THE RHODES BioSURE PROCESS IN THE TREATMENT OF ACID MINE DRAINAGE WASTEWATERS

by

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Abstract

While sulphate-enriched wastewaters are generated in a number of industrial processes, such as tanning, paper manufacture and metals processing, the principal contributors to large-scale pollution from this source in South Africa are the gold and coal mining industries. Both biological and physico-chemical processes, set in train by mining operations, give rise to the oxidation of sulphur species, and the resultant generation of AMD. The Vaal River system is most affected and receives large tonnages of mining related salinity as both direct discharges, and in diffuse runoff flows.

The long-term burden of this problem, and sustaining ongoing treatment over the time-frames involved will almost certainly resort to the community inhabiting the area, notwithstanding progressive mine closure legislation and comprehensive regulation governing the polluter-pays principle.

The volume and time-frame of the AMD problem, and the need for a long-term and sustainable response has focused interest in biological treatment approaches. These have concentrated on active and passive treatment systems, both of which rely on microbial activity related to the biological sulphur cycle. Notwithstanding the reactor type, and the particular treatment approach used, widespread application of active AMD treatment has not yet been seen on any large scale. Singular factors constraining process development are bioreactor design, cost of bioreactor construction, and the cost of the carbon source and electron donor for the biological sulphate reduction process. The SRB are able to utilise only a limited range of small organic molecules.

The studies reported here were motivated by the need to evaluate low-cost options and the treatment of high volume AMD flows. This has focussed research activity on bioprocess developments using complex organic compounds derived from waste streams as electron donor sources, and the integration of AMD treatment with other waste treatment objectives. The co-disposal of organic wastes with AMD treatment would enable the development of an 'integrated resource management' approach to the problem, including sustainability of treatment operations over the long time-frames involved. Apart from the cost advantages accrued to waste treatment, the recovery of the treated water as a resource to the wider community provides a potentially important value-added function to the combined operation.

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List of Abbreviations

ABR	Anaerobic Baffle Reactor
ALD	Anoxic Limestone Drains
AMD	Acid Mine Drainage
APS	Adenosine Phosphosulphate
ATP	Adenosine Triphosphate
CBA	Cost Benefit Analysis
COD	Chemical Oxygen Demand
DWAF	Department of Water Affairs and Forestry
EBG	Environmental Biotechnology Group
FSBR	Falling Sludge Bed Reactor
HDPE	High Density Polyethylene
HRAP	High Rate Algal Pond
HRT	Hydraulic Retention Time
MSR	Multi-Stage Falling Sludge Bed Reactor
PLC	Programmable Logic System
PVR	Precipitation Valley Reactor
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
SRB	Sulphate Reducing Bacteria
UASB	Upflow Anaerobic Sludge Bed Reactor
VFA	Volatile Fatty Acid

CHAPTER 1.

THE BIOREMEDIATION OF ACID MINE DRAINAGE WASTE WATERS

1.1. ACID MINE DRAINAGE WASTEWATERS

All the active gold mines in the major mining basins of South Africa are dewatering in order to remain operational (Scott, 1995). Water leaving the mine, also referred to as Acid Mine Drainage (AMD), may be characterised by one or more of the following: low pH, high Total Dissolved Solids (TDS), high sulphates (SO_4^{2-}), and/or high levels of heavy metals especially Iron (Fe), Manganese (Mn), Nickel (Ni) and/ or Cobalt (Co) (Scott, 1995).

AMD is generated due to geochemical trauma induced by mining operations (Rose *et al.,* 1998). The main sources of AMD in abandoned mine areas are usually old waste rock dumps and rock walls in tunnels and shafts. Open pits and underground workings will often be filled partly or completely with polluted water after the closure of a mine, and overflow from such systems may in some cases contribute significantly to the total transport of pollutants out of the area (Christensen *et al.*, 1996).

Mineral build-up caused by acid mine drainage presents a formidable problem in South Africa, particularly in view of the fact that it imposes a severe restriction on the beneficial use of water. The effects of this are compounded by the fact that the majority of gold and coalmines are located in the most highly populated areas in the country where the demands on the fresh water supplies for industrial use are the highest (Henzen & Pieterse, 1975)

Although mines only use 4.2 per cent of the total amount of water used in the Republic, the pollution loads carried in mine effluents can impose limitations on the usefulness of the fresh water resources. It has been estimated that when mine pumping operations finally cease, filling of the voids would occur within about a decade, and then to be followed by long term surface flows of AMD (Scott, 1995).

The Witwatersrand supergroup sediments contain varying proportions of sulphide minerals, the predominant sulphide being pyrite (FeS_2). In many of the gold bearing reefs this mineral may form up to three percent (by weight) of the rock. Various forms of pyrite occur, some are more susceptible to weathering breakdown than others, for example the Kimberley Reef has a higher pyrite content than the other reefs (Scott, 1995). Acidic drainage is a persistent environmental problem at many active and abandoned sulphide and coal mine sites. Mining of these sediments has produced surface rock piles, sand and slime dumps, underground backfilled rock piles and spoil heaps in stopes and haulage's. These all contain pyrite which on exposure to oxygen, water and in the presence of oxidising bacteria such as *Thiobacillus ferrooxidans*, oxidises to produce dissolved metals, sulphate and acidity (Gazea *et al.*, 1996).

Acid mine drainage (AMD) results from the oxidation of pyritic iron sulphide to sulphate and Fe^{2+}. Under acidic conditions the process proceeds by two reactions (Stumm and Morgan, 1981):

$$FeS_2 + {}^7/_2\, O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \text{ ----------------- (1)}$$

$$Fe^{2+} + 3\, O_2 + H^+ \rightarrow Fe^{3+} + 2\, H_2O \text{ ----------------- (2)}$$

The major inorganic oxidation reaction follows equation 1. At a pH of 4.5 the abiotic oxidation of Fe^{2+} slows down (Funke, 1990), but at pH values below 3.5 *T. ferooxidans*, an acidic chemolithotroph, increases the rate of oxidation of the Fe^{2+} ion to the Fe^{3+} ion (Obereke and Stevens, 1991). The Fe^{3+} ion is then hydrolysed by water to form the insoluble precipitate ferrihydrite and acidity by the following reaction:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \text{ ----------------- (3)}$$

In addition to reacting directly with oxygen, pyrite may also be oxidised by dissolved ferric iron to produce additional Fe^{2+} and acidity as shown in equation 4.

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \text{ ----------------- (4)}$$

Once the acid generating reactions have begun, oxygen is only necessary for the microbially catalysed oxidation of ferrous to ferric iron. Pyrite will continue to be oxidised, in the absence of oxygen, by ferric iron. At this stage the process becomes largely unstoppable (Brierly and Brierly, 1997).

Acid mine drainage does not only occur from the mine itself but also from rock dumps and tailings areas. These two sources contain a high concentration of sulphides and/or sulphosalts, which are associated with most ore and coal bodies. During mining, pyrite and marcasite are left on the ground surface. Exposure to oxygen and moisture results in oxidation of FeS_2 and the release of acids into the water (Funke, 1990; Johnson, 1995). Acid mine drainage may also result from slimes (pulps containing very finely ground minerals from the ore) which are contained in slimes dams (Querol, 1999). Mine drainage pollutants, such as iron and hydroxides, may also arise from the neutralisation of iron sulphate and are precipitated in riverbeds. The drainage of water from underground mining works located below the surface drainage levels also contributes to mine drainage pollution (Henzen and Pieterse, 1978).

1.2. GEOCHEMICAL PROBLEMS IN WITWATERSRAND GOLD MINES.

Gold was first discovered on the Witwatersrand in 1886 on the farm Langlaagte, 5 km west of the city of Johannesburg. This conglomeratic outcrop was found to stretch for a continuous distance of 50 km and has come to be known as the Central Rand Goldfield. Soon afterwards similar gold bearing outcrops were found in the East Rand, West Rand and around the Klerksdorp area. Further prospecting also led to the identification of the Carltonville and Klerksdorp Goldfield, and the Welkom and the Kinross/Evander Goldfields in 1956 (Department of Mineral and Energy Affairs Report, 1995). This led to the gold-bearing reefs being exploited along a strike of 480 kms and to depths of over four kilometres, making it the largest gold mining area in the world (Funke,1990).

In the 1970's the gold mining industry underwent a period of growth due to the rise in the world gold price, with South Africa responsible for 75% of the 'free world's' gold production. However, due to increased labour costs, labour and political unrest and a reduction in the gold price in the mid-1980's, the gold mining industry entered a slump. This, together with the emergence of Russia and China into the gold market led to a decline in South Africa's relative share of the gold market (Department of Mineral and Energy Affairs, 1995).

Although the poor quality of recycled service mine water in operating mines costs the mining industry approximately R300 million annually, based on its corrosive, scaling and fouling potential (McKay *et al.*, 1991; Juby *et al.*, 1996), the problem most likely to have major ecological and economic effects is pollution from water decanting from abandoned mines. Many mines have been forced to close due to economic constraints associated with the increased depths at which ore has to be mined and a falling gold price. In 1995, there were only four mines still working underground in the Witwatersrand compared to the 39 operational mines in the 1940's (Scott, 1995). The abandonment of mines has left behind surface rock piles, sand and slime dumps and spoil heaps in stopes and haulages, all of which contain pyrite. The oxidation of this material generates acidity and dissolved salts such as calcium, sulphate, sodium and chloride at levels of up to 11 000 mg/l (Funke, 1990).

In an investigation carried out by Scott (1995) the following influences on the environment of mine water discharge were identified:

- Increase in subsurface instability and seismic activity;
- Negative impacts on the natural environment around the discharge points;
- Water quality deterioration;
- Recharge of local aquifers by mine waters;
- Negative impact on water users downstream of the discharge points;
- Water inrushes into the remaining operational mines from the filling geohydrological basins.

1.3. THE GROOTVLEI MINE: A CASE STUDY

Gold Mining in the Far East Rand began at the turn of the century, leading to the establishment of a number of mines and excavation in an underground area known as the Far East Rand Basin. In order to continue operations, mines were forced to pump water from underground to either dewater areas for new development or to keep existing works dry. Due to their different positions on the basin and the fact that the mines were interconnected, this task was not equally shared, with mines on the periphery pumping intermittently and mines operating in the deeper part of the basin, pumping large volumes continuously (Scott, 1993). With the closure of many mines in the 1960's, the lower works were allowed to flood and dewatering became the responsibility of Grootvlei, SA Lands and Exploration Gold Mining Company (Sallies) and Vlakfontein Gold Mining Company (Vlakfontein). As is shown in Figure 1.1, dolomite is intercepted by the

Grootvlei mine on both sides of the Blesbokspruit, and by Sallies mine which is situated west of the Blesbokspruit. Both mines are interlinked and it is also suspected that the dolomite at Grootvlei mine is recharged with water probably from the Blesbokspruit, the principal drainage route of this catchment area (Department of Minerals and Energy Affairs, 1995).

When Sallies closed in 1976, pumping was taken over by Grootvlei. With the closure of Vlakfontein in 1977, the water level in the basin was allowed to rise further, reaching 1606 meters below datum where it was maintained from 1988. Pumping at Sallies was suspended in 1991 and a new pump station was installed at Grootvlei No.3 shaft. To prevent flooding of its underground workings, Grootvlei had then to pump an estimated 24 300 Ml.year water from both mines.

The pump station discharges millions of liters of highly contaminated water into the nearby Blesbokspruit wetland on a daily basis with severe ecological implications. This water is typical acid mine drainage (AMD) with low pH, a high Total Dissolved Solids (TDS) and sulphate concentration and contains numerous heavy metals, some in very high concentrations (Table 1.1). The Grootvlei Mine is one of three active gold mines which, over a period of 16 months (1988/1989) contributed 9% to the flow, 48% to the TDS due to salinity and 60% to the sulphate load of the Klip River, which is the main contributor to the salt load of the Vaal Barrage (Rand Water Board, 1988; 1989) (Figure 1.2).

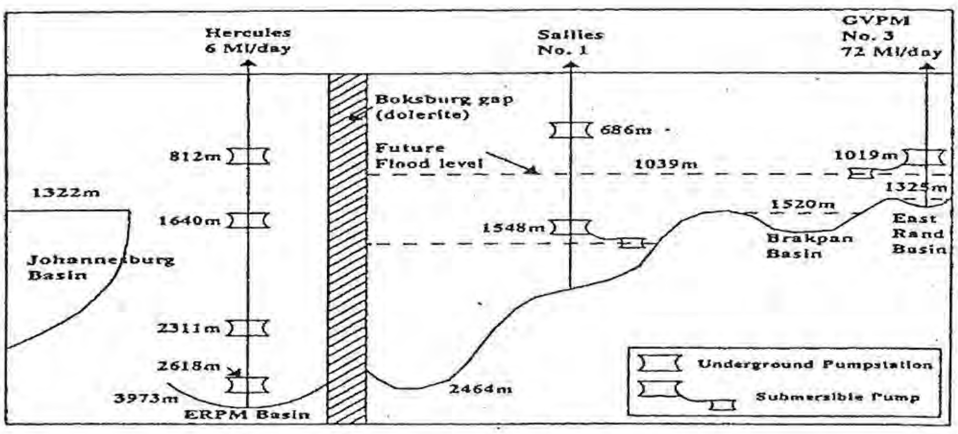

Figure 1.1. Underground water profile in the East Rand Basin with reference to Grootvlei and Sallies mines. (Department of Mineral and Energy Affairs Report, 1995)

In 1995 the government became aware of the environmental hazard caused by the pumping of mine drainage waste waters into the Blesbokspruit, but allowed the practice to continue in the interests of keeping the operation economically viable. The alternative would have been to cease pumping, leading to flooding of the underground workings, which in turn would cause the mine to close down, with the loss of 6000 jobs as well as R300 million in income to the mining company and the State. In early 1996, when the extent of pollution in the wetlands became obvious, the Minister of Water Affairs and Forestry ordered the mine to switch off pumps draining the mine. The environmental threat had also spread beyond the Blesbokspruit, with neighboring farmlands and the Marievale and Daggafontein Bird Sanctuaries being threatened. These are downstream of the Blesbokspruit and are registered Wetlands of International Significance under the Ramsar Convention. After a period of 2 weeks it was agreed that pumping could continue but only on condition that a permanent water treatment plant be installed to remove iron oxide deposits from the water.

Scott's report (1995) has noted that water flowing into the mining areas in the northern parts of the mine basin has a head of 20 meters over the lowest shafts connected to the basin. Thus when pumping finally stops it is likely that water will decant from those lowest shafts. The lowest shaft, which has the greatest potential to decant is the Nigel (Southgo) No. 3 shaft, located in the valley of a tributary of the Blesbokspruit, north of the central business district of the town Nigel. The expected outflow from this shaft would be in the region of 33Ml.day^{-1}. The decanting of such large volumes of water in close proximity to an urban settlement would have substantial implications, financially, socially and ecologically.

Table.1.1. Water quality analyses of mine water from Grootvlei Proprietary Mines, Ltd.

Water Quality Parameter	Guideline for aquatic life	Measured
Temperature (°C)		
pH	-	21
Dissolved Oxygen ($mg.l^{-1}$)	6.5-9.0	5.95
Electrical Conductivity($\mu S/cm$)	-	5.20
Total Dissolved Solids ($mg.l^{-1}$)	-	387
Alkalinity ($mg.l^{-1}$)	-	3788
Total Hardness ($mg.l^{-1}$)	>20	245
Ca-Hardness ($mg.l^{-1}$)	-	1700
Mg-Hardness ($mg.l^{-1}$)	-	980
Ammonia-N ($mg.l^{-1}$)	-	720
Nitrate-N ($mg.l^{-1}$)	0.016-4.5	5.4
Orthophosphate-P ($mg.l^{-1}$)	-	2.4
Sulphate ($mg.l^{-1}$)	0.1	<0.05
Fluoride ($mg.l^{-1}$)	Med:1400	1831
Chloride ($mg.l^{-1}$)	1.5	1.7
Iron ($mg.l^{-1}$)	50-400	250
Copper ($\mu g.l^{-1}$)	0.2-1.0	210
Nickel ($\mu g.l^{-1}$)	5-200	25
Lead ($\mu g.l^{-1}$)	25-50	762
Zinc ($\mu g.l^{-1}$)	20-100	340
Manganese ($\mu g.l^{-1}$)	30-100	40
Chromium ($\mu g.l^{-1}$)	100-1000	7060
Cadmium ($\mu g.l^{-1}$)	10-100	150
Sodium ($mg.l^{-1}$)	0.1-30	28
Potassium ($mg.l^{-1}$)	Med:500	258
	Med:50	18.2

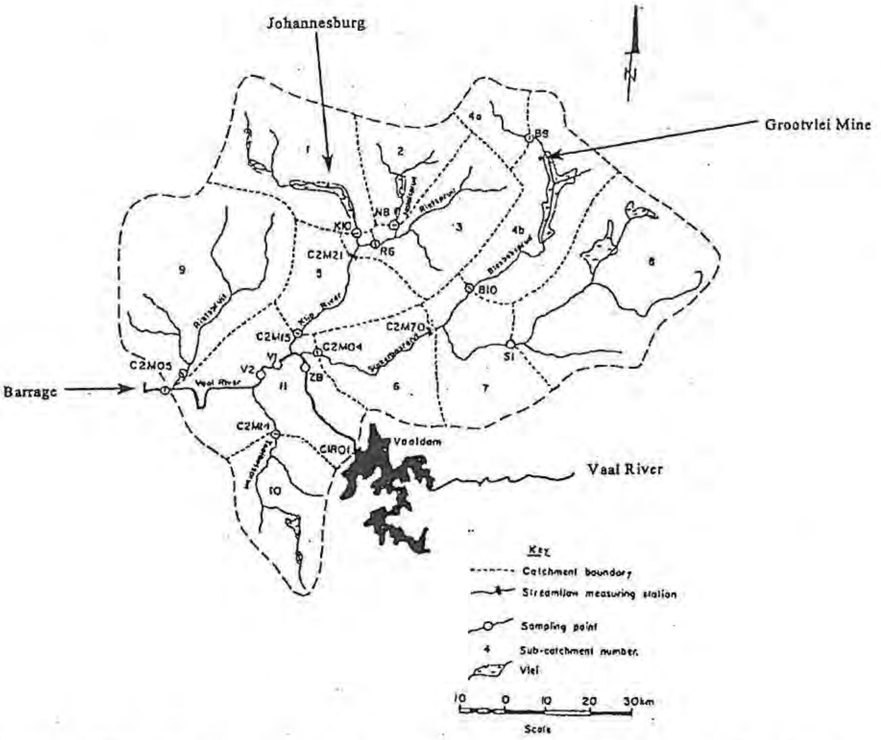

Figure 1.2. Map of Vaal Barrage catchment. (Department of Mineral and Energy Affairs Report, 1995).

1.3.1 Fate of the Pumped Water.

In order to allow mining in the Far East Rand Mining Basin to continue, The Grootvlei (Pty) Mines Ltd had by 1997 to discharge approximately 110ML/day of pumped mine water into the Blesbokspruit wetland (Cowan, 1995). Due to the unacceptable quality of this water, Professor Kader Asmal, Minister of Water Affairs and Forestry withdrew their water discharge permit, Permit 15M, on 15 May 1996. The mine was, however, informed this permit could be re-issued, should they, and the other affected mines, take concrete steps to treat the water to an acceptable standard. Grootvlei subsequently constructed a series of six temporary rock-walled plastic lined settling ponds in order to clarify the underground mine water by means of a combination of aeration, lime and flocculent dosing.

A second permit, Permit 17M, issued on 28 May 1996, authorised the discharging of semi-treated underground mine water for a further period of four months with the requirement that a permanent clarifier (High Density Sludge (HDS) plant) had to be established and commissioned before the permit was to expire on 30 September 1996.

On 30 September 1996 a third permit, Permit 18M, was issued authorising the discharge of underground mine water, after treatment in the new HDS plant, to continue for another six months. On the 27 March 1997 this permit was extended for an additional period of three months in order to allow the Cabinet to consider the conclusions and recommendations of the Grootvlei preliminary cost benefit analysis (CBA).

On instruction from Cabinet, the current permit, Permit 31M, was issued on 1 July 1997 allowing Grootvlei to discharge semi-treated underground mine water to the Blesbokspruit for an additional period of 18 months on condition that desalination pilot plant investigations be undertaken and be undertaken to the Department of Water Affairs and Forestry (DWAF) for consideration.

1.4. PROCESSES FOR THE TREATMENT OF ACID MINE DRAINAGE WASTE WATER

Treatment of the AMD problem has been investigated from the perspectives of both physico-chemical and biological processes.

1.4.1. Chemical Treatment Processes

A number of chemical processes have been applied to the treatment of AMD.

1.4.1.1. The High Density Sludge Process

Grootvlei Gold Mine currently utilises lime treatment in order to precipitate the majority of heavy metals in the effluents as metal hydroxides. A schematic diagram of the high-density sludge process (HDS) is shown in Figure 1.3.

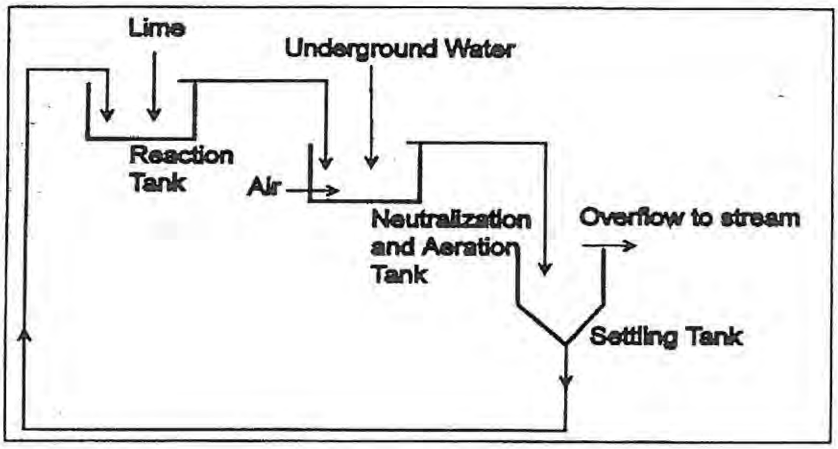

Figure 1.3. Systematic diagram of the HDS Treatment Process

Although the HDS plant has drawbacks, metal precipitation by means of pH control with lime or sodium hydroxide addition is used widely throughout the mining and refinery industries (Van Wyk & Munnik. 1997). Toxicity of the clarified AMD waters is reduced to the extent where the treated water is, in most cases, regarded as non-toxic to fish and indicator organisms. Recent studies of biodiversity in the Blesbokspruit surrounding the Grootvlei Mine, the receiving body for the treated mine effluent, indicates that some improvement has taken place in both the diversity and richness of waterbirds since the instillation of the HDS process (The Grootvlei Mines, *Monitoring of the Blesbok Spruit,* May/August 1997). The wetland is, however, still greatly impoverished in terms of bird numbers and diversity compared to previous years. Sensitive species have only been found at the bottom end of the wetland system, after dilution has taken place. The bio-diversity of macro-invertebrates has reduced significantly in most parts of the wetland, with the continued presence of species of low sensitivity being recorded.

1.4.1.2. Precipitation with Barium Salts

Barium has been extensively used in the treatment of boiler feed water for the removal of sulphates. Barium sulphate is a very insoluble compound, and one way of removing sulphate from water is its precipitation as the barium sulphate salt. The source of barium is usually barium carbonate. The removal of sulphate using barium salts consists of two stage barium carbonate and four stage barium sulphide processes (Maree *et al.*, 1989). The removal of sulphate and calcium from water by means of barium carbonate ($BaCO_3$) and barium sulphide (BaS) can be presented by the following reactions respectively:

$$Ca^{2+} + SO_4^{2-} + BaCO_3(s) \rightarrow BaSO_4\,(s) + CaCO_3 \text{ --(5)}$$

$$Ca^{2+} + SO_4^{2-} + BaS \rightarrow BaSO_4(s) + CaS^{2-} \text{ ---(6)}$$

In both processes, sulphate is precipitated as barium sulphate, calcium as calcium carbonate, magnesium as magnesium hydroxide where **M** represents heavy metals such as iron, zinc or copper, and heavy metals as either metal hydroxides or metal sulphide as show in equation 8 below.

$$BaCO_3 + MgSO_4 + Ca(OH)_2 \rightarrow BaSO_4\,(s)\; Mg(OH)_2 + CaCO_3 \text{ --------------------------------(7)}$$

$$\mathbf{MS}\,(OH)^{2+} + H_2O \rightarrow \mathbf{MS} + 2H_2O. \text{ ---(8)}$$

The raw materials, barium sulphide or barium carbonate, are recovered by thermal process from the precipitated barium sulphate, which has been used for treatment of various industrial effluents, or neutralised process water from slimes dam recovery, acid mine drainage, gold plant filter wash water and power station cooling water. By-products such as sulphur, sodium bisulphide and heavy metals can be recovered (King *et al.*, 1975).

1.4.1.3 Neutralisation with Limestone

Limestone ($CaCO_3$) can be used as an alternative to lime for the neutralisation of AMD as it is cheaper and occurs naturally in a pure state as limestone, and with magnesium as dolomitic limestone. Another advantage of neutralisation with calcium carbonate is the production of smaller sludge volumes than those produced from neutralisation with lime (Henzen & Pieterse, 1978). Several researchers have reported the use of $CaCO_3$ as a neutralising agent for acid waters (Thompson, 1980; Barnes *et al.*, 1991).

Maree *et al.*, (1992) investigated the practicality of using cheaper limestone instead of lime for the treatment of acidic effluents. From this study, it was determined that in case of lime treatment, the rate of neutralisation is fast when stiochiometric dosages of lime are applied.

