

BIOLOGICAL SULPHATE REDUCTION USING PRIMARY SEWAGE SLUDGE AS ENERGY SOURCE IN AN UPFLOW ANAEROBIC SLUDGE BED REACTOR

by

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ABSTRACT

BIOLOGICAL SULPHATE REDUCTION USING PRIMARY SEWAGE SLUDGE AS ENERGY SOURCE IN AN UPFLOW ANAEROBIC SLUDGE BED REACTOR

Since the economics of biological sulphate reduction (BSR) are driven by the economics of the organic carbon source, the BioSURE[®] process has been developed as a low-cost effective system where primary sewage sludge (PSS) is used as the energy source. This research investigates the use of PSS for BSR in an upflow anaerobic sludge bed (UASB) reactor in detail in order to exploit and further develop this novel technology. From the analyses of the extensive experimental data gathered, a number of significant outcomes have been accomplished, namely:

1. The capabilities and limitations of BSR with PSS in a UASB reactor configuration at 2 operating temperatures, 35 and 20 °C and at different organic and sulphate loading rates have been established. UASB reactor R1 (at T=35 °C) fed a PSS COD/Sulphate ratio of 1.25 (1875 mgCOD/1500 mgSO₄²⁻) achieved more than 90% sulphate reduction when operated at its lowest optimal hydraulic retention time (HRT) of 13.5h and sludge age of 18d. When fed 1800 mgSO₄²⁻/L (PSS COD/SO₄²⁻ = 1.44), R1 achieved >92% sulphate reduction at its lowest optimal HRT of 18h and bed sludge age of 21d. UASB R1 effluent sulphate and unfiltered organic COD concentrations were <250 mgSO₄²⁻/L and < 260 mgCOD/L respectively. UASB R2 (at T=20 °C) required a higher PSS COD/SO₄²⁻ of 1.75 (2625 mgCOD/1500 mgSO₄²⁻) to increase the availability of volatile fatty acids (VFA) for sulphate reduction. R2 achieved >93% sulphate reduction at its lowest optimal HRT of 20.4h and bed sludge age of 24d. R2 effluent sulphate and unfiltered organic COD concentrations were <250 mgSO₄²⁻/L and < 234 mgCOD/L respectively. The feed PSS COD/SO₄²⁻ ratio was increased to compensate for the slower hydrolysis rate at 20 °C, resulting in utilisation of only 2/3 of the PSS biodegradable organics. At ambient temperature a high % PSS biodegradable organics utilisation and low PSS COD/SO₄²⁻ ratio (1.25) can be maintained provided the sludge age is increased compared with 35 °C, thus requiring a larger bed and reactor volume. These high sulphate removals were facilitated by the introduction of a sludge recycle line from the top to the bottom of the reactor bed which initiated BSR processes as soon as the feed entered the reactor.

2. One very important design parameter of the UASB system is the upflow velocity (V_{up}) which is directly related to the HRT. HRT and V_{up} directly impact the sludge bed stability in the UASB system. By means of a settleometer the settling rate of the various solids fractions in the sludge bed was measured. From the settleability test it was found that bed expansion rather than sludge settleability was the capacity limiting process below the lowest optimal HRT. This finding helped to establish the optimum balance between the HRT (and V_{up}) and the bed expansion (which governs the sludge age). Further to the detailed laboratory investigation and the experimental data collected, the design and operating parameters of the UASB systems have been established.
3. New simple wet chemistry analytical procedures for the accurate determination and measurement of aqueous hydrogen sulphide to balance the mass of COD and sulphur around the UASB BSR system have been successfully developed. It was found that sulphide loss in the sulphide determination with the COD test must be minimised by immediately raising the pH above 10 at sample collection by adding 3 drops of 10M NaOH. Thereafter the sample can be vacuum membrane filtered for the COD test. These methods resulted in COD and S mass balances close to 100%. The 5-pH point titration method of Moosbrugger *et al.* (1992) can be used for BSR systems provided accurate sulphide concentrations are entered into the titration programme.
4. Both a steady state (SS) and a dynamic (UCTADM1-BSR) anaerobic digestion models for BSR were successfully developed. The model predicted results correlate very well to the experimental values. Both models can aid in the design of BSR systems in which PSS is used as energy source in AMD remediation. In addition, because they were developed with generic substrate formulation ($C_xH_yO_zN_a$), they can accommodate other substrate types such as VFA (or a mixture of SCFA) and therefore can be applied where these are used for BSR.
5. From the models it became evident that many organics, including PSS are carbon deficient for BSR, in that organics with $COD/C > 2.67$ can donate more electrons than C (CO_2) required for the alkalinity increase. The alkalinity shortfall is supplied by the sulphide (H_2S/HS^-) system which establishes the BSR reactor pH. From elemental (CHN) analysis of the PSS feed, the C in the PSS biodegradable organics utilised was recovered in the $H_2CO_3^*$ alkalinity yielding a $> 90\%$ C balance over the R1 and R2 reactors.

The benefits of the UASB BSR system using PSS as electron donor have already been implemented at pilot- and full-scale in the BioSURE[®] process at the Ancor (Germiston, South Africa) wastewater treatment plant based on the results of this study.

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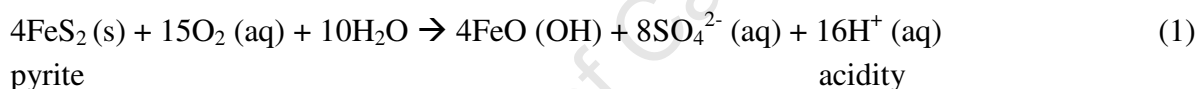
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Executive summary

1. BACKGROUND

1.1 Acid mine drainage (AMD) origin

Acid Mine Drainage (AMD) waters originate from both surface and underground mining activities either through intentional pumping to prevent mine flooding or through unintentional seepages. AMD is characterised by a low pH (2-3), high concentrations of heavy metals (e.g. iron concentration ranges from 10-6700 mg/L), sulphate (3000-30000 mgSO₄²⁻/L) and total dissolved solids (1800-45000 mg/L) (Christensen *et al.*, 1996). During mining activities, large surface areas of rock which often contain iron disulphide (FeS₂) are exposed to air and water. Iron disulphide, commonly known as Pyrite, is oxidised to soluble iron complexes and sulphuric acid, catalysed by the sulphur oxidising bacteria (Davison *et al.*, 1989).



The resulting highly acidic water dissolves a large variety of heavy metals into solution as long as the pH remains very low (<3.5). Because of these characteristics, mine waters pose a significant environmental hazard. The negative impacts of AMD are both short and long term and can be categorised as chemical (e.g. salinisation and increased acidity), physical (e.g. increased turbidity and decrease in light penetration), biological (e.g. acute and chronic toxicity resulting in death of sensitive species), ecological (e.g. food chain modification) and socioeconomic (e.g. decrease of drinking, agricultural, industrial and recreational water quality) (Gray, 1997; Jarvis and Younger, 2000). In addition, the liabilities as a result of AMD pollution can attain astronomical figures because of the large volumes (scores of ML/d) of mine water generated at the mine sites. For instance, the Canadian liability is estimated to C\$ 2-5 billion/year (Anon., 2005).

In view of the above, considerable effort has been made in the treatment of AMD with regard to the high acidity and heavy metals content. However, little attention has been focused on the mitigation of dissolved sulphate because of its lower toxicity compared with acidity and heavy metals. Nonetheless, there is a growing concern about high dissolved

sulphate concentrations and more stringent effluent sulphate standards are enforced by regulatory agencies. As a result, sulphate remediation is now required at many mine sites around the world.

1.2 AMD treatment

Several physical and chemical processes have been developed for AMD remediation, such as the high density sludge (HDS) (Pulles *et al.*, 1995), neutralisation (Maree *et al.*, 1996) or seeded ambient temperature ferrite (Morgan *et al.*, 2004) systems to remove iron and heavy metals, and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) precipitation to remove sulphate. However, the high costs of chemicals involved and large sludge volumes generated make the treatment of AMD via these processes disadvantageous. As supplement or alternative to the chemical/physical processes for AMD remediation, biological treatment would seem an attractive option for chemically pre-treated or relatively low sulphate ($<2000 \text{ mgSO}_4^{2-}/\text{L}$) mine water. Biological treatment usually forms one unit process in a treatment train encompassing additional chemical and/or physical treatment (Rose *et al.*, 2002; Maree, 2002) but can sometimes stand alone (Luptakova and Kusnierova, 2005).

Biological sulphate reduction (BSR), mediated by sulphate reducing bacteria (SRB), requires an organic substrate as electron and carbon source. Conventionally, organic substrates such as molasses, ethanol, acetate or lactate have been used as energy source (Herlithy *et al.*, 1987). Although all these pure substrates have been effective for BSR, they are expensive thereby making AMD treatment costly. As a consequence, BSR via these organics have in general been restricted to lab-and/or pilot scale levels.

Since the economics of BSR are steered by the economics of the organic source, the BioSURE[®] process has been developed as a low-cost effective system where BSR is achieved using primary sewage sludge (PSS) as energy source for the central BSR unit process (Rose *et al.*, 2002). PSS is available as a by-product at municipal wastewater treatment systems, and therefore co-treating this waste with AMD proposes an elegant solution to BSR. In its initial conception for BSR, the Rhodes BioSURE[®] process made use of a Recycling Sludge Bed Reactor (RSBR), which is a down-flow based configuration. However, the RSBR configuration has a number of disadvantages: (1) it requires a long hydraulic retention time of approximately 48h and a second post treatment step (Rose *et al.*,

2002) which demand relatively large reactor volumes with significant capital cost; (2) dissolved sulphate can “short-circuit” to the effluent requiring downstream BSR as proposed in the BioSURE[®] process and (3) BSR systems with PSS tend to produce higher non-settleable solids concentrations than equivalent methanogenic systems (Ristow *et al.*, 2005), which in the RSB configuration would cause high suspended solid concentrations in the effluent. As alternative, the use of an upflow configuration, based on the upflow anaerobic sludge bed (UASB) reactor has been proposed. This scheme should improve and maximise the contact between the PSS and the sulphate where all the sulphate would in effect flow through the entire sludge bed. Furthermore, the UASB will most probably have improved solids retention, allowing decoupling of the solid and liquid retention times, leading to higher sulphate loading rates and shorter hydraulic retention times, which would be a significant benefit.

1.3 Bioprocess mathematical modelling

To assist in the design, operation, control and research into the use of PSS in BSR, a mathematical kinetic model would constitute an invaluable process evaluation tool. Mathematical models provide quantitative descriptions of the treatment system of interest and are able to predict the system response and performance. From the model predictions, design and operational criteria can be identified to optimise the system performance. Evaluating these predictions make it possible to test hypotheses on the behaviour of the system (such as biological processes and their response to system constraints) in a consistent, reliable and integrated manner.

One of the objectives of this research was to integrate BSR into the integrated chemical, physical and biological processes methanogenic anaerobic digestion (AD) model (UCTADM1) and use it to model the UASB BSR system performance and compare with experimental and steady state model results. This required an evaluation of existing kinetic models for anaerobic digestion in the literature where the most suitable ones were selected for extension and integration as required. Accordingly, four existing kinetic models were evaluated, viz:

1. The kinetic model for BSR with PSS as substrate developed by Ristow *et al.* (2001). In this model, the focus was on the biological processes and they excluded the chemical and

physical processes which are of importance in BSR. They recognised that under steady state the hydrolysis of PSS was the rate-limiting step. In addition, Ristow *et al.* (2005) undertook an extensive investigation to describe and model the PSS hydrolysis step, under methanogenic, sulphidogenic and acidogenic conditions. They concluded that BSR does not affect the rate of PSS hydrolysis implying that the same methanogenic rate formulations and rate constants can be applied under BSR conditions.

