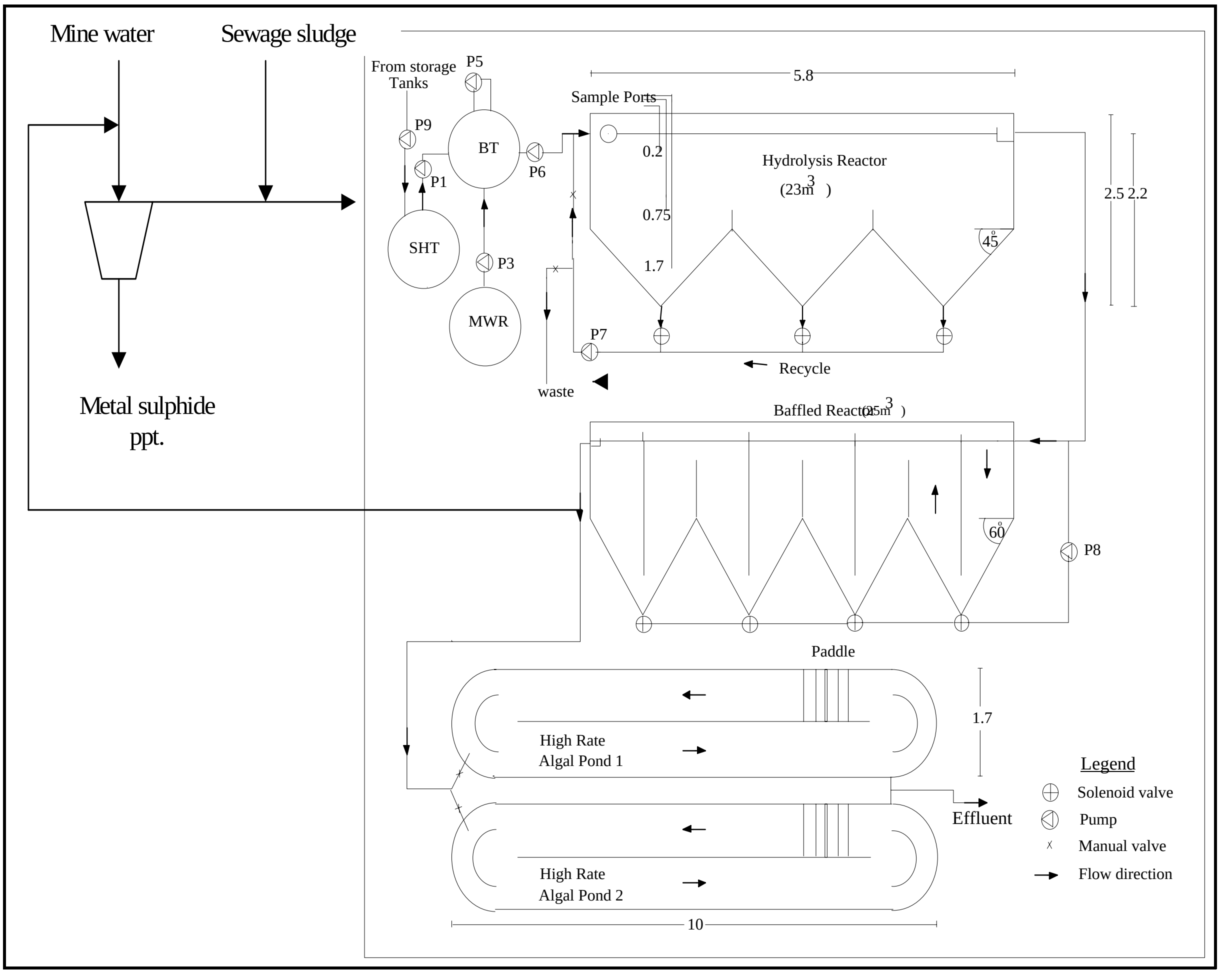

**Figure 3.1.** Process flow schematic of the Rhodes BioSURE® Pilot plant constructed in Grahamstown and located on site at the Grootvlei Gold Mine, Springs.

Two HRAP were constructed as portable units, using a galvanised steel tube frame, and fitted with prefabricated plastic liner inserts. Stainless steel paddle wheels were to be driven by a common motor and gear box. The linear flow velocity for the ponds was set at 30 cm.sec$^{-1}$.

Dimensions of the HRAP were as follows:

| | |
|---|---|
| Length | 10 m |
| Width | 1.7 m |
| Depth | 300 mm |
| Volume | 3 m$^3$ |
| HRT | variable |

Since the principles of the metal precipitation and the sulphide oxidation steps were under concurrent investigation at the time, it was decided to treat these as separate unit operations, to be developed, scaled-up and piloted on a different time scale to the core hydrolysis and sulphate reduction operations.

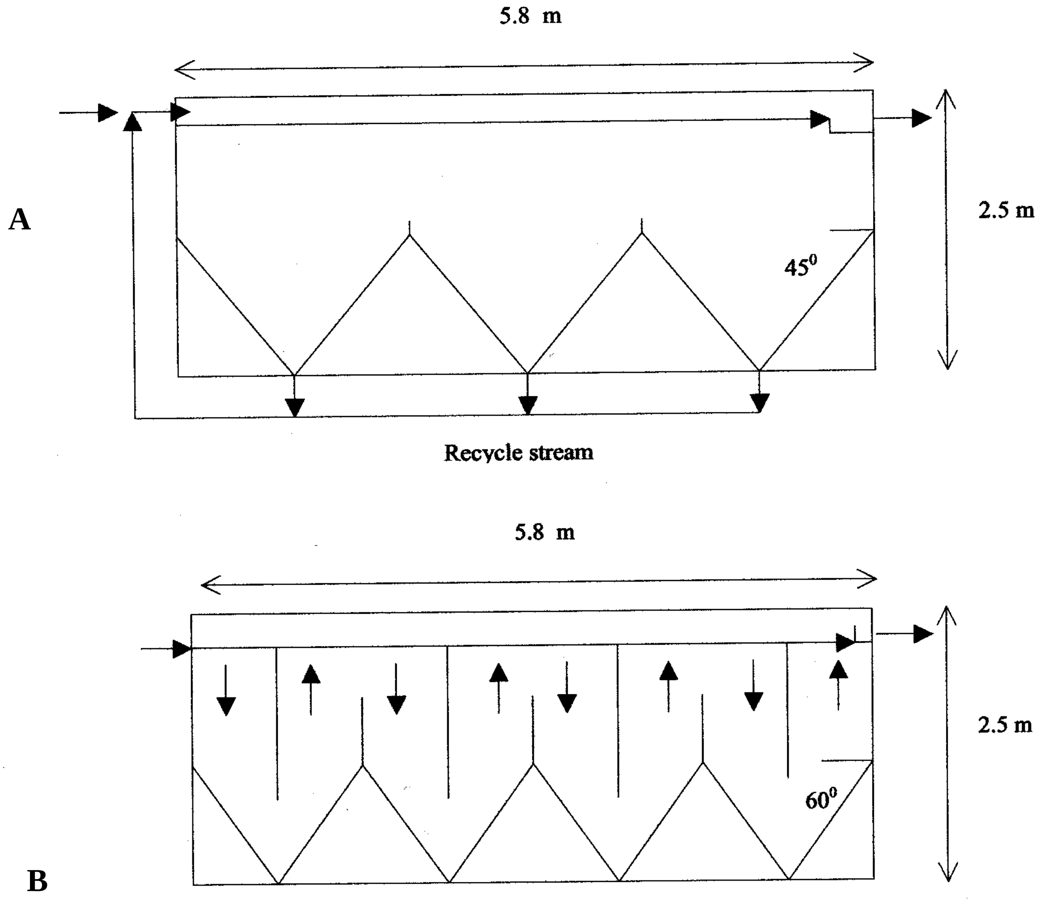

**Figure 3.2** The design and dimensions of the Recycling Sludge Bed Reactor (A), and the Anaerobic Baffle Reactor (B) used in the construction of the pilot plant.

The development of these unit operations are to be reported separately (see Appendix 1). The availability of neutralised AMD from the Grootvlei HDS lime treatment plant made it possible to proceed with pilot studies without the metal precipitation and neutralisation steps in place. The metal removal and sulphide oxidation unit operations were investigated separately in WRC Projects 1078 and 1336.

## 3.2 CONSTRUCTION AND COMMISSIONING

The construction of the pilot plant was undertaken by Grahamstown Engineering cc, electrical fittings were installed by BJ Electrical, and the PLC system for automated process control designed and installed by L. McLelland.

Construction was completed in Grahamstown early January 1998, and following hydraulic testing the plant was dismantled and transported to site at No 3 Shaft Grootvlei Mine in Springs on 24 January 1998 (Figure 3.3). The site had been prepared to provide a difference in level between R1 and R2, to enable gravity flow between the units. The reconstruction of the plant commenced on site on 26 January, 1998. Connection to the neutralised AMD stream from the mine's HDS plant was made, also to the fresh water supply and electrical connections from the mine. A small laboratory was established in the adjacent mine offices where operational analysis was undertaken. Sewage sludge was supplied by ERWAT from the Ancor Works. Full audit analyses were undertaken at ERWAT's ERTECH laboratories.

Commissioning and hydraulic testing of the plant commenced in early March 1998.

**Figure 3.3**.Headgear at the No.3 shaft Grootvlei Mine with the Rhodes BioSURE Process® pilot plant in the foreground.

## 3.3 PLANT OPERATION

The plant was operated in continuous mode with pumps, solenoid valves and level controls regulated by a PLC system. The flow rate was adjusted through the start-up period, and then fixed at 675 $L.h^{-1}$ giving a total HRT of 34 hours in the RSBR and 37 hours in the ABR. However, the RSBR operated as a settler with the liquid stream occupying only the top 0.3 m, and passing from inlet to outlet with an estimated HRT of around 8 hours. The sulphate and COD levels were analysed daily in the AMD and PSS respectively, and the $COD:SO_4$ ratio was adjusted, by manipulating pump flow rates, to maintain a ratio as close as possible to 2:1. Variability in the sulphate concentration of the AMD stream pumped from the mine over the course of the day, and the variable COD of the PSS delivered to site made this a demanding exercise, and at times fluctuations occurred quite widely around the 2:1 value.

The following operating regime was used for the management of the pilot plant (Figure 3.1):

1. Screened PSS was delivered twice weekly from the ERWAT Ancor Works by the Springs Municipality, and stored in 5 $m^3$ high density polyethylene holding tanks. The sludge was then pumped into the sludge holding tank (SHT) via P9 (Figure 3.1). A submersible pump was used to maintain solids in suspension in the SHT;

2. Neutralised sulphate feed water from which metals had been largely removed was drawn from the HDS lime treatment plant into the 5 $m^3$ mine water reserve tank (MWR), and the level regulated by a high pressure ball valve;

3. The feed water was pumped into the blend tank (BT) via P3, at a rate set daily to maintain the 2:1 COD:$SO_4$ feed ratio. The speed of P3 was PLC-controlled;

4. PSS was pumped via P1 from SHT to BT, and the pumps speed was similarly set daily and under PLC control;

5. A manually operated recirculation pump P5 was used to mix the two streams and maintain the solids in suspension until pumped to the RSBR;

6. The feed water/PSS mix was fed to the RSBR via variable speed P6;

7. RSBR sludge was recirculated via P7;

8. Recirculation in the ABR was provided for by P8;

9. Overflow from the RSBR passed to the ABR by gravity flow via an interconnecting pipe;

10. ABR overflow was split and fed to the two HRAP in equal volumes;

11. All tanks were fitted with high level and low level controls for pump protection.

Both the COD of the PSS delivered from the Ancor works, and the sulphate concentration in the feed water varied quite widely at times. An average analysis of these two components of the process is presented in Table 3.1. The analytical values for the raw AMD stream before treatment are also recorded.

**Table 3.1.** Average analytical values for the primary sewage sludge and the AMD (before and after lime treatment), as used in the study at Grootvlei Mine.

| Sewage Sludge | | Mine Water | | |
|---|---|---|---|---|
| | | | Before | After |
| pH | 5.3 | pH | 5.8 | 7.1 |
| Total COD (mg.L$^{-1}$) | 24 140 | Sulphate (mg.L$^{-1}$) | 2047 | 2300 |
| Filtered COD (mg.L$^{-1}$) | 3910 | TDS (mg.L$^{-1}$) | 3268 | 3300 |
| Suspended solids (mg.L$^{-1}$) | 16 995 | Suspended solids | - | 16 |
| Sulphate (mg.L$^{-1}$) | 56 | Iron (mg.L$^{-1}$) | 265 | 0.56 |
| TDS (mg.L$^{-1}$) | 2150 | Conductivity (mS.m$^{-1}$) | 398 | 237 |
| Total solids (mg.L$^{-1}$) | 19358 | Turbidity (NTU) | 371 | 45 |
| Total coliforms (cfu.mL$^{-1}$ ) | 397x10$^{6}$ | | | |
| *E. coli* | Positive | | | |
| *Ascaris* ova count | 37 | | | |

Of the total 18 month programme the plant was actually operated for 12 months until the end of March 1999. The results of the plant initialisation and process performance evaluation studies are outlined in subsequent sections. The piloting programme was undertaken by Chris Corbett (MSc, 2001).

# 4 PROCESS INITIALISATION AND MONITORING

## 4.1 INTRODUCTION

Following construction and assembly of the pilot plant at No 3 Shaft Grootvlei Mine, Springs, process initialisation commenced with the arrival to site of the first delivery of PSS from the Ancor Works, on 23 March, 1998. Sludge deliveries were made twice weekly thereafter by courtesy of the Springs Municipality ‘honey sucker’. A starter anaerobic sludge, containing an actively growing SRB population, was sourced from a local sewage works treating a sulphidogenic paper pulp effluent. Neutralised AMD was drawn from the mine’s HDS lime treatment plant, and feeding of the AMD/PSS blend commenced at a 2:1 COD:$SO_4$ ratio.

While pilot plant start-up and process initialisation proceeded smoothly, with respect to both mechanical and biological performance, numerous problems were experienced over a period of time in the provision of services to the system. Due to ongoing underground pumping problems, and process interruptions in the operation of the HDS plant, a variable quality of mine water was delivered to the pilot plant. The off-take of small volumes of sludge from the Ancor Works also resulted in a fairly wide variability in the quality of the PSS deliveries. These fluctuations in COD and sulphate levels in the feed streams required a continual adjustment of the blend to maintain a constant feed ratio.