Partial removal of sulphate is achieved if sufficient crystallisation times are provided and complete removal of heavy metals, depending on the pH of the treated water. With limestone processes, the rate of $CaCO_3$ neutralisation is directly related to the dosage of $CaCO_3$ and the particle size. Aeration marginally accelerated the rate of $CaCO_3$ neutralisation as a result of CO_2 stripping. The partial sulphate removal is achieved during $CaCO_3$ neutralisation as a result of $CaSO_4$ precipitation. Iron (III) and aluminium are effectively removed during $CaCO_3$ neutralisation. The rate of neutralisation is retarded by the presence of iron (II) in solution. The capital costs for lime and limestone neutralisation are similar, but the chemical cost in case of limestone neutralisation amounts to only 29% of that of lime (Maree *et al.*, 1992).

1.4.1.4 Slurry Precipitation Recycle Reverse Osmosis (SPARRO)

The SPARRO process is a novel design developed in South Africa by the Chamber of Mines, from a seeded RO concept originated in the USA (Chamber of Mines Research Organisation, 1988). Two of the main advantages of the process are that it produces a high quality solid gypsum by-product which could be sold, and can operate at very high recovery ratios, which reduces the quantity for brine disposal. The quality of the product water is related to the overall water recovery and this would be adjusted to each raw mine water treated. The process was successfully tested at pilot scale on scaling mine water from ERPM Hercules Shaft. However, the disadvantage of this process is that it entails high capital, maintenance and operational costs, and membrane fouling can occur.

1.4.1.5. Advantages and disadvantages of chemical treatment processes

Chemical treatment has the disadvantages of producing large volumes of unstable metal hydroxides mixed with gypsum which are costly to dispose of, especially when toxic metals content classifies it as hazardous waste (Rowley *et al.*, 1994). The sludges may also precipitate in the reactor, which may cause problems of plugging, abrasion and toxicity. Schemes for recovery and reuse of the chemicals would be the key for not only developing a satisfactory solution to the problem of ultimate sludge disposal, but also would lead to the development of a process wherein superior economic advantages could be demonstrated.

1.4.2. Biological treatment processes

Microorganisms are known to play an important role in the solubilisation, accumulation, transport and deposition of metals in the environment (Colleran, 1997). Their ability to accumulate metals from dilute solutions, and thereby concentrate them, has the potential for exploitation, with the remediation of metal contaminated waters and the possible recovery of valuable metals as the final objectives. A number of fungi (Muraleedharan and Venkobachar, 1990; Kapoor and Viraraghavan, 1998), bacteria (Komori *et al.*, 1990; Thompson and Watling, 1987) and yeasts (Brady *et al.*, 1994; Rapaport and Muter, 1995) have been investigated for their ability to accumulate heavy metals. The bioremoval capabilities of microalga has also been extensively studied (Ziminik, 1988; Kuyucak and Volesky, 1989; Volesky and Prasetyo, 1994), and some commercial applications have been initiated (Greene and Bedell, 1990). Constructed microbial mats, which utilise the metal accumulating ability of cyanobacteria coupled to nutrient removal by bacteria have shown promising results in field-site studies (Bender *et al.*, 1995; Phillips *et al.*, 1995). Systems utilising immobilised biomass such as Sphagnum peat moss (Hammack and Edenborn, 1992; Spinti *et al.*, 1995), *Rhizopus arrhizus* (Tsezos *et al.*, 1989), *Penicillium sp.* (Duran *et al.*, 1997), and a range of micro-algae (Holan and Volesky, 1994; Harris and Ramelow, 1990; Mahan and Holcombe, 1992) have also been investigated. However, their long-term use and regeneration ability appears to be limited. Liehr *et al.*, (1994) evaluated metal precipitation inside algal biofilms. Micro-alga are not unique in their capability to remove heavy metals but they do offer advantages over other biological materials in some conceptual bioremoval process schemes. Photosynthesis obliviates the need for an external organic carbon source. Micro-algae cultures can also be cultivated in large open ponds (Richmond and Preiss, 1980; Chaumont, 1993; Oswald, 1991) or in large-scale laboratory culture, providing a reliable and consistent supply of biomass (Wilde and Benemann, 1993).

Although much work has been done elucidating the mechanisms involved in metal uptake and internalisation by microorganisms (Ting *et al.*, 1995; Schenk *et al.*, 1988), the transfer of this technology to practical scale is still in its infancy. One of the few large-scale applications was developed by Gerhardt and Oswald (1990) and Gerhardt *et al.*, (1994) for the removal of selenium and nitrate from agricultural drainage water using both micro-algae and anaerobic bacteria. Algae were grown in high-rate oxidation ponds and removed NO_3^- from the water. The micro-algae and drainage water were then transferred to anoxic units where denitrifying and selenate reducing bacteria, fed on the micro-algae, further reduced the NO_3^- levels. Although the soluble selenium concentrations only decreased slightly, it was shown that selenate was reduced to selenite and other reduced forms. Unused micro-algae were fermented to methane in digesters.

Studies have shown that when sulphate-rich pollutants such as AMD reach aquatic environments, sulphate reduction in anoxic zones increases (Schindler *et al.*, 1980). This serves to remove sulphate from the overlying water, generates alkalinity and precipitates metals as sulphides. Lawrence and McCarty (1965) had also shown that the presence or addition of sulphide to a digester containing heavy metals results in the formation of metal sulphides that are insoluble salts. These observations led to the suggestion that biological sulphate reduction may have a role to play in mitigating these forms of pollution (Tuttle *et al.*, 1969).

1.4.2.1. Biological Sulphate Reduction

Biological approaches to the treatment of AMD have concentrated on both active and passive treatment systems, both of which rely on microbial activity related to the biological sulphur cycle. These include high sulphate reducing bacterial (SRB) growth rates and the associated precipitation of metals as sulphide salts (Johnson, 1995).

SRB are a large and diverse physiological group of anaerobic bacteria which are defined by their ability to utilise inorganic sulphate in an ATP-requiring reaction as one of their terminal electron acceptors (Peck and Lissolo, 1988). This process differs from assimilatory sulphate reduction which is purely a biosynthetic process in which sulphate is reduced to sulphide before incorporation into amino acids (Gibson, 1990). Dissimilatory sulphate reducing bacteria on the other hand utilise sulphate as an electron acceptor in the oxidation of the energy substrate and produce sulphide (Hansen, 1988). This takes place via the following reaction:

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO^{3-} \text{---} (9)$$

The sulphide may be converted to H_2S or HS^-, depending on the surrounding redox environment. The pathway for dissimilatory sulphate reduction is shown in Figure 1.4. The initial step of biological sulphate reduction involves the transport of exogenous sulphate across the bacterial cell membrane into the cell (Cypionka, 1987). Once inside the cell, sulphate dissimilation proceeds via the action of ATP sulphurylase. Sulphate combines with ATP to produce the highly activated molecule adenosine phosphosulphate (APS), and pyrophosphate (PPi) which may be subsequently cleaved to yield inorganic phosphate. APS is rapidly converted to sulphite (SO_3^-) by the cytoplasmic enzyme APS reductase (Gibson, 1990). Sulphite, in turn may be reduced via a number of intermediates to form the sulphide ion. The physiological electron donors for these reactions have not been conclusively identified (Peck and Lissolo, 1988). Candidates that have been considered include cytochrome C_3 and ferredoxin.

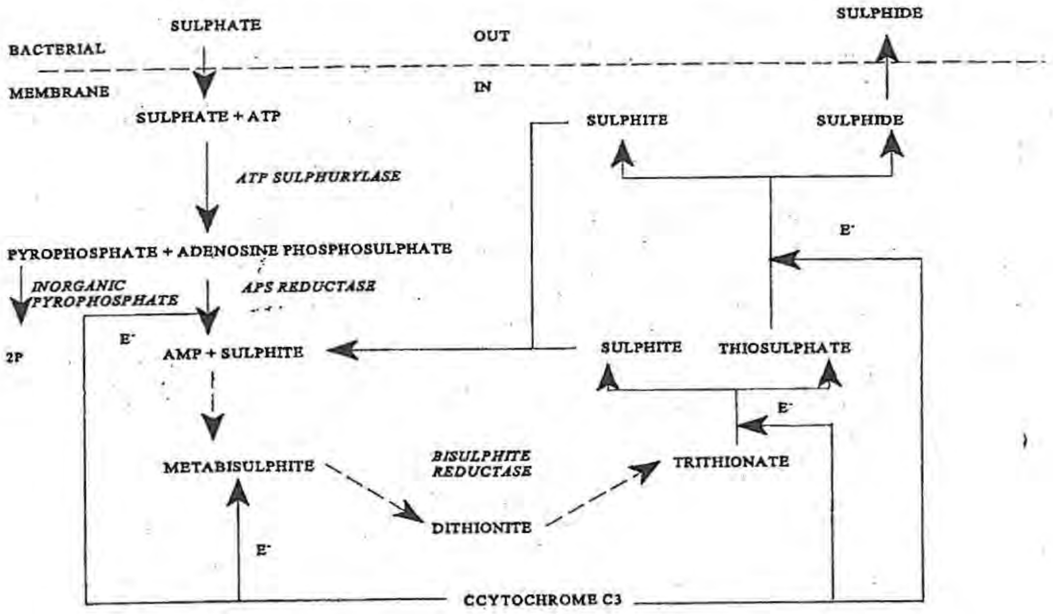

Figure 1.4. The sulphate regeneration pathway for dissimilatory sulphate reduction. (Gibson, 1990)

The physiology and growth of these bacteria has been studied and well-documented (Hansen, 1988; Peck and Lissolo, 1988; Gibson, 1990). Initial research concentrated on two groups of SRB: the genus *Desulfotomaculum*, which are characterised as being spore-forming straight or curved rods, and the genus *Desulfovibrio* which are non spore-forming vibrios capable of utilising sulphate as terminal electron acceptor together with hydrogen during growth on a limited number of organic substrates (Liu and Peck, 1981). The basic difference in the bioenergetics of sulphate reduction in these two genera is the enzymes involved in the removal of pyrophosphate formed during sulphate activation by ATP sulfurylase (Liu and Peck, 1981). Attempts were made to determine their preferred carbon source when grown in pure culture. However, data obtained in the field tended to conflict with laboratory data, suggesting the presence of previously unknown strains. Since then numerous new strains have been isolated and characterised. This has led to the reclassification of the bacteria and the addition of numerous genera. These include *Desulfobacter*, *Desulfonema*, *Desulfobacterium*, *Desulfomicrobium*, *Desulfococcus*, *Desulfobulbus*, *Desulfomonas*, *Desulfosarcina*, *Thermodesulfobacterium* and *Archaeoglobus* (Gibson, 1990).

The ecology, physiology, enzymology and bioenergetics of sulphate reducing bacteria have been discussed in a number of reviews (Widdel, 1988; Peck and Lissolo, 1988; Gibson, 1990), as well as their role in anaerobic corrosion. Sulphate reducing bacteria are found in a number of different environments: anoxic estuarine sediment (Compeau and Bartha, 1987), acid mine water (Herlihy and Mills, 1985; Herlihy *et al.*, 1987), saline water (Banat *et al.*, 1981), freshwater and generally in all soils (Watanabe and Furusaka, 1980). The temperature range at which they grow is also diverse and thermophilic sulphate reducing bacteria have been isolated at temperatures greater than 60°C in deep aquifers (Olson *et al.*, 1981). Hastings and Emerson (1988) found that sulphate reducers were also able to grow in anoxic surroundings in the water column of the Cariaco Trench, either in reducing micro-niches or because of the tolerance of some SRB to oxygen.

The ability of SRB to break down compounds or to convert metals, which are highly toxic, is also well known. Strains which are able to methylate mercury have been isolated from anoxic estuarine sediments (Compeau and Bartha, 1987) while another species of SRB, *Desulfuromonas acetoxidans* has been found to conserve energy by coupling the complete oxidation of organic compounds to the reduction of Fe (III) or Mn (IV) (Roden and Lovley, 1993). Lovley and Phillips (1992) investigated the possibility of SRB contributing to U (VI) reduction in sedimentary environments. Results indicated that the organism may be useful for the recovery of uranium from contaminated waters and wastewaters. Strains which are capable of degrading recalcitrant pollutants such as phenol, catechol, benzoate, cresol and vanillate and of growing in both saline and freshwater conditions have also been isolated (Kuever *et al.*, 1993).

SRB are well known for their role in oil formation souring where they accumulate as biofilms on reservoir porous media and use short-chain organic acids obtained from oil partitioning as energy sources (Chen *et al.*, 1994).

Numerous substrates have been reported as electron donors for SRB, some of which are recorded in Table 1.2. SRB do not degrade polysaccharides, proteins or lipids, but depend on the activity of fermentative bacteria for the supply of energy sources (Hansen, 1988). Most energy substrates are typical fermentation products, monomers of cell polymers or other cell components. With the exception of two strains, none of the SRB can utilise simple sugars as energy substrates. One of the most important substrates for SRB is hydrogen. This is especially important to the *Desulfovibrio* species, as their high affinity for hydrogen is considered to be the reason they are able to out-compete hydrogenotrophic methanogens in sulphate-sufficient environments. A number of *Desulfomataculum* species are also able to grow with hydrogen and sulphate as the sole source of energy (Klemps *et al.*, 1985).

Table 1.2. Compounds that can be used as energy substrates by sulphate-reducing bacteria (from Gibson, 1990).

Inorganic	Hydrogen, carbon monoxide
Monocarboxylic acids	Formate, acetate, propionate, butyrate, isobutyrate, 2- and 3-methylbutyrate, higher fatty acids up to C_{18}, pyruvate, lactate
Dicarboxylic acids	Succinate, fumarate, malate, oxalate, maleinate, glutarate, pimelate
Alcohols	Methanol, ethanol, propanal, butanol, ethylene, glycols (mono-, di-, tri- and tetra-), 1,2- and 1,3-propanediol, glycerol
Amino Acids	Glycine, serine, cysteine, threonine, valine, leucine, isoleucine, aspartate, glutamate, phenylalanine.
Miscellaneous	Choline, furfural, oxamate, fructose, benzoate, 2-, 3- and 4-OH-benzoate, cyclohexanecarboxylate, hippurate, nicotinic acid, indole, anthranilate, quinoline, phenol, p-cresol, catechol, resorcinol, hydroquinone, protocatechuate, phloroglucinol, pyrogallol, 4-OH-phenyl-acetate, 3-phenylpropionate, 2-aminobenzoate, dihydroxyacetone.

1.4.2.2. Treatment processes utilising biological sulphate reduction

Laboratory scale tests have shown promising results for the treatment of acid mine drainage by biological sulphate reduction. Numerous two-stage processes combining anaerobic biological sulphate reduction with an aerobic step have been developed at laboratory-scale (Maree and Hill, 1989); Cork and Cusanovich (1979) developed a variation in which the conversion of hydrogen sulphide to sulphur takes place in a second stage reactor. Hammack *et al.* (1994) in turn combined a limestone neutralisation step prior to sulphate reduction. Anaerobic packed bed reactors (Maree *et al.*, 1987; Hammack and Edenborn, 1992), stirred tank reactors (Maree and Hill, 1989), soil columns utilising *Clostridium* and *Desulfovibrio* bacteria (Kauffman *et al.*, 1986) and biofilms (Rivera, 1983) have also been studied, as has the selective removal of heavy metals from effluents by sulphide precipitation and pH manipulation (Hammack *et al.*, 1993; Hammack *et al.*, 1994).

1.4.2.3. Passive Processes

The wetland process is considered to be passive as it relies on naturally occurring geochemical and biological processes (Gazea *et al.*, 1996) such as ammonification, denitrification, methanogenesis and the reduction of iron and sulphur (Kalin *et al.*, 1991). Over 400 wetlands have been constructed for the treatment of AMD and the approach is very popular in the Eastern United States (Johnson, 1995), with artificial wetlands treating coal mine drainage (Hammack *et al.*, 1994) and effluent from sewage works, mines and industries (De Wet *et al.*, 1990; Mitsch and Wise, 1998). An advantage of wetlands is that they are inexpensive to construct and maintain in comparison to conventional chemical treatment plants (Johnson, 1995). However, recently the sustainability and stability of these systems under conditions of nutrient limitation has come under question. They also use large tracts of land, which in certain circumstances may not be feasible.

Kuyucak and St-Germain (1994) investigated a number of alternative processes, which may be used in conjunction with constructed wetlands, for the addition of alkalinity to acidic mine waters. Anoxic Limestone Drains (ALD), which are used as a pre-treatment step, consist of an excavated seepage interception trench that is filled with limestone and covered with plastic and clay to keep air out. ALD produce alkalinity at a lower cost than do compost wetlands, but their use is limited to mine waters with Fe^{3+} concentrations < 2mg/l, a net acidity < 300mg/l and $CaCO_3$ and dissolved oxygen < 1mg/l (Gazea *et al.*, 1996). Other alternatives include Lime Organic Mixture, which utilises a bed of limestone and manure to remove metals, and biotrenches which utilise nutrients such as straw, sawdust or woodshavings to establish microbial populations and increase the pH.

1.5. ADVANTAGES AND DISADVANTAGES OF BIOLOGICAL SULPHATE REDUCTION

The utilisation of biological sulphate reduction for the removal of heavy metals and sulphate from solution has received much attention and has been reviewed by Peters and Ku (1985). It has been determined that metal separation and settling rates obtained with hydroxide precipitation are lower than those obtained with sulphide precipitation, and that most metal sulphides have low solubilities even at acidic pH values (Singh, 1992; Hammack *et al.*, 1994). Metal sludge's containing Cu, Pb, Ni, Cd and Zn are three times less susceptible to leaching at pH 5 than an equivalent metal hydroxide sludge (Whang *et al.*, 1982). Sulphides are also highly reactive with metals, even in the presence of complexing agents (Bhattacharya *et al.*, 1979), thus allowing for a low retention time in the bioreactor (Peters and Ku, 1985). The low solubility of the metal sulphides, coupled with the high reactivity of sulphides with metals, leads to improved metal removal efficiency (Whang *et al.*, 1982). The metal sulphides have also been shown to be more compact and have faster settling velocities than metal hydroxides, thus exhibiting better thickening and dewatering characteristics than hydroxide sludges (Whang *et al.*, 1982; Peters and Ku, 1985; Kuyucak and St-Germain, 1994).

The hydrogen sulphide and hydrogen carbonates formed during sulphate reduction equilibrate into a mixture of H_2S, HS^-, S^{2-}, CO_2, HCO_3^- and CO_3^{2-}. If sufficient sulphate reduction takes place, this mixture will buffer the solution pH to a particular value (pH 6-7), but this differs depending on the specific quantities and types of organic end products (Dvorak *et al.*, 1992). It has also been shown that sulphides play a significant role in preventing the toxicity of most heavy metals in anaerobic treatment (Oleszkiewicz and Sharma, 1990). Hexavalent chromium, which is highly toxic, can be reduced to the trivalent form during sulphide treatment and subsequently precipitated as a hydroxide using lime or caustic soda (Lanouette, 1977).

Notwithstanding the reactor type, and the particular treatment approach used, widespread application of active biological treatment processes AMD treatment has not yet been seen on any large scale. Singular factors constraining process development are bioreactor design, cost of bioreactor construction and the costs of the carbon source and electron donor for the microbial sulphate reduction process (Rose *et al.*, 1996). The SRB are able to utilize only a limited range of small organic molecules.

Numerous SRB reactor design studies have been reported including trench reactors, anaerobic filters (De Walle *et al.,* 1979; Chian and De Walle, 1983), mixed reactors (Maree and Hill 1989), packed bed anaerobic bioreactors (Riviera 1983; Maree *et al.,* 1987), fluidised bed systems, sequencing batch reactors, the upflow anaerobic sludge bed (Buisman *et al.,*1993; Barnes *et al.,* 1991) and the baffled reactor (Grobicki and Stuckey, 1992). The evaluation, in the active AMD treatment application, of a range of carbon sources has also been reported (Rose *et al.,*1998), including sewage sludge (Bultin *et al.,*1956; Pipes 1961; Burgess and Wood 1961), animal waste slurries (Ueki *et al.,* 1988) and ethanol and methanol (Postgate 1984). In passive systems wetland plantings of *Sphagnum sp., Typha latifola* and *Phragmites australis* have been used, and may provide a carbon source to these systems of up to 40 tons.ha^{-1} per year (Wieder 1993).

1.6. DEVELOPMENT OF THE RHODES BioSURE PROCESS

Notwithstanding the wide range of bioreactor and electron donor options examined, the effective engineering of active biological AMD processes has concentrated largely to date on relatively high cost bioreactor systems and carbon sources such as ethanol and producer gas (Johnson, 1995).

Observations of efficient sulphate reduction in the tannery Integrated Algal Ponding System (IAPS) by Dunn (1998) and Boshoff (1996), and the apparently effective solubilisation and utilisation, in this activity, of the complex organic compounds present in these wastewaters, led to a sequence of activities culminating in the development of the WRC patented Rhodes BioSURE Process (Rose and Hart, 1998).

This research and development activity, which demonstrated the potential available in linking sulphur biocycle process development and the hydrolysis of particulate organic carbon was undertaken by the Rhodes University Environmental Biotechnology Group (EBG) and followed up in four related WRC projects. In the first instance, an IAPS approach to the sulphate salinity problem was investigated. This provided a number of indications that ponding systems might themselves be used for biological treatment of AMD on large-scale, with the anaerobic compartments in these systems serving as effective bioreactors for sulphate reduction (Rose *et al.,* 1998).

Work by Boshoff (1996) and Dunn (1998) in the WRC project 'Appropriate Low-cost Treatment of Sewage Reticulated in Saline Water Using the Algal High Rate Oxidation Ponding System', commenced in 1995 and was to undertake a preliminary evaluations of the co-disposal of sewage sludge and saline wastewaters. Results acquired here showed the use of tannery effluent and sewage sludges as potentially effective electron donors, and carbon sources, in sulphate-salinity reduction applications in particular. This development was followed up in 1997 in WRC project 'Biological Sulphate Desalination and Heavy Metal Precipitation in Industrial Mining Effluents using the AIPS' which ran concurrently with the previous WRC project mentioned, and resulted in the conceptual development of the Algal Sulphate Reducing Process for Acidic and Metal Wastewater Treatment'- the ASPAM Process (Rose *et al.,* 1998). This study showed that ponding systems might indeed be considered for the large-scale treatment of sulphate wastewaters, but also that the use of complex carbon as an electron donor might be managed as high rate processes in bioreactors, the design of which may be based on the particulate soulubilisation mechanisms observed both in natural environments and in wastewater ponding systems.

Scale-up evaluation studies for the use of sewage and tannery wastewaters as electron donor sources, was planned to be undertaken at Seton Leathers Co. at ERWAT's Bickley Sewage Works in Nigel, Gauteng Province. However, at this time the so-called Grootvlei eco-incident intervened. The increased pumping and dewatering of the Grootvlei Gold Mine into the Blesbokspruit, and resulting pollution impacts developed into a political issue of potentially international significance. Heavy metal and sulphate salinity pollution from the mine dewatering exercise threatened the Marievale and Daggafontein Bird sanctuaries – Wetlands of International Significance under the RAMSAR Convention, to which South Africa is signatory.

The various research outputs described above by Boshoff (1996), Dunn (1998), Molipane (1999) and Whittington-Jones (2000) led to the initial conceptualisation of what was to become known as the Rhodes BioSURE Process applied to the treatment of AMD. Given the volume of the treatment requirement at Grootvlei Mine it was decided to concentrate on the use of sewage sludge as the most freely available carbon source

1.6.1 Primary Sewage Sludge Solids

Investigations undertaken using PSS as the electron donor for sulphate reduction in $1m^3$ bioreactor studies had shown the effective degradation of particulate organic matter to be associated with efficient sulphate reduction (Molepane, MSc 1999).

Observations of effective degradation of organic carbon occurring within these reactor systems appeared to indicate a particular role for sulphate reduction in the solubilisation processes involved and these were apparently of importance in the processes by which complex carbon substrates were made available to SRB activity. In natural environments such as sulphate reducing sediments, and in high rate algal ponding systems, the size of particulate matter may be observed to decreases against increasing sulphide and alkalinity concentration gradients (Figure 1.5). Where an upwelling incident occurs, nutrients, partly degraded small organic molecules and residual slowly degrading organic particulate matter pass back up into the water column. Solubilised components support ongoing nutrient cycles, and the remaining undegraded settleable particulates return to the sediment for another round of solubilisation activity, yielding ultimately the full hydrolysis of the degradeable organic fraction.

Given the central importance of the solubilisation and hydrolysis reactions as the initial steps in which complex organic carbon structures are made available to biological processes, the apparent advantages of the reciprocating sedimentation process was subjected to more detailed investigation in the Falling Sludge Bed Reactor (FSBR) study described below.

The prototype FSBR was constructed as a 2L bench-scale single stage reactor (SSR) unit (Figure 1.6), and sulphate-enriched PSS was used as the feed (COD = 4000 mg/l; SO_4^{2-} = 2000 mg/l). In this unit solids settling in the reactor are drawn down into the falling sludge bed where sulphate reduction commences and the build-up of sulphide and alkalinity is observed. The sludge is drawn down the bed and is then recycled to blend with the influent flow simulating the upwelling events observed in the pond systems. Floc growth entraps new particulate matter which together with residual, and as yet undegraded, settleable solids returns to a further round of sludge recycling. Solubilised solids pass out of the reactor in the liquid stream. The subsequent use of the soluble organic fraction as electron donor for sulphate reduction was investigated in a multi-stage reactor (MSR) FSBR unit (Figure 1.6).

The results of this study have been reported by Whittington-Jones (PhD, 2000).