2. The International Water Association (IWA) Anaerobic Digestion Model No. 1 (ADM1) developed by (Batstone *et al.*, 2002). In this model the substrate, in this case PSS, is characterised into carbohydrates, lipids and proteins which are thereafter hydrolysed to their intermediate products. However, for PSS, measurements of carbohydrates, proteins and lipids and their COD equivalents are conducted virtually exclusively in research projects making application of ADM1 in the field for operation difficult.
3. The model developed by Van Rensburg *et al.* (2001) and extended and modified by Sötemann *et al.* (2005a) for methanogenic anaerobic digestion of sewage sludges. In this model the feed sludge is characterised with the usual COD, TKN and VSS measurements and the carbon, hydrogen, oxygen and nitrogen ($C_xH_yO_zN_a$) composition which can be derived from the tested measurements and CHN elemental analysis. Sötemann *et al.* (2005a) integrated the biological kinetic processes for methanogenic anaerobic digestion (AD) into a two phase (aqueous/gas) subset of the three phase mixed weak acid/base chemistry kinetic model of Musvoto *et al.* (1997). The model was calibrated and validated with data from the laboratory mesophilic anaerobic digesters of O'Rourke (1968), Izzet *et al.* (1992) and Ristow *et al.* (2005). The predicted PSS composition based on influent measurements and elemental analysis was within 5% of the average measured composition, providing persuasive validation of the model.
4. Van Wageningen, Masters student in the Water Research Group at UCT (2007) selected the model of Sötemann *et al.* (2005) (UCTADM1) as the basis for the development of the kinetic model for BSR with PSS as substrate. This required the development of the kinetics and stoichiometry for the biological, chemical and physical processes in BSR in two phases (aqueous/gas), and integration of these with UCTADM1, taking due cognisance of any interactions introduced by the integration. The stoichiometry and kinetics for the bioprocesses (growth and death) mediated by the propionate degrading,

acetotrophic and hydrogenotrophic sulphate reducing bacteria were formulated. These bioprocesses produce and consume *inter alia* sulphate and sulphide acid/base species which were not present in the original UCTADM1 model. Accordingly, following the approach in the UCTADM1 model, chemical processes for these were included. Further, in the BSR model the end product sulphide has a gaseous equilibrium not included in the UCTADM1 model, to give a complete kinetic model for competitive methanogenic and sulphidogenic anaerobic digestion with sewage sludge as substrate. The model was validated with the methanogenic and sulphidogenic data (flow through systems) of Ristow *et al.* (2005) and yielded a two phase biological, chemical and physical processes model for the AD of PSS with competitive methanogenesis and sulphidogenesis.

The kinetic model for BSR (UCTADM1-BSR) using PSS was updated and applied to model the UASB BSR system performance. It was extended by including a sulphide (namely undissociated H₂S) inhibition term. Moreover, a temperature function was incorporated to simulate the effect of temperature on BSR. Thereafter, the model was verified, calibrated and validated, after which, it was used to model the UASB BSR system performance.

2. RESEARCH SCOPE AND OBJECTIVES

Within the first year of commencing operation of the laboratory UASB reactors, it attracted the attention of mining industry such that the BioSURE[®] system at Grootvlei Mines Ltd, Johannesburg, South Africa was changed from a downflow recycling sludge falling bed reactor (RSBR) to an upflow anaerobic sludge bed (UASB) reactor. This provided greater impetus and significance to this research and made the need more urgent for the outcomes of the detailed investigation into the design and operating parameters, and understanding and modelling the behaviour of the UASB system.

The following **objectives** were identified for this research:

1. To understand the capabilities and limitations of BSR with PSS in the UASB system by operating 2 lab-scale UASB reactors – one (R1) at 35 °C and the other (R2) at ambient temperature (20 °C), each at different organic and sulphate loading rates. This will allow establishing the minimum bed hydraulic retention time (HRT) and bed sludge age for maximum utilisation of PSS and sulphate reduction. UASB reactor R1 will be operated

at two influent sulphate concentrations (namely 1500 and 1800 mgSO₄²⁻/L) while reactor R2 at an influent sulphate concentration of 1500 mgSO₄²⁻/L since the objective is to study the system performance at ambient temperature (20 °C).

2. To investigate the effects of sludge recycle from the top to the bottom of the sludge bed on system performance. It is envisaged that this recycle line would initiate rapid BSR from the bottom of the bed because the incoming feed to the reactor moves the sludge bed upward with the active biomass so that very little sulphate reduction occurs at the bottom. This in turn delays the sewage hydrolysis process due to high VFA concentrations. By introducing the sludge recycle line, BSR biomass is returned to the bottom of the reactor bed and keeping the biological processes active throughout the bed.
3. To measure the settling rate of the various solids fractions of the sludge to determine if bed expansion or sludge settleability is the capacity limiting process. At high upflow velocity, the sludge bed will expand and become unstable even though the sludge settleability might not be affected. The optimum balance of these two parameters needs to be established.
4. To develop simple wet chemistry analytical procedures (COD, VFA, Alkalinity, H₂S and SO₄²⁻) to monitor BSR systems for implementation in the field and achieve 100% COD, S and N mass balances. Sulphidogenic systems are complex since they contain mixed weak acid/base systems which are affected by the loss of H₂S and CO₂ during sampling procedures. Aqueous hydrogen sulphide measurement is problematic especially when it involves filtering the samples as H₂S escapes the system in the filtration process and sampling procedures. This study attempts to fix the sulphur balance on the system, which is an exercise scarcely reported in the literature. The development of simple wet chemistry analytical procedures for the accurate determination and measurement of aqueous H₂S to balance COD and sulphur around the UASB BSR system are required for operation and control of full-scale BSR systems, especially in developing countries where expensive equipment and highly skilled operators are scarce.

5. To develop a general steady state (SS) anaerobic digestion model for BSR and validate it using PSS as carbon source and electron donor. This model comprises three sequential parts: a COD based hydrolysis kinetics part, a CHONS, COD and charge mass balance based stoichiometry part and a mixed weak acid/base chemistry part. This SS model may give insight into the inter-relationship between the biological processes and weak acid/base chemistry systems and be used to predict steady state system performance, product generation and pH. In addition, it will also provide a basis for crosschecking the results from the UCTADM1-BSR model to be updated.
6. To revise, extend and fine-tune the integrated two phase (aqueous-gas) biological, chemical and physical processes kinetic model (UCTADM1-BSR) for competitive methanogenic and sulphidogenic anaerobic digestion with PSS as substrate. Thereafter the kinetic model will be validated by simulating the performance of the 2 lab-scale UASB BSR reactors and comparing the predictions with the SS BSR results and the experimental data. This model together with the steady state one (mentioned above) will provide an integrated mass balance based framework for the system and can give guidance to design, operation and research.

3. RESEARCH EXPERIMENTAL SET-UP

To meet the research objectives, two lab-scale upflow anaerobic sludge bed (UASB) reactors, named as R1 ($T=35\text{ }^{\circ}\text{C}$) and R2 ($T=20\text{ }^{\circ}\text{C}$), were operated with PSS as carbon source and fed sulphate based on different PSS COD/SO₄²⁻ ratios. Each reactor had a total volume of 9.1 L with an internal diameter of 93mm and height 1330mm. They were sealed and mixed by a vertical rod fixed to the centre and set to rotate for 5 revolutions every 5 minutes. Effluent draw-off was subsurface via an inverted “U”-tube which could be adjusted to control the reactor liquid volume. Sampling ports were designed at 10cm height intervals from bottom to top of the reactor. Reactor R1 was heated to approximately 35 °C with heating wires wrapped around the column, with a thermocouple inserted into one of the sample ports of the reactor and connected to a temperature controller, while R2 was maintained at the constant laboratory temperature of 20 °C.

Both UASB reactors were inoculated with sulphate reducing bacteria, and operated with a synthetic sulphate rich feed similar to low sulphate AMD, except for the deliberate omission

of heavy metals. PSS was added to the feed as substrate (carbon and electron) source for BSR. The reactors were operated with a sludge recycle line from the top to the bottom of the reactor sludge bed to initiate BSR as soon as the feed enters the reactor. In order to close the sulphur loop and do a sulphur mass balance around the system, hydrogen sulphide gas was collected from the top (gaseous phase) of the reactor and bubbled in ferric solution. Analyses of the ferric solution were conducted to determine the concentration of ferrous iron (Fe^{2+}) formed from the reduction of ferric iron (Fe^{3+}) using hydrogen sulphide as reductant as per the following equation:



During the reactors operation, the hydraulic retention time (HRT) was reduced stepwise to obtain the minimum value of stable operation, by increasing the feed flowrate. After each stepwise change, the system was allowed to stabilise, indicated by measured effluent alkalinity, pH, VFA and sulphate remaining constant for a period of about 4-7 days. The minimum stable HRT was accepted as the shortest HRT where the effluent VFA ($<100 \text{ mgHAc/L}$) and sulphate ($<250 \text{ mgSO}_4^{2-}/\text{L}$) were low, and the measured alkalinity and pH were almost constant. When the minimum stable HRT was reached, bed profiles through the sludge bed were done to gain insight into the process behaviour within the reactor bed. Bed profile tests were carried out by withdrawing a known volume of sludge (usually 100 ml) from the reactor bed via the sample ports at pre-determined bed heights (namely 10, 30, 50, 70 and 90 cm). The samples were $0.45 \mu\text{m}$ filtered and the filtrates analysed for sulphate, VFA and alkalinity concentrations. The solids concentrations were used to estimate the mass of solids in the bed and its sludge age. Also, a settleometer (a series of vertical columns with different diameters) was built to test the settleability of the UASB sludge bed particulate constituents.

4. OPERATION AND PERFORMANCE OF UASB REACTORS R1 (35 °C) AND R2 (20 °C)

At the beginning of this investigation, the main focus was on the potential of PSS to serve as an energy source in BSR using the UASB reactor. For the first 280 days, only one UASB reactor (R1 at 35 °C) was operated with an influent sulphate concentration of $1500 \text{ mgSO}_4^{2-}/\text{L}$ and COD 1875 mgCOD/L (COD/ SO_4^{2-} ratio = 1.25). It was concluded that a feed

sulphate concentration of $1500 \text{ mgSO}_4^{2-}/\text{L}$ was successfully reduced under sulphidogenic conditions with an average effluent sulphate concentration of $149 \text{ mgSO}_4^{2-}/\text{L}$ at a HRT of 13.5h. The UASB system effectively uncoupled of the solid and liquid retention times which is a significant advantage of the UASB reactor over the RSB. Excellent solid-liquid separation in the system was obtained with unfiltered organic COD $<260 \text{ mgCOD}/\text{L}$ at a HRT of 13.5h, with very low solids content in the effluent. The PSS and likewise the reactor sludge, which had a good settleability, appeared to effectively enmesh and entrap fine solids arising from biodegradable particulate organic breakdown.

In operating the reactor at a HRT lower than 13.5h (by increasing the influent feed rate) while maintaining the sludge bed height constant, effluent quality from the UASB reactor deteriorated. This deterioration was ascribed to the reduced sludge bed biomass caused by sludge bed expansion and sludge loss with the effluent as a result of the increased upflow velocity. Restoring the HRT to 13.5h re-established the steady state conditions where effluent quality was met. It was therefore deduced that the system optimal lowest HRT is 13.5h. The bed sludge age at 13.5h HRT was 18d.

Attention was given to the effect of sludge mass recycle from the top to the bottom of the reactor bed, by conducting profile tests along the bed. These results indicated that BSR processes commenced immediately at the bottom of the bed and continued throughout the bed height (Figure 1a). This was not the case without the recycle (Figure 1b). The sludge recycle distributed the SRB biomass throughout the bed, and despite increasing the upflow velocity provides considerable advantages in BSR using the UASB configuration. Based on the preliminary results of this investigation, the pilot plant of the Grootvlei Mines Ltd (Springs, South Africa) was scaled up from 2 ML/d to 10 ML/d.