In addition to the variability in feed quality, the process was also subjected to two substantial shock loads which are reflected in the plant performance reports shown in Figures 4.1-4.3. A concentrated stream of NaOH accidently entered the pipeline feeding the pilot plant. This caused a pH rise above 12.5, and severe disruption of the process between days 37 and 41. Following correction of this problem, active sulphate reduction had resumed by the following day, and stable operating conditions had been re-established 8 days later by day 50. Between days 78 and 80, a valve failure on the AMD pipeline to the plant resulted in the feeding of a fresh water stream instead of AMD. Here the resumption of active sulphate reduction followed by day 81, with the reestablishment of steady state operating conditions by day 85.

In addition to the above, the process was also subjected to a number of other shocks to the system in its first three months of operation. While this influenced average process performance values, these incidents also provided a graphic indication of the potential robustness of the process, and its capacity to respond to loading shocks. For these reasons the report on process performance evaluation has been considered here in two main phases. An initial period of 120 days is described (Phase 1) during which process initialisation and performance optimisation is documented, and during which period the major fluctuations occurred. Following this a period of steady state performance covered the remaining 8 months of the pilot study (Phase 2) and provided the basis for process performance evaluation studies.

## 4.2 MATERIALS AND METHODS

Sulphide and total settlable solids were measured according to Standard Methods (APHA, 1989). Merck Spectroquant test kits were used to determine concentrations of sulphate (kit number 14791) and COD (kit number 14541) using the Merck Spectroquant 1800 system. Prior to COD determination, all samples were acidified with concentrated HCl to pH 2 in order to remove residual dissolved sulphide. Samples used for determination of CODf were passed through a 0.45μm GFA filter (Whatman). CODp was calculated as the difference between total COD (CODt) and CODf of a particular sample. Sulphide concentrations were determined using the method described by Rees *et al*. (1971). Suspended solids were calculated as described in Standard Methods (APHA,1989). pH was measured using a Cyberscan 2500 pH meter.

## 4.3 PHASE 1: COMMISSIONING AND PROCESS INITIALISATION

The performance of the pilot plant for the Phase 1 period, covering process initialisation and optimisation (day 0-120), is reported in Figures 4.1 to 4.4. The pH values for the feed, RSBR and ABR streams provide an important indication of alkalinity generation, and thereby also the activity of the sulphate reduction process.

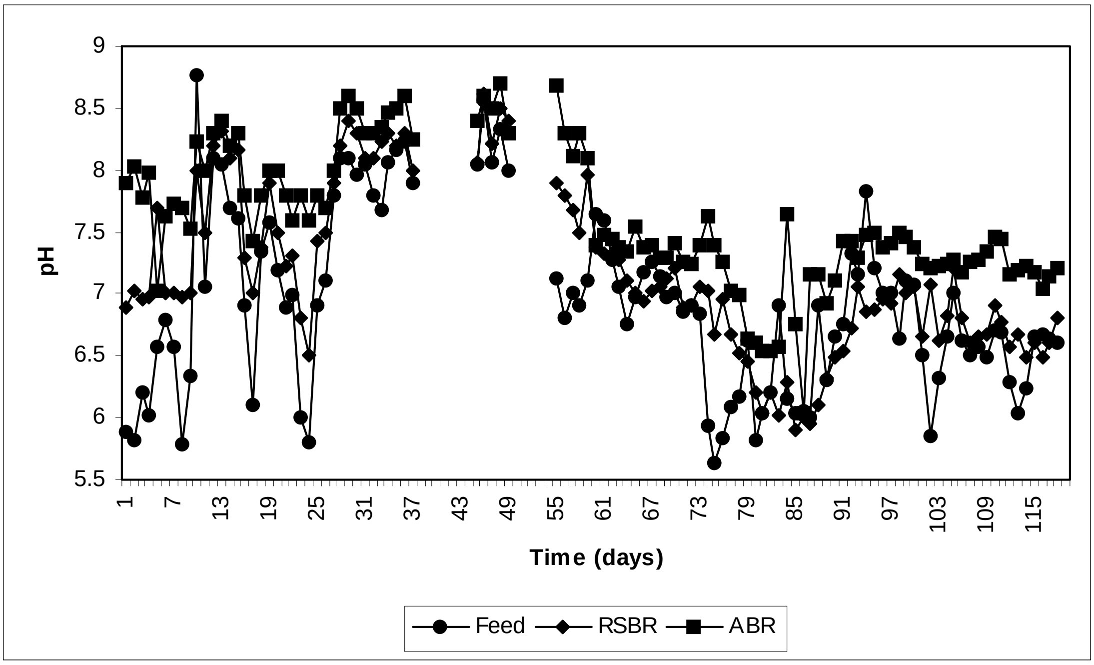

**Figure 4.1.** pH of the Feed, Recycling Sludge Bed Reactor and Anaerobic Baffle Reactor over the 120 day period of Phase 1operation.

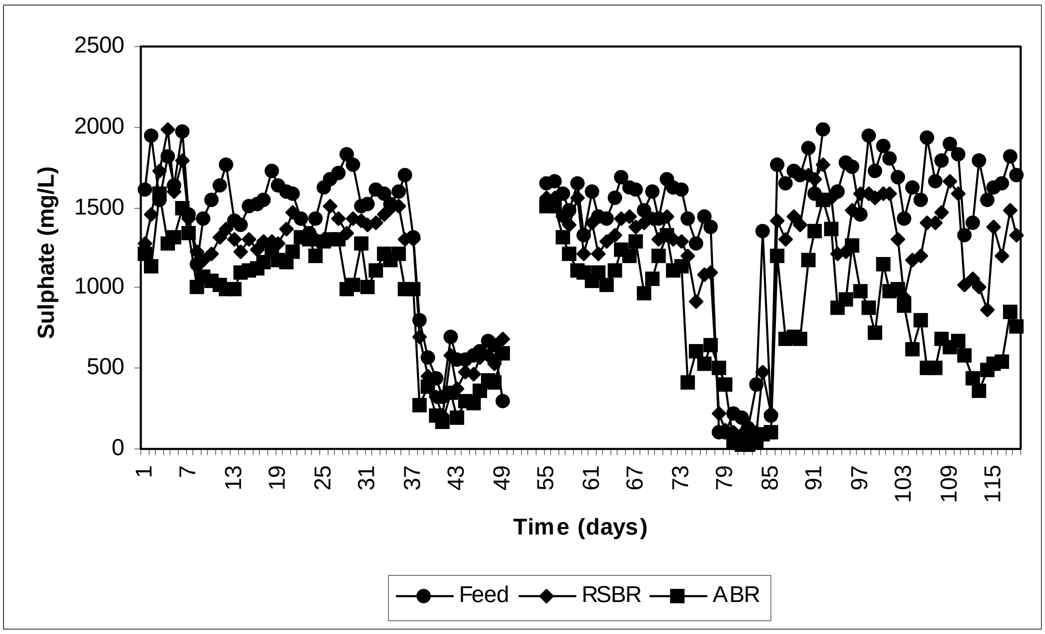

**Figure 4.2.** Sulphate concentration of the Feed,Recycling Sludge Bed Reactor and Anaerobic Baffle Reactor over the 120-day period of Phase 1operation.

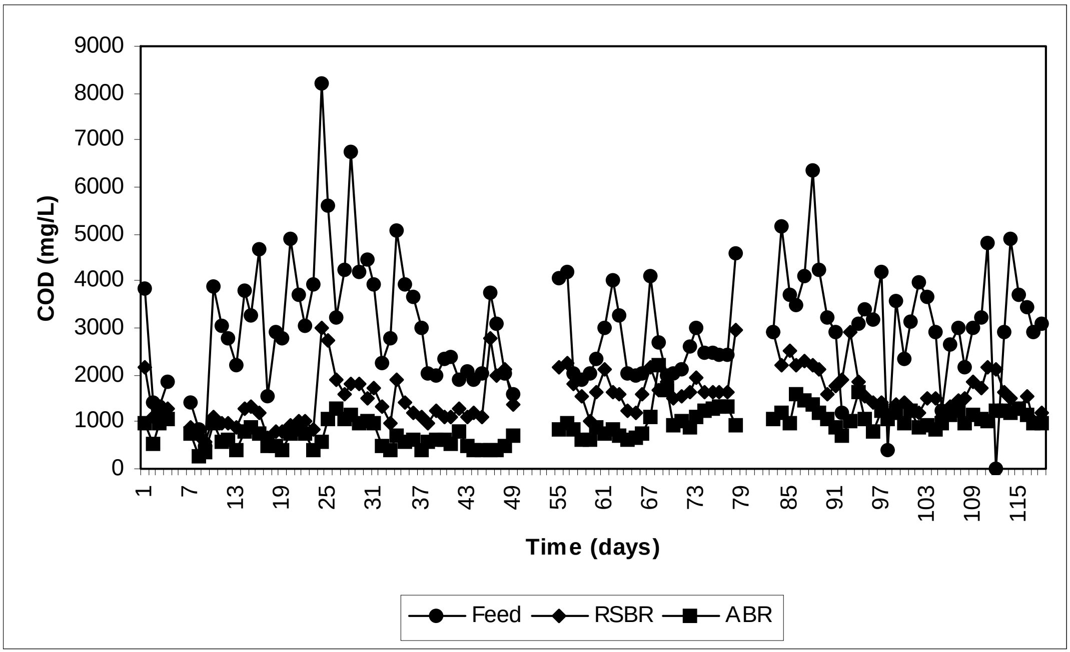

**Figure 4.3.** COD concentration of the Feed, Recycling Sludge Bed Reactor and Anaerobic Baffle Reactor over the 120-day period of Phase 1 operation.

Figure 4.1 shows a clear trend of alkalisation across the system with pH rising between 0.5 and 2 pH units from feed to ABR. Both alkalinity generation and sulphate reduction (Figure 4.2) commenced within days of start-up, with the graphs showing results from April 1, 1998 onwards. Figures 4.2 and 4.3, show sulphate and COD values across the system, and provide an indication of the variability in the feed values experienced throughout the pilot study. Nevertheless, a constant sulphate removal function is maintained outside the reported shock load incidents, and a 400-500 mg.L$^{-1}$ sulphate removal rises to around 1000 mg.L$^{-1}$ by the end of this period. Percentage sulphate removal is reported in Figure 4.4, with between 60-70% removed across the system at the end of the initialisation and optimisation period.

Tables 4.1 reports the averaged data values for the three stages of the initialisation and optimisation phase. It is apparent that average sulphate removal improves across the period from 25% to 66%. While COD removal was more active in the RSBR than in the ABR, sulphate removal values show the opposite effect with higher reduction in the ABR than the RSBR. It is also apparent that settleable solids are nearly completely retained in the RSBR (~98%), with COD passing to the ABR being mainly in the soluble form (Imhoff cone reading < 2 mL). The RSBR was not desludged during the entire 1 year pilot study, providing a further indication of the efficiency of hydrolysis and COD consumption in the RSBR. This high level of sludge solubilisation in the RSBR has been followed up and developed as a sludge disposal process in collaboration with ERWAT. The results of this study are detailed in Report 12 in this series.

**Table 4.1** Performance of the BioSURE® Pilot Plant during three periods over the initialisation and optimisation phase.

| | **RSBR** | **ABR** | **Overall Process** |
|---|---|---|---|
| **Days 1-31** | | | |
| COD influent | 3292 | 1259 | 3292 |
| COD effluent | 1259 | 778 | 728 |
| COD consumed | 2033 | 531 | 2564 |
| $SO_4$ influent | 1589 | 1391 | 1589 |
| $SO_4$ effluent | 1391 | 1185 | 1185 |
| $SO_4$ consumed | 198 | 206 | 404 |
| % $SO_4$ removed | 12.5 | 15 | 25 |
| % COD removed | 62 | 42 | 78 |
| %Settled solids removed | 92 | 90 | 99.2 |
| | | | |
| **Days 60-73** | | | |
| COD influent | 2529 | 1605 | 2529 |
| COD effluent | 1605 | 938 | 938 |
| COD consumed | 924 | 667 | 1591 |
| $SO_4$ influent | 1549 | 1348 | 1549 |
| $SO_4$ effluent | 1348 | 1133 | 1133 |
| $SO_4$ consumed | 201 | 215 | 416 |
| % $SO_4$ removed | 13 | 16 | 27 |
| % COD removed | 37 | 42 | 63 |
| %Settled solids removed | 97.9 | 52.4 | 99 |
| | | | |
| **Days 90-118** | | | |
| COD influent | 3323 | 1562 | 3323 |
| COD effluent | 1562 | 1118 | 1118 |
| COD consumed | 1761 | 444 | 2205 |
| $SO_4$ influent | 1689 | 1297 | 1689 |
| $SO_4$ effluent | 1279 | 579 | 579 |
| $SO_4$ consumed | 392 | 781 | 1110 |
| % $SO_4$ removed | 23 | 60 | 66 |
| % COD removed | 53 | 28 | 66 |
| % Settled solids removed | 97.2 | 56.6 | 98.7 |

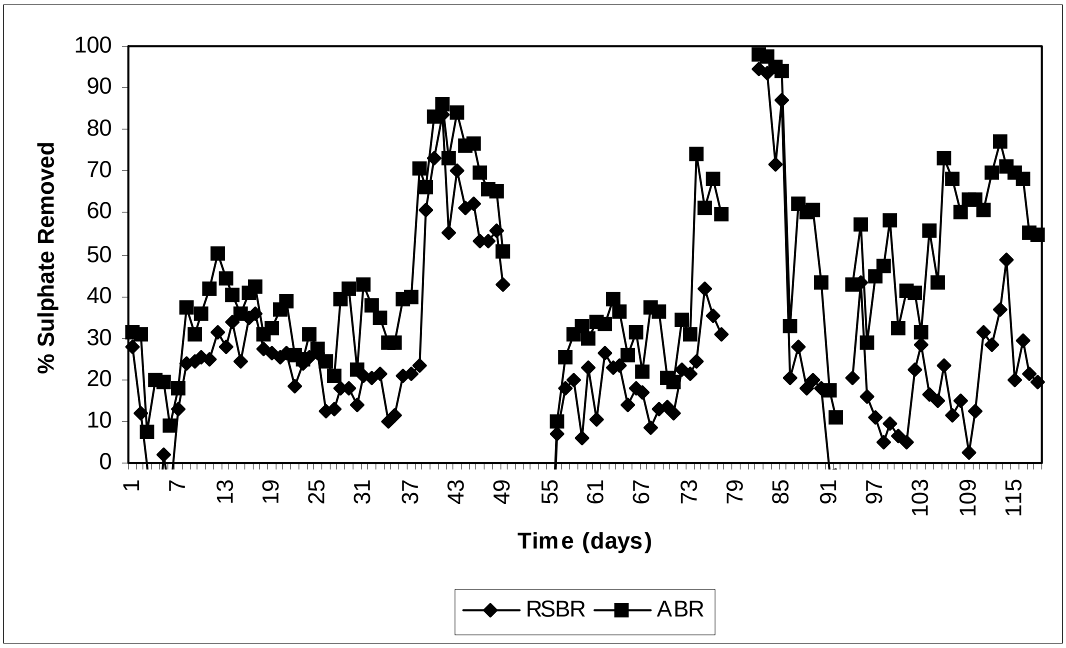

**Figure 4.4.** Cumulative percentage sulphate removal in the Recycling Sludge Bed Reactor and Anaerobic Baffle Reactor over the 120 day period of Phase 1 operation.