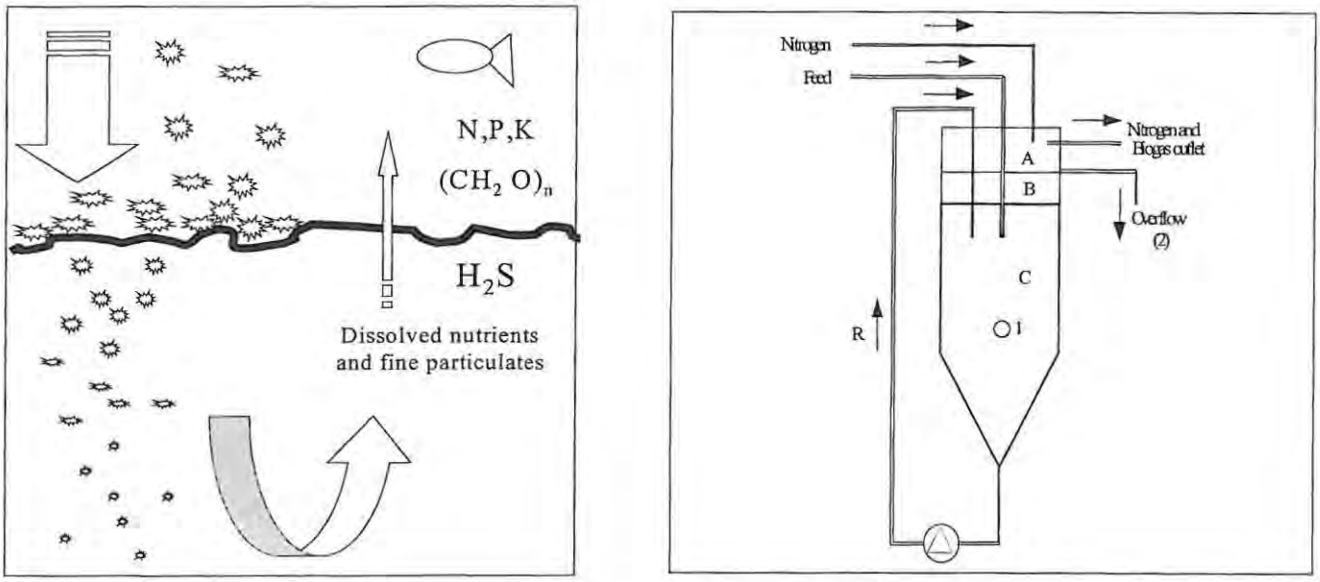

Figure 1.5. The breakdown of particulate organic matter in natural sulphidogenic settlement and sedimenting processes (A) was simulated in a 1L prototype study (B) of the Falling Sludge Bed Reactor (FSBR). The degrading sludge is returned via line R to blend with the incoming feed.

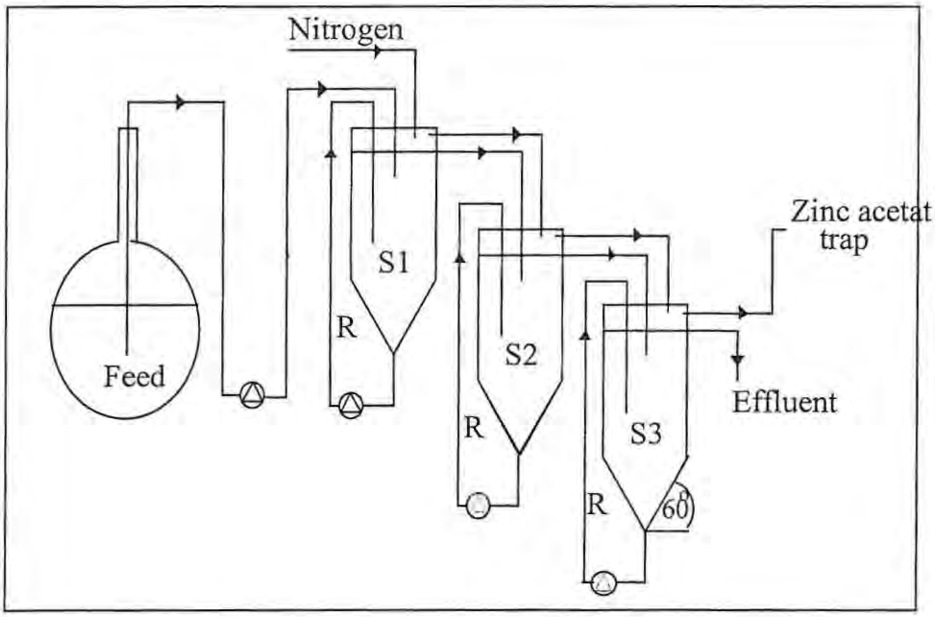

Figure 1.6. The Multi Stage Falling Sludge Bed Reactor used to investigate the solubilisation of primary sewage sludge and its utilisation as an electron donor source in sulphate reduction activity.

1.6.2 Solubilisation of Particulate Organic Carbon

Hydrolysis is generally regarded as the rate limiting step in anaerobic pathways responsible for the degradation of complex organic carbon structures, in both natural and bioprocess environments (Eliosov and Argaman, 1995; El-Fadel *et al.*, 1996; Vavilin *et al.*, 1995; Penaud *et al.*, 1997). The rate at which hydrolysis proceeds is described by first order kinetics and may be strongly influenced by both environmental and operational parameters, including the concentration of particulate substrate and soluble products (Eastman and Ferguson, 1978; Shimizu *et al.*, 1993). Particle size, in particular, has been shown to have a profound impact on the rate of the anaerobic digestion of complex substrates (Choi *et al.*, 1997; Madhukara *et al.*, 1997; Müller *et al.*, 1998), and Wentzel *et al.*, (1995) demonstrated a size related criterion of 0.1 mm separating rapidly- from slowly-biodegradeable, and refractory, COD.

Sewage sludge has received attention as a model system for studies in the degradation of particulate organic matter (Vavilin *et* al., 1995), due, in part, to the ubiquitous nature of the disposal problem, but also in the potential use of the solubilised product as an electron donor source in a range of bioprocess applications. These include biological nutrient removal processes in wastewater treatment (Brinch *et al.*, 1994; Skalsky and Daigger, 1995; Hatziconstantinou *et al.*, 1996; Banister and Pretorius, 1988), biological sulphate reduction in acid mine drainage (AMD) wastewater treatment (Molepane, 1999 and Whittington-Jones, 2000), and other potential bioprocess applications related to waste disposal operations including, more recently, an interest in the utilisation of organic wastes in sustainable 'integrated resource management' strategies.

However, solubilisation rates for PSS are slow in conventional anaerobic digestion systems (Pipyn and Verstraete, 1979), with maximum soluble product formation reported between 8 and 20 days, and at yields of 5-10% in the mesophyllic temperature ranges (Canziani *et al.*, 1996; Hatziconstantinou *et al.*, 1996; Banister and Pretorius, 1988; Elefsiniotis and Oldham, 1994; Shimizu *et al.*, 1993). Effective separation and recovery of the solubilised product from the residual sludge imposes further constraints on bioprocess applications (Banister and Pretorius (1988).

Pipes (1961) had suggested that stabilization of PSS under sulphate reducing conditions might offer particular advantages for disposal of sewage sludges, and Butlin *et al.* (1956), and Burgess and Wood (1961) had noted potential for sulphide and sulphur production from sulphate-enriched sewage. While these early suggestions of sulphate assisted PSS digestion have remained largely unexplored, more recent studies have shown that the rate and extent of ligno-cellulose solubilisation, an abundant compound in primary sludge (Elefsiniotis and Oldham, 1994), was enhanced in the presence of sulphur compounds in both sewage and landfill environments (Khan and Trottier, 1978; Kim *et al.*, 1997; Pareek *et al.*, 1998).

The simulation of the reciprocating sedimentation and upwelling events observed in the pond study, provided an experimental system with which to test a descriptive model of enhanced solubilisation of PSS under sulphidogenic conditions, and suggests that the mechanisms observed may have more general application in understanding degradation of particulate organic carbon structures in natural sulphate reducing environments. It is proposed that the solubilisation of PSS was enhanced under sulphate reducing conditions as a result of enhanced hydrolysis of the macromolecular protein and carbohydrate constituents. Furthermore, it was suspected that this would result in a reduction in the mean size of sludge flocs, and thus also contribute to the enhanced solubilisation of the PSS. Reactor configuration seemed to be important in the concentration of reactants achieved at the bottom of the settling cycle.

Jain *et al.* (1992) modelled the anaerobic digestion of complex particulate substrates, and showed that two factors which had the greatest impact on the rate-limiting hydrolysis step were, the concentration of the hydrolytic enzymes, and the contact between these enzymes and their substrates. Vavilin *et al.* (1996) proposed that the hydrolysis rate constant was a function of the ratio between the characteristic sizes of the hydrolytic bacteria and the substrate particles, and was thus dependent on the colonisation of the particle surface by hydrolytic bacteria. The efficiency of particulate solubilisation may, therefore, depend on more than just reaction mechanism and reactor configuration or operational factors which increase the enzyme concentration, or mass transfer limitations, should result in an increase in the rate of hydrolysis.

1.7. PROCESS CONCEPTULISATION

Work done by Whittington-Jones (2000) using the MSR to investigate the solubilisation of PSS and its utilisation as an electron donor source in sulphate reduction activity had shown that limitations of hydrolysis could be overcome in a system of reciprocating sludge movement under sulphate reducing conditions.

The development of a Falling Sludge Bed Reactor (FSBR) (Whittington-Jones, 2000) provided a useful design in the enhanced hydrolysis of PSS and the process (Figure 1.6) was divided into two stages of operation. Firstly the solubilisation of PSS and generation of small organic molecules was accomplished with some carbon being consumed in establishing the sulphidic environment. The solubilised fraction constituted the feedstock which passed to the second stage of operation where the major part of sulphate reduction occurred.

The research outputs in 2L reactors, described above, led to the initial conceptualisation of what was to become known as the Rhodes BioSURE Process for the treatment of AMD (Figure 1.7). In the process design (Figure 1.7) the MSR was incorporated as the first stage (Reactor 1) in a dual stage sulphate reduction operation. Although some sulphate and COD would be consumed in the MSR, its primary role would be the enhanced hydrolysis of the PSS as electron donor and carbon source. The solubilised product would pass to a second stage (Reactor 2) where the sulphate reduction reaction would be optimised. A baffle reactor was used in this application. A component of the alkalised and sulphide-enriched ABR effluent would pass to an AMD pre-treatment operation where neutralisation and heavy metal precipitation would be effected. An HRAP was used to effect polishing and disinfection of the final treated water.

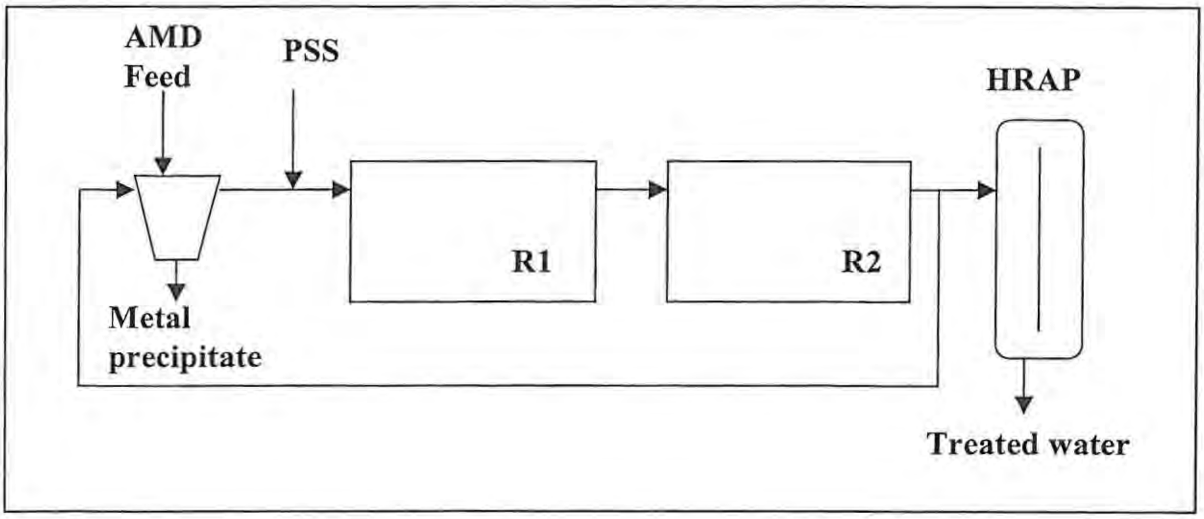

Figure 1.7. Process flow diagram of the Rhodes BioSURE Process applied to the treatment of acid mine drainage wastewater. R1 = falling sludge bed reactor; R2 = anaerobic baffle reactor. A side stream of sulphidic-containing water is blended with incoming minewater to precipitate contaminating heavy metals. The sewage sludge carbon source is added to the metal-free stream which passes to the FSBR where hydrolysis of particulates and some sulphate reduction occurs. The dissolved organic stream passes to a baffle reactor where it is used as the feedstock in the final sulphate reduction step. The treated water is then discharged via the HRAP polishing stage.

1.8. RESEARCH OBJECTIVES

The studies reported here were motivated by the need to evaluate low-cost options and the treatment of high-volume AMD flows. This has focussed research activity on bioprocess developments using complex organic compounds derived from waste streams as electron donor sources, and the integration of AMD treatment with other waste treatment objectives. The co-disposal of organic wastes with AMD treatment would enable the development of an 'integrated resource management' approach to the problem, including sustainability of treatment operations over the long time- frames involved. Apart from the cost advantages accrued to waste treatment, the recovery of the treated water as a resource to the wider community provides a potentially important value-added function to the combined operation (Rose *et al.,* 1998). The 'integrated resource management' approach places the sustainability requirement in the domain of the public utility operator, where treatment may be more effectively managed over the long-term.

This study reports the development of active biological treatment of sulphate saline wastewaters based on complex organic carbon utilisation including industrial effluent and sewage sludge co-disposal as the electron donor sources in bacterial sulphate reduction.

Having conceptualised a process, the Rhodes BioSURE Process, for the treatment of AMD waters and given the particular nature and extent of the South African AMD problem the objectives of this research programme were identified as follows:

(1) design, construct and operate a technical-scale pilot FSBR and to test the findings on the accelerated hydrolysis of PSS reported by Whittington-Jones (2000) in the laboratory-scale FSBR studies;
(2) design, construct and operate the proposed two-stage system at technical-scale and to evaluate preliminary findings that conversion of PSS to a hydrolysate in the FSBR would make complex carbon available to SRB activity;
(3) investigate the use of sulphide rich process recycle liquors from the sulphate reduction stage of the process for the metal removal and pH adjustment of raw influent AMD wastewaters prior to entry into the FSBR;
(4) systematic operation of the full process including the various unit operations;
(5) undertake a long-term study of the performance and feasibility of the system in AMD wastewater treatment

CHAPTER 2.

THE RHODES BioSURE PROCESS: PILOT PLANT DESIGN CONSTRUCTION AND OPERATION

2.1. PILOT PLANT DESIGN AND CONSTRUCTION

The Rhodes BioSURE process flow schematic presented in Figure 2.1 outlines the technical-scale development of the process following from the laboratory studies reported by Whittington-Jones (2000). The pilot plant was constructed at Grootveli Gold Mine Number 3 shaft and this study reports the development of the Rhodes BioSURE process at technical-scale.

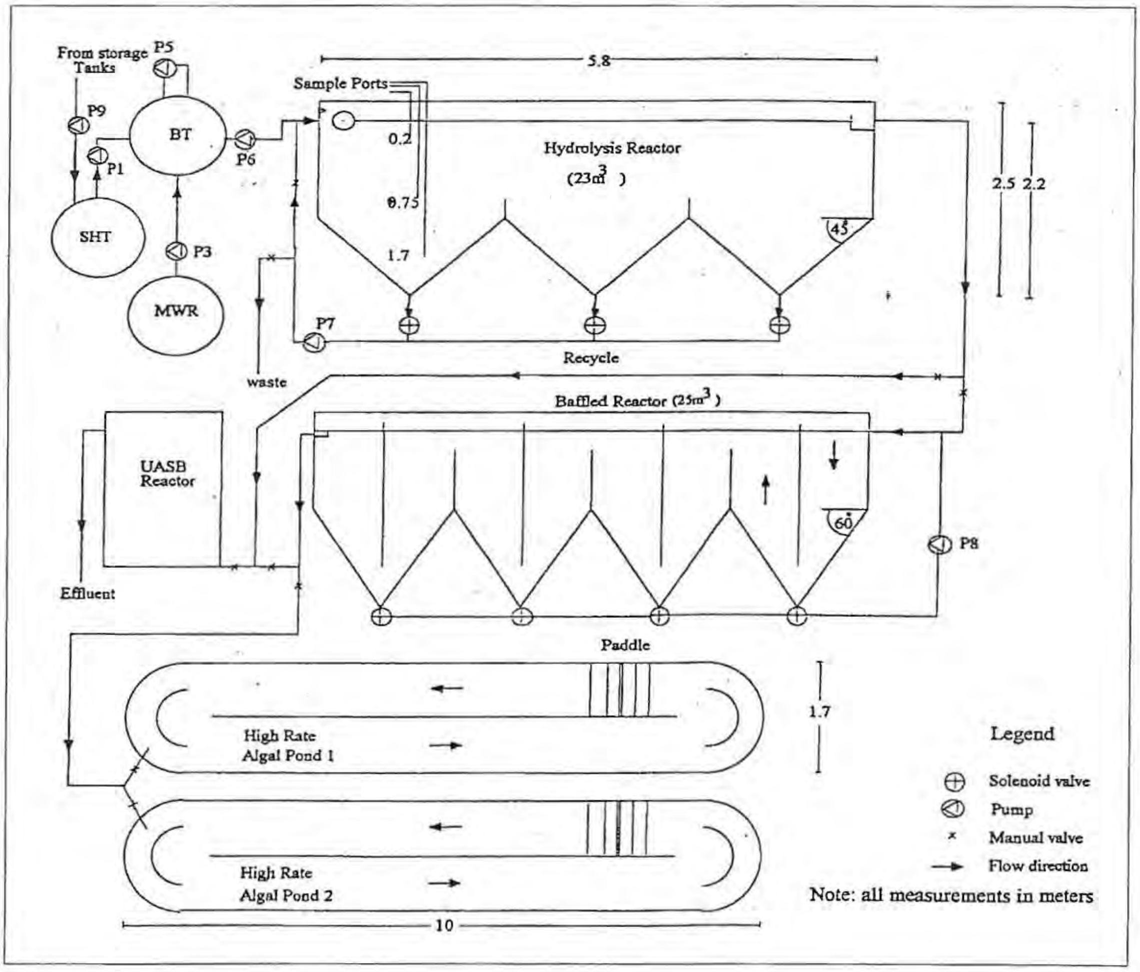

Figure 2.1. Process flow schematic of the Rhodes BioSURE process technical-scale pilot plant constructed at Grootvlei Gold Mine Number 3 shaft. All measurements are given in meters. BT = blend tank, SHT = sludge holding tank, MWR = mine water reservoir UASB = upflow anaerobic sludge bed

2.1.1. Reactor Design and Construction

Both the Falling Sludge Bed Reactor (FSBR) and Anaerobic Baffle Reactor (ABR) were constructed from modified metal shipping containers (6.0 2.5 x 2.5m), by Grahamstown Engineering Co. The volume of each container prior to modification was $30.4m^3$. After modification, the liquid volumes of the FSBR and ABR were $23m^3$ (Figure 2.2) and $25m^3$ respectively (Figure 2.3).

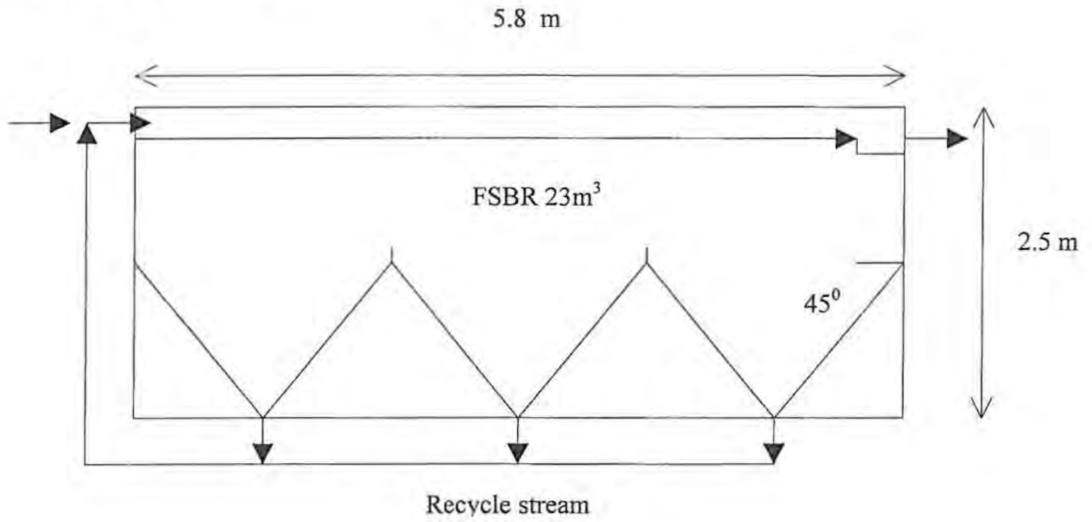

Figure 2.2. Design and dimensions of the FSBR constructed out a modified shipping container

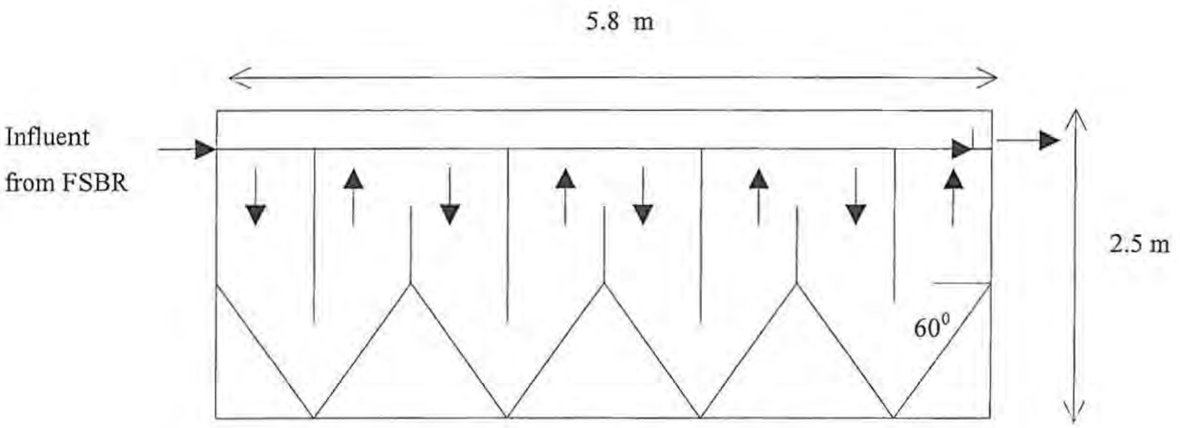

Figure 2.3. Design and dimensions of the ABR constructed out a modified shipping container with the volume being $25m^3$

2.1.1.1. Falling Sludge Bed Reactor

The container was divided into three contiguous sections of equal size, with the lower meter of each section forming a valley. These valleys were constructed by welding 10mm mild steel plates into the base of the container at 45^o angles. The joins between the plates and the reactor sides were not watertight. This allowed water to fill the dead-spaces under the plates to prevent buckling when the reactor was full. A pipe containing slots (i/d = 100 mm) was placed into the base of each valley. These pipes, which spanned the width of the reactor and passed through the wall on both sides, allowed for the recycle of settled sludge. Sludge was sucked sequentially from each of the valleys for pre-determined time periods, and was then pumped to the inlet of the reactor. Influent passed into the reactor via an 80mm steel pipe, with 40mm sockets placed just below water level, and pointing vertically downward. Effluent flowed over a crown weir, placed 2.2m above the reactor base, before it flowed, by gravity, into the baffled reactor. Three 2cm I/D pipes were inserted into each valley through the roof of the reactor. They allowed samples to be drawn from depths of 0.2, 0.75 and 1.7m below the surface of the reactor. Two inspection manholes with bolted steel covers were installed into both ends of the reactor roof.

2.1.1.2. Anaerobic Baffle Reactor

The ABR had a similar configuration to that of the FSBR, except that the container was divided into four equal compartments, with the valley sides having a slope of 60^o (see Figure 2.3). Each compartment was partially separated from adjacent compartments by steel baffles that extended to 0.2m below the water surface. Each of the four compartments was further divided into two equal compartments by a central baffle extending from above the water level to 0.2m above the base of each valley. Thus, any water flowing through the system would follow a tortuous flow path. Manholes identical to those in the FSBR were installed.

The hydrodynamics and degree of mixing that occur within this ABR strongly influence the extent of contact between substrate and bacteria, thus controlling mass transfer and reactor performance. Although the baffled reactor had the facilities to allow recycling of effluent to occur, this was not run on an automated PLC program as with the ABR.

The overall objective of the start-up during the initial phase of the programme was the development of the most appropriate microbial culture for high sulphate wastewaters. In order to ensure that these mixed populations of largely unknown species composition in the reactor systems were retained in the reactor by accumulation in a biosludge, the initial loading rates were kept low. This was not only to prevented slow growing micro-organisms from being overloaded, but also ensured that a 'wash-out' of micro-organism biomass did not occur.

2.1.1.3 Upflow Anaerobic Sludge Blanket Reactor (UASB)

This was constructed from a $5m^3$ High Density Polyethylene (HDPE tank). To obtain a uniform distribution of the influent over the bottom of the UASB reactor, a flow-splitting device was used to introduce the influent flow at several points on the reactor bottom. Feeding was accomplished using a gravity-feed system. The effluent was collected at the top of the UASB uniformly by means of 50mm PVC pipe with small notches at regular distances that acted as horizontal gutters. Anaerobic digestion process generates a corrosive environment, therefore plastic materials were used to avoid severe corrosion.

2.1.1.4. High Rate Algal Ponds (HRAP)

Design procedures for stabilisation ponds should include operations such as sedimentation, oxidation, and digestion, gas exchange and photosynthesis, mechanical aeration, and evaporation and seepage. The rate determining factors which had to be considered were: (1) the detention time, (2) pond depth, (3) pond loading, (4) the pond temperature, (5) visible light energy. With these determinants in mind two pre-fabricated HRAPs were constructed by Grahamstown Engineering Co. The materials for construction were as follows:

a) frame: 40x40mm square tube (galvanised steel)
b) sides: 6mm rods spaced 60mm apart
c) plastic liner made to fit pond frame
d) paddle wheel: stainless steel
e) The frame of each pond could be dismantled into 5 smaller sections for easy transportation.