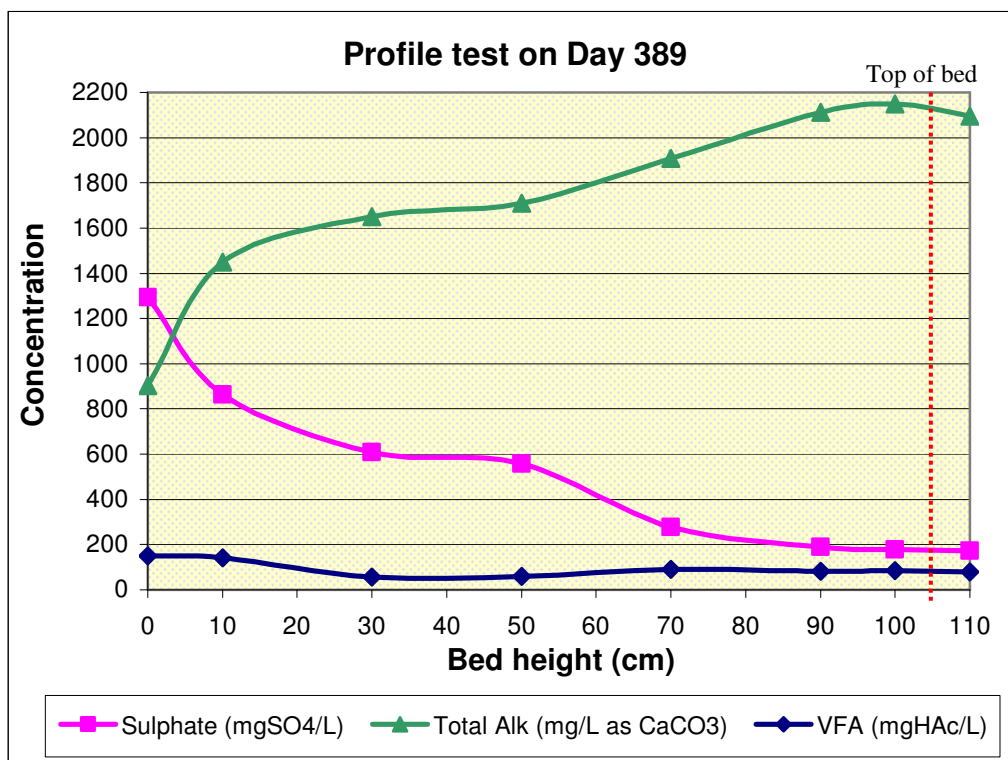


Figure 1a: Reactor alkalinity, VFA and sulphate concentration profiles up the sludge bed height (104 cm) for a BRT of 16.4h with a 0.5:1 sludge recycle from the top to bottom of the bed (UASB R1 fed 1800 mgSO₄²⁻/L).

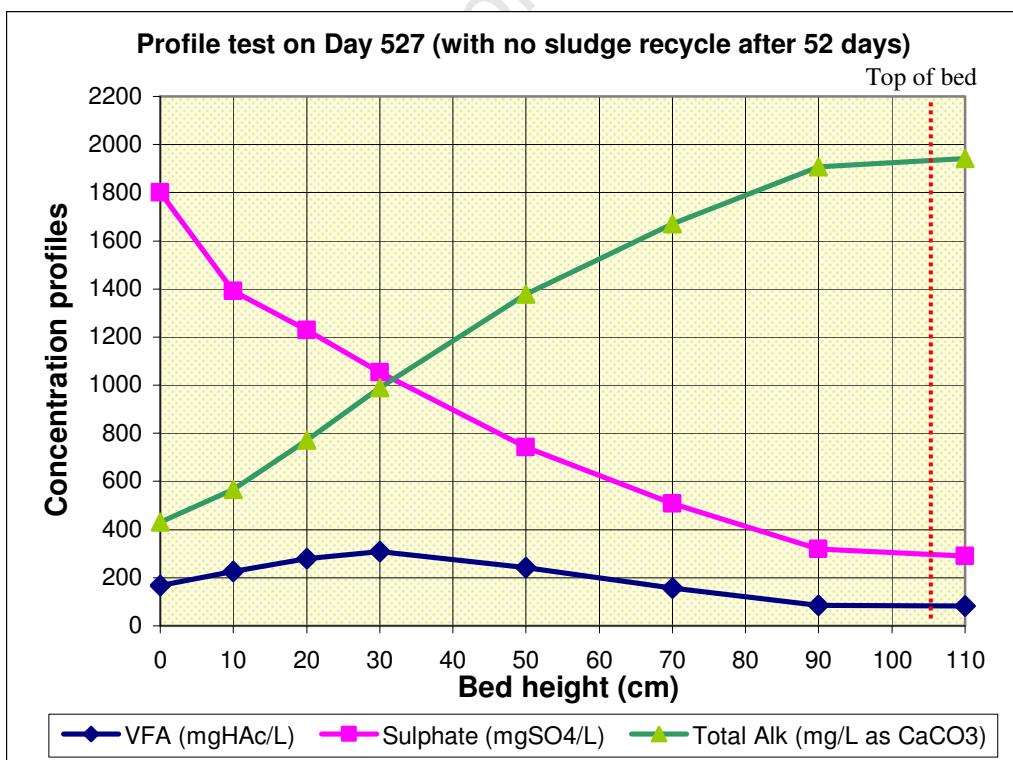


Figure 1b: Reactor alkalinity, VFA and sulphate concentration profiles up the sludge bed height (104 cm) for a BRT of 16.4h, 52 days after stopping the sludge recycle (UASB R1 fed 1800 mgSO₄²⁻/L).

During this part of the investigation, the COD, S and N mass balances conducted over the UASB R1 system averaged 88.8%, 68.7% and 97.1% respectively. The relatively low COD and S mass balances were ascribed to the loss of H₂S during sample handling (filtration, mixing and dilution) in analysis - a significant sulphide concentration was unaccounted for when compared with the sulphate reduced. This prompted an investigation to develop simple wet chemistry analytical procedures to fix the COD and S mass balances close to 100% (see Section 5 below). From Day 410, these developed methods yield > 96% COD and S mass balances and were used for the remainder of the investigation. After modifying the analytical procedures to minimise H₂S gas loss, very good COD, N and S mass balances were obtained on all the systems operated (Table 1).

Table 1: COD, Sulphur and Nitrogen mass balances of UASB reactors R1 and R2 under steady state conditions at their respective lowest optimal hydraulic retention times.

UASB reactor	Mass Balances (%)		
	COD	Sulphur	Nitrogen
R1 (1500 mgSO ₄ ²⁻ /L) at 35 °C	88.7 ± 0.8*	68.7 ± 3.4*	97.1
R1 (1800 mgSO ₄ ²⁻ /L) at 35 °C	96.5 ± 0.8	95.8 ± 2.9	102.5 ± 8.1
R2 (1500 mgSO ₄ ²⁻ /L) at 20 °C	98.8 ± 2.9	95.9 ± 0.1	104.5 ± 4.9

* Prior to the development of the new analytical methods for accurate H₂S measurement.

With the successful operation of the UASB reactor R1 at 35 °C (when fed 1500 mgSO₄²⁻/L for a period of 280 days), the performance of BSR using PSS was investigated in a second identical UASB reactor (R2) operated at ambient temperature, namely 20 °C. Reactor R2 (T=20 °C) was run with a feed sulphate and PSS concentrations of 1500 mgSO₄²⁻/L and 1995 mgCOD/L respectively representing a feed PSS COD to sulphate ratio of 1.33 mgCOD/mgSO₄²⁻ but this ratio later was increased to 1.75 to reduce effluent sulphate concentration below 250 mgSO₄²⁻/L. The results of the operation of UASB reactor R2 are of particular importance as they demonstrate the viability of treating sulphate-rich water at ambient temperature. In fact, the UASB BioSURE[®] process at the Ancor mine water treatment plant in Johannesburg is operating at ambient temperature. Besides the 2 critical parameters (sludge age, R_s and hydraulic retention time, HRT), the other important parameter to consider in the operation of BSR system using PSS is the PSS COD/SO₄²⁻ ratio where at low temperature the PSS hydrolysis process rate is slowed down. By decreasing

the temperature from 35 to 20 °C, less than 70% of the PSS is hydrolysed thereby generating inadequate VFA for BSR. Increasing the PSS COD/SO₄²⁻ from 1.25 (used in R1) to 1.75 (used in R2) increased the concentration of PSS hydrolysed to meet the VFA demand for sulphate reduction. Increasing the sludge age of the system by reducing the volumetric COD and sulphate load would increase the % biodegradable PSS hydrolysed and reduced the PSS COD/SO₄²⁻ to 1.25.

The UASB R1 (at 35 °C) was operated at a higher influent sulphate concentration (1800 mgSO₄²⁻/L) to study possible inhibition by higher undissociated hydrogen sulphide concentration. A high sulphate reduction (~ 92%) was achieved even at the relative low HRT of 18.5h. These R1 results were useful for calibrating the value of the acetotrophic SRB inhibition constant (K_I) used in the kinetic simulation model (UCTADM1-BSR).

Initially the influent to the UASB reactors was dosed with alkalinity to assist in establishing a reactor pH of 7-8. For the last 2 to 3 sludge ages of both R1 (35 °C) and R2 (20 °C), alkalinity dosing was stopped. The systems maintained a pH >7.0 indicating that the bioprocesses are pH self-regulatory, which is important for the economics of the system.

For R1 (35 °C), batch tests were conducted on top, bottom and mixed bed sludges to qualitatively and quantitatively assess the process rates taking place in the UASB reactor. The batch results confirmed the need to recycle sludge from the top to the bottom of the bed because without recycle sulphidogenesis (and not acidogenesis) is the rate limiting step at the bottom part of the sludge bed. The sulphate reduction rates with the top, bottom and mixed sludges were 1184, 595 and 929 mgSO₄²⁻/L/d respectively. These batch sulphate reduction rates were used to calculate the process kinetic rates. The value of the saturation maximum hydrolysis rate constant (K_M) was found to be 6.68, 5.01 and 3.67 gCODsubstrate/(gCODbiomass.d) from batch tests conducted on the reactor top, mixed and bottom sludge respectively. The first 2 rates are close enough to the value of 5.27 gCODsubstrate/(gCODbiomass.d) reported by Sötemann *et al.* (2005a) for methanogenic systems. Batch tests results using acetic acid as substrate gave sulphate reduction rates of 649.4-851.2 mgSO₄²⁻/L/d and yielded values of 0.502-0.658 (mgCOD/mgCODbiomass)/d for the maximum specific acetic acid utilisation rate (μ_{max}), closely similar to the μ_{max} value of 0.612 (mgCOD/mgCODbiomass)/d from Kalyuzhnyi *et al.* (1998).

From the experimental data of this detailed investigation, a summary of the design and operating parameters established for the 3 UASB BSR systems is listed in Table 2.

Table 2: Design and operating parameters for BSR UASB system using PSS as carbon and energy source.