The results observable at this early stage of the pilot study appeared to support the hypotheses which emerged from the laboratory investigations described in Part 2 of this report (Whittington-Jones *et al.*, 2002). While some sulphate reduction does occur in the RSBR during the first step in the process, it is primarily hydrolysis and COD consumption involved in the production of CODf which characterises the main activity in this unit. The CODf passing to the second stage of the process is primarily consumed in sulphate reduction.

## 4.4 PHASE 2: PROCESS MONITORING

While fluctuations in values for both the AMD and PSS feeds continued throughout the pilot study period, no further major shock loads were experienced following the second incident between days 78 - 85. A period of about a month following re-establishment of steady-state operating conditions was allowed, and day 120 provided an arbitrary point after which month-on-month averages could conveniently be used to report system performance. The monitoring period covers the remaining 8 months of the pilot study which ran from August 1998 to March 1999.

Figures 4.5 and 4.6 report sulphate and COD removal across the BioSURE® pilot plant for the 240 day Phase 2 period, and Table 4.2 reports average monthly performance results for the same period. Notwithstanding an ongoing wide fluctuation in the feed concentration, an average COD:$SO_4$ loading of 1.94:1 (0.93:1 actual) confirmed the sustainability of the 2:1 ratio which had been based on theoretical calculation and laboratory studies. Average sulphate removal achieved for the 240 day Phase 2 period was 67% with 72% COD consumption occurring during the process.

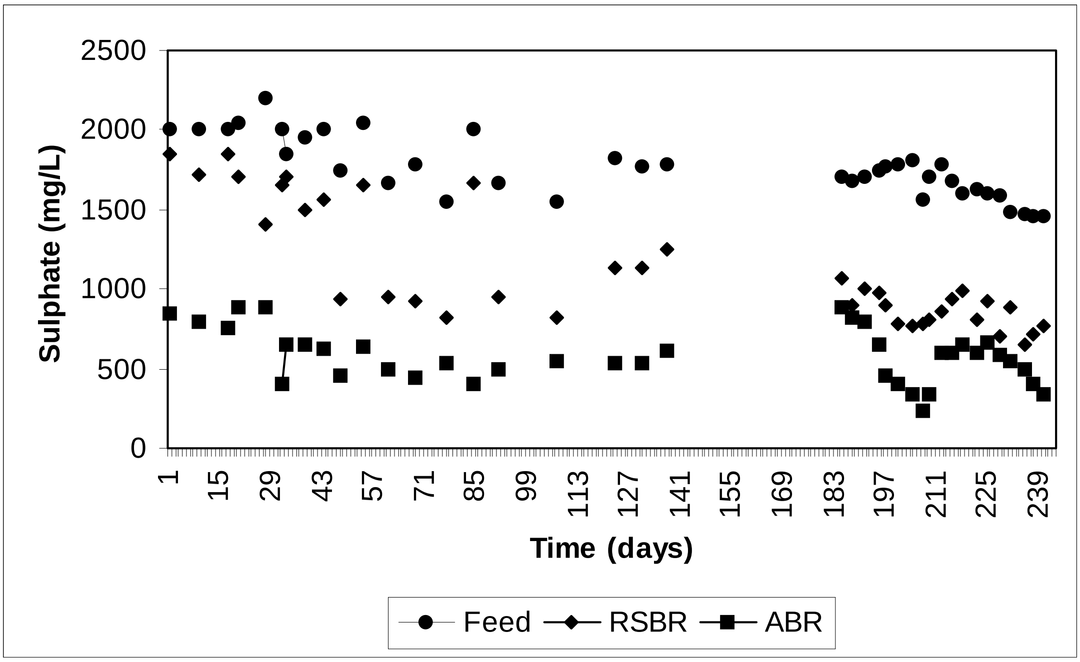

**Figure 4.5.** Sulphate concentration of the Feed, Recycling Sludge bed Reactor and Anaerobic Baffle Reactor over the 240-day period of Phase 2 operation of the pilot plant.

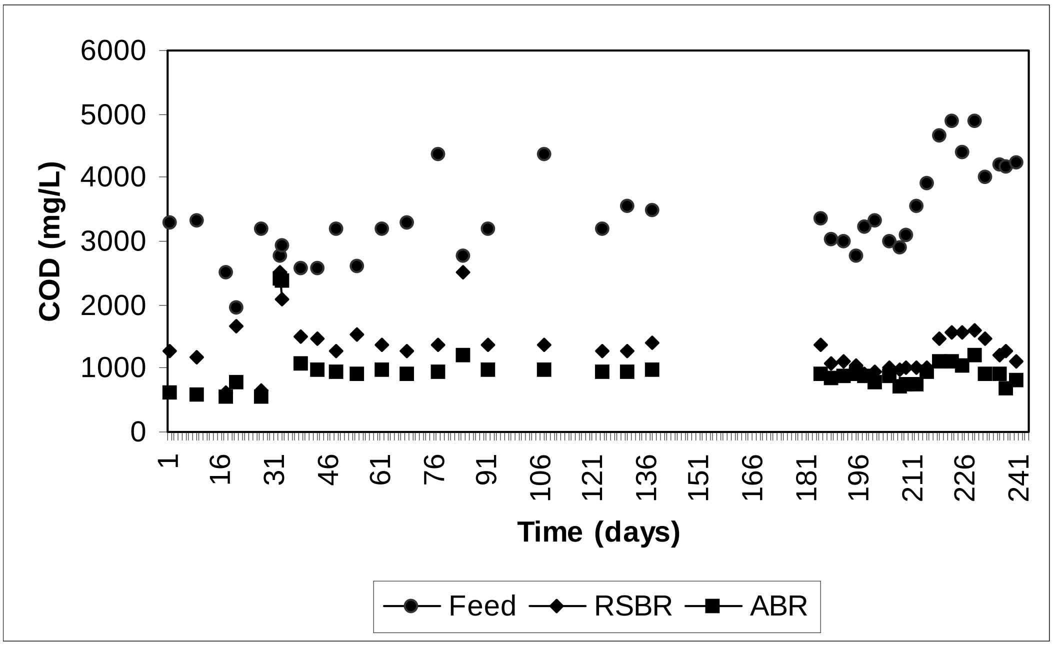

**Figure 4.6.** COD concentration of the Feed, Recycling Sludge Bed Reactor and Anaerobic Baffle Reactor over the 240-day period of Phase 2 operation of the pilot plant.

**Table 4.2** Process performance values averaged over the 240-day Phase 2 study.

| | Feed | RSBR | ABR | Total |
|---|---|---|---|---|
| COD ($mg.L^{-1}$) | 3412 | 1324 | 966 | |
| Consumption (%) | | 61 | 27 | 72 |
| $SO_4$ ($mg.L^{-1}$) | 1760 | 1113 | 580 | |
| Removal (%) | | 37 | 48 | 67 |

Table 4.2 also shows that while the major fraction of COD consumption occurred in the RSBR, sulphate removal was higher in the ABR. This accorded well with the principle of the process design which provides for PSS solubilisation and conversion to VFA intermediates in the RSBR and the consumption of these components as electron donors in the second stage ABR.

Table 4.3 reports average monthly performance results for August and December 1998 (comparing the first and last months of Phase 2 operation before shut down), and then following the January shut-down for February and March 1999. These results broadly confirm results obtained in the Phase 1 period with sulphate and COD removal values rising somewhat to monthly averages around 70% and 70-75% respectively.

Reoxidation of sulphide to elemental sulphur in a floating sulphur biofilm, which developed on the surface of the reactors, was observed throughout the early part of the study given that the headspace of the reactor was not completely sealed and exposed to the ingress of air. Following the January shut-down provision was made for the headspace of the reactors to be purged with nitrogen gas for short periods of time to inhibit re-oxidation of sulphide on the liquid surface. This was done continuously for a two-week period during February and resulted in an improvement in measured sulphate removal values by 10-15%, and total sulphide removals for this period. This finding should be taken into account in the interpretation of the overall sulphate removal results recorded for the rest of the study.

While the finding has important implications for reactor design, including establishing effective anaerobic conditions in the reactor headspace, the use of the floating sulphur biofilm as a sulphur recovery mechanism was also investigated in follow-up studies as a free-standing sulphur recovery unit operation of the BioSURE Process®. Studies of the development of a Sulphide Oxidation Bioreactor based on this principle have been reported separately in Report 11: ‘Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa, Volume 4. The Rhodes BioSURE Process®. Part 3: Sulphur Production and Metal Removal Unit Operations’.

The variations in feed composition also had an effect on the stable operation of the system. It is assumed careful regulation of COD and sulphate feed concentrations would also be necessary to maintain +80% as a standard performance for the system. Nevertheless a 70 - 75% sulphate removal was readily achievable under the robust operating conditions of the pilot study.

**Table 4.3.** Performance of the BioSURE® pilot plant during three periods over the monitoring phase.

| | RSBR | ABR | Process |
|---|---|---|---|
| **August 1998** | | | |
| COD influent | 3207 | 1362 | 3207 |
| COD effluent | 1362 | 986 | 986 |
| COD consumed | 1845 | 376 | 2221 |
| $SO_4$ influent | 1673 | 956 | 1673 |
| $SO_4$ effluent | 956 | 498 | 498 |
| $SO_4$ consumed | 717 | 458 | 1175 |
| % $SO_4$ removed | 42.8 | 47.9 | 70.2 |
| % COD removed | 57.5 | 27.6 | 69.3 |
| % Settled solids removed | 98 | 51 | 99 |
| **December 1998** | | | |
| COD influent | 3553 | 1274 | 3553 |
| COD effluent | 1274 | 937 | 937 |
| COD consumed | 2279 | 337 | 2616 |
| $SO_4$ influent | 1771 | 1128 | 1771 |
| $SO_4$ effluent | 1128 | 539 | 539 |
| $SO_4$ consumed | 643 | 589 | 1232 |
| % $SO_4$ removed | 36 | 52 | 69.5 |
| % COD removed | 64 | 26 | 73.6 |
| % Settled solids removed | 97 | 50 | 99 |
| **February 1999** | | | |
| COD influent | 3128 | 980 | 3128 |
| COD effluent | 980 | 810 | 810 |
| COD consumed | 2148 | 170 | 2318 |
| $SO_4$ influent | 1736 | 841 | 1736 |
| $SO_4$ effluent | 841 | 432 | 432 |
| $SO_4$ consumed | 895 | 409 | 1304 |
| % $SO_4$ removed | 52 | 48 | 75 |
| % COD removed | 69 | 21 | 90 |
| % Settled solids removed | 98 | 51 | 99 |
| **March 1999** | | | |
| COD influent | 4375 | 1366 | 4375 |
| COD effluent | 1366 | 967 | 967 |
| COD consumed | 3009 | 820 | 3829 |
| $SO_4$ influent | 1552 | 820 | 1552 |
| $SO_4$ effluent | 820 | 544 | 544 |
| $SO_4$ consumed | 732 | 276 | 1008 |
| % $SO_4$ removed | 47 | 34 | 65 |
| % COD removed | 69 | 30 | 77.9 |
| % Settled solids removed | 98 | 54 | 99 |

Trends with respect to COD and sulphate removal in the two reactors broadly confirmed the observations made during Phase 1 operation. Solids removal with hydrolysis of the CODt provided the principle reaction in the RSBR, with CODf consumption and sulphate reduction occurring as the main reaction in the ABR. The use of PSS as an electron donor source presents numerous potential health hazards with respect to the quality of the final treated water. A microbiological analysis of the effluent streams produced by the various unit operations in the process is reported in Table 4.4. This shows the effective reduction of fecal coliform counts across the system, and especially in the ABR and the HRAP units. Fecal coliforms, total coliforms and Ascaris ova were completely removed by the time the water had passed through the HRAP. Removal of virus particles was not investigated.

**Table 4.4.** Microbiological analysis of various stages of the process. (Plate counts in CFU.mL -1 )

| Sample | Fecal Coliforms | Total Coliforms | Plate count | Ascaris |
|---|---|---|---|---|
| Blend-tank | 4700000 | 26400000 | 3200000 | 37 |
| RSBR | 208000 | 113000 | 7300000 | |
| ABR | 17000 | 6100 | 42000 | |
| HRAP | negative | negative | | 0 |

## 4.5 CONCLUSIONS

1. The BioSURE® pilot plant was designed and constructed on the basis of laboratory and initial scale-up studies, and then established and operated on-site at Grootvlei Mine for a 12-month period.

2. The principles of the BioSURE Process® design were demonstrated in the study with PSS solubilisation and COD mobilisation to VFA intermediates being the primary events taking place in the RSBR, and sulphate reduction and VFA consumption taking place in the second stage ABR operation.

3. Enhanced hydrolysis of PSS in the RSBR was demonstrated with solubilisation values >90% recorded here. Sludge accumulation in the RSBR was hence extremely slow.

4. A COD:$SO_4$ ratio of 2:1 was shown to provide an effective feed blend to the process where PSS is the electron donor source.

5. Notwithstanding a number of shock loads and a variable feed composition over the course of the study period, the system maintained a 70 - 75% sulphate removal using PSS as the electron donor source. In addition to demonstrating a robustness of the process, given its rapid recovery from the shock loads, it may be anticipated that in a full-scale continuously-fed system fluctuation in feed values would be evened out to some extent.

6. It was demonstrated that rigorously maintained anaerobic conditions are necessary in the reactor headspace to prevent the re-oxidation of sulphide to elemental sulphur and sulphate. As a result of headspace nitrogen purging studies it was shown that the performance efficiency values recorded over the study period should be adjusted upward by around 10-15 %. The stable operation of the process should deliver consistent sulphate removal in the range of 80 - 85%.

7. A microbiologically acceptable final effluent can be produced by the system indicating that infectious elements in the PSS feed may be effectively removed in the system.