Dimensions and operating conditions were as follows:

Length:	10m
Width:	1.7m
Depth:	300mm
Volume:	3000L
Flow rate:	variable
HRT:	variable

2.1.1.5 Metal removal

Within the Rhodes BioSURE process, it was proposed that the principal metal ions be removed via metal sulphide precipitation by blending the incoming untreated AMD with a sulphide rich recycle effects such removal with a sulphide rich recycle. A novel precipitation valley reactor (PVR) for the effective removal of dissolved iron in AMD wastewater was designed. The PVR comprised of three settling tanks in series able to be operated as a continuos flow-through system. The three settling chambers were compartmentalised by the addition of baffles. The baffles were positioned to facilitate retardation of horizontal flow thus increasing the hydraulic retention time of the precipitating metal sulphide. The PVR had a volume of 1.1m^3. The results of the operation of the PVR are discussed in Chapter Six.

2.2 PROCESS DESIGN

2.2.1 Principles of process

As described above and in Chapter One, the initial conceptualization of Whittington-Jones's (2000) work gave rise to the process design illustrated in Figure 2.1 for the treatment requirement at Grootvlei Gold Mine.

The principles in the working of the process are described. Given the volume of the treatment requirements at Grootvlei Mine it was decided to concentrate on the use of sewage sludge as the most freely available carbon source. The PSS was blended with treated mine water from the HDS plant at a ratio of 2:1 (COD:SO_4) before being pumped to the FSBR (hydrolysis reactor). The FSBR was the first stage of the Rhodes BioSURE process and provided the reactor in which solubilisation of the PSS was effected. The solubilised product would then pass to the second stage, the ABR, where the sulphate reduction would be optimised and a component of this alkalised and sulphide enriched effluent would pass to the AMD PVR pre-treatment operation where neutralisation and heavy metal precipitation would be effected. The HRAP was used to effect polishing and disinfection of the final treated water.

2.2.2 *Operational parameters*

Electrical Aspects

All controls with fuses or starter switches and timers were housed in a control panel box mounted on the side of the FSBR. The system included the following:

a) A programmable logic system (PLC) for the automated control of some pumps and all of the solenoid valves
b) light indicators for all pumps and solenoid valves
c) manual overriding for all pumps and solenoids
d) overall on-off switches to activate/deactivate pumps and timers from SHT onwards.

The description and types of pump used is described in Table 2.1.

Table 2.1 Description and types of pumps used for the Rhodes BioSURE Process

Pump Number	Description	Flow Rate
P1	variable speed sludge pump	0-200L.h^{-1}
P3	variable speed centrifugal pump	
P5	high speed shear pump	$10m^3h^{-1}$
P6	variable speed open impeller pump	$0.3\text{-}8m^3h^{-1}$
P7	variable speed sludge pump	max. = $27m^3h^{-1}$
P8	high speed shear pump	$10m^3h^{-1}$
P9	Mini Monster Model 20 000 in-line grinder with 5 and 11 tooth double edge 4130 alloy steel cutters. 0.75kw. 525V. Max flow = 10L.s^{-1}.	

The reactors were operated in continuous mode with a retention time of 2 days. The anaerobic reactors were fed at a rate of 675 $L.day^{-1}$. Fresh primary sewage sludge was delivered twice weekly from ANCOR ERWAT disposal works. The sludge was passed through a sieve with pores 1cm in diameter, and then stored in $5m^3$ (HDPE) holding tanks. The sludge was then pumped into a $2.7m^3$ Sludge Holding Tank (SHT) via an online macerator (P9, Figure 2.1). A submerged macerator was suspended in the SHT to macerate the sludge and keep any particulate material in suspension. Based on daily analysis of the sewage and mine water, a predetermined volume of sewage sludge was mixed with metal-free mine water from the HDS process in a Blend Tank (BT), to maintain a $COD:SO_4$ feed ratio of approximately 2:1.

The reactors were operated as a continuous flow system for a period of 120 days, with the overflow going to drain. The blend ratio was kept constant for this phase of the operation, except for a period of six days in September 1999 during which the ratio was reduced to 1.5:1 and an 11 day period in March 2000 during which it was increased to 3:1 by manipulating the COD concentration respectively.

In order to maintain an operational temperature above 20^0C during winter, a counter-current heat exchange system was installed. The heat exchanger consisted of a series of 25mm plastic PVC pipes, submerged into the reactor, through which warm untreated underground mine water was allowed to flow. The mine water had a temperature of between 24 – 27^0C.

The operating regime for the pilot plant was as follows:

1. Screened primary sewage sludge was delivered to the Grootvlei Mine study site, twice weekly from Springs ANCOR (ERWAT) Water Care Works, and stored in $5m^3$ HDPE holding tanks. The sludge was then pumped into $2.7m^3$ sludge holding tank (SHT) via an online macerator (P9). A submerged macerator was suspended in the SHT to macerate the sludge and keep particulates in suspension. The sludge holding tanks were fitted with both high (HL) and low-level (LL) probes.
2. Flow of treated mine water from the High Density Sludge Process into a $5m^3$ Mine Water Reserve tank (MWR) was regulated by a high-level ball valve.
3. Mine water was pumped at pre-determined intervals, at a constant rate of 5780 litres per hour, into the blend tank (BT) by pump P3. P3 was controlled via the PLC

system, but was be switched off by the LL probe in MW and the HL probe in BT.

4. PLC-controlled pump P1 pumped raw sludge from SHT into BT at a pre-determined flow rate. The volume of sludge pumped into BT was dependent on the chemical oxygen demand (COD) of the raw sludge. The final COD:SO_4 ratio in the feed was set daily. The LL probe in SHT or the HL probe in BT automatically switched off pump P1.
5. A manually operated pump P5 recirculated the contents of BT in order to mix mine water with the sludge, and prevent settling of particulates. The LL probe in BT switched off P5.
6. Low levels in either SHT or MW will switch off P1, P3 and P6.
7. A PLC-controlled variable speed pump P6 pumped feed from BT to the FSBR at 610 l/hr. The LL probe in BT switched off P6.
8. The recirculation pump P7 and all 8 solenoid valves on the FSBR were PLC-controlled. The operator determined the sequences and duration of recirculation.
9. Recirculation times of the FSBR:

   valley 1: 60 seconds

   valley 2: 30 seconds

   valley 3: 10 seconds
10. Pump P8 was a manually controlled sludge Recirculation pump for the ABR. All the valves on the baffle reactor were operated manually.
11. After exiting the FSBR, equal portions of effluent flowed, by gravity, into the UASB and ABR
12. Equal volumes of effluent from the ABR were piped to each of the HRAPs.

2.3. PILOT PLANT OPERATION

As described in section 2.1 the construction of the Rhodes BioSURE process in Grahamstown was undertaken by Grahamstown Engineering Co. Following completion of construction, hydraulic tests were undertaken before the plant was dissembled and transported to Grootvlei Gold Mine No 3 Shaft where it was reassembled on-site (Figure 2.4).

Figure 2.4 Headgear at the No.3 shaft Grootvlei Mine with the Rhodes BioSURE Process pilot plant assembled in the foreground.

Following the reassembly of the BioSURE pilot plant at No.3 Shaft at Grootvlei Gold Mine, and after a period of stabilisation, during which a viable bioreactor sludge bed was established the plant was operated over a period of 18 months. Monitoring the performance of the BioSURE process at Grootvlei Mine is described over two time periods:

(1) **Process initialisation.** The plant was operated over an 8-month period of process initialisation that was characterized by sludge bed development, process optimisation, fluctuating results, mechanical breakdown and a number of unplanned process perturbations. During the course of this phase the system was exposed to a number of 'shock-loads' that had an immediate and profound effect on destabilizing the FSBR

and ABR, affecting both sulphate and COD concentrations. The first incident was due to the 'accidental' injection of concentrated NaOH into the mine water feed line. The second technical incident was the result of a fresh water leak into the mine water feed line.

(2) **Performance evaluation.** A 10-month period of steady-state operation followed in which process evaluation studies provided reliable data on performance characteristics of the process. Investigations into the associated removal of heavy metals was also undertaken during this phase of the investigation.

2.4. MATERIALS AND METHODS

2.4.1 Analysis

Sulphide, volatile fatty acids (VFAs) and total settable solids (TSS) were measured according to Standard Methods (APHA, 2000). 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 any dissolved sulphide. Samples used for determination of soluble COD (CODf) were passed through a 0.45μm GFA filter (Whatman). Particulate COD (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). The pH was measured using a Cyberscan 2500 pH meter.

The concentrations of CODt, sulphate and pH of the FSBR and ABR were determined daily. Samples were drawn from sample-ports (influent and effluent samples) within the reactor and analysed according to the methods described above. Faecal and total coliforms were analysed by an external accredited laboratory (ERWAT).

The chemical composition of the mine water was relatively constant (Table 2.2) except during periods of 'shock-loading' which will be discussed in Chapter Three. Table 2.3 gives a representative composition of the sewage sludge.

Table 2.2. Representative analysis of the mine water used in this study

Water Quality Parameter	Measured
pH	7.1
Sulphate (mg/l as SO_4)	2300
Total Dissolved Solids (mg/l)	3300
Total Solids (mg/l)	3316
Iron (mg/l Fe)	0.56
Conductivity mS/m	237
Suspended Solids	16
Turbidity (NTU)	45

Table 2.3. Representative analysis of sewage sludge used in the study

Water Quality Parameter	Measured
pH	5.3
Chemical Oxygen Demand (mg/l O_2)	24140
Suspended Solids (mg/l)	16995
Sulphate (mg/l SO_4)	56
Total Dissolved Solids (mg/l)	2150
Total Solids (mg/l)	19358
Chemical Oxygen Demand (filtered) (mg/l O_2)	3910
Total coliforms (cfu/1 ml)	397 000 000
Total plate count (cfu/1 ml)	>300
E-coli	Positive
Ascaris Ova Count	37

2.4.2 Metal removal

Solutions were prepared with varying concentrations of Fe^{3+}, Fe^{2+}, sulphide and pH. For a particular Fe^{2+} and S^{2-} content the Fe^{3+} was added so that a range of values Fe^{2+}: Fe^{3+} were investigated. This procedure was repeated for a number of sulphide concentrations. The pH in each experiment was adjusted at the start using NaOH so that the mixture after precipitation had a pH $\approx$ 6.5 (pH initial is given in table 6.1); after flocculation and settling pH tended to decrease slightly to a final value recorded as pH final in Table 6.1.

Solutions were prepared with distilled water and fixed Fe^{2+} (200mg/l), SO_4^{2-} (1600mg/l) concentrations. Alkalinity was introduced to the waters in the form of sodium bicarbonate (200mg/l) to simulate the Grootvlei waters. Solutions were mixed using a floculator (Sunonwealth electrical machine model no: 23080A) initially under rapid mix conditions, 192 rpm, for the initial 20 seconds. Thereafter a slow mix of 16.5rpm was applied for 20 minutes to allow flocculation. Finally the solution was allowed to settle for half an hour. Concentrations of Fe^{2+} and sulphide in the supernatant after settling were measured using a Nova 60 spectroquant by MERCK. pH was measured using a 744 Metrohm meter. Mn and Zn metals were analysed using Atomic Adsorption Spectrophotometer (Spectra AA-30 Varian).

For the simulation of the Rhodes BioSURE process with the addition of lime (Section 6.4) solutions were again prepared, as above, with distilled water and fixed Fe^{2+} (200mg/l), and SO_4^{2-} (1600mg/l) concentrations but variable sulphide and ferric content (see below) with dissolved O_2 ($\approx$ 7mg/l) and pH 6. Alkalinity was introduced to the waters in the form of sodium bicarbonate (200mg/l) to simulate the Grootvlei waters, and simultaneously NaOH was added to the solution to elevate the pH (>7.8). Solutions were mixed in the same way, as in the simulation of the Rhodes BioSURE process (above), using the flocculater. Initially the only metal ions added were iron species. A second set of experiments were later undertaken in which the water was 'spiked' with $Mn(Cl)_2$ and $Zn(Cl)_2$ at concentrations similar to those encountered at Grootvlei.

In order to investigate removal of colloidal sulphide from solution (resulting from coagulation and flocculation of iron hydroxide precipitant), solutions were prepared with varying ratios of Fe^{3+} to total iron (10 and 20 percent), representing figures likely to be encountered in practice. For each of these two ratios the Fe^{2+} to total sulphide content was prepared in molar ratios of 1:1 and 1:0.5. After mixing solutions were allowed to settle for 30 minutes and concentrations of Fe total and total sulphides in the supernatant were measured using a Nova 60 spectroquant by MERCK. pH was measured using a 744 Metrohm meter. Mn and Zn metals were analysed using Atomic Adsorption Spectrophotometer (Spectra AA-30 Varian).

CHAPTER 3.

PILOTING OF THE RHODES BioSURE PROCESS: PROCESS INITILISATION

3.1. INTRODUCTION

The performance of the Rhodes BioSURE process at Grootvlei Mine has been divided into two distinct time phases of operation: process initilisation and performance evaluation. This chapter reports on the initilisation and establishment period of the Rhodes BioSURE process at Grootvlei Gold Mine from early 1998 to late September 1998.

During this time, of establishment and initilisation, the FSBR and ABR were seeded with PSS in order to develop and maintain an active population of SRB. However, this period of 'reactor seeding' and 'sludge-bed development' was not without problems. Faulty solenoid valves in conjunction with troubleshooting of the programmable logic system (PLC), for the automated control of some solenoids resulted in the loss of the sludge-bed, in the FSBR, which had taken weeks to build up. Unpredictability of service providers (PSS delivery, mine water supply, electricity and engineering modifications) had a substantial impact and complicated the early stages of the research programme.

During the course of the project the system was also exposed to a number of 'shock-loads' that had an immediate and profound effect on destabilizing the FSBR and ABR, affecting both sulphate and COD concentrations. Once the source of the disturbance had been removed, however, the systems quickly returned to steady-state operation. The first incident was due to the 'accidental' injection of NaOH into the mine water feed line The second technical incident was the result of fresh water leaking into the mine water feed line.

The results and insights observed during the initilisation period of the Rhodes BioSURE process are presented here. The results are reported in three ways. Firstly, concentrations and data sets of sulphate, COD, and pH of the pilot-plant performance over a 120-day operational period are presented. Secondly, during this 120-day operational period two technical incidents were encountered, as mentioned above, and the effects of these perturbations on the pilot-plant are assessed and discussed. Thirdly three periods where no gross perturbations of the system occurred namely, days 0-31, 60-73 and 106-118, are presented and are compared to periods of stable operation discussed under performance evaluation studies reported in Chapter Four.

3.2. RESULTS AND DISCUSSION

Figures 3.1, 3.2 and 3.3 show the actual performance of the, FSBR and ABR, with respect to sulphate concentration, COD concentration and pH over a 120 day period. During days 37-55 the effect of an increased pH (Figure 3.1) due to NaOH and the dilution of influent sulphate stream (days 78-85) due to a fresh water injection occurred. Except for the periods of these perturbations influent sulphate concentrations (feed) remained relatively constant but fluctuating around 1700mg/l (Figure 3.2). The rate of sulphate removal in the FSBR showed an initial decline over the first 11 days of operation during stabilization. However, following this the removal rate increased with sulphates falling to 1391mg/l in the FSBR and down to 1185 mg/l in the ABR. These rates of sulphate removal increased steadily over the first 37 days of operation. The microbial population appeared to establish itself quickest in the ABR with an average sulphate removal of 206mg/l more effective than the FSBR. Sulphate reduction rates were not constant throughout the operation of the piloting exercise. Poor sulphate removal was initially obtained, probably due to a low bacterial concentration at start up.

The two different anaerobic reactors (FSBR and ABR) were compared in terms of substrate utilization and removal efficiency rate as well as sulphate reduction efficiency. The sulphate removal efficiency refers to the difference in sulphate levels between the influent (feed) and outflow and thus takes into account the dilution factors which occur with the blending of the mine and sewage waters.

COD concentrations in the various reactors are illustrated in Figures 3.3 Sewage sludge added a COD value of approximately 2800-4900mg/l to the sulphate rich wastewaters. The rate of COD removal for both the FSBR and ABR reactors increased from the time of commissioning of the reactor from 0 mg $COD.day^{-1}.l^{-1}$ to over 2000mg $COD.day^{-1}.l^{-1}$except for days 60-73 where the mean COD removal was only 1589 mg $COD.day^{-1}.l^{-1}$.

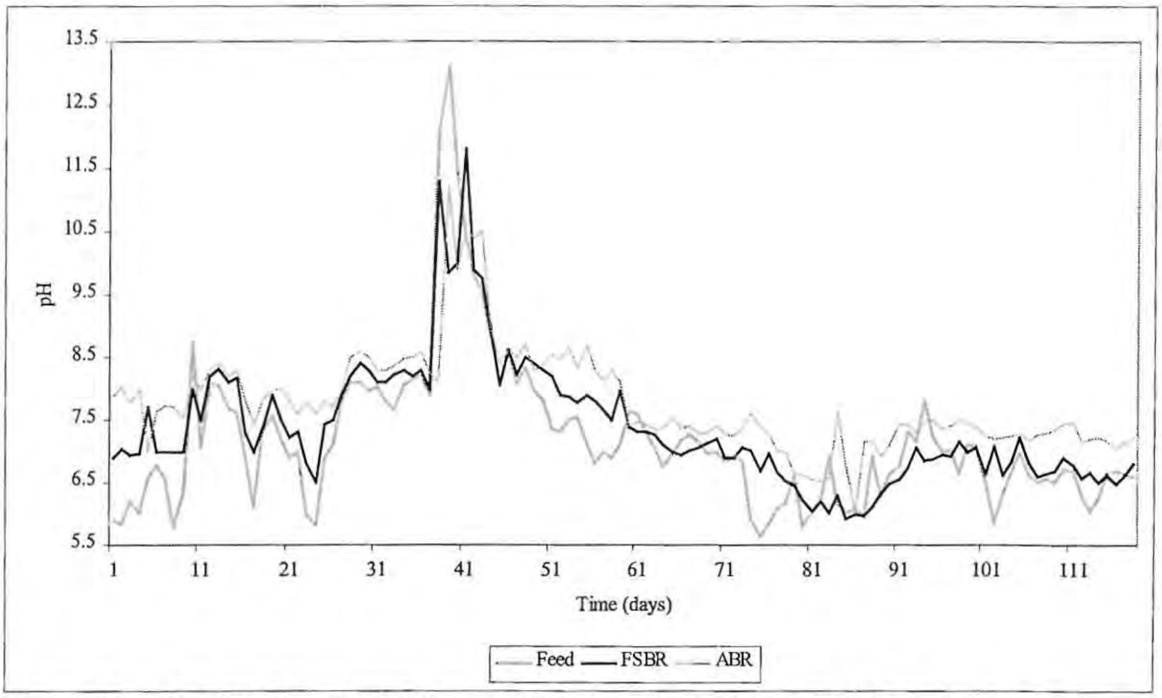

Figure 3.1. pH of the Feed, FSBR and ABR over the 120 day period of operation

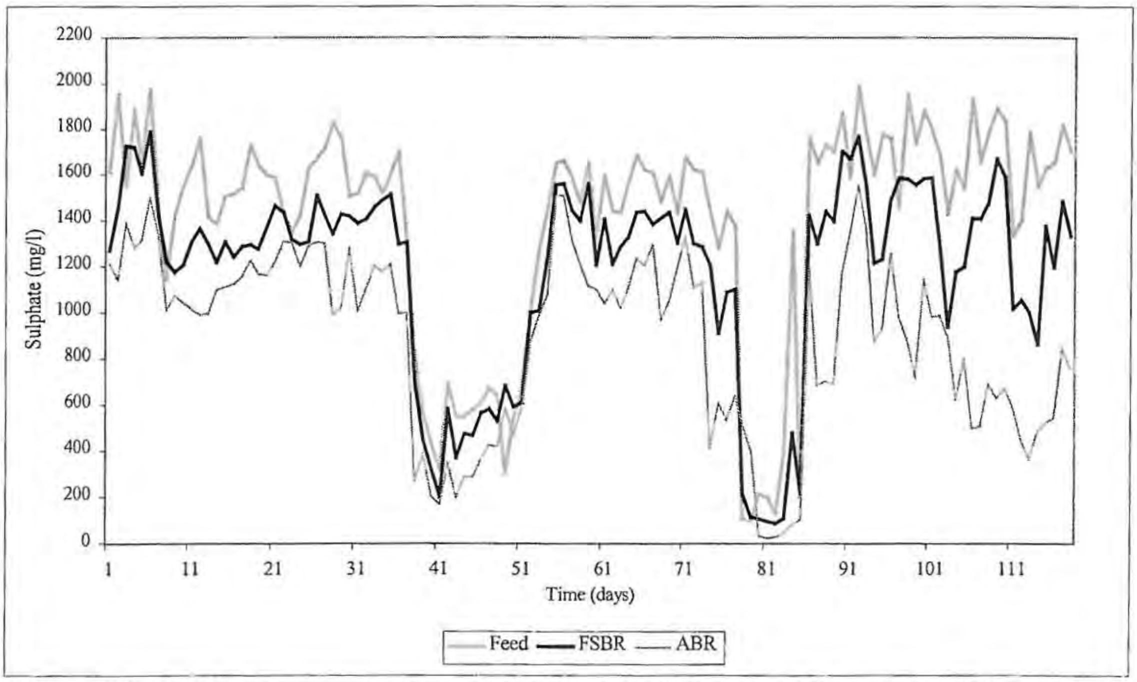

Figure 3.2. Sulphate concentration of the Feed, FSBR and ABR over the 120-day period of operation

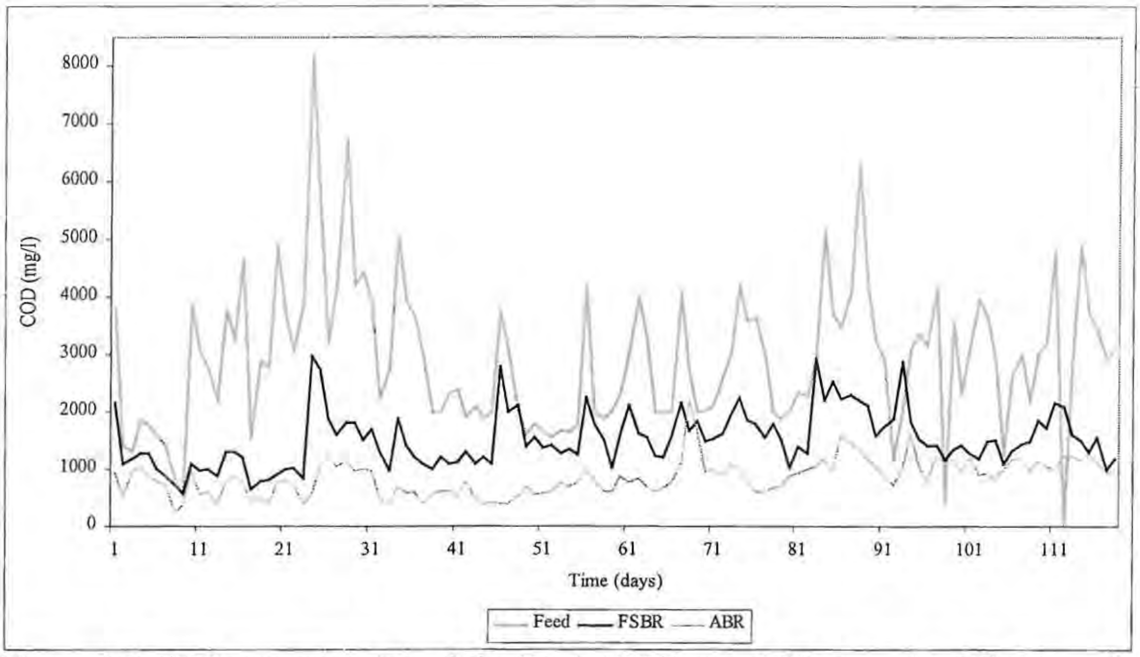

Figure 3.3. COD concentration of the Feed, FSBR and ABR over the 120-day period of operation

3.2.1 Effect of pH

The first technical incident occurred during the start up phase of the program, and was due to the injection of NaOH into the mine water feed line. This resulted in unstable operating conditions, characterized by an increase in pH to 11 on days 37-55 (Figure 3.1). Sulphate removal during this period exceeded 60% on some days (Figure 3.4). This may be explained either by enhanced sulphate reduction under alkaline conditions, or the sulphate ions precipitating as $NaSO_4^{2-}$. Although literature suggests that a pH value above 9 results in the inhibition of sulphate reducing bacteria, it can be supposed that the sulphate reducers in the alkali environment occurred in microniches of a higher, more favourable pH and therefore exposed to less alkalinity.

The increased pH had little effect on the COD levels in the reactors (Figure 3.3). The sludge blanket at the bottom of the valleys was not disturbed (results not shown). A slight increase in COD levels would have been expected due to the net increased substrate flux (even though the loading rate remained constant) and also due to a reduced sulphate influx in that most of the sulphates were precipitated as $NaSO_4$. The flattened COD peaks over the shock-loading period were most probably the result of increased substrate concentrations (due to reduced

SO_4^{2-} levels) which increased the substrate flux into the bioaggregates, thereby increasing the growth rate of the microbial population.

It may be observed from this data, that with the fluctuations in pH, the anaerobic reactors proved to be quite stable in their return to normal operating conditions. This can be seen in Figure 3.1 (day 55 – 77) where rapid stabilisation of the processes in the reactors with pH returning to 7.27 (± 0.29) in the FSBR and 7.6 (± 0.34) in the ABR.