Design and operating parameters	Unit	Average values		
		R1 (35 °C)	R1 (35 °C)	R2 (20 °C)
Feed PSS COD based on f_{PSSup} of 0.36	mgCOD/L	1880	2584	2596
Feed sulphate	mgSO ₄ ²⁻ /L	1500	1800	1500
Influent pH	-	7.20 ^a	5.99	5.94
Influent flow rate, Q_i	L/d	13.6	10.4	9.2
Organic loading rate, OLR	g/m ³ /d	3886	3788	3224
Sulphate loading rate, SLR	g/m ³ /d	3100	2637	1863
Reactor liquid volume	L	7.8	7.8	7.8
Reactor bed volume	L	6.7	7.1	7.4
Sludge recycle ratio (w.r.t. Q_i)	-	0.5	0.5	0.5
Upflow velocity, V_{up}	m/h	0.127	0.096	0.085
Hydraulic retention time, HRT	h	13.8	18.0	20.4
Sludge aspect ratio (bed height/diameter)	-	10.5	11.2	11.6
Bed hydraulic retention time, BRT	h	11.8	16.4	19.3
Sludge retention time (Sludge age), R_s	d	18	21	24
Waste flow rate, Q_w	L/d	0.37	0.34	0.31
Expected sulphate removal rate	g/m ³ /d	2792	2423	1737
Expected sulphate reduction	%	90.1	91.9	93.3

a: Alkalinity dosage to feed but concluded not necessary since the system is pH self-regulatory

5. DEVELOPMENT OF SIMPLE WET CHEMISTRY ANALYTICAL PROCEDURES

Initially the measurements of the total aqueous hydrogen sulphide, S_T ($= \text{H}_2\text{S}$ and HS^-) were inaccurate. For calibration of models based on mass balances, and operation of full-scale systems, it was imperative to develop simple wet chemistry analytical procedures for the accurate measurement of parameters like sulphide, COD, alkalinities and VFA in order to monitor BSR systems and achieve 100% COD and S mass balances.

To address the issue of poor S balances, three different analytical methods were investigated to minimise the loss of undissociated H_2S . Method 1 which is the recommended Standard Methods (1985) COD test method resulted in poor S mass balance (64-75%) due to loss of H_2S during sample handling, mainly vacuum filtration. Method 2, in which 3 drops of 10 M NaOH are added immediately upon effluent sample collection to raise the pH to > 10 and converting undissociated H_2S species into the HS^- species resulted in minimal sulphide is lost during sample vacuum filtration, dilution, mixing and standing. Method 3, in which a polyelectrolyte is added to the effluent sample to coagulate the organic particles and uses centrifugation for solid-liquid separation instead of vacuum filtration. Results from Method 3 showed an improvement in the S mass balance with respect to Method 1 - 91% against 75% without a long sample standing period and 88% against 65% with a long sample standing period). However, S mass balance with Method 3 was still relatively low when compared with Method 2 (86-91% against 92-95%). Therefore, Method 2 was the best simple wet chemistry analytical procedure to accurately measure S_T ($= \text{H}_2\text{S} + \text{HS}^-$) and achieve close to 100% COD and S mass balances. Accurate S_T measurement is essential to correctly speciate the total alkalinity into H_2CO_3^* alk. and Alk H_2S .

With the measurement problem of S_T resolved, the effects of S_T loss were investigated on the total and subsystem alkalinities as determined with the 5-pH point titration method of Moosbrugger *et al.* (1992). This method for measuring the H_2CO_3^* alk. and volatile fatty acid (VFA) concentrations requires the sulphide concentration to be known when above negligible concentration. By testing standard solutions with known carbonate, acetate and sulphide species and UASB effluent samples, it was found that (1) the total alkalinity concentration is not affected by H_2S (and CO_2) loss as the subsystem alkalinities re-speciate due to a change in pH and (2) to obtain accurate H_2CO_3^* alk, and volatile fatty acid (VFA) concentrations, accurate sulphide concentrations are required, i.e. those obtained from Method 2.

Because one of the objectives of this research was to develop simple (but accurate) wet chemistry methods for operation and control of full-scale BSR systems, the prospect of developing a 7-pH point titration method was explored with standard solutions but found not feasible. To characterise a system with e.g. the phosphate, ammonium, sulphide, acetate, carbonate and water weak acid/base subsystems, 6 measurements are required, one for each subsystem. For the first four, these are the total species concentrations (P_T , N_T , S_T and A_T),

for the carbonate subsystem the H_2CO_3^* alk. and for the water subsystem the pH. The H_2CO_3^* alk. allows loss of CO_2 without affecting the accuracy of the results. Because significant S_T (H_2S) loss was observed during the titration S_T measurement falls away requiring a substitute to be found. The Alk H_2S cannot be substituted because the titration approach allows only one subsystem to change – with two the change in each is not known. It is possible to change the 5-pH point titration programme to assume H_2S loss but no CO_2 and obtain C_T from an inorganic carbon analyser. Because this defeated the objective of developing simple and inexpensive analytical procedures to monitor BSR systems, this approach was abandoned – the method of determining S_T separately with the COD test (Method 2) is better. With S_T accurately known before the 5-pt titration, H_2S loss during the titration does not affect the accuracy of the H_2CO_3^* alk. and VFA concentrations obtained.

6. MEASUREMENT OF SLUDGE SETTLEABILITY

The success of the UASB reactor depends largely on the settling properties and stability of the sludge bed which consists of active biomass. A stable sludge bed provides a long sludge retention time and a high sludge mass, and these are key features to ensure process stability and high substrate loading rates, thereby optimising the UASB system. From the operation of the R1 (35 °C) and R2 (20 °C) UASB reactors, it was found that decreasing the HRT below the optimal (13.5h for R1 at 1500 $\text{mgSO}_4^{2-}/\text{L}$, 18h for R1 at 1800 $\text{mgSO}_4^{2-}/\text{L}$ and 20h for R2 at 1500 $\text{mgSO}_4^{2-}/\text{L}$) resulted in unstable bed conditions and progressive system failure, indicated by poor effluent quality - high effluent VFA, SO_4^{2-} and particulate COD.

To examine bed dynamics, a sludge settleability device (called a settleometer) was designed following the principle outlined by Moosbrugger (1994). The principle of the settleometer is relatively simple: A pre-determined volume (say 1L) of sludge is taken from a UASB reactor and placed in the first column (smallest one). A constant flow rate (Q) was applied in an upflow mode similar to the UASB reactor (Figure 2). Since the upflow velocity (V_{up}) decreased incrementally in the subsequent columns (from smallest to largest), the sludge sample is fractionated according to particle size and density. The percentage sludge mass retained in each tube was determined by dividing the mass of sludge retained in each column by the mass of sludge of the original sample. The sludge concentration in each column was further determined by dividing the mass of sludge retained in each tube by the initial sludge sample volume. Both the percentage sludge masses and the sludge

concentrations were plotted against their respective upflow velocities, resulting in a graph describing the settling profile of the sludge at different hydraulic upflow velocities.



Figure 2: Picture of the settleometer showing R1 sludge fraction retained in each column at steady state ($Q = 10.17 \text{ L/h}$ and $V_{up} = 1.16 \text{ m/h}$ in the largest column).

From the mass of total settleable solids measured in each column, it is concluded that both R1 and R2 sludges settled well as 99% of the total sludge settled faster than 1.16 m/h . This upflow velocity was 9.1 and 13.7 times higher than the maximum operating upflow velocity (V_{up}) of R1 (0.127 m/h) and R2 (0.085 m/h). Tests were also done to observe the effect of upflow velocity on sludge bed expansion. Based on V_{up} at minimum HRT, it was found that R1 sludge had a bed expansion ratio of 1.8 at V_{up} of 0.127 m/h while R2 sludge had a bed expansion ratio of 2.0 at V_{up} 0.085 m/h . Since the bed was maintained at constant volume, the mass of sludge removed from the system increased with increasing upflow velocity, causing reduction in the sludge bed mass, the sludge age and concomitantly a reduction in the biomass available to mediate the BSR reactions. It was concluded that bed expansion rather than the sludge settleability causes system failure at upflow velocities higher than the optimum. The R1 sludge (35°C) had a better settleability and expanded less compared with R2 sludge (20°C) at the same upflow velocity. Hence the shorter minimum HRT for R1 compared with R2 at the same influent sulphate concentration.

7. STEADY STATE AND KINETIC MODELS FOR BIOLOGICAL SULPHATE REDUCTION

The core unit process in the BioSURE[®] system is biological sulphate reduction (BSR) with primary sewage sludge (PSS). To assist in and optimise the design, operation of and research into this unit process, mathematical models (both steady state and kinetic) would represent very useful process evaluation tools. Mathematical models provide quantitative descriptions of the treatment system of interest that allow predictions of the system response and performance to be made. Two models for BSR have been successfully developed and validated – the steady state (SS) and the UCTADM1-BSR kinetic simulation models.

The SS model for BSR using PSS as carbon source and electron donor comprises three sequential parts: (i) a COD based kinetic part for PSS hydrolysis from which the % PSS COD, sulphate removal and (acidogen) biomass concentration are calculated for a given sludge retention time (sludge age). This is the same as that developed by Sötemann *et al.* (2005b) for methanogenic AD systems; (ii) a C,H,O,N,S, COD and charge mass balance based stoichiometry part from which the alkalinity generated (from both the HCO_3^- and HS^-) are determined from the % COD and sulphate removal and (iii) a mixed weak acid/base chemistry part from which the digester pH is calculated from the HCO_3^- and $\text{H}_2\text{S}/\text{HS}^-$ species formed.

In the kinetic part it is accepted that the hydrolysis/acidogenesis process is the overall BSR rate limiting step and proceeds at the same rate as under methanogenic conditions (Ristow *et al.* 2005). Accordingly, the hydrolysis kinetics of PSS were taken from Ristow *et al.* (2005) and Sötemann *et al.* (2005b). From the stoichiometry, it was found that the PSS with composition $\text{C}_{3.35}\text{H}_{7.0}\text{O}_{1.45}\text{N}_{0.45}$ (determined from CHN elemental analysis) is C-deficient in that it does not generate sufficient HCO_3^- alkalinity for the sulphate reduction, i.e. its COD/C ratio is too high (>2.67) which accounts for the observed (and predicted) zero gas (CO_2) generation. This CO_2 deficiency causes respeciation of the $\text{H}_2\text{S}/\text{HS}^-$ system which provides the alkalinity shortfall and establishes the system pH. The absence of a gaseous CO_2 generation allowed the carbon released from the biodegraded organics to be measured via the H_2CO_3^* alk.. From this and the CHN elemental analysis 98.4, 94.0 and 90.3 % carbon mass balances were achieved over the R1 (1500 $\text{mgSO}_4^{2-}/\text{L}$), R1 (1800 $\text{mgSO}_4^{2-}/\text{L}$) and R2 systems.

The SS model predicted results including pH, correlate very well with the experimental results from 3 lab-scale UASB BSR systems (Table 3). This provides support for the developed BSR stoichiometry which gives considerable insight into the inter-relationship between the biological processes and weak acid/base chemistry systems. The SS BSR model also provides a basis for crosschecking the results from the UCTADM1-BSR model developed.

Following the development of the SS BSR model, the integrated 2 phase (aqueous-gas) mixed weak acid/base chemistry and biological processes simulation model for BSR (UCTADM1-BSR) developed by van Wageningen (2007) was revised and fine-tuned to simulate the lab-scale UASB BSR systems operated in this research investigation. In the development of this dynamic model, some of the relevant processes and kinetics for BSR were extracted from Kalyuzhnyi *et al.* (1998) and Fedorovich *et al.* (2003). Where required, other relevant processes and kinetics were modified or added to the existing ones and integrated into the PSS methanogenic anaerobic digestion model (UCTADM1) developed by Sötemann *et al.* (2005a) to yield the UCTADM1-BSR dynamic model for competitive methanogenic and sulphidogenic anaerobic digestion with PSS as energy source.

In modifying the BSR dynamic model, a sulphide inhibition term for the acetotrophic SRB growth rate equation and a temperature dependency term for the maximum specific hydrolysis rate and the half saturation coefficient in the saturation hydrolysis rate equation (in the case of UASB R2 at 20 °C) were incorporated. The K_{I-as} value for the acetotrophic SRB was found to be 206 mgS/L for a 94% growth inhibition by the undissociated H_2S using an exponential inhibition term $\exp[-([H_2S]_i/0.60056K_{I,j})^2]$. The θ temperature dependency value was 1.114, representing a 30% decrease in the PSS biodegradable organics hydrolysed when the temperature is decreased from 35 °C to 20 °C. The kinetic simulation model predictions (restricted to steady state conditions) conform favourably well to the experimental measurements and the SS model results (Table 3) and therefore provides support for the successful development, calibration and validation of the kinetic simulation model.