# 5 PROCESS PERFORMANCE EVALUATION

## 5.1 INTRODUCTION

The studies described in sections three and four had shown that the availability, to biological sulphate reduction, of complex organic carbon structures as electron donors, was dependant not only on the relevant hydrolysis reactions, but also on the configuration of the reaction environment. With reactor conceptualisation informed, to a degree, by the simulation of natural sedimenting environments, the RSBR was found to offer advantages in the optimisation of the solubilisation process. It was also found that the partial separation of carbon solubilisation and sulphate reduction reactions, in sequential unit operations, offered opportunities for the more effective optimisation of the overall sulphate reduction process. Although a component of the influent COD and sulphate is consumed in the establishment of the enhanced hydrolysis environment, the solubilised product is made available as a feedstock to downstream sulphate reduction activity.

The most important products of SRB activity in the anaerobic degradation of organic matter are acetate, propionate and butyrate (Gujer and Zehnder, 1983). When sulphate is present in wastewater, SRB are able to use several intermediates of the anaerobic mineralisation process, and the following reactions can occur:

- Oxidation of fatty acids with more than two carbon atoms by SRB. Two oxidation patterns can be distinguished here. Firstly an incomplete oxidation with acetate and sulphide as end products, and secondly a complete oxidation with only sulphide as the end product;
- Oxidation of acetate by acetotrophic SRB and molecular hydrogen by hydrogenotrophic SRB.

The hydrolysis and solubilisation reactions as the initial steps in which complex carbon structures, such as PSS, are made available to biological processes, are of central importance. Given the complex range of the products of hydrolysis and the difficulty involved in their accurate individual analysis, it was necessary to relate the efficiency of hydrolysis in the RSBR in this study in terms of the combined products of acidogenesis and acetogenesis. These were expressed as acetate equivalents and calculated from the stoichiometric sulphate reduction value measured in the system at a COD:$SO_4$ value of 0.61:1. Based on Equation 5.1 the COD:$SO_4$ value of 0.61:1 was used in the calculation of the acetate equivalent value. Since components of lactate and the other products of anaerobic digestion would have been consumed by microorganisms other than SRB, the estimation of carbon consumption by sulphate reduction activity would be both a crude and a minimum value.

$$CH_3COO^- + SO_4^{2-} \Longleftarrow H_2O + CO_2 + HCO_3^- + S^{2-} \qquad (5.1)$$

. G = -12.41kJ/reaction (Widdel, 1988)

It is apparent, therefore, that the efficiency of the hydrolysis and sulphate reduction events may be measured in terms of the rate and extent of acetate production. However, at this stage neither of the reactors necessarily sustained fully optimised systems and, given a limited ability to manipulate HRT in the pilot plant, there was no way to determine how efficient the production of acetate equivalents might have been if the reaction time had been extended. This was undertaken in a series of flask studies where an additional HRT was provided for each process stream, and the reactions allowed to proceed to an end point.

The COD:$SO_4$ feed ratio of 2:1 had been set for the pilot study on the basis of the laboratory investigations undertaken previously on PSS utilisation. In determining the efficiency of process performance it would also be important to test this assumption, and therefore a series of studies were undertaken where the ratio of the feed to the pilot plant was elevated from 2:1 to 3:1 and lowered again from 2:1 to 1.5:1.

## 5.2 RESEARCH OBJECTIVES

1. To evaluate the performance of the system in terms of PSS hydrolysis and sulphate reduction efficiency, by measuring the production and use in the process of hydrolysis products calculated as acetate equivalents;

2. To determine optimum efficiency in terms of HRT settings for the individual unit operations by allowing reactions to proceed to completion;

3. To determine optimum COD:$SO_4$ feed ratios for the process.

## 5.3 RESULTS AND DISCUSSION

### 5.3.1 Formation of Acetate Equivalents from Primary Sewage Sludge

Table 5.1 lists values for COD and $SO_4$ consumed in the RSBR and ABR individually, and for the combined overall process. From these values the COD:$SO_4$ consumption ratios can be determined as well as the acetate equivalent value using the theoretical COD:$SO_4$ ratio of 0.61:1.

In terms of overall process, the COD:$SO_4$ consumption ratio (with the COD as PSS consumed in the process) was close to 2:1 over extended periods of steady-state operation for the pilot plant. The actual measured values for the COD:$SO_4$ consumption ratio ranged from 2.6 – 4.5:1 in the RSBR and between 0.57 – 0.82:1 in the ABR. Given the close approximation in the ABR to the theoretical value for COD consumption as acetate equivalent (0.61:1), it could broadly be assumed that sulphate reduction in the ABR was largely driven by VFA products generated by PSS hydrolysis occurring in the RSBR. As may be anticipated, the products of hydrolysis would be consumed by a range of the consortial bacteria in addition to SRB, and the COD:$SO_4$ consumption ratio of 4.5:1 is consequently larger than the second stage of the process where the hydrolysis products are consumed largely in sulphate reduction. In terms of total sulphate reduction measured across the system, the hydrolysis reactions achieve a 32% conversion of PSS to acetate equivalents.

Where the value for consumption of acetate equivalent was in excess of 100%, as in the months of September and December (i.e. 107.3 and 106%), there is an indication that not only was acetate consumed but that both hydrogen and formate may have been electron sources for sulphate reduction as well.

**Table 5.1**. COD:$SO_4$ consumption ratio and carbon utilization values for the Recycling Sludge Bed Reactor and Anaerobic Baffled Reactor and the combined overall process calculated as the acetate equivalent used in sulphate reduction reported for the September, November and December monitoring periods.

| **September** | **RSBR** | **ABR** | **Overall Process** |
|---|---|---|---|
| COD consumed (mg.L$^{-1}$) | 1761 | 444 | 2205 |
| $SO_4$ consumed (mg.L$^{-1}$) | 392 | 781 | 1110 |
| Consumption ratio | 4.5 | 0.57 | 1.99 |
| Acetate equivalents used in $SO_4$ reduction (%) | 13.5 | 107.3 | 30.7 |
| **November** | | | |
| COD consumed (mg.L$^{-1}$) | 1845 | 376 | 2221 |
| $SO_4$ consumed (mg.L$^{-1}$) | 717 | 458 | 1175 |
| Consumption ratio | 2.6 | 0.82 | 1.9 |
| Acetate equivalents used in $SO_4$ reduction (%) | 23.7 | 74.3 | 32.3 |
| **December** | | | |
| COD consumed (mg.L$^{-1}$) | 2279 | 337 | 2616 |
| $SO_4$ consumed (mg.L$^{-1}$) | 643 | 589 | 1232 |
| Consumption ratio | 3.5 | 0.57 | 2.1 |
| Acetate equivalents used in $SO_4$ reduction (%) | 17.2 | 106.6 | 28.7 |

### 5.3.2 Effects of Feed Ratio Adjustment on Acetate Equivalents Produced

Once the system had stabilised, the COD:$SO_4$ feed ratio to the Rhodes BioSURE Process® was adjusted from 2:1 to 3:1 and 2:1 to 1.5:1 for short periods, in order to assess effects of feed ratio on carbon consumption, and on the overall performance of the process. These results are reported in Table 5.2.

During the period of increased COD loading to the system (COD:$SO_4$ ratio of 3:1), the values for the COD:$SO_4$ consumption ratio measured in each reactor were 4.1:1 in the RSBR and 1.45 in the ABR respectively. When the COD:$SO_4$ ratio was decreased to 1.5:1 acetate equivalent produced and used in sulphate reduction was 37% - twice that of the 3:1 COD:$SO_4$ loading value. These results indicate the consumption of hydrolysis products by microorganisms other than SRB where carbon is in excess, and mainly by SRB where the COD:$SO_4$ ratio falls below 2:1 (Speece, 1993). The observed sensitivity of the system to manipulation of the COD:$SO_4$ ratio supports the use of the acetate equivalent unit as an indicator of the efficiency of hydrolysis of PSS.

**Table 5.2**. COD:$SO_4$ consumption ratio and utilisation calculated as the acetate equivalent used in sulphate reduction reported for the two periods of feed ratio alteration (COD:$SO_4$). Results reported for the Recycling Sludge Bed Reactor and Anaerobic Baffled Reactor and the combined overall process.

| **Period of 3:1 loading** | **RSBR** | **ABR** | **Overall Process** |
|---|---|---|---|
| COD consumed (mg.L) | 3009 | 399 | 3408 |
| $SO_4$ consumed (mg.L) | 732 | 276 | 1008 |
| Consumption ratio (COD:$SO_4$ ) | 4.1 | 1.45 | 3.4 |
| Acetate equivalents used in $SO_4$ reduction (%) | 14.8 | 42.2 | 18.0 |
| **Period of 1.5:1 loading** | | | |
| COD consumed (mg.L) | 798 | 317 | 1115 |
| $SO_4$ consumed (mg.L) | 376 | 403 | 679 |
| Consumption ratio (COD:$SO_4$ ) | 2.9 | 0.79 | 1.6 |
| Acetate equivalents used in $SO_4$ reduction (%) | 28.7 | 77.5 | 37.1 |

### 5.3.3 Volatile Fatty Acid Production

VFAs can be used directly as electron donors by the SRB. As such, the concentration of VFA in a reactor at any one time provides some idea of the relative rates of VFA production (hydrolysis plus acidogenesis) less VFA consumption. Consumption is usually by either sulphate reducers or methanogens, depending on the available electron acceptor.

Figure 5.1 reports the measured values for VFA in the various stages of the reactor, together with the estimates of acetate equivalents based on sulphate reduction. Previous results had shown that effective hydrolysis/acidogenesis of PSS takes place in the RSBR, that the end products of this conversion process are VFA, and high concentrations of these products would be expected in the effluent. As some sulphate reduction did take place in the RSBR, a certain proportion of the available VFA would have been consumed, thus resulting in only a portion of the total products exiting in the RSBR effluent. The concentration of VFA in the effluent of the RSBR does not appear to depend on the influent VFA concentration. This suggests either that a certain percentage of the VFA produced in the RSBR is not available to sulphate reducers, or that reactions that produce the VFA are in some way inhibited. This may indicate that further optimisation of reactor operation may be required.

### 5.3.4 Process Efficiency and Reactor Retention Times

Due to the complexity of pilot-plant operation it was not practical to substantially vary the HRT settings of 8 hours for the liquid stream in the RSBR, and 37 hours in the ABR. However, since neither reactor had been fully optimised during the scale-up exercise, it was important to gather some idea how close they were operating to optimal performance. This information would also be necessary in planning the optimisation studies which would need to follow this initial piloting exercise.

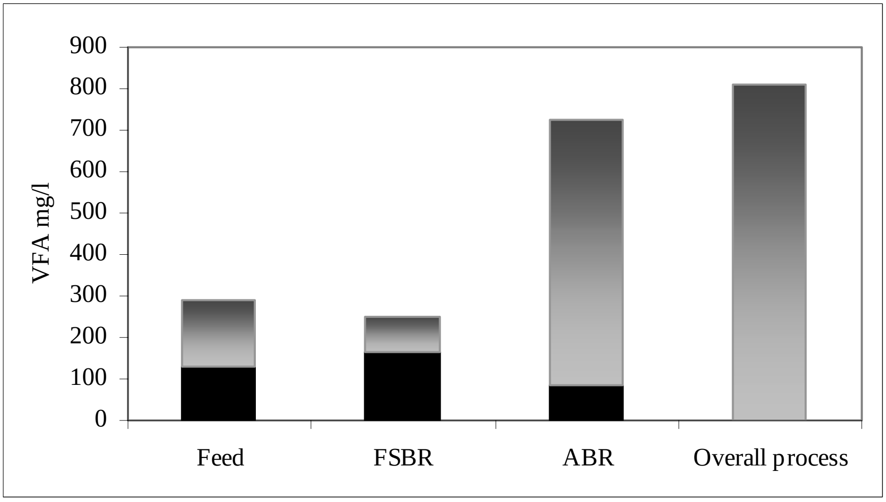

**Figure 5.1**. Volatile fatty acid produced from primary sewage sludge in the BioSURE® pilot plant. Measured VFA values across the system are compared with calculated values for total production of acetate equivalent, based on COD consumed in sulphate reduction. Results reported for the Recycling Sludge Bed Reactor and Anaerobic Baffled Reactor and the combined overall process. Dark shading = measured, and light shading = calculated values.

A series of laboratory flask study experiments were undertaken where the effluent stream from each reactor was incubated under comparable conditions for a period of an additional nine days. Cumulative changes in COD and sulphate were monitored daily, and process efficiency was evaluated in terms of increased COD and sulphate removal, changes in the $COD:SO_4$ consumption ratio, and an increase in the production of acetate equivalents.

The results of this study are reported in Figures 5.2 a-c, 5.3 a-c, 5.4 and 5.5, and Table 5.3.

Figure 5.2. shows changes in COD values for the RSBR and ABR over the 9-day period. The additional loss in the RSBR stream of CODt (497 $mg.L^{-1}$) and CODp (585 $mg.L^{-1}$) would have been anticipated given that this reactor is designed to produce a soluble product from COD solids. This is borne out in the CODf result which shows an increase of some 511 $mg.L^{-1}$, over the course of the first 3 days, apparently at the expense of CODp. The correlation in values for the increase in CODf and the decrease in CODp are impressively close.