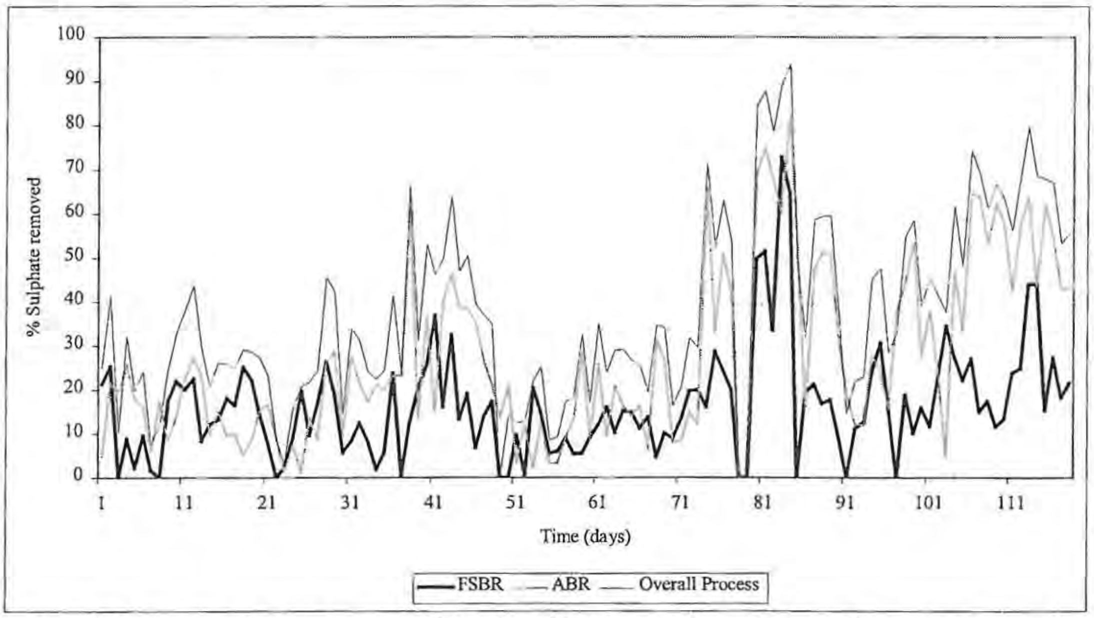

Figure 3.4. Percent Sulphate removal in the FSBR, ABR and overall process over the 120 day period of operation

3.2.2 Effect of Sulphate Dilution

Sulphate levels in the FSBR fell to well below 1000 mg/l and 500 mg/l in the ABR (Figure 3.2) during days 78-85. COD removal efficiencies decreased slightly in the FSBR reactor during this period, however this was presumably due and an influx in COD concentration and an increase in the feed concentrations (Figure 3.3). Despite this increase in COD concentrations the ABR's COD concentration remained fairly constant throughout the shock-loads. The percentage sulphate removal showed a significant improvement, although this was probably an artefact of dilution.

In order to observe the performance of the Rhodes BioSURE process without the disturbances of NaOH and fresh water injection, modified graphs with data for the periods of disturbance omitted are presented in (Figures 3.5-3.8). It can be seen that the operation of the system is relatively stable and apparently capable of dealing with the variable nature of industrial wastes. From Figures 3.5, it can be seen that with the disturbances omitted on days (37-55) and (78-85), the influent sulphate concentrations were around 1674mg/l which was around normal operating concentrations for the system.

Although there was little difference in the COD concentration (Figure 3.6) during the first shock-load (results not shown), the second shock load showed a significant increase in COD removal, however, this should be seen purely as an artefact of dilution.

From Figure 3.7, a stable pH is evident after both incidents of shock loading. After the second shock-load (days 78-85) there was a general improvement in sulphate removal (Figure 3.8) with 40% being removed from the overall process in (days 90-105) and 66% removal in (days 106-118).

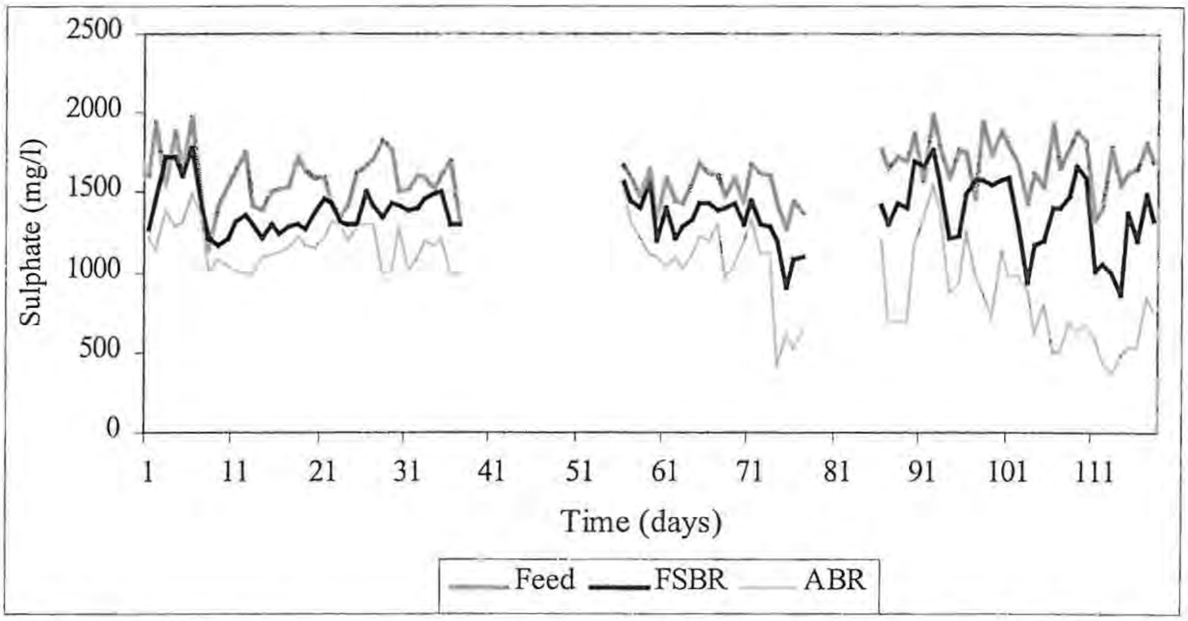

Figure 3.5. Sulphate concentration of the Rhodes BioSURE Process with periods of disturbance omitted.

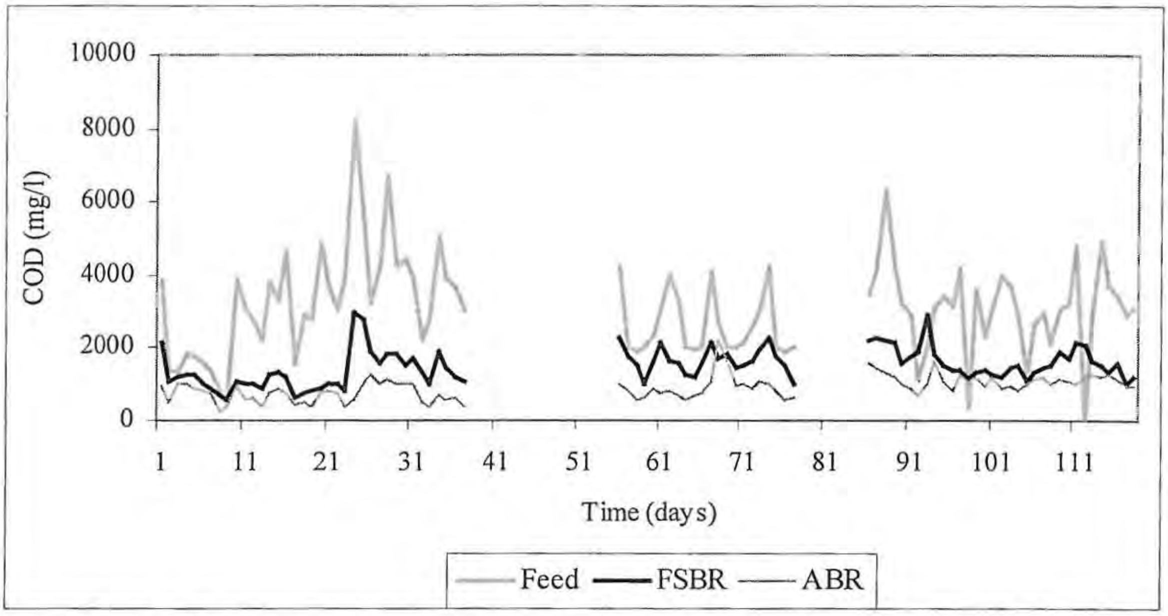

Figure 3.6. COD concentration of the Rhodes BioSURE Process with periods of disturbance omitted

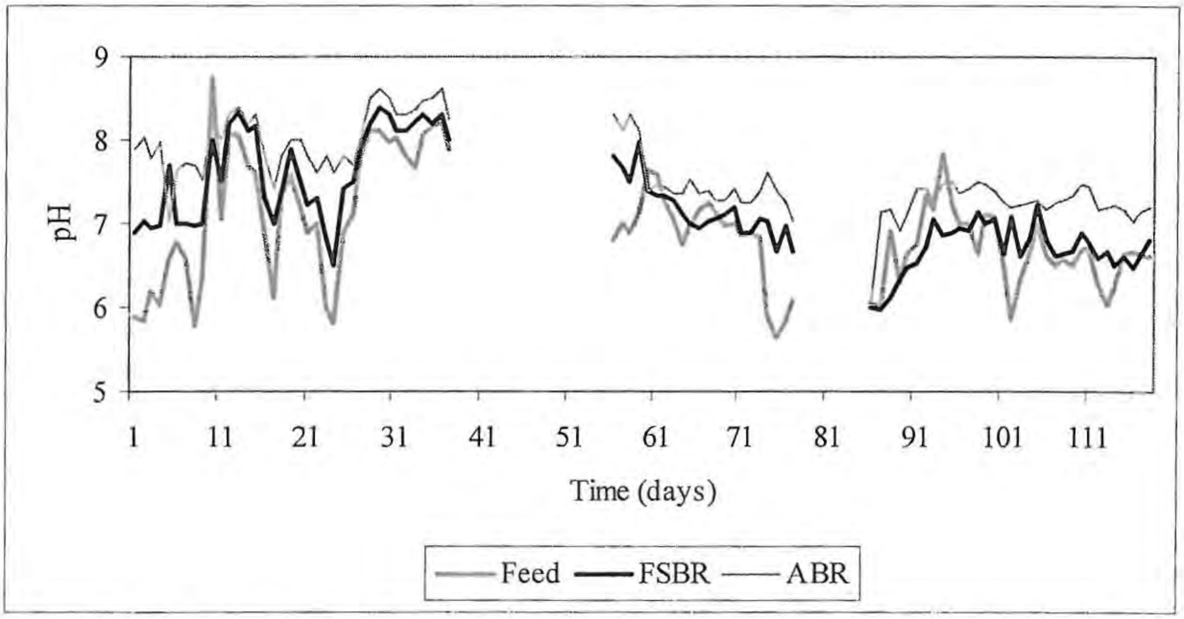

Figure 3.7. pH of the Rhodes BioSURE Process with periods of disturbance omitted

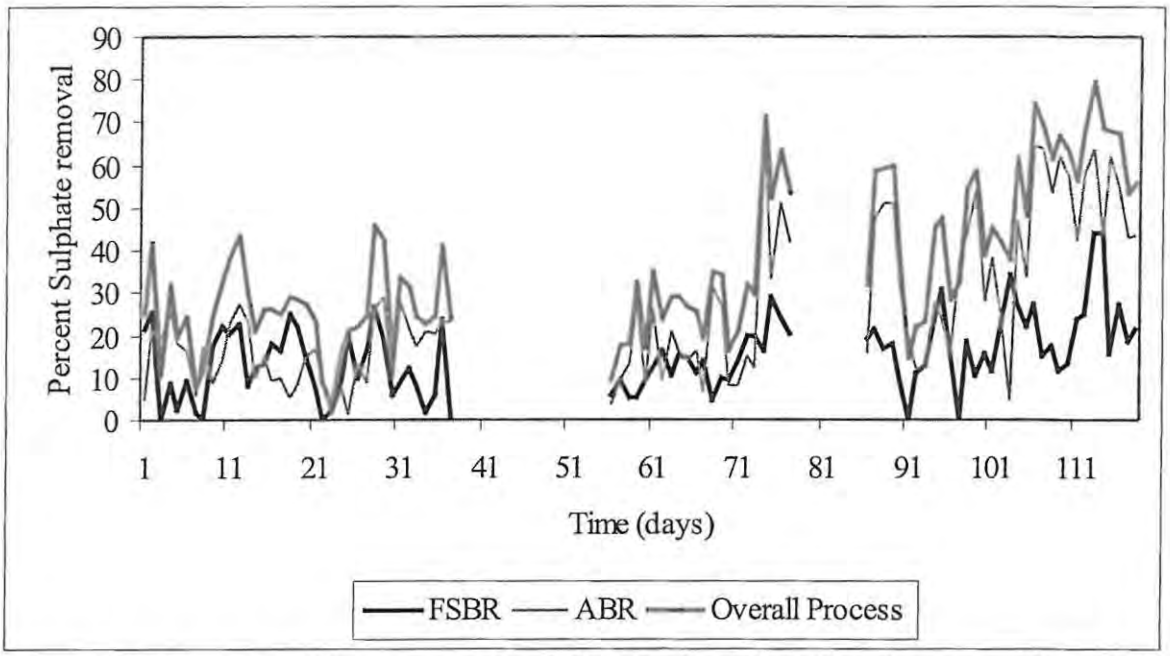

Figure 3.8. Percent Sulphate removal of the Rhodes BioSURE Process with periods of disturbance omitted

3.2.3 *Mean monthly sulphate performance*

Mean monthly removals of sulphate for the various stages of the process are graphed in Figure 3.9. Sulphate reduction in the ABR ranged from 14.8% (April) to 55.3% (September) falling well within discharge limits (<500mg/l) set out by the Department of Water Affairs & Forestry (DWAF).

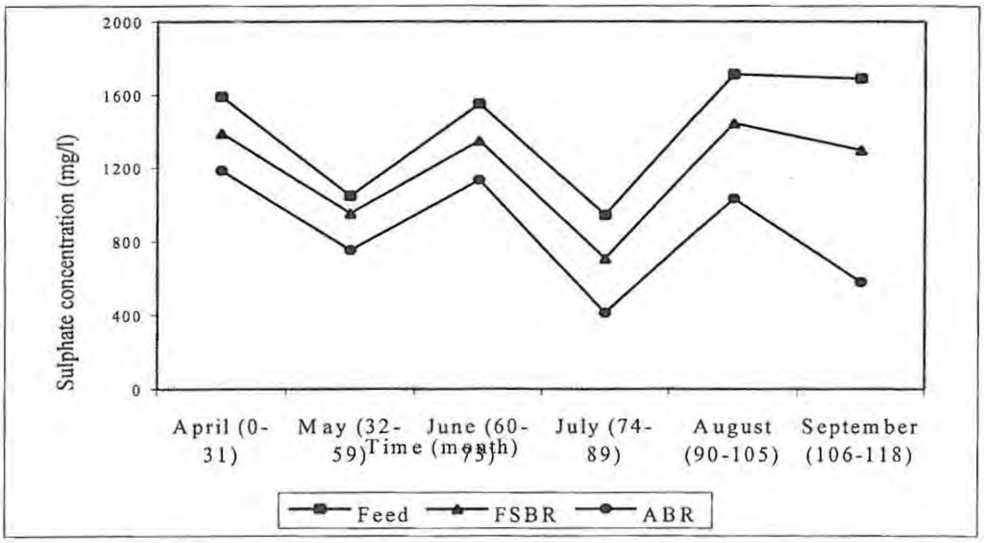

Figure 3.9. Mean monthly sulphate concentrations in the various stages of the BioSURE Process pilot study.

The results discussed below all refer to Figure 3.9. The FSBR exhibited a COD removal of between 36.5% and 62% over the 120-day operational period. Cumulative removal of COD after the effluent passed through the ABR was relatively constant at approximately 42% over the 120 operational period. The COD removal performance of the ABR did not appear to depend on influent COD values, suggesting that the ABR might be capable of withstanding shock-loads. The COD of the effluent varied between 622mg/l (May) - 1189 mg/l (July).

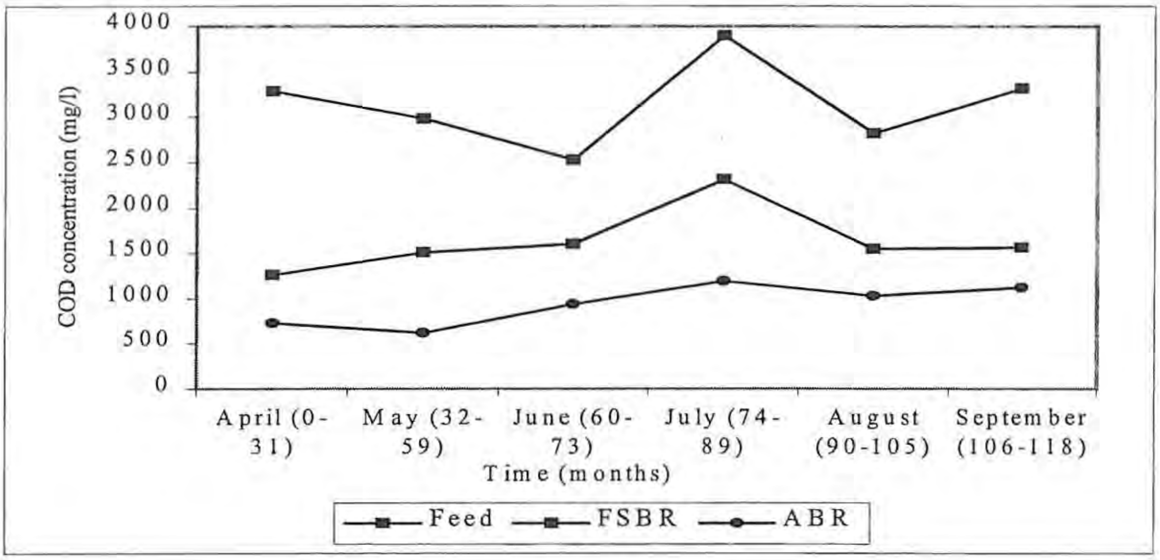

Figure 3.10. Mean monthly COD concentrations of BioSURE Process

3.2.4 *Process performance analysis*

Three periods where no gross perturbations occurred during the 120-day initialisation and establishment period are presented in Table 3.1. These three periods were the months April (day 0-31), June (days 60-73) and September days (106 – 118). The results of these periods of initialisation and establishment are compared to periods of stable operating conditions discussed in Chapter Four.

Table 3.1. Performance of the Rhodes BioSURE Process during three periods of the initialisation and establishment period where no perturbations occurred.

April (days 1-31)	**FSBR**	**ABR**	**Process**
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

June (days 60-73)	**FSBR**	**ABR**	**Process**
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

September (days 106-118)	**FSBR**	**ABR**	**Process**
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

Influent COD and sulphate concentrations entering the Rhodes BioSURE Process remained constant during days 1-31 and 106-118. Days 60-72, however, showed a slight decrease in COD concentrations with the COD feed ≈ 778mg/l less than the two periods mentioned above.

The FSBR removed a COD fraction of 37% (days 60-73), 53% (days 106-118) and 62% (1-31), during the initialisation phase. The ABR was less effective at solubilising and hydrolyzing the PSS and a COD removal rate of 42% (days 0-31 and 60-73), and 28% (days 106-118) was achieved. The overall COD removal was 63% (days 60-73), 66% (days 106-118) and 78% (days 1-31).

The sulphate removal during the initial stages of establishment, showed poor sulphate removal efficiencies with 25% (days 1-31) and 27% (days 60-73) being removed from the overall process. Days 106-118 showed a considerable improvement in the sulphate being removed from the AMD waters. A 66% overall sulphate removal was achieved with the majority of the removal taking place in the ABR (60%). Solubilisation of the PSS in the FSBR (days 106-118) was reflected in a net increase in VFAs (see Chapter Five), resulting in maximum consumption associated with sulphate reduction in the ABR. The Rhodes BioSURE process appeared to have established approximate steady state operation after 8 months operation.

Solids solubilisation in the Rhodes BioSURE Process was excellent with over 98% of all SS being converted to solubilised form during all three periods. Influent SS ranged in concentration from 130-83mg/l (entering the FSBR) and left the ABR at ± 1mg/l during all three periods.

3.3. CONCLUSION

The development of the Rhodes BioSURE Process and the technical-scale pilot plant study undertaken at Grootvlei Gold Mine had shown the potential value of using PSS as carbon source for SRB activity. The PSS was efficiently hydrolysed in the FSBR as suggested in Whittington–Jones's Study (2000).

The first eight months on site were characterised by supply problems in electricity, sludge delivery, mine water, faulty pumps and valves and more importantly two incidents of NaOH and fresh water injection into the system. However, these technical incidents indicated the robustness and speedy recovery of the Rhodes BioSURE Process.

Organic and sulphate loading rates varied with time. However, an average removal of 27-66% sulphate and 63-79% COD was achieved. The rates of removal were difficult to calculate accurately due to fluctuations in the effluent as well as the instability of the system due to the perturbations as noted. High levels of sulphide were obtained (results not shown) and alkalinity was generated from the reduction of sulphate. Both these products have a role to play in the removal of heavy metals from the acid mine drainage effluent and their use in this application will be discussed in subsequent chapters.

The three periods where no gross perturbations occurred during the initialisation and establishment phase showed consistent results with efficient COD and sulphate removal taking place. A decrease in the settlable solids fraction of the effluent FSBR and ABR indicated the effectiveness of both reactors in removing particulate matter with an efficiency of 99%.

CHAPTER 4.

PILOTING OF THE RHODES BioSURE PROCESS: PERFORMANCE EVALUATION AND OPTIMISATION

4.1. INTRODUCTION

The second phase of the process piloting study was characterised by stable and steady state operation conditions. The objectives of this research phase were to obtain accurate and reliable data under steady state operating conditions and to use this as a basis optimise the Rhodes BioSURE Process.

Three periods of stable operating conditions are reported. These are the months of November, December 1998 and March 1999. These periods of stable operation are compared to the periods of initialisation and establishment (early January 1998 - late September 1998) as discussed in Chapter Three.

Apart from the daily sample analysis performed in the site laboratory, an independent audit analysis was undertaken by an accredited laboratory (ERWAT). During the evaluation process samples were taken and collected by an ERWAT employee from set points in the process, and then transported to ERWAT for analysis. This allowed direct monitoring of the performance of the various stages of the pilot plant. All temperatures and pH were taken immediately using a hand operated DO (Hanna Instruments).

4.2. RESULTS AND DISCUSSION

4.2.1 Performance analysis of Rhodes BioSURE Process during November and December 1998 and March 1999

Mean removal of COD and reduction of sulphate for the three audit periods, November and December 1998 and March 1999, are listed in Table 4.1 and discussed below.

Between 57.5% and 69% of the total COD entering the FSBR was removed during the three audit periods. Sulphate removal in the FSBR varied between 36% and 47%. The ABR had COD removal efficiencies less effective in comparison to the FSBR with between 26-30% being removed. The difference in COD and settlable solids removal between the FSBR and

ABR indicates that the rate of solubilization in the FSBR was high as the system was run at steady state with no desludging. The average volume of settleable solids in the primary sludge was 990ml. This dropped to 90ml in the feed, due to dilution, and was between 1 and 3ml in the effluent of the FSBR.

The overall performance of the Rhodes BioSURE Process showed results of 69.3%-77.9% COD removal and between 65%-70.2% sulphate removal being achieved. The initialisation and establishment period of the Rhodes BioSURE process (Chapter Three) had shown similar COD removal rates of between 63%-78%.

From the results above it can be seen that there is a clear difference in both sulphate and COD removal efficiencies in the FSBR and ABR. Although some COD was consumed in the ABR, its primary role was sulphate reduction using COD product generated in the FSBR.

Table 4.1. Summary of the overall performance of the Rhodes BioSURE Process over three audit periods. All values in mg/l unless otherwise stated.

November 1998	**FSBR**	**ABR**	**Process**
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 1999	FSBR	ABR	Process
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

March 1999	FSBR	ABR	Process
COD influent	4375	1366	4375
COD effluent	1366	967	967
COD consumed	3009	820	3408
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

4.2.2 Independent System Evaluation

As noted, the Rhodes BioSURE Process was the subject of an independent audit and technology evaluation exercise. Table 4.2. reports some of the parameters assessed during this evaluation period in September 1998.

A large percentage of sulphate removal was accomplished in the ABR in comparison to the FSBR. There is a clear difference in the removal capacities of both systems, that could perhaps be attributed to a lower consumption rate of volatile fatty acids (VFA) in the FSBR, compared to the ABR. It can be assumed that an increase in VFAs result in an increase in substrate removal. The sulphate removal efficiency of the FSBR was very poor with 23% sulphate removal taking place. The bulk of the sulphate removal took place in the ABR reactor with between 60% sulphate removal occurring here. The loading ratio of the system was fairly constant with a COD:SO_4 ratio of 2:1. The results for sulphate removal are satisfactory in terms of meeting final discharge standards. The overall process achieved a sulphate removal of 66%.

COD reduction rates were not constant throughout the operation of the reactors. It can be seen that the consumption and removal of COD varies greatly. From the data tabled in 4.2 it appears that the COD:SO_4 exceeds what is required for sulphate removal. Sulphide toxicity can also cause the erratic COD removal values observed. Most of the COD removal took place in the FSBR, with between 9%–56% removal taking place. Day 107 results indicate a net gain of an additional 21% COD. The ABR only removed between 29%–48%. Even though the loading of the system remained fairly constant the rates of COD consumption did differ with influent COD:SO_4 ratios. This observation is supported by the decrease in sulphate removal seen with an increase in the consumption ratio. The highest sulphate removal (72%) was measured in the reactor fed medium with a COD:SO_4 consumption ratio of 0.4, followed by 65%, 62%, 60% and 54% removal with COD:SO_4 ratios of 1; 2.3; 2.4; and +4.5 respectively. Results obtained using sewage sludge as a carbon source in previous experimental programmes showed that a COD:SO_4 loading ratio of at least 2:1 is required for efficient sulphate reduction as not all carbon present is readily degradable (results not shown).