Table 3: Comparison of experimentally Measured (M) effluent values with the Steady State (SS) BSR and the UCTADM1-BSR kinetic (Sim) model predictions.

Parameters	Units	UASB R1 at 35°C (fed 1500 mgSO ₄ ²⁻ /L)			UASB R1 at 35°C (fed 1800 mgSO ₄ ²⁻ /L)			UASB R2 at 20°C (fed 1500 mgSO ₄ ²⁻ /L)		
		M	SS	Sim	M	SS	Sim	M	SS	Sim
Effluent sulphate	mgSO ₄ ²⁻ /L	149	149	136	146	145	115	101	104	103
Sulphate removal	mgSO ₄ ²⁻ /L	1351	1351	1364	1654	1355	1685	1399	1396	1397
Organic COD removal	mgCOD/L	1624	1632	1757	2153	2242	2264	2309	2444	2410
Effluent total soluble COD	mgCOD/L	761 ^a	761 ^b	1031	1234	1234 ^b	1442	951	951 ^b	1116
Effluent organic soluble COD	mgCOD/L	141	141 ^b	123	229	229 ^b	320	96	96 ^b	186
Effluent HS/H ₂ S	(mgS/L)/(mgS/L)	209/101 ^a	277/173	336/120	318/184	339/213	409/153	261/166	280/185	321/145
Reactor pH	-	7.15	7.05	7.19	7.08	7.04	7.17	7.21	7.20	7.26
Effluent sum of H ₂ CO ₃ * alk and Alk H ₂ S	mg/L as CaCO ₃	1938 ^a	2063	2039	1855	1974	1982	1558	1672	1668
Effluent H ₂ CO ₃ * alkalinity	mg/L as CaCO ₃	1611 ^a	1627	1516	1358	1441	1343	1144	1234	1166
Effluent VFA	mgHAc/L	48	48 ^b	22	72	72 ^b	82	62	62 ^b	42
Effluent FSA	mgN/L	32	50	57	46	60	76	38	48	57
H ₂ S effluent gas stream	mgS/L influent	0	0	0	0	0	0	0	0	0
CO ₂ effluent gas stream	mol/L	0	0	0	0	0	0	0	0	0

a: H₂S measurement problem during the first 280 days of UASB R1 operation period, system total alkalinity unaffected by loss of H₂S while H₂CO₃* alk. and Alk H₂S are affected.

b: The Steady State (SS) model for BSR is based on substrate utilisation, hence the concentration of the effluent solubles is given the experimental values.

Both the steady state and kinetic simulation models are very useful tools for the design of BSR systems in which PSS is used in the treatment of AMD. Furthermore, because they were developed for multi-organic general substrate formulation, they can accommodate other substrate types such as VFA (or a mixture of SCFA) and therefore can be applied where other organics are used for BSR.

8. CLOSURE AND FURTHER RESEARCH

Laboratory scale research on the UASB system for BSR using PSS has been completed in this research project and all aspects relevant for determining the important design and operating parameters have been investigated in detail. Further research should focus on

applying the test methods – sulphide via COD, 5-pH point titration and settleometer – to operation and control of full-scale systems in particular the BioSURE[®] system at Ancor WWTP. While additional data on UASB sludge settleability and bed expansion would be useful, these results are probably fairly site specific and would need to be measured *in situ* to optimise a particular UASB system.

With regard to modelling, both a steady state and a dynamic simulation kinetic model have been developed, calibrated and validated against the UASB system data. These models allow multi-organic variable composition feed specification. Should a BSR model with the sole biological processes consuming the SCFA and H₂ substrates generated from PSS hydrolysis and acidification be required, the methanogenic processes can be switched off in the UCTADM1-BSR model resulting in an exclusive sulphidogenic model. Moreover, although UCTADM1-BSR has been developed purposely for situation where PSS serves as the feed substrate, it offers nonetheless a much broader potential application. For instance, should the feed be a particulate substrate (e.g. a mixture of PSS and compost, compost alone or a mixture of PSS and waste activated sludge), only the feed substrate composition and kinetic constants for hydrolysis would require modification. For soluble organics (e.g. acetate or a mixture of SCFA), they would be used directly as input to the model as they serve as intermediates in the processes already included in the model. In fact, other organic sources have been explored for BSR in South Africa such as grass cuttings (work conducted by the CSIR) and high strength organic wastes such as Sasol's Coal to liquid Fischer Tropsch reaction (Rx) water (work commenced at the University of Cape Town). This water is produced in South Africa in such high concentration (18 gCOD/L) and volume (30 ML/d) that it may be worth transporting to other acid mine drainage sites and used for BSR. It would be interesting to apply and test the steady state and UCTADM1-BSR models against these organic sources.

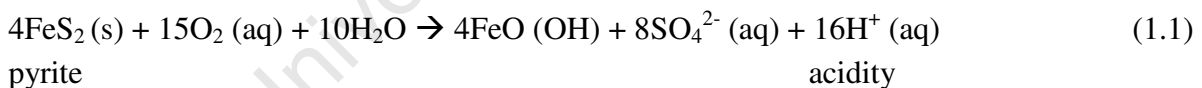
Another aspect of BSR that requires research is the removal of hydrogen sulphide from the BSR effluent. Though this stream can be recycled to precipitate the metals in the raw mine water, a relative high H₂S concentration still remains in the residual stream which needs to be removed before discharge. The conversion of H₂S (stripped from the effluent) into elemental sulphur which has a market value seems to be a feasible option for investigation.

Chapter 1

Introduction

1.1. BACKGROUND AND PROBLEM STATEMENT

Acid Mine Drainage (AMD) poses a significant environmental threat. The AMD waters emanate from both surface and underground mine workings, intentionally through pumping to prevent mine flooding or unintentionally through seepages. These waters are characterised by low pH (2-3), high iron (10-6700 mg/L) and sulphate (3000-30000 mgSO₄²⁻/L) and variable non-ferrous (usually heavy) metals and total dissolved solids (TDS) concentrations (1800-45000 mg/L) (Christensen *et al.*, 1996). These characteristics occur as a result of sulphide oxidation in rock exposed to air and water (Thomas and Jonathan, 1994). Mining activities expose to air large surface areas of rock which frequently contains iron disulphide (FeS₂), commonly known as Pyrite. In the presence of oxygen and water, pyrite is oxidised to form soluble iron complexes and sulphuric acid, catalysed by the sulphur oxidising bacteria (Davison *et al.*, 1989):



The resulting water is therefore high in acidity and dissolves a wide variety of metal (usually heavy) ions into solution. These metals stay dissolved in solution until the pH rises to a level where precipitation occurs.

The impacts of AMD discharges are both short term and long term. Low pH AMD often cannot be re-used in mineral processing since it damages mine infrastructure and machinery. Aquatic ecosystems downstream can be damaged or destroyed. Ecosystems on the banks of rivers and drainage channels also can be affected. Death of trees is common and these changes can lead to secondary effects such as increased erosion and sediment load in streams. Moreover, underground water resources are contaminated by the acidic nature of

the AMD and its heavy metal contents (Anon., 2005). The Department of Environment and Heritage in Australia (Anon., 2005) estimate the Canadian liability from AMD as C\$ 2-5 billion/year, the Australian liability as A\$ 60M/year, that 20000 km of streams and rivers are adversely affected in the USA, and that for USA coal mines only, the liability in 1990 was US\$ 1 million/day. Movin and Hutt (2001) estimated that the Chinese mining industry produces about $2.5 \times 10^9 \text{ m}^3$ of polluted water annually ($\sim 80 \text{ m}^3/\text{s}$).

Considerable effort has been made in the treatment of AMD with regard to the high acidity and heavy metals content, due to their toxicity and the associated environmental hazards. However, less attention has been directed to the treatment of sulphate in AMD despite the elevated concentrations. This was due to the fact that dissolved sulphate is of lower toxicity than that for acidity and heavy metals. However, there is an increasing concern about high dissolved sulphate concentrations and regulatory agencies are enforcing more stringent standards for sulphate in effluents. Consequently, sulphate treatment is now required at many mine sites around the world. Countries with an important mining industry, such as Canada, United States, Australia and South Africa, are investigating various sulphate treatment processes to meet their respective effluent sulphate guidelines (INAP, 2003).

Various physical and chemical processes have been developed to treat AMD, such as neutralisation (Maree *et al.*, 1996), the high-density sludge (HDS) (Pulles *et al.*, 1995) or ambient temperature ferrite (Morgan *et al.*, 2004) systems to remove heavy metals, and barium sulphate or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) precipitation to remove sulphate. However, in these systems the high costs of chemicals and the large sludge volumes generated (Johnson and Hallberg, 2005) are disadvantageous. Furthermore, for the chemical removal of sulphate, the precipitation of gypsum is more a consequence of neutralisation with Ca-based neutralising agents (e.g. lime, limestone (Maree *et al.*, 1996)) than a direct treatment for sulphate removal, and leaves a significant sulphate residual ($\sim 2000 \text{ mgSO}_4/\text{L}$) (Potgieter-Vermaak *et al.*, 2006). As supplement or alternative to the chemical removal of sulphate, biological sulphate reduction (BSR) would seem an attractive option for chemically pre-treated or relatively low sulphate ($< 2000 \text{ mg/L}$) AMD. Biological sulphate reduction, mediated by sulphate reducing bacteria (SRB), requires an organic substrate as electron and carbon source. Conventionally, for BSR organic substrates such as molasses, ethanol, acetate or lactate have been used as electron donor and organic carbon source (Herlithy *et al.*, 1987). However, these organics are relatively expensive making AMD remediation via

BSR costly and consequently BSR using these organics have in general been limited to lab- and/or pilot scale levels.

1.2 BIOLOGICAL SULPHATE REDUCTION (BSR) USING PRIMARY SEWAGE SLUDGE (PSS) AS ENERGY SOURCE

Since the economics of BSR are driven by the economics of the organic energy source, the use of a low-cost effective electron donor was considered the most significant factor steering the BSR process. Recently, Rhodes University has developed a novel system, the Rhodes BioSURE® process in which BSR is achieved using Primary Sewage Sludge (PSS) as carbon source and electron donor (Rose *et al.*, 2002). PSS is freely available as a by-product at municipal wastewater treatment systems, and thus this co-disposal process proposes an elegant solution to BSR. Initially, for BSR the Rhodes BioSURE® process made use of a Recycling Sludge Bed Reactor (RSBR), which is a down-flow based configuration. However, the RSBR configuration requires a hydraulic retention time of approximately 48h (Rose *et al.*, 2002) and this in turn requires a relatively large reactor size. Moreover, in the RSBR configuration, dissolved sulphate can “short-circuit” to the effluent requiring downstream BSR as proposed in the BioSURE® process. In addition, BSR systems with PSS tend to produce higher non-settleable solids concentrations than equivalent methanogenic systems (Ristow *et al.*, 2005), which in the RSBR configuration would cause high suspended solid concentrations in the effluent. As alternative, it has been proposed to make use of an upflow configuration, based on the upflow anaerobic sludge bed (UASB) reactor. This scheme should facilitate improved contact between the PSS and the sulphate (all sulphate flows through the entire sludge bed). Furthermore, the UASB probably will have improved solids retention, allowing decoupling of the solid and liquid retention times, leading to higher sulphate loading rates and shorter hydraulic retention times, which would be of significant benefit.