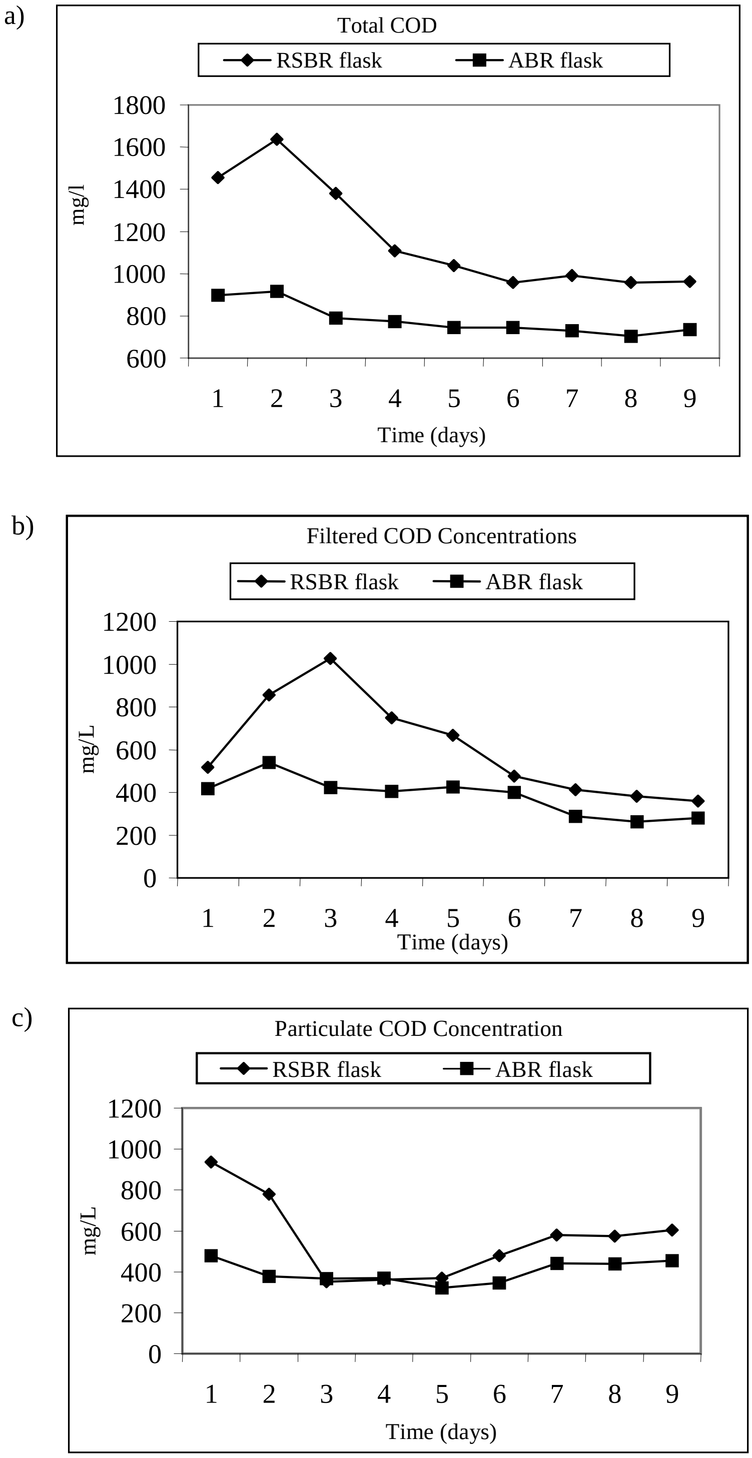

**Figure 5.2.** Changes in total, particulate and filtered COD in flask studies extending the reaction time in Recycling Sludge Bed Reactor and Anaerobic Baffle Reactor effluent by 9 days.

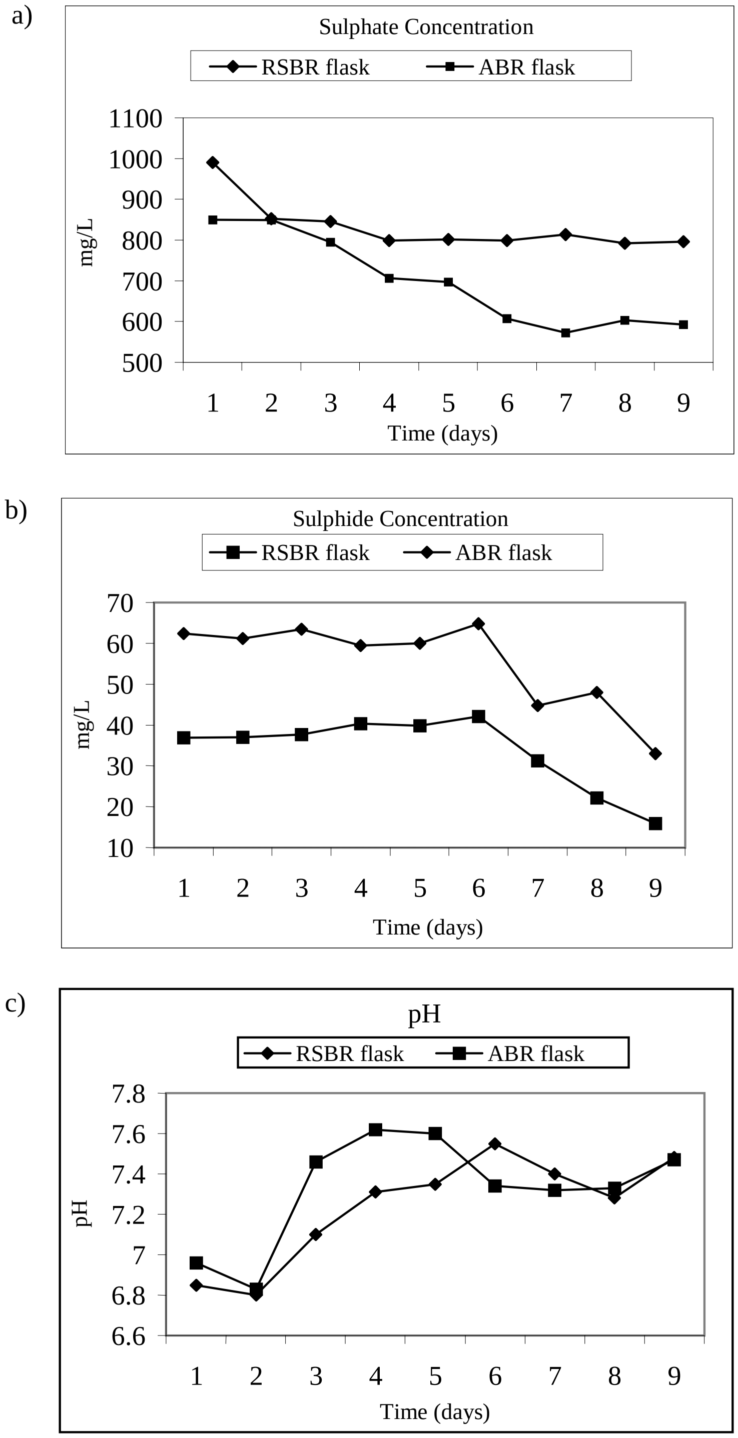

**Figure 5.3.** Changes in sulphate sulphide and pH in flask studies extending the reaction time in Recycling Sludge Bed Reactor and Anaerobic Baffle Reactor effluent by 9 days.

In contrast, the ABR shows relatively little change in COD values over the course of the flask study. Sulphate reduction shows the opposite to the COD result. While substantial additional carbon is solubilised in the RSBR stream with an extended incubation, sulphate reduction only increases by 24 mg.L$^{-1}$ over the 9-day period. This compared to 277 mg.L$^{-1}$ sulphate reduction over the same period in the ABR stream. This result may also have been anticipated, with the consumption ratio at 24 hours of 0.65 and 0.95 reported in Table 5.3 being close to the theoretical value of 0.61.

**Table 5.3.** An evaluation of pilot plant hydraulic retention time extension from 46 hours. Effluent from the Recycling Sludge Bed Reactor (8 hr HRT) and Anaerobic Baffle Reactor (38 hr HRT) was inoculated in flasks and incubated under anaerobic conditions for a further 142 hours.

| | **RSBR (8 hours)** | **ABR (38 hours)** | **Process (46 hours)** |
|---|---|---|---|
| **Pilot Plant (HRT 46 hours)** | | | |
| COD consumed mg.L$^{-1}$ | 1733 | 361 | 2094 |
| SO4 consumed mg.L$^{-1}$ | 434 | 583 | 1017 |
| Consumption ratio | 3.99 | 0.62 | 2.05 |
| Acetate equivalents produced mg.L$^{-1}$ | 264.7 | 355.6 | 620.3 |
| Acetate equivalents used in sulphate reduction % | 15.2 | 98.5 | 30.0 |
| **Pilot Plant + 24 hours** | | | |
| COD consumed mg.L$^{-1}$ | 74 | 108 | 182 |
| SO4 consumed mg.L$^{-1}$ | 144 | 114 | 256 |
| Consumption ratio | 0.53 | 0.95 | 0.71 |
| Acetate equivalents produced mg.L$^{-1}$ | 87.8 | 69.5 | 156.2 |
| Acetate equivalents used in sulphate reduction % | 118. | 64.3 | 85.8 |
| **PlantPilot + 96 hours** | | | |
| COD consumed mg.L$^{-1}$ | 423 | 44 | 467 |
| SO4 consumed mg.L$^{-1}$ | 48 | 186 | 234 |
| Consumption ratio | 8.81 | 0.24 | 1.99 |
| Acetate equivalents produced mg.L$^{-1}$ | 29.3 | 113.5 | 142.7 |
| Acetate equivalents used in sulphate reduction % | 6.92 | 25.7 | 30.6 |
| **Pilot Plant+ 142 hours** | | | |
| COD consumed mg.L$^{-1}$ | 0 | 11 | 11 |
| SO4 consumed mg.L$^{-1}$ | 2 | 4 | 6 |
| Consumption ratio | 0 | 2.8 | 1.8 |
| Acetate equivalents produced mg.L$^{-1}$ | 0 | 2.4 | 3.66 |
| Acetate equivalents used in sulphate reduction % | 0 | 22.2 | 33.2 |

These results serve to confirm the initial hypothesis that the RSBR would adapt to function primarily as a generator of CODf products, and that these products, mainly in the form of VFA, would be consumed in sulphate reduction, primarily in R2. Results for acetate equivalent production show this increased substantially in the first 24 hours, with a high level of efficiency in terms of COD conversion. This increase had tailed off by day 4.

The results show that most of the major changes in COD and sulphate values, due to an increase in retention time, were completed within around 36 - 48 hours following flask innoculation (Figures 5.4 and 5.5).

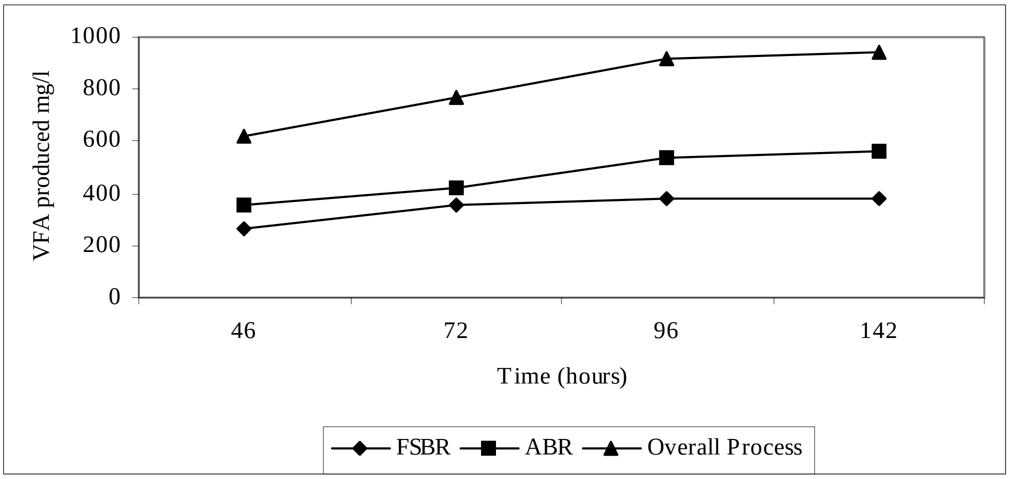

**Figure 5.4.** Primary sewage sludge converted to acetate equivalents utilised in sulphate reduction as a result of the extension of hydraulic retention time.

Since settleable solids in the RSBR are removed by up to 98%, it does not seem that any reduction in retention time from 8 hours would serve a useful purpose. While hydrolysis is still active in this stream when it leaves the RSBR, COD is mainly in the form of suspended and dissolved solids. The ABR, however, benefits substantially from an extension of HRT, and sulphate removal may be improved from around ~75 % to over 85%. It is apparent that the ABR might not be the best reactor design for this system and that reactors offering improved contact might work better in this application. The alternative would be to pond the treated water from the short ABR retention time, and allow the slower final removal to take place in this low-cost reactor environment with substantially increased HRT. This would utilise aspects of the ASPAM concept.

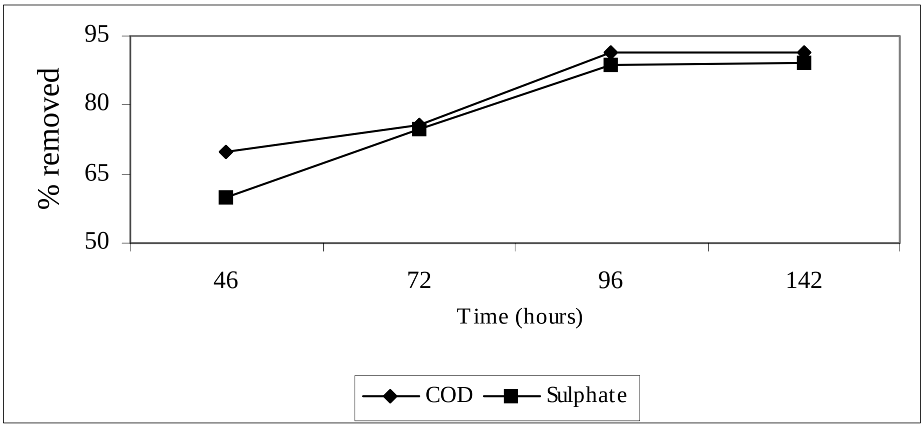

**Figure 5.5.** Flask studies showing the percent sulphate and COD removal where hydraulic retention time is extended.

Figure 5.5 summarises the results of the sulphate and COD removal as a result of an extension of retention time. From the results it can be seen that both the sulphate and COD removal efficiencies improve with time. Sulphate removal after 46 hours was 60%. If the HRT was extended to 142 hours a cumulative sulphate removal of 89%

could be achieved. The same trend applies to COD removal. Where the initial COD removal was 69.7%, a total 91.6% COD could be removed if the HRT was extended to 142 hours.

The flask studies indicated that an extension of the HRT from 46 to 96 hours would yield an optimum performance for the system (sulphate reduction +85%), and that this increase in reaction time should be mainly allocated to the R2 stage of the operation. This might be achieved by including an initial period of ABR contact, and then followed by a more protracted period in a lower-cost reaction environment such as an anaerobic pond.

# 6 CONCLUSION

In many respects the study reported here is still a work in progress. What started out as a circumscribed project to undertake the scale-up application of the ASPAM process in AMD treatment, resulted in the conceptualisation of the RSBR, and the design and evaluation, at pilot scale, of the Rhodes BioSURE Process®, and its development through laboratory- and pilot-scale studies.

During previous studies observations had been made on the microbial ecology of tannery waste stabilisation ponds (WRC Project K5/495), of recycling interactions between the sludge bed and water column in these systems, and the influence of this activity on sulphate reducing microbial consortia and the degradation of particulate COD. The observation was incorporated into a development of an IAPS approach to the management of these wastewaters, and the effectiveness of particulate removal evaluated in the retrofitting of a ponding system at Mossop-Western Leathers Co. in Wellington.