Table 4.2. Independent audit of the Rhodes BioSURE process showing COD:SO_4 relationships during the evaluation period. All mg/l (+indicating a net gain)

Day 105	FSBR	ABR	Process
COD feed	2766	2525	2766
COD effluent	2525	2400	2400
COD consumed	241	125	366
SO_4 influent	1407	1650	1407
SO_4 effluent	1650	900	400
SO_4 consumed	243	1250	1007
Loading ratio	1.97	1.53	1.97
Consumption ratio	1	0.1	0.4
% SO_4 removed	17	76	72
% COD removed	9	5	13

Day 106	FSBR	ABR	Process
COD feed	3662	2080	3662
COD effluent	2080	2380	2380
COD consumed	1582	-300	1282
SO_4 influent	1838	1700	1838
SO_4 effluent	1700	650	650
SO_4 consumed	138	1050	1188
Loading ratio	2	1.2	2
Consumption ratio	11.5	-0.3	1
% SO_4 removed	7.5	62	65
% COD removed	43	+12.6	+35.1

Day 107	FSBR	ABR	Process
COD feed	3146	6950	3146
COD effluent	6950	7075	7075
COD consumed	-3804	-125	-3929
SO_4 influent	1590	1550	1590
SO_4 effluent	1550	725	725
SO_4 consumed	40	825	865
Loading ratio	1.9	4.5	2
Consumption ratio	-95	+15	+4.5
% SO_4 removed	3	53	54
% COD removed	+21	+1.8	+55.54

Day 108	FSBR	ABR	Process
COD feed	3441	1950	3442
COD effluent	1950	1006	1006
COD consumed	1491	944	2436
SO_4 influent	1734	1700	1734
SO_4 effluent	1700	700	700
SO_4 consumed	34	1000	1034
Loading ratio	1.98	1.2	1.99
Consumption ratio	44	0.94	2.4
% SO_4 removed	2	59	60
% COD removed	43	48	71

Day 109	FSBR	ABR	Process
COD feed	3398	1500	3398
COD effluent	1500	1064	1064
COD consumed	1898	436	2334
SO_4 influent	1709	1500	1709
SO_4 effluent	1500	650	650
SO_4 consumed	209	850	1059
Loading ratio	2	1	1.9
Consumption ratio	9	0.51	2.2
% SO_4 removed	12	57	62
% COD removed	56	29.1	68.7

4.2.2.1 pH Values

pH plays an important role in the sulphate reduction process. The SRB prefer an environment around pH 7 and are usually inhibited by pH values lower than 6 or higher than 9 (Pfening *et al.*, 1981). From Figure 4.1. the pH values of the audit study period are depicted. From the results it can be seen that the operation is an alkalinity generating process, and the pH remains fairly stable in each stage of the operations.

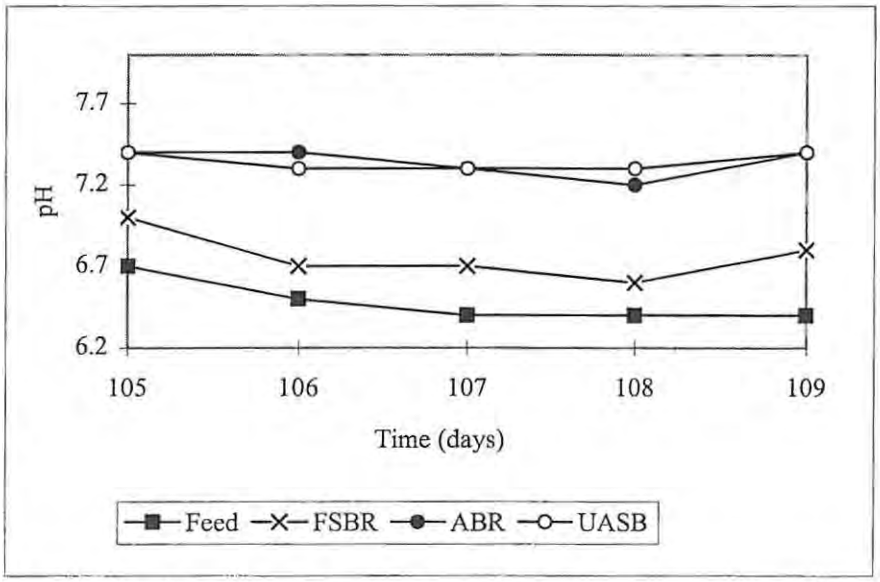

Figure 4.1. pH profile of Rhodes BioSURE Process over the evaluation period

4.2.2.2. Microbiological Analysis

Both the FSBR and the ABR are effective in killing coliforms, and thus lowering the numbers of these potentially hazardous microbes in the treated effluent. This ability of the reactors to trap biomass also suggests that the reactors may be effective in retention of those bacteria involved in hydrolysis, acidogenesis and sulphate reduction reaction. Removals of fecal and total coliforms in the FSBR were 95.1% and 99.6% respectively. After passing through the ABR, 99.6% of fecal coliforms and 97.6% total coliforms had been removed (Table 4.3.). Removal of biomass by the ABR was not unexpected, as the primary advantage of the baffle reactor over other designs is its ability to retain biomass, irrespective of the binding and floc-forming capabilities of the biomass. The ability of the UASB reactor to retain coliforms compared well to that of the baffle reactor, with combined removal of fecal coliforms of 99.1%.

The final effluent passed through the High Rate Algae Ponds (HRAP) (post-treatment step) achieved removal of a large proportion of the remaining coliforms.

Table 4.3. Results of the microbiological analysis ($CFU.mL^{-1}$)

Sample	Faecal Coliforms	Total Coliforms	Estimated plate count
Blend-tank	4700000	26400000	3200000
FSBR	208000	113000	7300000
ABR	17000	6100	42000
UASB	39000	620000	24000
HRAP	negative	negative	

4.2.2.3 Total Solids

A comparison of the concentration of total solids between each reactor is given in Figure 4.2. Results over the five-day evaluation period indicate there was a general decrease in concentration of total solids from the feed to the UASB. The feed total solid concentrations were considerably higher than the FSBR throughout the five-day evaluation period. The FSBR total solid concentrations were considerably higher than both the ABR and UASB concentrations throughout the evaluation period. The concentrations of total solids in the ABR and UASB did not show any clear trends, for example the UASB concentration (2970 mg//) on day 106 was greater than in the ABR (2214 mg/l), however, on day 108 the concentration of total solids in the ABR (2618 mg/l) was greater than in the UASB (2536 mg/l).

The FSBR was found to be highly effective in removing total solids at a retention time of 8 hours. A large proportion of the removed total solids were not hydrolysed immediately, but were rather removed from the liquid phase by sedimentation. Through the process of sludge recirculating the non-refractory component of the settled sludge was degraded over time. The ABR was designed in such a way so as to retain a maximum biomass. Thus, the effective removal of a large proportion of the remaining total solids was expected.

4.2.2.4 Total Dissolved Solids

Figure 4.3. compares the concentration of TDS for each reactor. Whilst there is no clear trend, a general decrease between the feed and UASB is apparent. The TDS concentration of the Blend-tank and the FSBR were considerably greater than the ABR and UASB. Again, there are no trends with the ABR and UASB TDS concentration. For example on day 105 the UASB concentration (2606 mg/l) was greater than the ABR (2516 mg/l), however, on days 106 to 109 the TDS concentration of the ABR was greater than the UASB.

The high TDS concentration of mine water can be attributed to the quantity of various inorganic salts dissolved in the water. This inorganic component includes salts such as calcium, magnesium, sodium, potassium, sulphate and bicarbonate. The increase in TDS in the FSBR (day105) could possibly be attributed to an increase in solubilised carbon and bacteriological biomass. The FSBR is involved mainly in the breakdown of complex carbon and high TDS levels are evident due to less organic materials being consumed in sulphate reduction.

In the ABR and UASB the sulphate/COD are used in conjunction with dissolved inorganic material for the production of biomass. This results in the organic as well as the inorganic components being removed and a reduction in total dissolved solids being achieved.

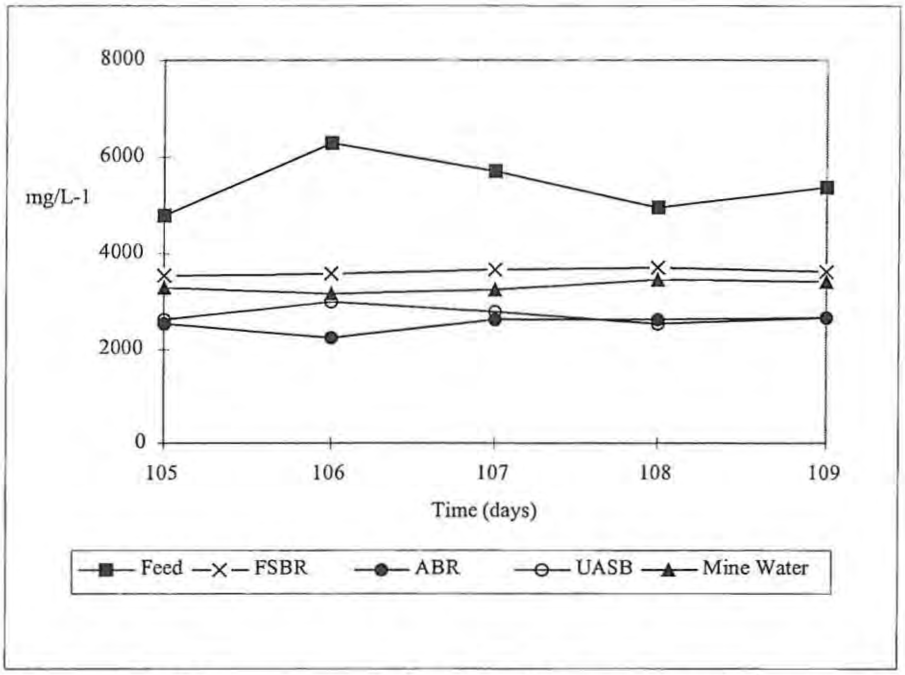

Figure 4.2. Measurement of total solids concentration across the pilot plant made during the audit period.

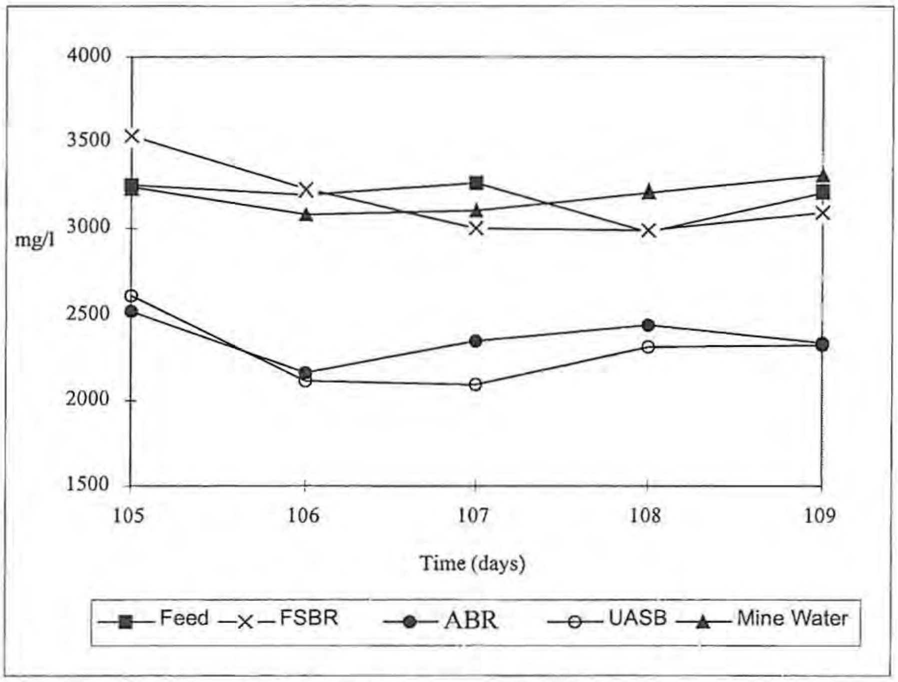

Figure 4.3. Measurement of total dissolved solids concentration across the pilot plant made during the audit period.

4.2.3. Optimisation studies

4.2.3.1. Feed ratio change

Development and system optimisation studies involved the adjustment of the COD:SO_4 ratio undertaken downward from 2:1 to 1.5:1 and upward to 3:1. A detailed record of COD removal and sulphate reduction is shown in Table 4.4. The COD: SO_4 ratio of the feed was maintained at 2:1 for the duration of the pilot plant study, except for a period of six days in November and eleven days in March 1999 (Figure 4.5-4.6). During this period (November 1998) the ratio was reduced to 1.5:1, by decreasing the COD concentration. This change had little influence on the overall performance of the reactor (Table 4.4.). However, within 24 hours after the change was introduced, there was a dramatic increase in gas production, and solids began to rise to the surface of the reactor.

Table 4.4. Summarised performance of the FSBR during November 1998. All values in mg/l

Date	COD:SO_4 (feed)	CODt removed (influent – effluent)	Sulphate reduced	Theoretical COD used in sulphate reduction	% removed COD accounted for by sulphate reduction
2	2:1	917	304	253	27.6
3	2:1	1505	763	636	42.3
4	2:1	1838	194	162	8.8
5	1.5:1	400	258	215	53.8
9	1.5:1	596	453	378	63.4
10	1.5:1	1078	215	171	15.9
11	1.5:1	1118	180	150	13.4
12	2:1	602	248	207	34.4
13	2:1	1611	465	388	24.1
16	2:1	1494	704	587	39.3
17	2:1	1851	798	665	35.9
18	2:1	1845	717	598	32.4
19	2:1	1954	720	600	31

During the period March 1999, the COD:SO_4^{2-} was increased to 3:1 (Table 4.5). Again this change had no significant influence on the overall performance of the reactors with a mean COD removal accounted for by sulphate reduction of 22.16% (± 2.1). It was possible to estimate what fraction of the CODt retained in the FSBR was used for sulphate reduction and consequently, what percentage was likely to have been removed by settling. Values, based purely on CODt of the influent and effluents and sulphate reduced, are between 16% and 22.7% of the CODt removed during March must have been utilised for sulphate reduction, with a mean value of 20.16% (± 2.064). Although not yet fully optimised, most of the particulate COD in primary sewage was effectively solubilized in the FSBR in the presence of an active SRB population. When the system was operated at a COD:SO_4^{2-} loading ratio of 2:1 the removal of COD (32.5%) due to sulphate reduction correlates with published maximum yields of around 35% (Hatziconstantinou *et al.*, 1996).

Taking the mean data from March 1999 (see Table 4.6), 732 mg/l and 276 mg/l of sulphate was reduced by the FSBR and ABR respectively. The concentration of CODt removed was 3009 mg/l for the FSBR and 399 mg/l for the ABR. Thus 69% of the CODt was removed in the FSBR, and 30% in the ABR. The concentration of CODp remaining in the FSBR was 2490 mg/l. This meant that a minimum of 75.6% of the particulate COD that remained in the reactor had to have been hydrolysed to again produce enough soluble COD to support the amount of sulphate reduction that took place.

4.5. Summarised performance of the FSBR during March 1999. All values in mg/l.

Date	$COD:SO_4$ (feed)	CODt removed (influent – effluent)	Sulphate reduced	Theoretical COD used in sulphate reduction	% removed COD accounted for by sulphate reduction
1	3:1	2880	707	589	20.4
2	3:1	3189	610	508	16
3	3:1	3305	821	684	20.6
4	3:1	2852	674	562	19.7
5	3:1	3300	882	735	22.3
8	3:1	2522	601	501	19.8
9	3:1	3012	821	684	22.7
10	3:1	2887	749	624	21.6
11	3:1	3134	691	576	18.4

Table 4.6. Summary of the FSBR and ABR performance during March 1999. CODt = total COD; CODp = particulate COD; CODf =soluble COD

Parameter	FSBR	ABR
CODt in	4375	1366
CODt out	1366	967
CODp in	3558	1099
CODp out	1068	760
CODf in	817	298
CODf out	298	207
Sulphate in	1552	820
Sulphate out	820	544
CODt removed	3009	399
% CODt removed	69	30
Sulphate removed	732	276
% sulphate removed	47	34
pH in	6	7
pH out	7	7.2

4.3. GENERAL CONCLUSIONS

The second phase of the process piloting study was characterised by stable and steady state operation conditions. Three periods of stable operating conditions (November 1998, December 1998 and March 1999) were evaluated and the system exposed to other operating parameters that answered critical questions.

Overall performance of the Rhodes BioSURE Process showed results of 69.3%-77.9% COD removal and between 65%-70.2% sulphate removal being achieved. There was a clear difference in both sulphate and COD removal efficiencies in the FSBR and ABR. The ABR, although it consumed some COD, primary role was sulphate reduction using solubilised COD generated in the FSBR.

An accredited laboratory (ERWAT) undertook an independent audit assessment of the Rhodes BioSURE Process. A clear difference in the removal capacities of the FSBR and ABR was again identified and was assumed to be attributed to a lower consumption rate of VFA in FSBR, compared to ABR.

Development and system optimisation studies concerning the removal of sulphate at different $COD:SO_4^{2-}$ ratios were also investigated. It was found that adjustment of the $COD:SO_4$ ratio downward from 2:1 to 1.5:1 resulted in characteristic signs of methanogenesis, such as gas bubbles and lifting of the sludge bed due to gas formation. However, when the system was returned to a $COD:SO_4^{2}$ ratio of 2:1 the system recovered rapidly. A $COD:SO_4^{2}$ ratio adjustment upward to 3:1 was also attempted, however due to an increase in the available COD fraction this resulted in residual carbon available to re-oxidize sulphur to sulphate.

CHAPTER 5.
SYSTEM PERFORMANCE

5.1. INTRODUCTION

The studies described in Chapter 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 FSBR 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, offer opportunities for the more effective optimisation of the overall sulphate reduction process. Although a component of the influent COD and sulphate are consumed in the establishment of the enhanced hydrolysis environment, the solubilised product may be made available as a feedstock to downstream sulphate reduction activity.

A significant proportion of the total organic matter in primary sewage sludge is in the form of complex macromolecules (Heukelekian and Balms, 1959; Levine *et al.,* 1985). During the process of anaerobic digestion, these macromolecules are hydrolysed by a variety of extracellular bacterial enzymes, to produce smaller constituent molecules that can be internalized by the bacterial community (Eastman and Ferguson, 1978; Novaes, 1986; Pavlostathis and Giraldo-Gomez, 1991; Jain *et al.*, 1992; Confer and Logan, 1997a, 1997b, 1998).

A schematic representation of the anaerobic degradation of organic matter is illustrated in Figure 5.1. The process can be divided into the following steps:

- *Hydrolysis:* Complex organic compounds in the form of carbohydrate, protein and lipid structures are hydrolysed to the monomer sugars, amino acids, polyols and long chain fatty acids, respectively.
- *Acidogenesis:* Fermentation of the soluble compounds (sugars, amino acids and polyols) to volatile fatty acids, hydrogen, carbon dioxide and small amounts of ethanol and lactic acid.

- *β-Oxidation:* Oxidation of long chain fatty acids yielding acetate for even numbered fatty acids and acetate plus propionate for the odd numbered fatty acids.
- *Acetogenesis:* Oxidation of volatile fatty acids formed in the acidogenesis yielding acetate, hydrogen and depending on the chain length of the fatty acids also carbon dioxide.
- *Methanogenesis:* Formation of methane by decarboxylation of acetate by acetotrophic methanogenic bacteria and hydrogenation of carbon dioxide by hydrogenotrophic methanogenic bacteria (Visser, 1995).

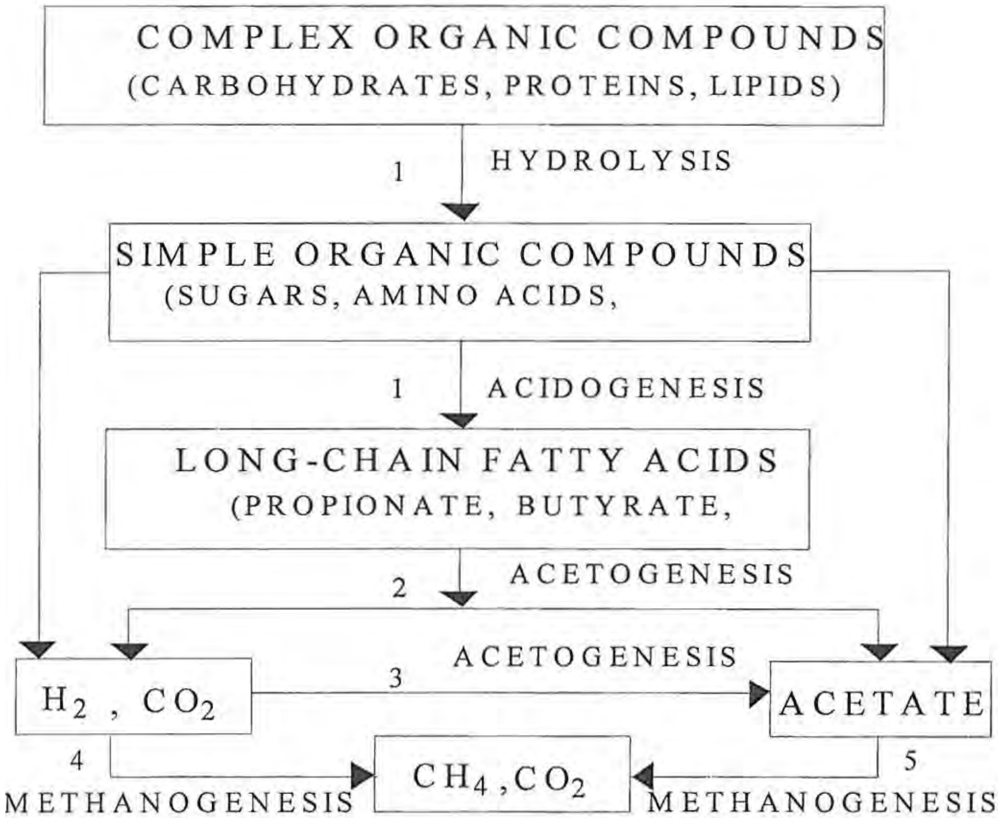

Figure 5.1. Metabolic steps and microbial groups involved in anaerobic digestion:
1) fermentative bacteria; 2) H_2-producing acetogenic bacteria; 3) H_2-consuming acetogenic or homoacetogenic bacteria; 4) CO_2-reducing methanogenic bacteria; 5) acetoclastic methanogenic bacteria (Novaes, 1986).

The most important products for SRB activity of 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 sulphide as the end product.
- Oxidation of acetate by acetotrophic SRB and molecular hydrogen by hydrogenotrophic SRB

Given the central importance of the hydrolysis and solubilisation reactions as the initial steps in which complex carbon structures such as PSS are made available to biological processes, the complex range of the products of hydrolysis and the difficulty involving the accurate individual analysis, it was necessary to relate the efficiency of hydrolysis in the FSBR in this study in terms of the combined products of acidogenesis and acetogenesis. These were expressed as acetate equivalents and calculated from the sulphate reduction value measured in the system at a $COD:SO_4$ value of 0.61:1 and based on equation 5.1 the $COD:SO_4$ value of 0.61:1 was used in the calculation of acetate equivalent rather than the 0.67:1 value which relates carbon consumption as COD. 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 to sulphate reduction would be both a crude and a minimum value.

$CH_3COO^- + SO_4^{2-} \rightarrow H_2O + CO_2 + HCO_3^- + S^{2-}$ -- (1)

$\Delta G = -12.41$kJ/reaction (Widdel, 1988)

Using the above calculation of hydrolysed PSS into acetate equivalents the COD: SO_4 consumption ratios and the resultant carbon utilisation values were calculated for the FSBR and ABR in the Rhodes BioSURE process.

5.2. RESULTS AND DISCUSSION

5.2.1. Formation of acetate equivalents from primary sewage sludge

Table 5.1 lists values for COD and SO_4 consumed in the FSBR 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.

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 in the FSBR and between 0.57 – 0.82 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 be broadly assumed that sulphate reduction in the ABR was largely driven by VFA products generated by PSS hydrolysis occurring in the FSBR. 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 is consequently larger than the second stage of the process where the hydrolysis products are consumed largely in sulphate reduction. Where the overall objective of the Rhodes BioSURE Process is taken into account the utilisation of complex carbon as electron donor for sulphate reduction indicates a PSS conversion in the process to acetate equivalent utilised in sulphate reduction of around 32%.

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 primarily be electron sources for sulphate reduction as well.

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

September	**FSBR**	**ABR**	**Overall Process**
COD consumed (mg/l)	1761	444	2205
SO_4 consumed (mg/l)	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	**FSBR**	**ABR**	**Overall Process**
COD consumed (mg/l)	1845	376	2221
SO_4 consumed (mg/l)	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	**FSBR**	**ABR**	**Overall Process**
COD consumed (mg/l)	2279	337	2616
SO_4 consumed (mg/l)	643	589	1232
Consumption ratio	3.5	0.57	2.1
Acetate equivalents used in SO_4 reduction (%)	17.2	106.6	28.7

5.2.2. Effects of feed ratio adjustment on acetate equivalents produced

As mentioned in Chapter Four, 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 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 in the FSBR 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 twice that of 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, 1996). The sensitivity of this system for this manipulation of COD: SO_4 ratio indicates validity for the use of the acetate equivalent unit as an indication 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). Falling Sludge Bed Reactor (FSBR) and Anaerobic Baffled Reactor (ABR) and the combined overall process.