1.3 MODELLING ANAEROBIC DIGESTION SYSTEMS

The core unit process in the BioSURE® system is BSR with PSS as electron donor. To assist in and optimise the design, operation of and research into this unit process, mathematical models (both steady state and kinetic) would represent very useful process evaluation tools. Mathematical models provide quantitative descriptions of the treatment system of interest

that allow predictions of the system response and performance to be made. Based on the predictions, design and operation criteria can be identified to optimise the system performance. The model predictions can be evaluated and as such make it possible to test hypotheses on the system behaviour, such as biological processes and their response to system constraints, in a consistent and integrated fashion.

Ristow *et al.* (2001) developed a kinetic model for BSR with PSS as substrate. In this model, the focus was on the biological processes and they excluded the chemical and physical processes which are of importance in BSR. They recognised that under steady state the hydrolysis of PSS was the rate-limiting step. However, they were not able to determine the most appropriate kinetic rate formulations for this rate controlling process (hydrolysis) since there was no consensus in the literature which was best. Due to these limitations, Ristow *et al.* (2005) undertook an extensive investigation to describe and model the PSS hydrolysis step, under methanogenic, sulphidogenic and acidogenic conditions. They concluded that BSR does not affect the rate of PSS hydrolysis implying that the same methanogenic rate formulations and rate constants can be applied under BSR conditions. They also showed that for simple steady state models first order kinetics (which are analytically simpler to apply) for PSS hydrolysis are adequate, but that for more extensive kinetic models surface saturation (Contois) kinetics would be more suitable, in concordance with Vavilin *et al.* (2001) and later supported by Sotemann *et al.* (2005a)(see below).

The International Water Association (IWA) task group for mathematical modelling of anaerobic processes developed the Anaerobic Digestion Model No. 1 (ADM1) (Batstone *et al.*, 2002). In this model the substrate, in this case PSS, is characterised into carbohydrates, lipids and proteins. That is, in the characterisation of complex organic like PSS, the three organic types are generated in a disintegration step together with inert particulate and soluble compounds. The resultant carbohydrates, proteins and lipids are thereafter hydrolysed separately to their intermediate products. However, for PSS, measurements of carbohydrates, proteins and lipids and their COD equivalents are not routinely available, so a different approach was adopted in the development of methanogenic anaerobic digestion models, both steady state (Sötemann *et al.* 2005b) and dynamic simulation (Sötemann *et al.* 2005a).

In contrast to the IWA ADM1, the model developed by Van Rensburg *et al.* (2001) and extended and modified by Sötemann *et al.* (2005a) for methanogenic anaerobic digestion of sewage sludges, the sludge is characterised with the usual COD, TKN and VSS measurements and in addition carbon, hydrogen and nitrogen (CHN) composition obtained from elemental analysis. Van Rensburg *et al.* (2001) and Sötemann *et al.* (2005a) integrated the biological kinetic processes for anaerobic digestion (AD) into a two phase (aqueous/gas) subset of the three phase mixed weak acid/base chemistry kinetic model of Musvoto *et al.* (1997). The model was calibrated and validated with data from the laboratory mesophilic anaerobic digesters of Izzet *et al.* (1992) and Ristow *et al.* (2005). The sewage sludge COD was found to be 32-36% unbiodegradable (depending on the kinetic formulation selected for the hydrolysis process) and to have a $C_{3.5}H_7O_2N_{0.196}$ composition. The measured composition of PSS from two Cape Town wastewater treatment plants ranged between $C_{3.38}H_7O_{1.91}N_{0.21}$ and $C_{3.91}H_7O_{2.04}N_{0.16}$. The predicted PSS composition based on influent measurements and mass balances in model application was within 5% of the average measured composition, providing persuasive validation of the model.

Accordingly, the model of Sötemann *et al.* (2005a) (UCTADM1) was selected as the basis for the development of the kinetic model for BSR with PSS as substrate. This would require development of the kinetics and stoichiometry for the biological, chemical and physical processes in BSR in two phases (aqueous/gas), and integration of these with UCTADM1, taking due cognizance of any interactions introduced with the integration. Essentially, this would result in a two phase biological, chemical and physical processes model for the AD of PSS, with competitive methanogenesis and sulphidogenesis.

This current investigation forms part of a greater objective to treat AMD using cost-effective carbon sources. As the main objective of her Masters research, van Wageningen (2007) undertook the task of developing a kinetic model for BSR (UCTADM1-BSR) using PSS. This model will be updated and applied to model the UASB BSR system performance as one of the objectives of this present research. The UCTADM1-BSR was developed by extending the UCTADM1 to incorporate BSR. The stoichiometry and kinetics for the bioprocesses (growth and death) mediated by the propionate degrading, acetotrophic and hydrogenotrophic sulphate reducing bacteria were formulated. These bioprocesses produce and consume *inter alia* sulphate and sulphide acid/base species which were not present in the original UCTADM1 model. Accordingly, following the approach in the UCTADM1

model, chemical processes for these were included. Further, in the BSR model the end product sulphide has a gaseous equilibrium not included in the UCTADM1 model, to give a complete kinetic model for competitive methanogenic and sulphidogenic anaerobic digestion with sewage sludge as substrate. Van Wageningen (2007) calibrated and validated the model using the Ristow *et al.* (2005) sulphidogenic completely mixed reactor AD data set.

The kinetic model UCTADM1-BSR developed by van Wageningen (2007) will be extended in this investigation by including a sulphide (namely undissociated H_2S) inhibition term. Moreover, a temperature function will also be included to simulate the effect of temperature on BSR. Thereafter, the model will be verified, calibrated and validated, after which, it will be used to model the UASB BSR system performance.

1.4 RESEARCH SCOPE AND OBJECTIVES

Within the first year of commencing the research work above, it had already attracted the interest of mining industry such that the BioSURE[®] system at Grootvlei Mines Ltd, Johannesburg, South Africa was changed from a downflow recycling sludge falling bed reactor (RSBR) to an upflow anaerobic sludge bed (UASB) reactor. This provided greater impetus and significance to this research and making the need for the outcomes of the detailed investigation into the design and operating parameters, and understanding and modelling the behaviour of the UASB system more urgent.

The following **objectives** were identified for this research:

1. To understand the capabilities and limitations of BSR with PSS in the UASB system by operating 2 lab-scale UASB reactors – one (R1) at 35 °C and the other (R2) at ambient temperature (20 °C), each at different organic and sulphate loading rates. This will allow establishing the minimum bed hydraulic retention time (HRT) and bed sludge age for maximum utilisation of PSS and sulphate reduction. UASB reactor R1 will be operated at two influent sulphate concentrations (namely 1500 and 1800 $mgSO_4^{2-}/L$) while reactor R2 at an influent sulphate concentration of 1500 $mgSO_4^{2-}/L$ since the objective is to study the system performance at ambient temperature (20 °C) (Chapters 4 and 6).

2. To investigate the effects of sludge recycle from the top to the bottom of the sludge bed on system performance. It is envisaged that this recycle line would initiate rapid BSR from the bottom of the bed and thus is worthwhile investigating. It is thought that the incoming feed to the reactor will move the sludge bed upward thereby pushing up the active biomass and that very little biological processes will occur at the bottom. This will in turn delay the sewage hydrolysis process and hence sulphate reduction will be slowed down. So, by introducing the sludge recycle line, active biomass will be returned to the bottom of the reactor bed and this will keep the biological processes active all through the entire bed (Chapters 4 and 6).
3. To measure the settling rate of the various solids fractions in the sludge particle to determine if bed expansion or sludge settleability is the capacity limiting process. At high upflow velocity, the sludge bed will expand and become unstable even though the sludge settleability might not be affected. The optimum balance of these two parameters needs to be established (Chapter 6).
4. To develop simple wet chemistry analytical procedures (COD, VFA, Alkalinity, H_2S and SO_4^{2-}) to monitor BSR systems for implementation in the field and achieve 100% COD, S and N mass balances. Sulphidogenic systems are complex since they contain mixed weak acid/base systems which are affected by the loss of H_2S and CO_2 during sampling procedures. Aqueous hydrogen sulphide measurement is problematic especially when it involves filtering the samples as H_2S escapes the system in the filtration process and sampling procedures. This study attempts to fix the sulphur balance on the system, which is an exercise scarcely reported in the literature. The development of simple wet chemistry analytical procedures for the accurate determination and measurement of aqueous H_2S are required to balance the mass of COD and sulphur around the UASB BSR system (Chapter 5).
5. To develop a general steady state (SS) anaerobic digestion model for BSR and validate it using PSS as carbon source and electron donor. This model comprises three sequential parts: a COD based hydrolysis kinetics part, a CHONS and COD mass balance based stoichiometry part and a mixed weak acid/base chemistry part. This SS model may give insight into the inter-relationship between the biological processes and weak acid/base chemistry systems and be used to predict steady state system

performance, product generation and pH. In addition, it will also provide a basis for crosschecking the results from the UCTADM1-BSR model to be updated (Chapter 7).

6. To revise, extend and fine-tune the integrated two phase (aqueous-gas) biological, chemical and physical processes kinetic model (UCTADM1-BSR) for competitive methanogenic and sulphidogenic anaerobic digestion with PSS as substrate. Thereafter the kinetic model will be validated by simulating the performance of the 2 lab-scale UASB BSR reactors and comparing the predictions with the SS BSR results and the experimental data. This model together with the steady state one (mentioned above) will provide an integrated mass balance based framework for the system and can give guidance to design, operation and research (Chapter 7).

To meet the research objectives, two lab-scale upflow anaerobic sludge bed (UASB) reactors, named as R1 (T=35 °C) and R2 (T=20 °C), were operated with PSS as carbon source and fed sulphate based on different PSS COD/SO₄²⁻ ratios. The reactors were operated with a sludge recycle line from the top to the bottom of the reactor sludge bed to initiate BSR as soon as the feed enters the reactor. In addition to that, a settleometer (a series of vertical columns with different diameters) was built and operated to test the settleability of the UASB sludge at different flow through rates. The necessary experimental data will be collected and analysed and appropriate conclusions will be made.

Chapter 2

Literature Review

2.1 INTRODUCTION

The main objectives of this research investigation have been described in Chapter 1. In this Chapter, the relevant literature on the various AMD abatement methods is reviewed briefly, to highlight the importance of biological sulphate reduction (BSR) in the various treatment schemes. Particular attention is paid to the existing sulphate treatment processes to place this research project into context, that is the use of a cost-effective organic carbon source in BSR. Thereafter the existing kinetic models of relevance to this research will be reviewed with particular focus on anaerobic digestion models with PSS as substrate and those containing processes of significance to sulphate reduction.

2.2 ACID MINE DRAINAGE (AMD)

Acid Mine Drainage (AMD) waters emanate from both surface and underground mine workings, either intentionally through pumping to prevent mine flooding or unintentionally through seepages, and are characterised by low pH, high iron and sulphate concentrations and variable non-ferrous (usually heavy) metals and total dissolved solids (TDS). Due to these characteristics, AMD poses a significant environmental threat (Akcil and Koldas, 2006).



Figure 2.1: Picture of a typical acid mine drainage stream and its effects to the surrounding environment.