By the mid 1990s, increasing realisation of serious long-term environmental implications arising in the management of mine drainage wastewaters, and the focus of the EBG on the biotechnology of saline pollution, led to an investigation of ponding systems applied in AMD treatment (Project K5/656). During the development of the ASPAM system it became apparent that not only had the IAPS approach to AMD treatment received scant previous attention, but that the biosulphidogenic hydrolysis of organic solid wastes would play a crucial role in the provision of electron donor sources for sulphate reduction. Little was known about the mechanism involved.

This report, which covers the initial development of what became known as the Rhodes BioSURE Process®, followed a two-prong approach in the concurrent investigation of both basic and applied aspects of enhanced biosulphidogenic hydrolysis. The studies reported in Parts 1 and 2 on the development of the Rhodes BioSURE Process® (Reports 9 and 10 in the series) were undertaken in WRC Projects K5/869 and K5/972.

## 6.1 THE RHODES BioSURE PROCESS®

The core operation of the BioSURE Process® involves the mobilisation of electron donors for sulphate reduction using the enhanced hydrolysis of complex organic carbon substrates. Basic studies on the nature and mechanism of the processes involved in the enhanced hydrolysis operation led to the development of the RSBR, and its scale-up to pilot plant evaluation as a component of the Grootvlei desalination technology evaluation exercise, initiated by the decision of Cabinet in February 1997. The establishment of a WRC/EBG partnership with the ERWAT led to the investigation of PSS/AMD co-disposal as the primary focus of the pilot plant study undertaken at Grootvlei Mine in 1998/1999.

While previous studies have reported the solubilisation of PSS to provide a feedstock for nutrient removal in tertiary water treatment operations, these processes have been slow, and the yields of utilisable intermediates have generally been low (Whittington-Jones, 2000). In the dual-stage operation of BioSURE® the PSS solubilisation and sulphate reduction operations are optimised in separate unit processes.

Studies in this programme showed that in the RSBR a recovery of acetate equivalents from PSS of around 30%-35% (> 50% measured in laboratory studies) may be practically sustained over long periods of operation at the pilot-scale. This translated into a removal of sulphate from the Grootvlei minewater stream of around 70 - 75% in a relatively un-optimised system. Preliminary optimisation studies then showed that this might be increased to +85% sulphate removal, where an additional retention time would increase the recovery of PSS hydrolysis products to around 50% acetate equivalents. This represents the most efficient recovery of PSS intermediates recorded in the literature.

The results of the pilot study served to strengthen the preliminary hypothesis, derived from the initial ponding studies, that a reaction configuration, including settling and upwelling events, may be directly related to the observed enhanced hydrolysis of complex organic carbon structures in biosulphidogenic environments. The reaction mechanism of these two components of the RSBR system were subjected to further investigation and the results are detailed in Part 2 of this report (Whittington-Jones, 2002).

## 6.2 CONCLUSIONS

A number of conclusions may be drawn from the studies which have resulted in the development of the Rhodes BioSURE Process®.

1. Initial observations of enhanced hydrolysis of complex organic carbon substrates in biosulphidogenic environments have been followed up, and the broad effects confirmed in laboratory and pilot-scale studies. A descriptive model has been developed explaining the phenomenon in terms of reaction configuration and enzymatic effects. The establishment of dynamic sulphate reducing populations and sulphide gradients has been shown to enhance the activity of specific hydrolytic enzymes responsible for the breakdown and solubilisation of complex organic substrates such as PSS. Computer modeling of the RSBR operation has been undertaken;

2. The sulphidogenic hydrolysis reaction has been used in the conceptualisation and development of the Rhodes BioSURE Process® as a multi-stage operation in which complex organic carbon waste may be hydrolysed as an electron donor source. Sulphate reduction utilising the VFA intermediates produced is optimised in a separate unit operation, while the sulphide and alkalinity generated is used to precipitate heavy metals and neutralise AMD streams. A biodesalination of the stream may be effected where the influent sulphate is removed as elemental sulphur. The core operations of solubilisation and sulphate reduction have been reported here and other units of the overall process will be detailed in separate reports in this series;
3. Reactor design, scale-up, pilot plant construction and operation and

monitoring of the process treating AMD on-site at a gold mine over the period of a year has been reported;

4. The principles of the Rhodes BioSURE Process® design were demonstrated in the pilot study with PSS solubilisation and COD mobilisation to VFA intermediates being the primary events taking place in the RSBR, and sulphate reduction and VFA consumption taking place in the second stage (R2) operation;

5. Enhanced hydrolysis of PSS in the RSBR was demonstrated with solubilisation values > 98% recorded here. Sludge accumulation in the RSBR was hence extremely slow and the reactor was not desludged during the study period;

6. A COD:$SO_4$ ratio of 2:1 was shown to provide an effective feed blend to the process where PSS is the electron donor source;

7. Notwithstanding a number of shock loads and a variable feed composition over the course of the study period, the system maintained a ~75% sulphate removal using PSS as the electron donor source;

8. It was demonstrated that rigorously maintained anaerobic conditions are necessary in the reactor headspace to prevent the re-oxidation of sulphide to elemental sulphur and sulphate. It was shown in nitrogen headspace sparging studies that the performance efficiency values recorded over the study period should be adjusted upwards by around 10-15%. Stable operation of the process with this adjustment demonstrated sulphate removal in the range of 80-85%;

9. It was shown, in addition to the above, that an increase in HRT in the ABR would serve to increase sulphate reduction rates due to improved utilisation of VFA, and producing a potential sulphate removal ~90%. This indicates that while the ABR offers advantages of a low-cost reactor environment, it may not be the most efficient, and that other reactor configurations should be considered where more efficient throughput is required;

10. Using the HRAP in the final polishing operation, a microbiologically acceptable final effluent can be produced with infectious elements in the PSS feed effectively removed from the system.

## 6.3 RECOMMENDATIONS

A number of recommendations are made on the basis of the studies reported here:

1. Fundamental studies in the descriptive and quantitative modeling of the process should be continued in order to develop suitable kinetic criteria for the design of large-scale BioSURE Process® systems;
2. Follow-up studies on metal removal and sulphur recovery unit operations should be undertaken;

3. The observations of efficient PSS solubilisation should be followed up and possible sludge disposal application of the BioSURE Process® should be investigated;

4. Application of the BioSURE Process® in the solubilisation of other organic wastes should be investigated.

## 6.4 RESEARCH PRODUCTS

A number of research products were generated during the course of the studies associated with the development of the BioSURE Process® including 7 PhD and 8 MSc theses, 7 patents, 1 paper, 2 reports, 11 international and 19 local conference presentations.

## 6.5 FOLLOW-UP STUDIES

The initial observations of sulphidogenic enhanced hydrolysis, where complex organic carbon substrates were utilised as the electron donor source, led to the development of the RSBR and the sulphate reducing unit operations of the Rhodes BioSURE Process®. However, to effect a complete biodesalination function the final removal of the sulphate and metal loads from the wastewater stream is required. The development of the sulphide oxidation and sulphur and metal removal unit operations were tackled in a number of follow-up WRC projects. Follow-up actions have also included process development and modeling studies and applications of the principles of the BioSURE Process® in a number of areas.

### 6.5.1 Metal Removal

Studies reported in the ASPAM development had shown the feasibility of metal sulphide precipitation by recirculation of mixtures of the sulphidic organic stream from the sulphate reduction step with alkalised waters from the HRAP units. Follow-up studies on the processes involved in these reactions, and their potential application in process development were undertaken in collaboration with Prof Richard Loewenthal, Civil Engineering Department, UCT. These results will be the subject of a separate report.

The relationship of algal/sulphide metal precipitation reactions has also been the subject of studies by Prof John Duncan in the Department of Biochemistry, Microbiology and Biotechnology at Rhodes University. These will also be the subject of separate WRC reports.

### 6.5.2 Sulphide Oxidation and Sulphur Recovery

Final removal of sulphur species from the AMD wastewater requires the linearisation of the biological sulphur cycle and this may be effected by the oxidation to elemental sulphur of the sulphide produced in the RSBR. Development of a biologically-founded process for sulphur formation was investigated based on the preliminary description of floating sulphur biofilms observed during studies on the microbial ecology of tannery ponding systems. This approach to biological sulphur formation was developed into a sulphide oxidising floating sulphur biofilm reactor (Appendix 3).

These studies were undertaken in WRC Projects K5/1078 and K5/1336 and will be detailed in Report 11 of the series, 'Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa, Volume 4. The Rhodes BioSURE Process®. Part 3: Sulphur Production and Metal Removal Unit Operations'.

### 6.5.3 Modeling of the BioSURE Process®

Where the initial stages of BioSURE Process® development were founded in studies of microbial ecology, environmental biotechnology and bioprocess development, the reliable engineering of scale-up requires a quantitative basis for process modeling. Modeling studies were undertaken in collaboration with Prof Geoff Hansford and Dr Alison Lewis of UCT Chemical Engineering Department, and their students Neil Ristow and Anthony Knoble. Both AQUASIM and ASPEN approaches were undertaken in the modeling of the RSBR, and the results of these studies will be reported separately.

### 6.5.4 The Enzymology of Enhanced Hydrolysis

Studies on the mechanisms of enhanced hydrolysis of PSS, undertaken by Molepane (2000) and Whittington-Jones (2001), had shown the involvement of an interaction between sulphide gradients and enhanced enzyme activity. The studies became the subject of a follow-up study in the Environmental Enzymology Group, by Prof Chris Whiteley, in the Department of Biochemistry, Microbiology and Biotechnology at Rhodes University. Work by Drs Francois van Jaarsveld and Bret Pletschke has provided a theoretical model for the enzymology of enhanced hydrolysis. This work will be reported in WRC Project K5/1170.

### 6.5.5 Extension of BioSURE Process® Applications

Where the core insight of the BioSURE Process® involves the enhanced hydrolysis of complex carbon substrates to sustain active sulphate reduction, it became apparent that the reactions involved might usefully be related in other application areas. Full-scale commercial application of the Rhodes BioSURE Process® has become an important objective, and industrial partnerships to undertake this procedure have been established. The development of the Rhodes BioSURE Process® and the RSBR has been the subject of a number of patents (Appendix 2).

1. Follow-up studies in partnership with ERWAT have been undertaken applying the BioSURE Process® to sewage sludge solubilisation and disposal (WRC Project K5/1169).

2. The use of the enhanced hydrolysis reaction has been investigated in the mobilisation of lignocellulosic wastes to be used as electron donor sources in passive minewater treatment systems. The development of this approach is the subject of a DACST Innovation Fund Project led by Pulles, Howard and De Lange.

3. A study has been undertaken with ESKOM support to investigate the use of the BioSURE Process® for mobilisation of maize wastes as electron donor sources in active systems treating coal mine wastewaters.

The above studies are described in some detail in Appendix 3 and are also be the subject of independent reports.

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# 8 APPENDICES

## APPENDIX 1

## WRC STUDY 'SALINITY SANITATION AND SUSTAINABILITY' - PROJECT REPORTS

The WRC study which has been summarised here, developed out of a number of closely interrelated studies, undertaken for the WRC by the Rhodes University Environmental Biotechnology Group, over a 10 year period. The detailed findings associated with this work will be published separately as individual project reports. The following lists the WRC reports which cover the various investigations dealt with in the programme. The individual WRC projects under which the various studies were undertaken are listed separately below:

Report 1

Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 1. Overview.

Report 2

Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 2. Integrated Algal Ponding Systems and the Treatment of Saline Wastewaters.
Part1: Meso-saline Wastewaters - The *Spirulina* Model.

(Project K5/495: A Biotechnological approach to the removal of organics from saline effluents - Part 1.)

Report 3

Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 2. Integrated Algal Ponding Systems and the Treatment of Saline Organic Wastewaters.
Part 2: Hyper-saline Wastewaters - The *Dunaliella* Model.

(Project K5/495: A biotechnological approach to the removal of organics from saline effluents - Part 2.)

Report 4

Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.

Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters. Part1: The AIWPS Model.

(Project K5/651: Appropriate low-cost sewage treatment using the integrated algal high rate oxidation ponding process.)

Report 5

Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters. Part 2: Abattoir Wastewaters.

(Project K5/658: Algal high rate oxidation ponding for the treatment of abattoir effluents.)

Report 6

Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters.
Part 3: Mine Drainage Wastewaters - The ASPAM Model.

(Project K5/656: Appropriate low-cost treatment of sewage reticulated in saline water using the algal high rate oxidation ponding system.)

Report 7

Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters.
Part 4: System Performance and Tertiary Treatment Operations.

(Project K5/799: Development and monitoring of integrated algal high rate oxidation pond technology for low-cost treatment of sewage and industrial effluents;
Project K5/1073: Extension of applications and optimisation of operational performance of algal integrated ponding systems technology in appropriate low-cost treatment of industrial and domestic wastewaters.
Project K5/1362: Development and technology transfer of IAPS applications in upgrading water quality for small wastewater and drinking water treatment systems.)

Report 8

Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology

and Integrated Wastewater Beneficiation in South Africa.
Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters.
Part 5: Winery and Distillery Wastewaters.

(Project K5/1073: Extension of applications and optimisation of operational performance of algal integrated ponding systems technology in appropriate low-cost treatment of industrial and domestic wastewaters.)

Report 9

Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 4. The Rhodes BioSURE Process®.
Part 1: Biodesalination of Mine Drainage Wastewaters.

(Project K5/869: Biological sulphate desalination and heavy metal precipitation in industrial and mining effluents using the IAPS.)

Report 10

Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 4. The Rhodes BioSURE Process®.
Part 2: Enhanced Hydrolysis of Organic Carbon Substrates - Development of the Recycling Sludge Bed Reactor.

(Project K5/972: Process development and system optimisation of the integrated algal trench reactor process for sulphate biodesalination and heavy metal precipitation in mining and industrial effluents.)

Report 11

Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 4. The Rhodes BioSURE Process®.
Part 3: Sulphur Production and Metal Removal Unit Operations.

(Project K5/1078: Development and piloting of the integrated biodesalination process for sulphate and heavy metal removal from mine drainage water incorporating co-disposal of industrial and domestic effluents;
Project K5/1336: Scale-UP development of the Rhodes BioSURE Process® for sewage sludge solubilisation and disposal.)

Report 12

Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.

Volume 4. The Rhodes BioSURE Process®.
Part 4: Treatment and Disposal of Sewage Sludges:

(Project K5/1169: Intermediate scale-up evaluation of the Rhodes Process for hydrolysis and solubilisation of sewage sludges in a sulphate reducing bacterial system.)

## PROJECTS

The following lists the WRC Projects under which the studies in this series have been undertaken, and also the relevant reports in which the detailed results have been documented:

Project K5/410

A Biotechnological approach to the removal of organics from saline effluents.

Report: 1. Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 1. Overview.

Project K5/495

A Biotechnological approach to the removal of organics from saline effluents.