Period of 3:1 loading	**FSBR**	**ABR**	**Overall Process**
COD consumed (mg/l)	3009	399	3408
SO_4 consumed (mg/l)	732	276	1008
Consumption ratio	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	FSBR	ABR	Overall Process
COD consumed (mg/l)	798	317	1115
SO_4 consumed (mg/l)	376	403	679
Consumption ratio	2.9	0.79	1.6
Acetate equivalents used in SO_4 reduction (%)	28.7	77.5	37.1

5.2.3. Volitile Fatty Acids (VFA)

VFAs can be used directly as electron donors by 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 5.2 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 sewage sludge takes place in the FSBR, that the end products of this conversion process are VFA and, as such, one would expect high concentrations of these products in the effluent. As some sulphate reduction did take place in the FSBR, a certain proportion of the available VFA would have been consumed, thus resulting in only a portion of the total products exiting in the FSBR effluent. The concentration of VFA in the effluent of the FSBR does not appear to depend on the influent VFA concentration. This suggests either that a certain percentage of the VFA produced in the FSBR is not available to sulphate reducers, or that reactions that produce the VFA are in some way inhibited.

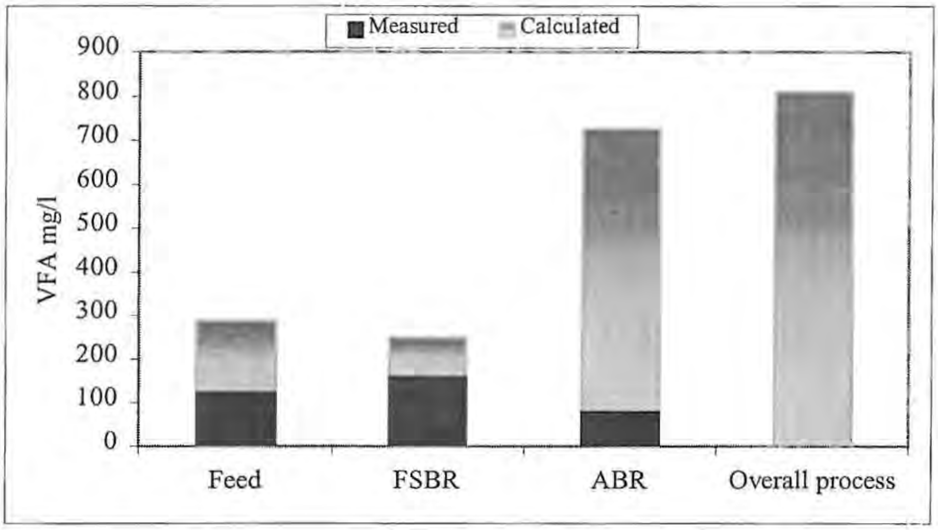

Figure 5.2. Volatile fatty acid produced from primary sewage sludge in the BioSURE pilot plant. Measured VFA values across the system are compared with calculated values for total production of acetate equivalent, based on COD consumed in sulphate reduction. Falling Sludge Bed Reactor (FSBR) and Anaerobic Baffled Reactor (ABR) and the combined overall process.

5.2.4. Flask-study degradation experiments

As discussed earlier the Rhodes BioSURE Process was operated as a dynamic system with an HRT of approximately 8 hours in the FSBR before passing to the ABR which had a HRT of 37 hours. Due to the complexity of operating the pilot-plant with extended HRTs in excess of 48 hours, a series of flask study experiments were performed to determine the possible effects on system productivity of an extended HRT. 500ml samples of effluent leaving the FSBR and ABR were drawn and performance measured over a 9-day period according to the procedure as noted in section 2.3.1.

The results of this study are reported in Figures 5.3. (a-c) and 5.4. (a-c).

Figure 5.3. (a) Illustrates the CODt of the effluent from the FSBR and ABR in flasks over a 9-day period. The results show the FSBR CODt on day 1 being 1454 mg/l. From day 2 to day 6 the CODt drops substantially and reaches a concentration of between 957 and 992 mg/l from day 6

onwards i.e. a net loss of 497 mg/l COD. The ABR, although a small drop in CODt is evident, clearly does not reflect a dramatic CODt removal (net loss of 194 mg/l COD) over time as in the FSBR. This is due to the fact that most of the sludge is effectively solubilised in the FSBR as mentioned earlier. The ABR had a CODt concentration of 897 mg/l. From day 3 onwards the concentration of the effluent reached a plateau of between 703 and 789 mg/l.

Figure 5.3. (b) and (c) show the concentrations of the CODf and CODp found during the degradation experiments. The CODf of the FSBR increased from 517 mg/l (day 1) to 1028 mg/l (day 3). From day 3 onwards the concentration continued to drop until day 9 where the concentration reached 359 mg/l. The CODf of the ABR also showed a gradual drop in concentration, however, not as predominant as in the FSBR. The concentration of the ABR effluent plateaued from day 7 to a concentration of between 263 and 288 mg/l. The CODp concentration showed the inverse relation to that of the CODf. The CODp concentration of the FSBR dropped from day 1 (937 mg/l) to (352 mg/l) on day 3. From day 3 to day 7 the concentration then increased from 352 to 580 mg/l respectively. From day 7 to day 9 the concentration plateaus between 576 to 603 mg/l. The ABR too showed the inverse relation to that of the CODf (Figure 5.3. (b). The concentration of the CODp for the initial 5 day period showed a decrease from 480 mg/l (day 1) to 321 mg/l (day 5). From day 6 onwards the concentration increased from 346 mg/l to 455 mg/l (day 9).

Figure 5.4. (a) Illustrates the sulphate concentration of the effluent in the FSBR and ABR, during the flask-study experiments, over a 9-day period. The sulphate concentration of both the FSBR and ABR shows a decrease in sulphate concentration over the experimental period. The FSBR showed a removal of 990 mg/l sulphate (day 1) being reduced to 796 mg/l sulphate (day 9). The ABR showed a far better removal, and the concentration of sulphate was reduced from 849 mg/l (day 1) to 572 mg/l (day 7). The concentration then increased to 603 and 593 mg/l on days 8 and 9 respectively.

Figure 5.4. (b) depicts the sulphide concentrations over the experimental period. The sulphide concentration for the FSBR is rather consistent until day 6 where it ranges from 36.8 to 42.1

mg/l. From day 7 onwards the concentration continues to drops to 15.9 mg/l. The ABR shows a similar trend to that of the FSBR, however the sulphide concentrations are much higher. The concentration ranges from 59.5 to 64.8 mg/l during the first 6 days. Again, the sulphide levels drop from day 7 (44.7 mg/l) to 33 mg/l on day 9.

Figure 5.4. (c) shows the pH profile of the effluent from the FSBR and ABR. The pH for the FSBR starts off at 6.85 (day 1) and after an initial slump during day 2 (6.8), it continues to increase to 7.55 (day 6). It then drops again slightly during days 7-9 and plateaus between 7.28 and 7.48. The ABR pH increases from 6.83 (day 2) to 7.6 (day5). From day 6 to 8 the pH plateaus and increased slightly to 7.47 on day 9.

a)

b)

c)

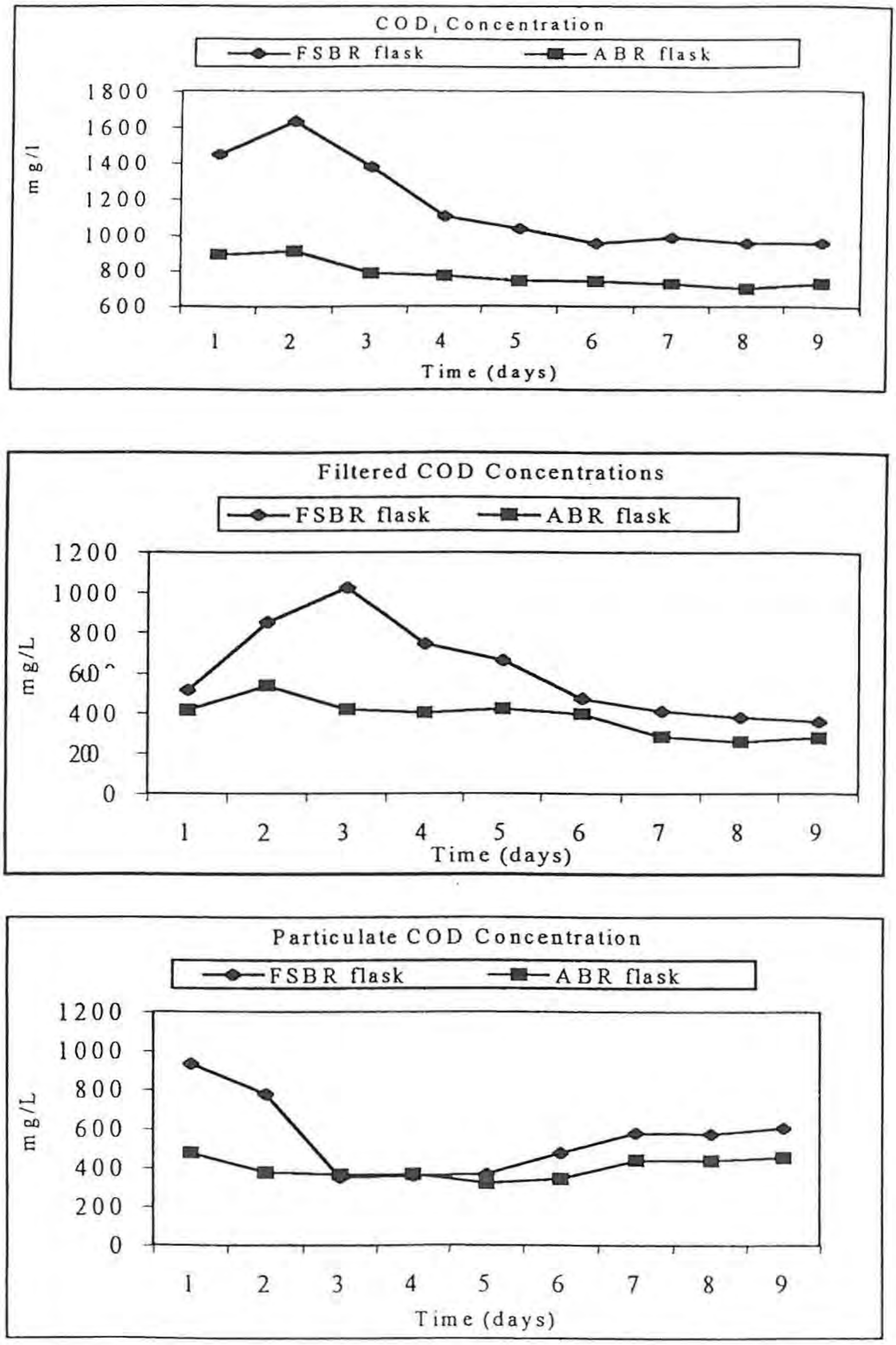

Figure 5.3 (a-c). Concentrations of various COD fractions during the flask study degradation experiments. Falling Sludge Bed Reactor (FSBR) and Anaerobic Baffled Reactor (ABR).

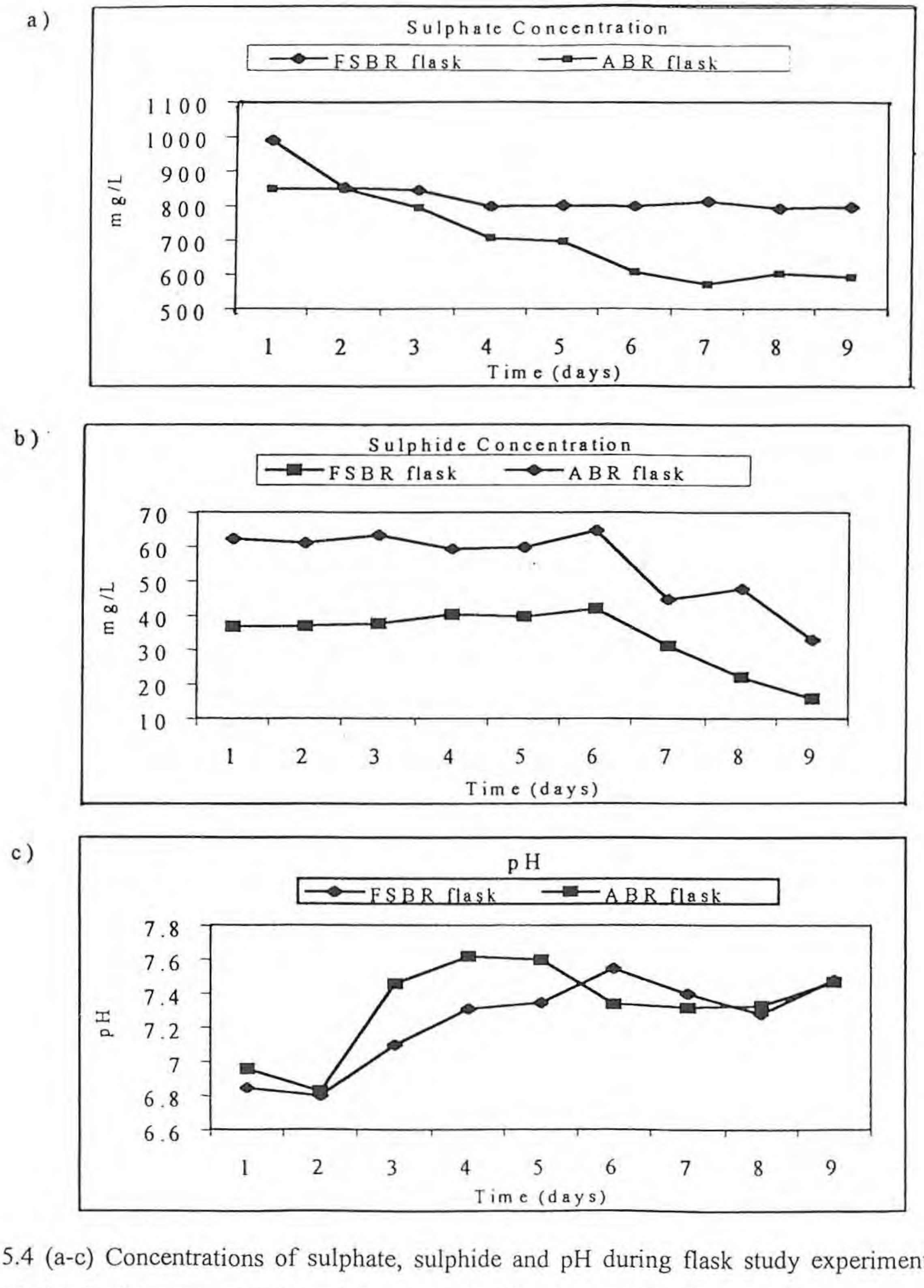

Figure 5.4 (a-c) Concentrations of sulphate, sulphide and pH during flask study experiments. Falling Sludge Bed Reactor (FSBR) and Anaerobic Baffled Reactor (ABR).

Table 5.3 reports the improvements in process effluents for various additional HRTS in the flask study.

Figure 5.5. illustrates the effects of an increased HRT with calculated cumulative acetate equivalents produced, on continuous operation with a HRT of 46 hours, a PSS conversion to acetate equivalent utilised in sulphate reduction was measured at 620mg/l. Where the HRT was increased by an additional period of 24 hours-totaling 72 hours (three days) a PSS conversion to acetate equivalent produced an additional 152.2mg/l for the overall process. The HRT was increased by a further 96 hours, resulting in 142.2mg/l of acetate equivalent production. An additional HRT 142 hours resulted in 33.2mg/l of the acetate equivalent produced. The cumulative acetate equivalent produced for the overall process was 946mg/l. This means that an extension of the HRT by an additional 144 hours, simulated in the flask studies, resulted in the production of an additional 326mg/l acetate equivalent above the 622mg/l produced during the 46 hours in the Rhodes BioSURE Process.

Where the overall objective of the process is to maximize VFA production that is in turn associated with maximum sulphate reduction, the longer the HRT the greater the PSS conversion to acetate equivalent utilised in sulphate reduction. Given the complexity of running a full-scale process at a HRT in excess of 48 hours, it appears from the results that a HRT between the current 46 hours and 72 hours (maximum) provides sufficient acetate equivalent from the hydrolysis of PSS to drive the sulphate reduction process and achieve a water quality of acceptable standards.

Table 5.3. Extension of process hydrolytic retention time in flask studies using effluent from the FSBR and ABR and from a baseline process of 46 hours.

Pilot plant	FSBR (8 hours)	ABR (38 hours)	Process (46 hours)
COD influent mg/l	3005	1272	3005
COD effluent mg/l	1272	911	911
COD consumed mg/l	1733	361	2094
SO_4 influent mg/l	1699	1265	1699
SO_4 effluent mg/l	1265	682	682
SO_4 consumed mg/l	434	583	1017
Consumption ratio	3.99	0.62	2.05
% SO_4 removed	25.5	46.0	60.0
% COD removed	57.6	28.3	69.7
Acetate produced mg/l	264.7	355.6	620.3
Acetate equivalents used in sulphate reduction %	15.2	98.5	30.0

46 + 24 hours	FSBR	ABR	Process
COD influent mg/l	1454	897	1454
COD effluent mg/l	1380	789	789
COD consumed mg/l	74	108	182
SO_4 influent mg/l	990	894	990
SO_4 effluent mg/l	846	780	780
SO_4 consumed mg/l	144	114	256
Consumption ratio	0.53	0.95	0.71
% SO_4 removed	14.5	12.8	27.3
% COD removed	5.1	12.0	17.1
Acetate produced mg/l	87.8	69.5	156.2
Acetate equivalents used in sulphate reduction %	118.7	64.3	85.8

46 + 96 hours	FSBR	ABR	Process
COD influent mg/l	1380	789	1380
COD effluent mg/l	957	745	745
COD consumed mg/l	423	44	467
SO_4 influent mg/l	846	795	846
SO_4 effluent mg/l	798	607	607
SO_4 consumed mg/l	48	186	234
Consumption ratio	8.81	0.24	1.99
% SO_4 removed	5.6	23.4	29.0
% COD removed	30.6	5.6	36.2
Acetate produced mg/l	29.3	113.5	142.7
Acetate equivalents used in sulphate reduction %	6.92	257	30.6

48 + 142 hours	FSBR	ABR	Process
COD influent mg/l	957	745	957
COD effluent mg/l	957	734	734
COD consumed mg/l	0	11	11
SO_4 influent mg/l	798	607	798
SO_4 effluent mg/l	796	603	593
SO_4 consumed mg/l	2	4	6
Consumption ratio	0	2.8	1.8
% SO_4 removed	0.3	0.7	1
% COD removed	0	1.5	1.5
Acetate produced mg/l	0	2.4	3.66
Acetate equivalents used in sulphate reduction %	0	22.2	33.2

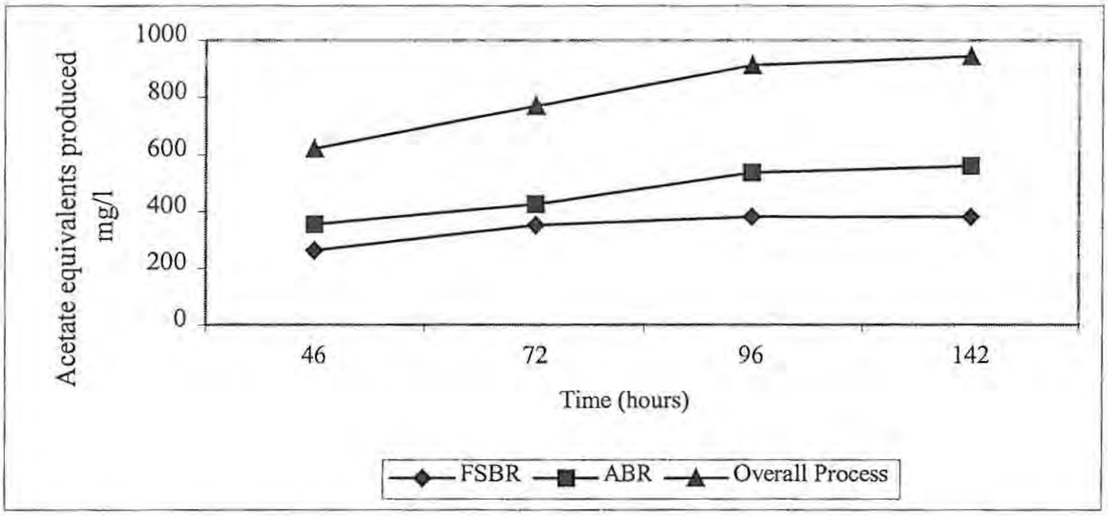

Figure 5.5. Primary sewage sludge converted to acetate equivalents utilised in sulphate reduction as a result of the extension of hydrolytic retention time.

Figure 5.6 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 during the Rhodes BioSURE process was 60%. If the HRT was extended to an additional 142 hours a cumulative sulphate removal of 89% could be achieved. The same trend applies to COD removal. The COD removal after the Rhodes BioSURE process was 69.7%. However, in an extended HRT by 142 hours, a total 91.6% COD could be removed.

The flask studies indicated an optimum retention time for the process of 96 hours, around the HRT used in the pilot study.

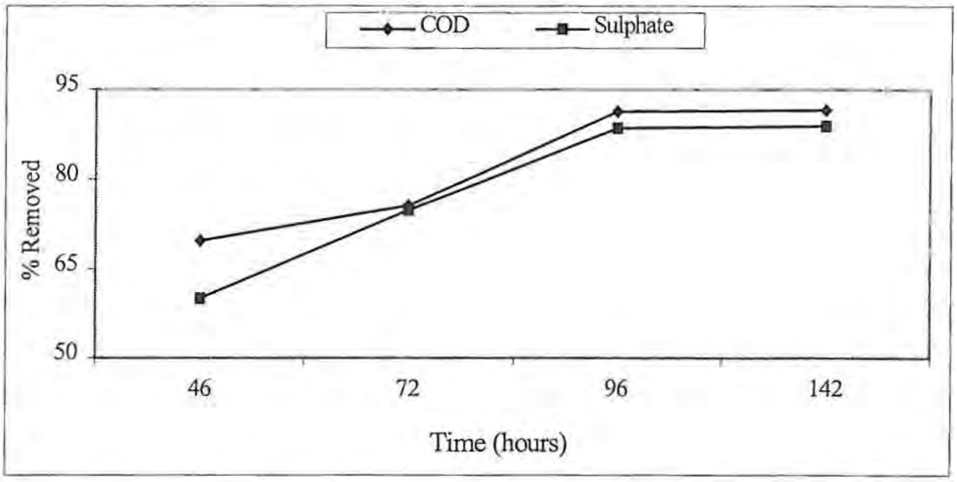

Figure 5.6. Percent Sulphate and COD removed in flask studies as a result of the retention time being extended after passing through the Rhodes BioSURE Process.

5.3. CONCLUSION

The studies reported here indicated an average recovery of around 30% PSS as acetate equivalents at a $COD:SO_4$ loading ratio of 2:1, and at a process HRT of 2 days. The soluble product of the hydrolysis step was successfully used as an electron donor biological sulphate reduction with PSS hydrolysis mainly occurring in the FSBR and sulphate reduction in the ABR.

The efficiency of PSS conversion to acetate equivalents in the process could be improved to around 52% where the HRT would be extended to 96 hours. If the HRT of the Rhodes BioSURE process was extended from 46 to 96 hours the acetate equivalent produced gave an additional 326mg/l acetate equivalent produced. This in turn resulted in sulphate and COD removal increasing from 60% and 69.7% to 89% and 91.7% respectively.

CHAPTER 6
METAL REMOVAL

6.1. INTRODUCTION

In the conceptulisation of the Rhodes BioSURE Process (Figure 1.7) the recycle of sulphide-rich treated waters would promote the precipitation of metals present in AMD as metal sulphides, and possibly also metal carbonates. Preliminary studies had indicated the feasibility of this step as a unit operation in the overall process. However, this unit process was not investigated in the pilot plant to any further extent due to time constraints. This resulted in a more intensive laboratory scale investigation into the feasibility of the metal ion precipitation/coagulation/flocculation process. These investigations are reported in this chapter after first dealing with theoretical aspects of the aqueous chemistry involved.

6.2. BASIC CHEMISTRY OF ACID MINE DRAINAGE WATERS

With regard to the chemistry of the blended water resulting from a mix of high-sulphide process recycle water and the raw untreated AMD waters, successful precipitation of the metals will depend on a number of factors including: pH; sulphide concentration and metal ion concentration of the blend.

pH established will depend principally on two factors: firstly, aqueous phase weak acid/base considerations that is, on the alkalinity and acidity of the blend; secondly, on the molar masses of metal sulphide (and metal carbonates) that precipitate. Such precipitation removes S^{2-} species and perhaps CO_3^{2-} and OH^- species thereby reducing alkalinity and pH. These effects can be explained in terms of equilibrium chemistry.

6.2.1 Aqueous phase equilibrium

The blended water contains three weak acid base systems and these in turn govern pH. The three systems are the sulphide system (H_2S, HS^-, and S^{2-} species); carbonate systems (H_2CO_3, HCO_3^- and CO_3^{2-} species) and the water system itself (H^+ and OH^- species). Aqueous phase equilibrium equation relationships for each of these systems are set out below. System mass and capacity equations are then formulated.

6.2.1.1 Sulphide system

$H_2S \leftrightarrow HS^- + H^+$

Gives us the concomitant equilibrium equation:

$$\frac{(H^+)(HS^-)}{(H_2S)} = K_{s1} \text{ --(1)}$$

($pK_1 = 7.06$ at 20^0C) and

$HS^- \leftrightarrow H^+$ and S^{2-}

Giving

$$\frac{(H^+)(S^{2-})}{(HS^-)} = K_{s2} \text{ --(2)}$$

Where $pK_2 = 13.89$ at 20^0C

With regard to pH buffering, equation 2 above can be ignored because pH of the AMD/high sulphide blend is pH of $\approx$ 6.8, which is very far away from the pKa of 13 and S^{2-} species concentration is negligible.