2.3 FORMATION AND CHEMICAL CHARACTERISTICS OF ACID MINE DRAINAGE

The origin of AMD is extensively described in the literature by Kuenen and Robertson (1992); Pronk and Johnson (1992); Robb (1994); Johnson (1995); Banks *et al.* (1997); Ristow (1999); Kaksonen *et al.* (2004); Johnson and Hallberg (2005); Akcil and Koldas (2006) and can be summarised as follows:

During mining activities large surface areas of rock are exposed to air (oxygen) and water. These rocks usually contain sulphide minerals, predominantly iron disulphide (FeS_2) commonly known as iron pyrite (fool's gold), but other metal sulphides such as pyrrhotite (FeS), chalcopyrite (CuFeS_2) may also be present. Taking pyrite as an example, in the presence of oxygen and water, it is chemically oxidised into ferrous iron (Fe^{2+}), sulphate (SO_4^{2-}) and protons (H^+):

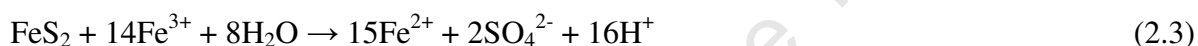


The release of H^+ ions in the reaction causes a decrease in pH. The ferrous iron (Fe^{2+}) produced in Reaction (2.1) is released into the water, where it is oxidised with oxygen as electron acceptor to ferric iron (Fe^{3+}), consuming H^+ :



Under most abiotic conditions Reaction (2.2) is the rate limiting step in the oxidation of pyrite, since at a pH < 5, the chemical oxidation of Fe²⁺ to Fe³⁺ is a slow reaction (Skousen *et al.*, 1998). However, the reaction is mediated by sulphur oxidising bacteria, of which the most important are *Acidithiobacillio ferro-oxidants* (formerly *Thiobacillus ferro oxidans*), which greatly accelerate the reaction rates. If *A. ferro-oxidants* are present, then oxygen may become rate limiting. The availability of oxygen will depend on the specific conditions present (Skousen *et al.*, 1998).

Due to the net production of H⁺ in the above two processes, the pH will decrease. At a pH < 4, the ferric iron generated in Reaction (2.2) above reacts with pyrite to form ferrous iron, SO₄²⁻ and H⁺:



The H⁺ generated in Reaction (2.3) causes a further decrease in pH, thereby slowing the rate of Reaction (2.1). However, the ferrous iron generated now enters Reaction (2.2) creating a cyclical propagation of rapid pyrite oxidation and the generation of both sulphate and acid. The overall effect is therefore an increase in the sulphate and dissolved metals concentrations (particularly iron), and a decrease in pH. The resultant water is thus high in acidity and dissolves a wide variety of heavy metals into the solution. Similar to pyrite, other sulphide minerals are oxidised releasing metals and sulphate in solution. However, in this case, the oxidation of metal sulphides of the type MS does not release acid, for instance sphalerite is oxidised as follows (Banks *et al.*, 1997):



Accordingly, AMD waters are typically characterised by high concentrations of heavy metals (e.g. Al=50 – 2000 mg/L; Fe=10 – 6700 mg/L; Zn=10 – 100 mg/L), sulphate (3000 – 30000 mg/ℓ) and total dissolved solids (1800 – 45000 mg/L), coupled with a low pH (2 - 3) (Christensen *et al.*, 1996). These heavy metals stay dissolved in solution until the pH rises (>3.5), due to dissolution of alkalinity or following discharge of the AMD to surface water, where ferric hydroxide Fe(OH)₃ will form and precipitate :



$\text{Fe}(\text{OH})_3$ also known as “yellow boy” gives rise to the yellow or reddish colours frequently seen in water bodies polluted with AMD (Figure 2.2).



Figure 2.2: Yellow boy in a stream receiving acid drainage from surface coal mining.

2.4 ENVIRONMENTAL IMPACTS OF ACID MINE DRAINAGE

As mentioned above, AMD discharge is either intentional (e.g. pumping) or unintentional (e.g. seepages). It has significant short and long term impact, both for water re-use and environmentally. Low pH AMD often cannot be re-used in mineral processing since it damages mine infrastructure and machinery. The environmental impacts are severe and widespread in many countries and arise principally through the acidification of receiving water bodies and the toxic metal contents. The prime impact areas are rivers, estuaries, lakes and coastal waters (Gray, 1997). Groundwater resources can also be adversely affected by AMD, namely metallurgical waters (Barnes *et al.*, 1991a, 1991b). Aquatic ecosystems downstream can be damaged or destroyed by a number of direct and indirect pathways (Gray, 1997). The acidic nature of the water can cause direct toxic effects to fish by harming their gills (Johnson, 2000). Ecosystems on the banks of rivers and drainage channels also

can be affected. Death of trees is common and these changes can lead to secondary effects such as increased erosion and sediment load in streams. Moreover, underground water resources are contaminated by the acidic nature of the AMD and its heavy metal contents (Anon., 2005). Even where the receiving water body has sufficient capacity to buffer pH changes, the increase in pH causes precipitation of ferric hydroxide ($\text{Fe}(\text{OH})_3$) which can blanket water bodies blocking sunlight penetration and thus reducing primary production. This may dramatically impact the food chain in these water bodies. Compared to non-polluted waters, AMD impacted water courses are inclined to be devoid of fish and tend to have limited biodiversity in planktonic and benthic organisms (Johnson, 2000). This corroborates the findings of Mills and Mallory (1987) who stated that the microbial community structure and function in AMD contaminated waters are very different from those of non-polluted waters. In addition, the high total dissolved solids (TDS) content of AMD (principally sulphate and metals) can significantly impact the salinity of the receiving waters.

Further, due to increased toxicity and hardness, the receiving waters of the AMD discharge may be unsuitable and unusable for agricultural, industrial as well as for recreational purposes (Dugan, 1975; Clarke, 1995). Table 2.1 summarises the negative effects of AMD which can be categorised as chemical, physical, biological, ecological and socioeconomic impacts (Gray, 1997; Jarvis and Younger, 2000).

Table 2.1: Major impacts of acid mine drainage (adapted from Gray, 1997; Jarvis and Younger, 2000).

Chemical	Physical	Biological	Ecological	Socioeconomic
▪ Increased acidity ▪ Destruction of bicarbonate buffering ▪ Increase in soluble and particulate metal concentrations ▪ Salinisation	▪ Increased turbidity ▪ Decrease in light penetration ▪ Sedimentation ▪ Adsorption of metals into sediments and organisms	▪ Behavioural ▪ Respiratory ▪ Reproduction ▪ Osmoregulation ▪ Acute and chronic toxicity ▪ Death of sensitive species ▪ Acid/Base balance failure in organisms ▪ Migration or avoidance	▪ Habitat modification ▪ Niche loss ▪ Bioaccumulation in food chain ▪ Loss of food source or prey ▪ Reduction in primary productivity ▪ Food chain modification	▪ Flooding ▪ Subsistence ▪ Corrosion ▪ Aesthetic loss ▪ Decrease of drinking, agricultural, industrial and recreational water quality ▪ Decrease in catch of fish ▪ Health effects

In 2005, the Department of Environment and Heritage in Australia (Anon., 2005) reported the scale of AMD problem and estimated the Canadian liability from AMD as C\$ 2-5 billion/year, the Australian liability as A\$ 60M/year, that 20000 km of streams and rivers are adversely affected in the USA, and that for USA coal mines only, the liability in 1990 was US\$ 1 million/day. Movin and Hutt (2001) estimated that the Chinese mining industry produces about $2.5 \times 10^9 \text{ m}^3$ of polluted water annually ($\sim 80 \text{ m}^3/\text{sec}$).

Due to the above-mentioned impacts and liabilities, it is clear that the prevention and/or treatment of AMD represent a crucial issue that necessitates more and more attention.

Considerable effort has been made in the treatment of AMD with regards to the high acidity and heavy metals content, due to their toxicity and the associated environmental hazards (INAP, 2003). However, less attention has been directed to the treatment of sulphate in AMD despite the elevated concentrations. This was due to the fact that dissolved sulphate is of lower toxicity than that for acidity and heavy metals. However, there is an increasing concern about high dissolved sulphate concentrations and regulatory agencies are enforcing more stringent standards for sulphate in effluents. Consequently, sulphate treatment is now required at many mine sites around the world. Countries with an important mining industry, such as Canada, United States, Australia and South Africa, are investigating various sulphate treatment processes to meet their respective effluent sulphate guidelines (INAP, 2003).

2.5 ACID MINE DRAINAGE POLLUTION CONTROL

The prevention of AMD is well documented in the literature and can be found in Skousen *et al.*, 1998; Hilson and Murck, 2001; Kaksonen *et al.*, 2004; Johnson and Hallberg, 2005; Chen *et al.*, 2006. AMD prevention is aimed at either eliminating or minimising water and / or air contact with the pyrite containing material, or inhibiting the rate limiting step in the formation of AMD, namely the bacterially mediated oxidation of the ferrous iron (Fe^{2+}), Reaction (2.2) above. Evangelon and Zhang (1995) reviewed and described the various physical, chemical and biological techniques for source and migration control of AMD. These techniques are summarised in Table 2.2 below.

Table 2.2: Available techniques for acid mine drainage prevention (adapted from Kaksonen *et al.* 2004).

Technique	Principle	Reference(s)*
Exclusion of air	Flooding and sealing of underground mines and underwater storage of mine tailings	Evangelou and Zhang (1995); Perry <i>et al.</i> (1998)
Exclusion of water	Storage of waste rock in heaps sealed with e.g. clay cover or plastic liners	Banks <i>et al.</i> (1997); Perry <i>et al.</i> (1998)
Revegetation	Establishing vegetation on mined land for preventing erosion, and reducing the amount of water and oxygen entering the soil	Tichy and Mejstrik (1996); Strock (1998)
Alkaline addition	Mixing of alkaline waste rock with pyritic material or injecting alkaline chemicals to neutralise acidity and precipitate metals	Sherlock <i>et al.</i> (1995); Perry <i>et al.</i> (1998); Smith and Brady (1998)
Immobilisation	Capturing the contaminants within the soil mass by using physico-chemical additives and cementation	Jang <i>et al.</i> (1998)
Rock phosphate addition	Complexation of Fe^{2+} with rock phosphate in order to reduce Fe^{3+} formation	Evangelou and Zhang (1995)
Micro-encapsulation	H_2O_2 - induced iron phosphate coating of pyrite surfaces	Evangelou and Zhang (1995)
Sacrificial anodes	Scrap iron as sacrificial anode to suppress the oxidation of metal sulphide ores	Shelp <i>et al.</i> (1995)
Microbial inhibitors	Application of anionic surfactants, organic acids or food preservatives that inhibit the activity of iron and sulphur oxidising microbes	Dugan (1975); Evangelou and Zhang (1995); Kleinmann (1998); Jozsa <i>et al.</i> (1999); Seidel <i>et al.</i> (2000)
Grazing	Application of acidophilic protozoa that graze on iron oxidising bacteria	Johnson (1995)

* References not listed – see Kaksonen *et al.* (2004) for reference details.

However, AMD formation generally cannot be prevented due to the practical and economic difficulties associated with it.

2.6 OVERVIEW OF EXISTING ACID MINE DRAINAGE TREATMENT TECHNOLOGIES

As an alternative or supplement to AMD prevention, AMD treatment represents the only viable option. Systems for AMD treatment incorporate various chemical, physical and biological processes. The chemical processes are principally aimed at neutralisation of the acidic AMD, but also include precipitation of heavy metals and sulphate salts, and ionic exchange or adsorption onto a variety of resins or materials. The physical processes are for phase separations, typically of resultant precipitants through gravity sedimentation, but also

include membrane filtration. The biological processes are dominated by biological sulphate reduction (BSR) to remove sulphate and generate alkalinity (or consume acidity) which therefore represents an added benefit of neutralising AMD.

In the literature, AMD treatment is broadly divided into “passive” and “active”, but there does appear to be some overlap between these two categories or combinations of unit operations from each. Generally (but not exclusively) the passive systems are those that do not require continual dosing of chemicals or substrates, whereas the active systems do.

2.6.1 Passive treatment

Compared with passive treatment, active treatment systems often carry considerable financial cost due to continual chemical or substrate addition and management requirements. Passive treatment processes commonly replace the conventional neutralisation techniques where alkaline reagents such as lime and limestone are used to neutralise the AMD. In most of the passive treatment technologies, the AMD remediation is aided by the naturally occurring chemical and biological processes so much so that these technologies require less energy and chemicals and the maintenance cost is relatively low.