Report: 2. Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 2. Integrated Algal Ponding Systems and the Treatment of Saline Wastewaters. Part1: Meso-saline Wastewaters - The *Spirulina* Model.

Report: 3. Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 2. Integrated Algal Ponding Systems and the Treatment of Saline Organic Wastewaters. Part 2: Hyper-saline Wastewaters - The *Dunaliella* Model.

Project K5/651

Appropriate low-cost sewage treatment using the integrated algal high rate oxidation ponding process.

Report 4: Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.

Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters. Part1: The AIWPS Model.

Project K5/656

Appropriate low-cost treatment of sewage reticulated in saline water using the algal high rate oxidation ponding system**.**

Report 6: Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters. Part 3: Mine Drainage Wastewaters - The ASPAM Model.

Project K5/658

Algal high rate oxidation ponding for the treatment of abattoir effluents.

Report 5: Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters. Part 2: Abattoir Wastewaters.

Project K5/799

Development and monitoring of integrated algal high rate oxidation pond technology for low-cost treatment of sewage and industrial effluents.

Report 7: Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters. Part 4: System Performance and Tertiary Treatment Operations.

Project K5/869

Biological sulphate desalination and heavy metal precipitation in industrial and mining effluents using the IAPS.

Report 9: Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 4. The Rhodes BioSURE Process®. Part 1: Biodesalination of Mine Drainage Wastewaters.

Project K5/972

Process development and system optimisation of the integrated algal trench reactor process for sulphate biodesalination and heavy metal precipitation in mining and industrial effluents.

Report 10: Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 4. The Rhodes BioSURE Process®. Part 2: Enhanced Hydrolysis of Organic Carbon Substrates - Development of the Recycling Sludge Bed Reactor.

Project K5/1073

Extension of applications and optimisation of operational performance of algal integrated ponding systems technology in appropriate low-cost treatment of industrial and domestic wastewaters.

Report 7: Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters. Part 4: System Performance and Tertiary Treatment Operations.

Report 8: Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters. Part 5: Winery and Distillery wastewaters.

Project K5/1078

Development and piloting of the integrated biodesalination process for sulphate and heavy metal removal from mine drainage water incorporating co-disposal of industrial and domestic effluents.

Report 11: Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 4. The Rhodes BioSURE Process®. Part 3: Sulphur Production and Metal Removal Unit Operations.

Project K5/1169

Intermediate scale-up evaluation of the Rhodes Process for hydrolysis and solubilisation of sewage sludges in a sulphate reducing bacterial system.

Report 12: Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 4. The Rhodes BioSURE Process®. Part 4: Treatment and Disposal of Sewage Sludges.

Project K5/1336

Scale-up development of the Rhodes BioSURE Process® for sewage sludge solubilisation and disposal.

Report 11: Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 4. The Rhodes BioSURE Process®. Part 3: Sulphur Production and Metal Removal Unit Operations.

Project K5/1362

Development and technology transfer of IAPS applications in upgrading water quality for small wastewater and drinking water treatment systems.

Report 7: Salinity, Sanitation and Sustainability: A Study in Environmental Biotechnology and Integrated Wastewater Beneficiation in South Africa.
Volume 3. Integrated Algal Ponding Systems and the Treatment of Domestic and Industrial Wastewaters. Part 4: System Performance and Tertiary Treatment Operations.

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# APPENDIX 2. RESEARCH PRODUCTS

## 2.1. STUDENTS TRAINED

### 2.1.1 Post-Doctoral Fellows

Dr N. Nagabushana (2000) - Carbon digestion in mine water treatment.

### 2.1.2 PhD Students

G. Boshoff (1998) - Development of integrated biological processing for the biodesalination of sulphate and metal-rich wastewaters.

K. Whittington-Jones (2000) - Sulphide-enhanced hydrolysis of primary sewage sludge: implications for the bioremediation of sulphate-enriched wastewaters.

A. Clarke (current) - Molecular microbial ecology of sulphate reducing environments degrading complex organic carbon substrates.

L. Dekker (current) - IAPS in the treatment of acidic and saline organic wastewaters.

C. Ehlers (current) - The degradation of aromatic compounds in sulphate reducing environments.

H. Roman (current) - Digestion of cellulose in sulphate reducing environments.

D. Sanyahumbi (current) - The manipulation of immobilised sulphate reducing bacterial systems.

### 2.1.3 MSc Students

C.J. Corbett (2001) - The Rhodes BioSURE Process in the Treatment of Acid Mine Drainage Wastewaters.

J. Gilfillan (2000) - Biological sulphide oxidation and sulphur recovery from mine drainage wastewaters.

P. Molepane (2000) - Sulphate reduction utilising hydrolysis of complex carbon sources.

M. Bowker (2002) - The biology and molecular ecology of floating sulphur biofilms.

G. Chauke (2002) - The molecular microbial ecology of sulphate reduction in the Rhodes BioSURE Process.

M. Madikane (2002) - Biosulphidogenic hydrolysis of lignin and lignin model compounds.

J. Molwantwa (2002) - The enhanced hydrolysis of sewage sludge in sulphate reducing environments.

N. Rein (2002) - Biological sulphide oxidation in heterotrophic environments.

## 2.2. PATENTS

Rose P.D., Boshoff, G.A., Hart, O.O., Barnard, J.P. 1997. The double deck trench reactor.
RSA 97/4165 (Final).
Australia 711069(Final).

Rose P.D., Duncan, J.R., van Hille, R.P., Boshoff, G.A. 1998. Alkalinity and biorefining.
RSA 98/3204 (Final).

Rose,P.D., and Hart, O.O. 1988. Treatment of Water-modification.
RSA 98/9429 (Final).

Rose,P.D. and Hart, O.O. 1988. Treatment of sewage.
RSA 98/9428 (Final).

Rose, P.D. 1998. Treatment of sulphate containing metaliferous wastewater.
RSA 98/3202 (Final).

Rose P.D., Duncan, J.R., van Hille, R.P., Boshoff, G.A. 1999. Use of ponds to treat sulphate solutions and ASPAM process.
RSA 99/4585 (Final). US patent pending.

Van Hille, R.P., Boshoff, G.A., Rose, P.D., Duncan, J.R. 1999. A continuous process for the biological treatment of heavy metal contaminated acid mine drainage water.
RSA 99/3867.

## 2.3. PAPERS

Rose,P.D., Boshoff, G.A., van Hille, R.P., Wallace, L.M.C., Dunn, K.M. and Duncan, J.R. 1998. An integrated algal sulphate reducing high rate ponding process for the treatment of acid mine drainage wastewaters. Biodegradation 9:247-257.

## 2.4. INTERNATIONAL CONFERENCES

Boshoff, G.A., Duncan, J.R., Burton, S.G. and Rose, P.D. 1995. The removal of heavy metals from industrial effluents by sulphate reducing bacteria. Proceedings of Society for General Microbiology first Joint meeting with the American Society

for Microbiology on Bioremediation, Aberdeen, Scotland, 1995.

Boshoff, G.A., Duncan, J.R. and Rose, P.D. 1996. Algal integrated ponding system for the treatment of mine drainage waters. Proceedings of 7th International Conference of Applied Algal Biotechnology, Knysna, April 1996.

Rose, P.D. and Dunn, K. 1996. The integrated photosynthetic high rate oxidation pond for treating tannery waste waters. Proceedings of 7th International Conference of Applied Algal Biotechnology, Knysna, April 1996.

Boshoff, G. and Rose, P. 1998. Algal biomass as a carbon source in sulphate reducing ponding treatment of acid mine drainage water. European Union Summer School: The Biological Sulphur Cycle - Environmental Science and Technology. Wageningen, The Netherlands, April 19-24, 1998.

Boshoff, G. and Rose, P. 1998. The use of tannery wastewater as a carbon source for sulphate reduction and heavy metal removal. European Union Summer School: The Biological Sulphur Cycle - Environmental Science and Technology. Wageningen, The Netherlands, April 19-24, 1998.

Rose, PD., Boshoff, GA., van Hille, RP., Wallace, L., Dunn, KM. and Duncan, JR. 1998. An integrated algal sulphate reducing high rate ponding process for the treatment of acid mine drainage wastewaters. Sulphur Environmental Science and Technology Workshop, Wageningen, Holland.

Duncan, JR., van Hille, RP., Boshoff, GA., Wallace, L. and Rose, PD. 1998. Biological treatment of metal containing wastewater using an integrated approach. 4th Intl. Symposium on Envir. Biotechnol., Belfast, Ireland.

Duncan, JR., van Hille, RP., Boshoff, GA., Wallace, L. and Rose, PD. 1998). Biological treatment of metal containing wastewater using an integrated approach. Proc. 4th Intl. Symp. Envir. Biotechnol., Belfast, Ireland.

van Hille, RP., Boshoff, GA., Rose, PD. and Duncan, JR. 1998. A continuous process for the biological treatment of heavy metal contaminated acid mine water. Proc. 4th Intl. Symp. Envir. Biotechnol., Belfast, Ireland.

Boshoff, GA., Duncan, JR. and Rose, PD. 1998. Heavy metal sequestration by microalgal photosynthate released in high rate algal ponding treatment of acid mine drainage. 4th Intl. Symp. Envir. Biotechnol., Belfast, Ireland.

Boshoff, GA., Duncan, JR. and Rose, PD. 1998. Microalgal biomass: An independent carbon source for sulphate reduction in an algal ponding treatment of acid mine drainage. Proc. 4th Intl. Symp. Envir. Biotechnol., Belfast, Ireland.
Rose, P.D., Boshoff, G.A., van Hille, R.P., Wallace, L.C.M., Dunn, K.M. and Duncan, J.R. 1999. Acid mine drainage wastewater treatment in an integrated algal ponding operation. IAWQ Conference on Waste Stabilization Ponds, Morocco, 20 -23 April.

Rose, P.D. 1999. Integrated Biological Treatment of Metal and Sulphate Enriched Drainage Waters Utilising Low-cost Complex Organic Carbon Sources. European Union Conference on the Aznalcolar disaster. Seville, January, 1999.

## 2.5. LOCAL CONFERENCES

Boshoff, G., Leukes, W., Jacobs, E., Sanderson, R. and Rose P.D. 1994. Efficiency of zinc removal by microalgae immobilised on hollow-fibre ultrafiltration membranes. Proc. Eighth Biennial Conference South African Society for Microbiology Grahamstown.

Boshoff, G., Duncan, J and Rose, P. 1994. The precipitation of heavy metals by sulphate reducing bacteria in a mixed bioreactor. Proc. Eighth Biennial Congress of the South African Society of Microbiology. Rhodes University, Grahamstown, June.

Boshoff, G., Leukes, W., Jacobs, E., Sanderson, R and Rose, P. 1994. Efficiency of zinc removal by microalgae, immobilised on hollow fibre ultrafiltration membranes. Proceedings of First WISA/MTD Seminar, Van Stadens, November, 1994.

Boshoff, G., Duncan, J and Rose, P. 1995. The utilisation of algal biomass as a carbon source for sulphate reducing bacteria. Proceedings of All-African Biotechnology Conference, Pretoria, November, 1995.

Boshoff, G.A., Duncan, J.R. and Rose, P.D. 1996. The removal of heavy metals from industrial effluents by sulphate reducing bacteria. Proceedings of Water Institute of Southern African Biennial Conference, Port Elizabeth, May, 1996.

Boshoff, G.A., Duncan, J.R. and Rose, P.D. 1996. The production of extracellular polysaccharides by the salt-tolerant alga under different environmental conditions. South African Society for Microbiology, June, 1996.

Rose, P.D., Hart, O.O., Barnard, J., Shipin, O. and Boshoff, G. 1997. Algal biotechnology and water treatment. Second South African Biotechnology Conference, Biotech SA '97, Grahamstown, January.

Boshoff, G.A., Radloff, S., Duncan, J.R. and Rose, P.D. 1997. Biological sulphate removal for the treatment of acid mine drainage - a statistical perspective. Second South African Biotechnology Conference, Biotech SA '97, Grahamstown, January.

Molipane, N.P., Boshoff, G.A. and Rose, P.D. 1997. The culture of *Dunaliella* and the production of extracellular polysaccharide under different environmental conditions. Second South African Biotechnology Conference, Biotech SA '97, Grahamstown, January.

van Hille, R.P., Wallace, L.C.M., Boshoff, G., Rose, P.D. and Duncan, J.R. 1997.

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Rose, P.D., Boshoff, G.A., van Hille, R.P., Wallace, L.M.C., Dunn, K.M., Hart, O.O. and Duncan, J.R. 1998. Treatment of acid mine drainage water in an integrated sulphate reducing high rate ponding process. WISA ‘98, Cape Town.

Wallace, L.M.C., Boshoff, G.A., Duncan, J.R. and Rose, P.D. 1998. A microbial sulphate reducing system utilised for the precipitation of heavy metals from refinery wastewaters. WISA ‘98, Cape Town.

van Hille, R. P., Boshoff, G.A., Rose, P.D. and Duncan, J.R. 1998. A continuous process for the biological treatment of heavy metal contaminated acid mine drainage. WISA ‘98, Cape Town.

Boshoff, G.A., Duncan, J.R. and Rose P.D. 1998. Sulphide toxicity to microalgae. WISA ‘98, Cape Town.

Dekker, L.G., Clark, S,J., Hart, O.O. and Rose, P.D. 2000. Dentirification and tertiary treatment of domestic wastewaters using stress manipulation in algal ponds. Biotech SA 2000, BIOY2K Grahamstown, January.

Nightingale, L., van Hille, R.P., Rose, P.D. and Duncan, J.R. 2000. Algal alteration of carbonate species equilibria: bioremediation potential. Biotech SA 2000, BIOY2K Grahamstown, January.

Wallace, L.C.M., Rose, P.D. and Duncan, J.R. 2000. Competitive metal ion removal from zinc refinery wastewater treated with sulphide-containing anaerobically digested sewage sludge. Biotech SA 2000, BIOY2K Grahamstown, January.

Whittington-Jones, K., Corbett, C.J.,. Whiteley, C., van Jaarsveld, F. and Rose, P.D. 2000. Enhanced hydrolysis of primary sewage sludge under sulphate reducing conditions. Biotech SA 2000, BIOY2K Grahamstown, January.

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# APPENDIX 3. TECHNOLOGY TRANSFER ACTIVITIES

The current report is a component investigation of the WRC research programme 'Salinity, Sanitation and Sustainability', as noted in Appendix 2 above. This study was based on previous developments of IAPS in treatment of saline wastewaters (WRC Project K5/495), and in turn led to a number of follow-on spinoff developments of which the Rhode BioSURE Process® became the principal focus. Technology diffusion and technology transfer activities initiated during the course of the study involved interactions with industry partners and led to scaled-up evaluations of the technology under development.