6.2.1.2 Carbonate system

A similar set of weak acid equilibrium equations as set out above for the sulphide system can be formulated for the carbonate system.

$$\frac{(H^+)(HCO_3^-)}{(H_2CO_3)*} = K_{c1} \text{ --(3)}$$

Where $(H_2CO_3)*$ = sum of CO_2 dissolved and $H_2CO_3^-$ and $pK_{c1} = 6.38$

$$\frac{(H^+)(CO_3^{2-})}{(HCO_3^-)} = K_{c21} \text{ --(4)}$$

Where $pK_{c2} = 10.32$

6.2.1.3 Water system

The single equilibrium equation:

$(H^+)(OH^-) = K_w$

Capacity equations for the system are formulated as the proton accepting (alkalinity) and donating (acidity) capacities with respect to selected reference species. For alkalinity, selecting the most protonated species (i.e. $H_2CO_3^*$ and H_2S) and pure water as reference species:

Alkalinity = $2[CO_3^{2-}] + [HCO_3^-] + 2[S^{2-}] + [HS^-] + [OH^-] - [H^+]$ ------------------------------(5)

Where [ ] = molarities.

In the pH region of the blended water ($pH_{\approx}$ 6.8) the alkalinity equation simplifies to:

Alkalinity = $[HCO_3^-] + [HS^-]$ --(6)

For acidity, selecting the least protonated species (CO_3^{2-} and S^{2-}) and pure water as reference species:

Acidity = $2[H_2CO_3]^* + [HCO_3^-] + 2[H_2S] + [HS^-] + [H^+] - [OH^-]$ -----------------------------(7)

And the pH region under consideration this approximates to:

Acidity = $2[H_2CO_3]^* + [HCO_3^-] + 2[H_2S] + [HS^-]$ --(8)

The system mass parameters are simply the sums of the individual species comprising each weak acid base sub-system. For the carbonate system, the total dissolved carbonate system, the total dissolved carbonate species dissolved in solution (C_T) is given by:

$C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$ ---(9)

And for the sulphide system (S_T), total dissolved sulphide species by:

$S_T = [H_2S] + [HS^-] + [S^{2-}]$---(10)

In order to characterize the aqueous phase, one parameter needs to be known for each of the three sub-systems: carbonate, sulphide and pure water. That is, if S_T, C_T and pH are known, each of the weak acid species concentration in solution can be determined using the above set of equations. This becomes important when determining the saturation state of the solution with respect to certain minerals which may precipitate.

6.2.2 Aqueous solid phase equilibrium

Various carbonate, sulphide and hydroxide species may precipitate when the recycled sulphide-rich high pH water is blended with incoming raw AMD water. For the Fe^{3+} species in the pH region of the blend, the Fe^{3+} concentration will be controlled by $Fe(OH)_3$ mineral or sulphated ferric hydroxide (jarosite) (Schwertman and Fechter, 1994; Drissi *et al.*, 1995) i.e.

$$(Fe)(OH)_3 = K_{sp} \text{ --- } (11)$$

Where $K_{sp} = 10^{-37.5}$

For the Fe^{2+} species any one or all of hydroxide, sulphide and/or carbonates may precipitate. For $Fe(OH)_2$:

$$(Fe)(OH)_2 = K_{sp} \text{ --- } (12)$$

Where $K_{sp} = 14.7$

For ferrous carbonate (siderite):

$$(Fe^{2+})(CO_3^{2-}) = K_{sp} \text{ --- } (13)$$

Where $K_{sp} = 10.7$

For Ferrous sulphide, this is commonly given in terms of the HS^- concentration, i.e. the equilibrium reaction:

$$FeS + H^+ \leftrightarrow Fe^{2+} + HS^- \text{ --- } (14)$$

This leads to the solubility product:

$$\frac{(Fe^{2+})(HS^-)}{(H^+)} = pK$$

Where $K_{sp} = 4.10^{-19}$

In general, the remaining heavy metal ions will be present at lower concentrations relative to the iron species, the metal sulphide will dictate the concentration of these species in solution.

In addition to the above precipitants that occur in the region $\approx$pH7 it was found that if the blend pH is artificially lifted to pH 8 and greater, green rust (II), a Fe^{2+}/Fe^{3+} sulphated hydroxide also precipitates. The importance of this mineral precipitate is similar to that of $Fe(OH)_3$, that is it forms flocculent precipitates that effect good removal of the colloidal metal sulphide precipitants (Bessiere *et al.*, 1999).

Laboratory-scale investigations were initiated in order to assess the metal removal using the proposed Rhodes BioSURE process. While this proved disappointing a further investigation was undertaken to investigate the feasibility of operating at a higher pH using lime at the blending point. These investigation are reported below with principle objectives being to investigate:

1. metal sulphide precipitation using sulphide-rich overflow liquor from biological sulphate reducing digesters fed on a complex carbon source, namely primary sewage sludge,
2. the coagulant properties of ferric ions with regard to destabilizing the FeS and metal sulphide colloidal suspensions at various ratios,
3. the effects of lime dosage on enhancing metal removal,
4. the effects of varying the sulphide concentration has on metal-sulphide precipitation.

6.3. RESULTS AND DISCUSSION

6.3.1 Simulaion of iron removal in the Rhodes BioSURE process

In the pilot plant studies iron removal (and other metal ions) was effected by establishing a blend of sulphide-rich process recycle water with incoming raw AMD waters, such that the ratio of sulphide to total iron in the blend was stoichiometric (on the molar scale 1:1). It should be noted that in the preliminary pilot plant investigation the Fe^{3+} component of the total iron was not measured. Recognising that ferric sulphide does not precipitate the sulphide: Fe^{2+} ratio was therefore some value in excess of unity. However, the Fe^{3+} species present should form $Fe(OH)_3$ with excellent coagulation/flocculation properties.

Table 6.1 lists the results of laboratory-scale experiments using various Fe^{3+} iron concentrations in order to assess the effects of Fe^{3+}/Fe^{2+} ratio on iron removal. The concentration of Fe^{3+} ranged from 10%–70% of the total iron available in the experiment. It should be noted that the iron remaining, i.e. $Fe_{(t)(f)}$ is composed of both dissolved and colloidal (suspended) iron species.

Table 6.1. Laboratory-scale simulation of iron removal from acid mine drainage wastewaters

Exp. No	% Fe^{3+} of $Fe_{(t)(i)}$	Ratio $Fe^{2+}_{(t)(i)}$:$S^{2-}_{(t)}$	$pH_{(i)}$	$pH_{(f)}$	$Fe_{(t)(i)}$	$Fe_{(t)(f)}$
1	10	1 to 1	6.56	6.37	200 mg/l	159 mg/l
2	20	1 to 1	6.51	6.41	214 mg/l	104 mg/l
3	20	1 to 1	6.45	6.33	207 mg/l	132 mg/l
4	30	1 to 1	6.57	6.4	208 mg/l	123 mg/l
5	37	1 to 1	6.54	6.23	223 mg/l	131 mg/l
6	39	1 to 1	6.56	6.4	213 mg/l	119 mg/l
7	40	1 to 1	6.51	6.38	199 mg/l	109 mg/l
8	43.8	1 to 1	6.54	6.39	199 mg/l	91 mg/l
9	50	1to 1	6.49	6.37	199 mg/l	86 mg/l
10	60	1 to 1	6.53	6.46	199 mg/l	77 mg/l
11	70	1 to 1	6.46	6.3	199 mg/l	93 mg/l
12	70	1 to 1	6.53	6.4	199 mg/l	82 mg/l

$_{(i)}$ = initial, $_{(f)}$ = final and $_{(t)}$ = total concentration

In Figure 6.1is shown plotted is the residual iron remaining versus Fe^{3+} added. The plot shows a decrease in non-settlable iron remaining with increase in percent Fe^{3+}. Generally the experiments indicate poor iron removal. The best result being residual Fe total content of $\approx$ 90mg/l (at pH 6.5 investigated) was with 70 percent Fe^{3+} added.

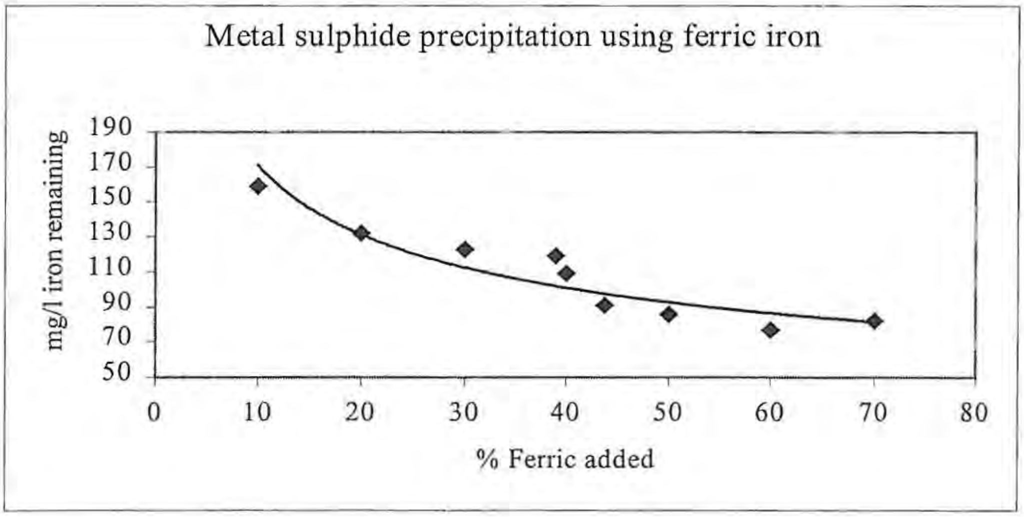

Figure 6.1. Observations on the effects of increased Fe^{3+} and showing the residual iron concentration remaining in solution for solutions with ferrous to sulphide ratios (molar scale) of unity.

The poor results obtained perhaps reflects that the Fe^{3+} did not all precipitate as $Fe(OH)_3$, and that the sulphide species did not all precipitate as metal sulphides. Most likely some of the sulphide species were oxidised to elemental sulphur. The electron acceptor in the oxidation process would be Fe^{3+} species being reduced to the Fe^{2+} species, i.e.

$HS^- \rightarrow S^o + H^+ + 2e^-$ ---(15)

$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$ ---(16)

Giving the resultant redox reduction:

$HS^- + 2Fe^{3+} \rightarrow S^o + 2Fe^{2+} + H^+$ ---(17)

This reaction is extremely fast and forms the basis for sulphide removal in the oil refinery industry.

The effects of such a redox reaction would be a Fe^{2+}: sulphide ratio that is very much greater than unity (leaving a residual Fe^{2+} in solution). Furthermore, the Fe^{3+} species would be reduced thereby impairing the good coagulating properties. The resultant effect being ineffective removal of metal sulphide colloids (Table 6.2). If this hypothesis is correct some modification to the existing process needs to be made.

Table 6.2. Laboratory-scale simulation of iron removal from acid mine drainage wastewaters with the Fe^{II}/S_{Total} ratio being altered.

Exp. No	**PH(i)**	**pH(f)**	**Fe(t)(i)**	**Fe(t)(f)**	**%Fe^{3+} of Fe(t)(i)**	**Ratio $Fe^{2+}_{(t)(i)}$: $S^{2-}_{(t)}$**
1	6.53	6.42	200mg/l	89mg/l	60	1 to 1.3
2	6.49	6.39	200mg/l	86mg/l	60	1 to 1.3
3	6.48	6.39	200mg/l	137mg/l	30	1 to1.5
4	6.47	6.37	200mg/l	141mg/l	30	1 to1.5

$_{(i)}$ = initial, $_{(f)}$ = final and $_{(t)}$ = total species concentration

6.3.2 Simulation of iron removal with addition of lime

The poor results obtained from the blending of a sulphide-rich process recycle with influent, required that further investigations be effected to obtain acceptable metal removal. In this regard it was found, at laboratory-scale, that an increase in pH ($\geq$ 7.8) using lime resulted in a thick green precipitate being formed. This occurred provided that, either or both the ferric component to total iron was in the region of 10%–20% and/or the untreated water contained more than 3mg/l dissolved oxygen. The settling characteristics of this floc were excellent. A literature review of processes involving metal removal at this elevated pH gave no indication as to the nature of the precipitants involved. A more recent review involving current fundamental chemistry research into the iron system indicates that the flocculant precipitate is green rust (II), a Fe^{3+}/Fe^{2+} sulphated hydroxide ($Fe_2^{III}\,Fe_4^{II}\,SO_4(OH)_{12}$) (Lowe *et al.*, 1988).

The formation of green rust II under these conditions is hypothesised to follow reaction 11 and perhaps either or both of reaction 19 and 20:

$$6Fe(OH)_2 + SO_4^{2-} + \tfrac{1}{2}\,0_2 + 2H^+ \leftrightarrow Fe_2^{III}\,Fe_4^{II}\,SO_4(OH)_{12} + H_20 \text{ --------------------(18)}$$

$$4Fe(OH)_2 + 2Fe^{3+} + SO_4^{2-} + 4OH^- \leftrightarrow Fe_2^{III}\,Fe_4^{II}\,SO_4(OH)_{12} \text{ --------------------------(19)}$$

$$6Fe(OH)_2 + 2Fe^{3+} + SO_4^{2-} \leftrightarrow Fe_2^{III}\,Fe_4^{II}\,SO_4(OH)_{12} + 2Fe^{2+} \text{ --------------------------(20)}$$

Over and above green rust II, precipitant, one may also expect co-precipitation of $Fe(OH)_3$ (Jarosite) and $Fe(OH)_2$ (part of which is transformed to green rust II as depicted in reaction (1)) (Schwertman and Fechter, 1994). The fractions of the various precipitants depend on the concentrations of Fe^{2+}, Fe^{3+}, O_2 and SO_4^{2} in the AMD waters. These precipitants are labile intermediates in the formation of goethite, lepidocrocite (FeOOH) and magnetite (Fe_3O_4). However the transformation of the fresh green rust precipitate to the stable end products is relatively slow from a process point of view (> 6 hours) and requires an internal electron acceptor (Genin, 1999).

Although the occurrence of the mineral green rust (II) has been shown to occur using various crystallographic techniques (Lowe *et al.*, 1988; Lowe and Genin, 1991; Schwertman and Fechter, 1994), the authors do not give solubility product data. Consequently it was not possible to formulate a quantitative model for the removal of metals. Therefore an empirical approach has been adopted via treatment of simulated AMD waters blended with a sulphide-rich process recycle stream and an elevated pH.

Considering treatment of the AMD high-sulphide blend at elevated pH, it is important to note that various metal hydroxides and carbonates are also likely to precipitate in addition to the metal sulphides and green rust (II). Again no attempt at mathematical modelling was attempted because this would be meaningless without incorporating the green rust component. However, one is still able to assess the efficacy of metal iron removal from measurements on laboratory-scale tests.

In order to investigate the efficacity with which the green rust (II) precipitant is capable of removing metal sulphide colloids, a number of experiments were effected and the results are reported below

The first set of experiments was set up to enquire into the removal of FeS colloids, and a second set that considers iron $Mn(Cl)_2$ and $Zn(Cl)_2$ removal.

6.3.3 Iron sulphide colloid removal

In table 6.3 below, are listed the results of an investigation into iron sulphide colloid removal. At 'high' pH in each experiment a colloidal FeS precipitation occurred. Flocculation occurred during a slow-mix period and excellent settling was attained. In all cases the final iron content was undetectable reflecting excellent removal of the FeS (this quantifies the visual observation, which was a relatively clear supernatant). However from a visual point of view the 20 percent initial Fe^{3+} solution gave a clearer solution.

Table 6.3. Iron sulphide colloid removal at high pH with varying ferric concentrations and ferrous to sulphide ratio in laboratory-scale experiments

Exp. No	**$pH_{(i)}$**	**$pH_{(f)}$**	**$Fe^{2+}_{(i)(t)}$**	**$Fe_{(t)(f)}$**	**$\%Fe^{3+}$ of $Fe_{(t)(i)}$**	**Ratio $Fe^{2+}_{(t)(i)} : S^{2-}_{(t)}$**
1	6.2	8.2	200mg/l	<5mg/l	10	1 to 1
2	6.19	8.17	200mg/l	<5mg/l	10	1 to 0.5
3	6.17	8.27	200mg/l	<5mg/l	20	1 to 1
4	6.21	8.13	200mg/l	<5mg/l	20	1 to 0.5

$_{(i)}$ = initial, $_{(f)}$ = final and $_{(t)}$ = total species concentration

6.3.4 Metal sulphide removal

In table 6.4 below, are listed results of an investigation into the removal of the metal irons: iron, manganese and zinc from simulated Grootvlei AMD waters. In all experiments the Fe^{3+} component of the initial total iron ($Fe_{(i)(t)}$) was 20 percent, as it was felt that this reflected most closely the real world situation. The initial concentration of ferrous, zinc and manganese were 200mg/l, 2mg/l and 10mg/l respectively. The molar ratio of ferrous to total sulphide ($Fe^{2+}_{(t)}$: $S^{2-}_{(t)}$) was varied between 1:1; 1:0.5; and 1:0.25.

Lime was added in a rapid mix phase for approximately 20 seconds, and thereafter flocculation was attained under a slow mix period (20 minutes). In all cases, excellent flocculation and coagulation occurred and fast-settling sludges resulted. The supernatant was sampled for analysis after 30 minutes of settling.

Referring to Table 6.4, in all cases iron was removed to a non-detectable level; for the zinc and manganese species significantly better removal was obtained at the higher total sulphide value. Recognising that all waters were treated to approximately the same pH and had the same initial total carbonate species concentration, one may conclude that metal sulphide precipitation was responsible for this improvement and not metal carbonate or hydroxide precipitation. Furthermore, it is important to note that the improvement in removal of zinc and manganese as sulphides was effected even though there was high mineral precipitation competition with ferrous sulphide.

Table 6.4. Metal sulphide colloid removal at high pH with ferric concentration at 20% and varying ferrous to sulphide ratio in laboratory-scale experiments

Exp. No	**$pH_{(i)}$**	**pH(f)**	**$Fe_{(i)(t)}$**	**$Fe_{(t)(f)}$**	**%Fe^{3+} of $Fe_{(t)(i)}$**	**Ratio $Fe^{2+}_{(t)}$: $S^{2-}_{(t)}$**	**$Zn_{(i)}$**	**$Mn_{(i)}$**	**$Zn_{(f)}$**	**$Mn_{(f)}$**
1	6.15	8.22	200mg/l	<5mg/l	20	1 to 1	2mg/l	10mg/l	0.03mg/l	1.46mg/l
2	6.16	8.27	200mg/l	<5mg/l	20	1 to 0.5	2mg/l	10mg/l	0.11mg/l	2.16mg/l
3	6.11	8.17	200mg/l	<5mg/l	20	1 to 0.25	2mg/l	10mg/l	0.21mg/l	2.18mg/l

$_{i)}$ = initial, $_{(f)}$ = final, $_{(t)}$ = total species concentration

6.4. CONCLUSION

A number of conclusions maybe drawn from these studies:

(1) In practice AMD waters contain iron species in both Fe^{2+} and Fe^{3+} forms.

(2) Blending untreated AMD waters with sulphide recycle water results in flocculation caused by $Fe(OH)_3$ precipitation at $\approx$ pH 6.8. The effluent however is turbid with relatively high iron content probably arising from colloidal FeS.

(3) The blending of untreated AMD waters with sulphide recycle probably causes oxidation of sulphide to elemental sulphur with Fe^{3+} acting as electron acceptor forming Fe^{2+} species. The elemental sulphur increases turbidity. More important however, reduction of the Fe^{3+} to Fe^{2+} reduces the coagulation/flocculation efficacy of the Fe^{3+} in the untreated water.

(4) Raising pH of the sulphide AMD blend to pH>8 results in excellent iron removal with a clear supernatant. This probably results from the coagulating properties of green rust (II) ($Fe_2^{III} Fe_4^{II} SO_4(OH)_{12}$) which coagulates iron sulphide colloids.

(5) Ninety percent of manganese and zinc were removed from the supernatant at the operational pH and the resultant colloids probably were flocculated by the green rust (II) precipitation.

CHAPTER 7
GENERAL CONCLUSION

Work undertaken by the Environmental Biotechnology Group at Rhodes University had focussed on the role of complex carbon substrates as electron donors for biological sulphate reduction. This had significant environmental application especially where large water volumes were involved. Based on the widespread availability of PSS in comparison to other complex carbon sources, studies were undertaken by Whittington-Jones (2000), to investigate the mechanisms involved in the degradation of complex organic compounds.

The observations of effective degradation of organic carbon occurring within these reactor systems appeared to indicate a particular role for sulphate reduction in the solubilisation process involved and these were of importance in the process by which complex carbon substrates were made available to SRB activity. The scale-up development of Whittington-Jones's prototype FSBR was undertaken and subjected to more rigorous examination at technical-scale. The studies of hydrolysis, sulphate reduction and use of sulphide product to precipitate metals in AMD waste water were incorporated into features that formed the basis of the Rhodes BioSURE pilot plant constructed at Grootvlei Gold Mine.

The performance of the Rhodes BioSURE process at Grootvlei Mine was divided into two distinct time phases of operation: (1) Process initilisation and (2) performance evaluation.

The first eight months on site (process initilisation phase) was characterised by supply problems in electricity, sludge delivery, mine water, faulty pumps and valves and more importantly two incidents of NaOH and fresh water injection. However, these technical incidents indicated the robustness and speedy recovery of the Rhodes BioSURE Process.

Organic and sulphate loading rates varied with time during this phase however, and an average removal of 27%-66% sulphate and 63%-79% COD was achieved. The rates of removal were difficult to calculate accurately due to fluctuations in the effluent as well as the instability of the system due to the perturbations as noted. High levels of sulphide were obtained and alkalinity was generated from the reduction of sulphate. Both these products had a role to play in the removal of heavy metals from the acid mine drainage effluent.

The second phase of the process piloting study was characterised by stable and steady state operation conditions. Three periods of stable operating conditions (November 1998, December 1998 and March 1999) were evaluated and the system exposed to other operating parameters that answered critical questions.

Overall performance of the Rhodes BioSURE Process showed results of 69.3%-77.9% COD removal and between 65%-70.2% sulphate removal being achieved. There was a clear difference in both sulphate and COD removal efficiencies in the FSBR and ABR. The ABR, primary role, although it consumed some COD was sulphate reduction using solubilised COD generated in the FSBR.

An accredited laboratory (ERWAT) undertook an independent audit assessment of the Rhodes BioSURE Process. A clear difference in the removal capacities of the FSBR and ABR was again identified and was assumed to be attributed to a lower consumption rate of VFA in FSBR, compared to ABR.

The results of studies reported have demonstrated the development of active biological treatment of AMD wastewaters based on the utilisation of complex organic carbon as the electron donor source in bacterial sulphate reduction. The following points have been demonstrated:

(1) The hydrolysis reaction primarily occurred in the FSBR with a 98% reduction in settlable solids achieved in this reactor unit. Although some sulphate (20%-30%) and COD were consumed in the FSBR, its primary role would be the enhanced hydrolysis of PSS as electron donor and carbon source

(2) The solubilised product of PSS hydrolysis (simple organic compounds), which were termed and calculated as acetate equivalents, would then pass to the second stage (ABR) where sulphate reduction would be optimised. Based on a theoretical $COD:SO_4$ ratio of 0.61 (calculating COD as acetate equivalents), and the close

approximation of COD consumption in the ABR to the theoretical value for COD consumption as acetate, it is assumed that sulphate reduction in the ABR was largely driven by VFA production generated by hydrolysis of the sludge in the FSBR. Where the overall objective of complex carbon utilisation as the electron donor for sulphate reduction is taken into account theses values indicate a PSS conversion to acetate equivalent utilised in sulphate reduction of around 30% with a HRT of 46 hours.

Manipulation of feed ratios as noted by Van Houten *et al.*,(1994) and Speece, (1993), were investigated and the COD:SO_4 feed rates were adjusted by increasing to 3:1 and decreasing to 1.5:1 accordingly. At a low COD:SO_4 feed ratios more carbon was consumed as a result of sulphate reduction. When the COD:SO_4 feed ratios were increased consumption was not used exclusively for sulphate reduction. The acetate equivalents used in sulphate reduction were 37% at COD:SO_4 feed ratio of 1.5:1 and showed more than a two-fold improvement in COD utilisation as acetate equivalents consumed compared to the COD:SO_4 feed ratio of 3:1 showing 18% acetate equivalents used.

The Rhodes BioSURE Process was run at steady state with a HRT of 46 hours throughout the experimental investigation. Due to the complexity and practical problems associated with extending the retention time of the pilot plant operation, flask studies were undertaken which added an additional 142 hours experimental retention time. Optimum results showed the acetate equivalent yield being increased from 30% to 36% as a result of increasing the retention time by an additional 96 hours. Sulphate and COD removal improved as a result of increased acetate equivalent production due to increased HRT to 89% and 91% respectively.

Alternatives to hydroxide precipitation for removal of heavy metals in AMD wastewaters, as routinely carried out at Grootvlei Gold Mine were investigated using sulphide-rich process recycle waters. In studies undertaken in the UCT Chemical and Civil Engineering Departments it was shown that by blending untreated AMD waters with sulphide recycle waters results in flocculation caused by $Fe(OH)_3$ precipitation at $\approx$ pH 6.8. The effluent, however, was turbid with relatively high iron content due to colloidal FeS.

Settling and precipitating metal sulphides that occur in a colloidal form was necessary to prevent them from being passed through the system. In this regard raising the pH greater than pH 8 results in excellent iron removal with a clear supernatant. This probably results from the coagulating properties of green rust (II) (Fe_2^{III} Fe_4^{II} $SO_4(OH)_{12}$) which precipitates with stoichiometric iron sulphide in the blend. Ninety percent of manganese and zinc were removed from the supernatant at the pH operation and again flocculated by the green rust (II) precipitate.

Given the particular nature and extent of the South African AMD problem – the large volume flows and long time frame anticipated over which they will be produced, the low-cost linkage to utility sewage treatment operations, and recovery of value in the form of treated water and elemental sulphur, the pilot study of the Rhodes BioSURE Process indicate real opportunities for achieving water resource sustainability in AMD management.

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