## 3.1 OFFICIAL OPENING OF THE RHODES BIOSURE® PILOT PLANT

The investigation of sulphate saline wastewater treatment and the resulting scale-up developments of the Rhodes BioSURE Process® largely took place at sites remote from the EBG laboratories in Grahamstown. As a result it was decided to establish a BioSURE® pilot plant on-site at the EBFS to facilitate both fundamental and up-scale/down-scale investigations.

The BioSURE® and Sulphur Biology Pilot Plants, located at the Rhodes University Environmental Biotechnology Field Station, at the Grahamstown Works, was opened during the Mine Water Conference at the BIOY2K meeting in January, 2000, by the Executive Director of the Water Research Commission, Mr P Odendaal. The event was attended by around 150 people including conference delegates from academia, industry and government.

**Figure A 3.1.** The Rhodes BioSURE® Pilot Plant at the Environmental Biotechnology Field Station opening by the Executive Director of the Water Research Commission, Mr P Odendaal. At left Dr D Woods, Vice Chancellor, Rhodes University.

## 3.2 BIODESALINATION - SULPHIDE OXIDATION AND SULPHUR RECOVERY

The final removal of sulphur species is necessary to effect the linearisation of the biological sulphur cycle, and thereby providing a biodesalination of the sulphate-saline wastewater system. Where sulphidogenesis provides the initial step in the biodesalination operation, sulphide may be removed in a number of ways, including its oxidation to $S^o$. Following the final precipitation and removal of $S^o$ from the treated stream, it may serve as a value-added end-product of the waste treatment process.

The formation of sulphur biofilms have been observed at the air/water interface in sulphidogenic systems under specific conditions, including high soluble sulphide concentrations. These had been reported in the Wellington tannery ponding system where sulphur had been observed to occur and form thick white layers on the pond levees (Figure A3.2).

The microbial ecology of sulphur biofilm formation in the Wellington tannery ponds has been investigated by the EBG. The underlying mechanisms controlling the formation of $S^0$ in these systems has been described by Bowker (MSc, 2002), Chauke (MSc, 2002) and Rein (MSc, 2002), and production of sulphur has been replicated under controlled conditions in the laboratory. Sulphur biofilms form at the air/water interface at high sulphide concentrations and a redox potential around -150mV. A biologically initiated production of polysulphide is catalysed by extracellular bacterial sulphur production, and this in turn leads to the crystalisation of ortho-rhombic sulphur, which may be settled as a heavy precipitate of mainly $S^0$ (Figure A33).

**Figure A3.2.** Floating sulphur biofims in the tannery ponds at Wellington. Biofilms of sulphur form at the air/water interface in the presence of high sulphide concentrations.

The above studies led to the development of a number of SOB configurations which have been evaluated at both laboratory- and pilot-scale at the Experimental Field Station in Grahamstown. This development was undertaken in association with the DACST Innovation Fund project on Passive Systems for mine water treatment described below. The Floating Sulphur Biofilm Reactor (Figure 7.20), operates with sulphide feed waters from an RSBR, or second stage sulphate reducing bioreactor, containing >100 mg.L$^{-1}$ sulphide. By establishing controlled redox conditions at the air/water interface a biofilm forms, the molecular microbial ecology of which has been described by Bowker (2002). Once sulphur formation commences the film develops rapidly and at a stage separation from the biofilm and settling commences. Harvesting of the film is managed to recover a maximum settleable sulphur precipitate. Results of this work will be reported in WRC Project: 'The Rhodes BioSURE Process®. Part 3: Sulphur Production and Metal Removal Unit Operations'.

**Figure A3.3.** Bacterial extracellular sulphur catalyses the formation of polysulphide in the presence of sulphide at redox values around -150 mV. At the air/water interface this is followed by the crystalisation of ortho-rhombic sulphur.

## 3.3 TREATMENT FOR SEWAGE SLUDGE SOLIDS

The use of sewage sludge as a carbon source for the Rhodes BioSURE Process® led to observations of accelerated hydrolysis of both primary and secondary sludges in sulphidogenic environments. In collaboration with ERWAT a joint WRC/ERWAT/Rhodes University project (K5/1169) has commenced to develop an application of the process for sewage sludge disposal. In addition to solids solubilisation and the removal of heavy metals, high levels of sludge disinfection are achieved.

## THE RHODES BioSURE PROCESS®: 2 - TREATMENT AND DISPOSAL OF SEWAGE SLUDGES

Sewage solids and latrine wastes have been used for millennia as soil amendments and fertilisers, and due to parasite and bacterial infections, and also heavy metal contamination, are the source of major public health and sanitation problems, affecting millions of human beings today. Yet in the implementation of public health programmes, removal of this nutrient resource from agricultural production, particularly in the developing world, presents a severe loss to 'closed system' and 'integrated wastewater resource management' objectives. At the same time sludges present a major disposal problem in the developed world, with few solutions remaining as landfill and marine disposal options are terminated.

Research results emerging from the AMD studies, using sewage sludge as the carbon and electron donor source for sulphate reduction and mine wastewater treatment, provided an early indication that the Rhodes BioSURE Process® might also offer an efficient method for disposing sewage sludges (Figure A3.4). By manipulating sulphate and sludge ratios, the process as described above delivers a substantial reduction in overall solids levels in PSS. Apart from the solids reductions achieved in this way, the process also effects the precipitation of contaminating heavy metals as metal sulphides, hydroxides and possibly carbonates, and the disinfection of the feed sludges. Residual organic solids may then be disposed via biological filtration, activated sludge or similar treatment, to final land disposal as a safe humus material. Results of the study showed that fed to a HRAP system, a high grade algal biomass may be produced, and also a final water quality which meets the general standard requirement suitable for surface discharge.

Where the external sulphate source is limited and the maintenance of a sulphate inventory within the system is required, the SOB may be used to recover $S^0$, oxidise it fully and return it to the process as sulphate. In principle, the primary source of sulphate could be derived from a number of industrial effluents, in addition to AMD, or from naturally occurring sulphate sources in the sewage feed.

The full-scale evaluation of the process has been undertaken by ERWAT at the Ancor Works in Springs, close to the Grootvlei Mine. A technical-scale plant has been constructed on site and a pipeline laid from Grootvlei Mine for the delivery of high-sulphate waters (Figure 3.5). This work will be reported in WRC Report: 'The Rhodes BioSURE Process®. Part 4: Treatment and Disposal of Sewage Sludges'.

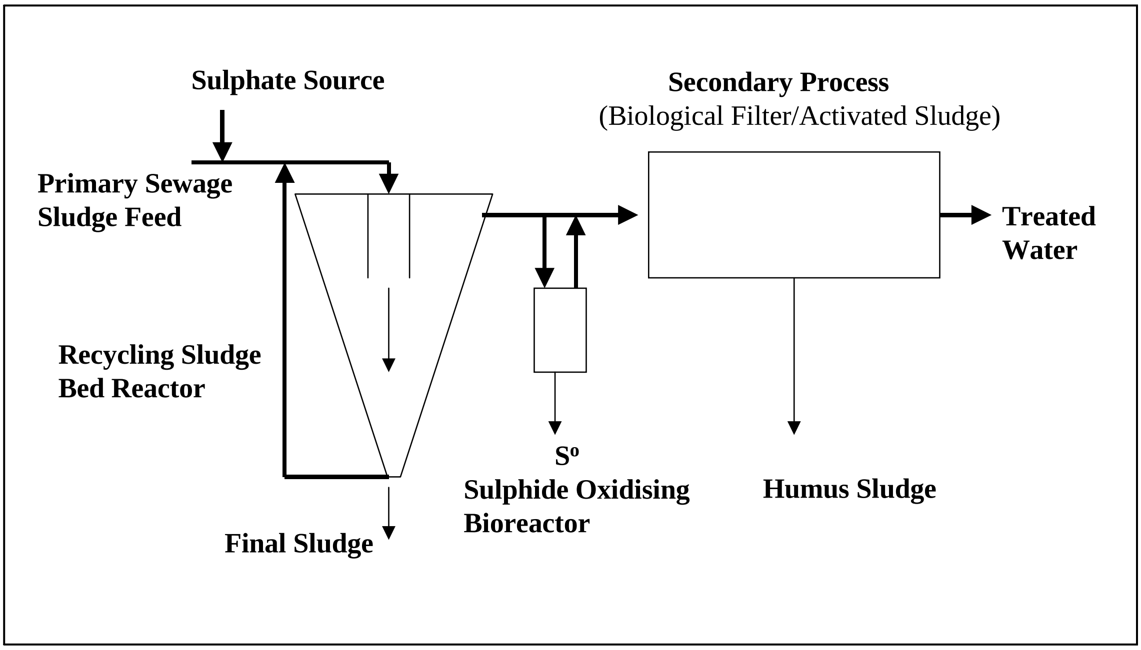

**Figure A3.4.** Application of the BioSURE Process® in the solubilisation of primary sewage sludge. The solubilised fraction passes from the Recycling Sludge Bed Reactor to a secondary process where organics are converted to a humus sludge, and treated water is produced. A final sludge containing metals, cysts and ova is recovered in a small volume from the Recycling Sludge Bed Reactor. Reduced sulphate may be recovered as $S^0$ in a Sulphide Oxidising Bioreactor.

## 3.4 ESKOM INTEGRATED MANAGEMENT OF COAL MINE WASTEWATERS

ESKOM have funded the application of various aspects of the WRC study in a programme to establish a comprehensive ‘integrated wastewater resource management’ approach to coal mining wastewaters. In addition to water treatment the project aims to develop aspects of the value recovery and beneficiation findings which have developed in the WRC study, including job creation and community rehabilitation initiatives in preparation for mine closure. This undertaking involves the use of the Rhodes BioSURE Process® as a pretreatment to RO membrane desalination, effecting the removal of metals, sulphate, calcium and other scaling salts, and the return of the treated water to mining and power generation requirements. The saline reject streams will pass to *Spirulina* and *Dunaliella* solar evaporation ponding cascades where biomass and fine biochemical production will be used as a component of downstream beneficiation operations. The ESKOM project will ultimately handle a minewater stream of 20 $ML.DAY^{-1}$, and provides an opportunity for the large-scale evaluation of the ‘integrated wastewater resource management’ objectives which formed one of the major motivations for the WRC programme. The integrated treatment system is shown in Figure A3.6.

**Figure A3.5** The 2 ML scaled-up Recycling Sludge Bed Reactor in the BioSURE® sewage sludge solubilisation technical-scale plant constructed at ERWAT's Ancor Works in Springs. Surface struts provide supports for a covering membrane.

## 3.5 PASSIVE SYSTEMS AND THE INNOVATION FUND PROJECT

Passive treatment systems for the remediation of mine drainage wastewaters have been under investigation by William Pulles of PHD Co. The Rhodes EBG was invited to participate in the DACST Innovation Fund project in which the commercialisation of sulphate removing passive treatment systems was to be investigated. Current research is investigating the application of the degrading bed reactor for the solid state digestion of lignocellulosic wastes as a feedstock in the passive treatment operations. The sulphate reducing degrading packed bed reactor has been based on the RSBR development associated with the BioSURE Process®.

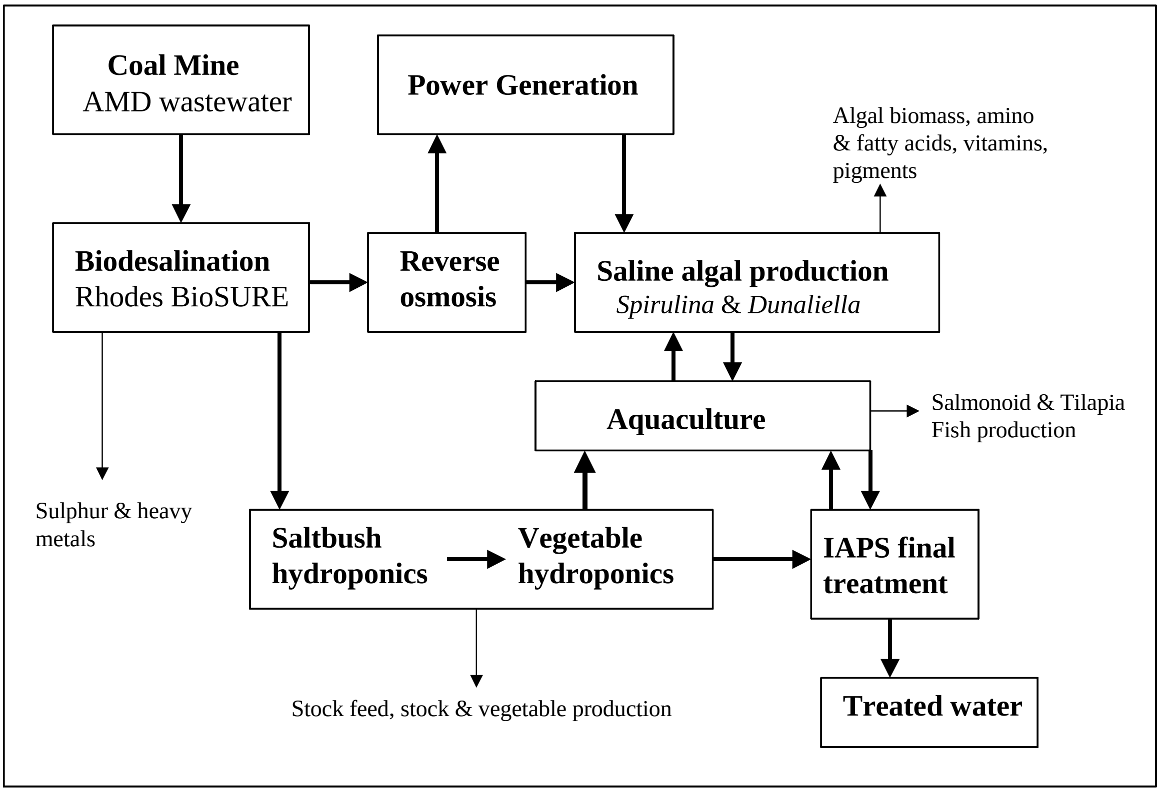

**Figure A3.6.** The ESKOM Sustainable Development Project in 'integrated wastewater resource management' based on the biodesalination and treatment of coal mine wastewaters using the Rhodes BioSURE Process® as the initial process step. Following biodesalination the partly demineralised stream containing residual chloride salinity passes to reverse osmosis and back to power generation. The chloride saline reject stream passes to meso- and hyper-saline algal production systems. Residual partly treated water may be used in aquaculture, salt bush, stock rearing and intensive horticulture production operations. Treated water may pass via an IAPS polishing step to discharge in the public water system.