Accordingly, a number of different passive treatment systems have been developed, including natural wetlands, aerobic and anaerobic wetlands, anoxic limestone drains, successive alkalinity producing systems, limestone ponds, open limestone channels, diversion wells, iron oxidation bioreactors (Gazea *et al.*, 1996; Skousen *et al.*, 1998; Johnson and Hallberg, 2005). Skousen *et al.* (1998) summarised the selection of the appropriate passive treatment system based on water chemistry and flow. This is depicted in Figure 2.3.

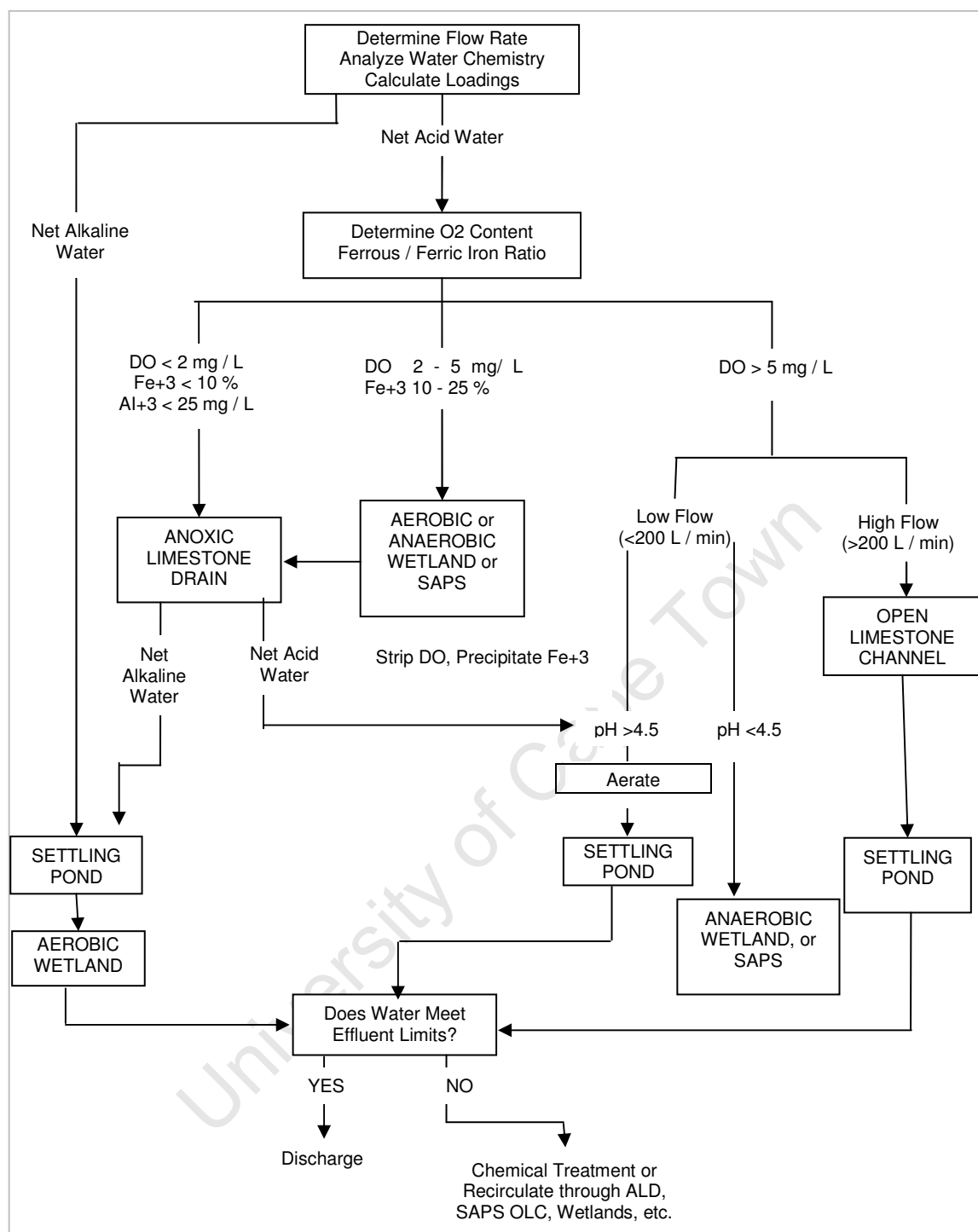


Figure 2.3: Flowchart summarising the selection of passive AMD treatment system based on water chemistry and flow (Skousen *et al.*, 1998).

The various concepts and systems of passive treatment of AMD appear to be considerably cheaper than active treatment systems. However, the low efficiency of the process, a large land requirement, metal recovery difficulty, poor control and predictability due to seasonal variations (in the case of anaerobic wetlands) (Gazea *et al.*, 1996) are among the main drawbacks. These passive systems are accordingly subject to sporadic failure in the long

term (Skousen, 2006). Additionally, the management of possible toxic sludges in passive systems necessitates due attention for sustainable long term treatment (Johnson and Hallberg, 2005).

2.6.2 Active treatment

Active treatment technologies are highly efficient compared with the passive treatment processes. Active treatment requires continual management of the system and input of chemicals and / or substrates in a controlled environment. Active treatment methods employ chemical / physical processes, principally for neutralisation and metals removal, and / or biological processes, for sulphate removal, alkalinity generation and metal sulphide precipitation. They require higher maintenance cost and manpower compared to passive processes. However, these costs are offset by the high efficiency of the processes. Active treatment holds the prospect of water reclamation from AMD (Gunther *et al.*, 2006) and allows control of the system efficiency and effluent quality. In the following sections, some of the active treatment technologies are described briefly.

2.6.2.1 Physico-chemical processes

The most widespread AMD active treatment method is the addition of chemical neutralising agents (Johnson and Hallberg, 2005). This increases the alkalinity and consequently raises the pH, which causes the precipitation of a number of metals as hydroxides and carbonates (Aubé, 2006). The resultant sludge encapsulates the precipitants which is then physically separated from the AMD, usually through gravity (Johnson and Hallberg, 2005; Aubé, 2006), but also through the use of membranes (Juby and Schutte, 2000). Various alkaline chemicals have been used as “pure” chemicals such as quick lime (CaO), slaked (hydrated) lime (Ca(OH)_2), calcium carbonate (CaCO_3), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), magnesium oxide (MgO), magnesium hydroxide (Mg(OH)_2) and ammonia (NH_3). Mined materials such as limestone (CaCO_3) (Maree and Hill, 1989) or dolomite ($\text{CaMg(CO}_3)_2$) (Potgieter-Vermaak *et al.*, 2006) or as industrial byproducts such as blast furnace slag (Feng *et al.*, 2004) or fly ash (Potgieter-Vermaak *et al.*, 2006) can also be used to neutralise the pH. The choice of the chemical neutralising agent depends on economic and technical considerations (Skousen *et al.*, 1998).

There is a general consensus that limestone is the most economical neutralising chemical (Sibrell and Watten, 2003), but is subject to slow reaction rates and limestone armouring (Maree *et al.*, 1996). Fluidised limestone beds (Maree *et al.*, 1996) and pulsed limestone bed reactors attempt to overcome this problem (Sibrell and Watten, 2003). Where calcium containing neutralising agents are used, removal of sulphate as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and / or as ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$) may be achieved, if the solubility products are exceeded (Potgieter-Vermaak *et al.*, 2006; Aubé, 2006). However, the chemical removal of sulphate leaves a significant sulphate residual ($\sim 2000 \text{ mgSO}_4^{2-}/\text{L}$; Potgieter-Vermaak *et al.*, 2006). Therefore, alternative or supplementary unit processes are required to reduce the sulphate concentration.

The metal laden sludge formed by the addition of chemical neutralising agents would need to be separated from the water. This separation is principally achieved by gravity in ponds, pits or clarifiers (Aubé, 2006), but limestone columns or fluidised beds have also been utilised (Maree *et al.*, 1996), as well as membranes (Juby and Schutte, 2000).

To facilitate gravity sludge separation, various system refinements have been developed, such as the sludge recycling, high density sludge (HDS) and Geco processes (Aubé, 2006). These systems return sludge to the lime neutralisation/precipitation reactor to provide surfaces for crystal growth thereby increasing the density of the sludge. Traditionally the solids content of the sludges has been 2 – 7 %, but the HDS achieves densities of >30 %, (Kalin *et al.*, 2005). Addition of coagulants and flocculants has also been used to facilitate sludge separation (Skousen *et al.*, 1998).

Alternative chemical/physical processes such as ion exchanges with resins or natural zeolites and bio-adsorption with low cost adsorbents (Santos *et al.*, 2004) have also been implemented (Skousen *et al.*, 1998). These processes together with other active physico-chemical techniques used for the removal of metals from aqueous sulphide are summarised in Table 2.3. Recently, Morgan *et al.* (2004) developed a novel chemical/physical process called the seeded ambient temperature ferrite for the removal of metal ions. In this system, the AMD is dosed with lime in a short retention mixed contact reactor with low oxygen concentration (either from the AMD influent or through limited aeration); this simulates the formation of green rust (ferric ferrous sulphato hydroxide). The green rust is settled and enters an oxidation reactor where air is supplied, the green rust is oxidised to magnetite

(Fe₃O₄), provided an aging period is included. The magnetite is settled and wasted, but some magnetite is recycled to the initial contact reactor to serve as a surface for green rust formation, thereby facilitating settlement. Non-iron metals are removed as hydroxides or are incorporated in the green rust matrix to give ferrite.

Table 2.3: Alternative physico-chemical techniques for the removal/recovery of metals from water.

Technical	Principle	Reference(s)
Cementation	Metal replacement process in which an ionised metal is recovered from solution by reduction to the elemental metallic state with subsequent oxidation of a sacrificial metal, such as scrap iron	Lanouette (1977); Peters <i>et al.</i> (1985)*
Coagulation-flocculation	Coagulation: charge neutralisation of particles using e.g. ferric sulphate, alum or sodium aluminate. Flocculation: slow mixing to promote the agglomeration of destabilised particles	Peters <i>et al.</i> (1985)*
Foam flotation	Use of gas bubbles and surfactants to decrease the apparent density of aggregates which float to the liquid/air interface	Peters <i>et al.</i> (1985); Rubio <i>et al.</i> (1996)*
Membrane filtration	Filtration through semipermeable membrane (reverse osmosis, micro/nano/ultrafiltration)	Lanouette (1977); Peters <i>et al.</i> (1985); Rubio <i>et al.</i> (1996); Banks <i>et al.</i> (1997); Kozłowski and Walkowiak (2002)*
Electrolytic recovery of metals	Deposition of positively charged metal ions on negatively charged cathodes by applying a direct current through the metal containing aqueous solution (electrowinning)	Peters <i>et al.</i> (1985)*
Electro-dialysis	Use of electric potential to transport ionic species through cation or anion exchange membranes	Peters <i>et al.</i> (1985); Chartrand and Bunce (2003)*
Ion exchange	Exchange of ions on the resin for those in wastewater	Lanouette (1977); Peters <i>et al.</i> (1985); Rubio <i>et al.</i> (1996); Chmielewski <i>et al.</i> (1997); Bosso and Enzweiler (2002)*
Liquid-liquid extraction	Extraction of metals using an organic solvent that flows countercurrent to the wastewater	Peters <i>et al.</i> (1985); Rubio <i>et al.</i> (1996); Chmielewski <i>et al.</i> (1997)*
Membrane extraction	Extraction of metals through membranes which separate aqueous and organic solvent carbon	Peters <i>et al.</i> (1985)*
Adsorption	Adsorption of metals on e.g. activated carbon	Lanouette (1977); Peters <i>et al.</i> (1985); Rubio <i>et al.</i> (1996)*
Evaporation/distillation	Recovery of metals by evaporation/distillation	Peters <i>et al.</i> (1985)*
Ferrite process	Controlled formation of ferrite from ferrous solutions using magnetite seed	Morgan <i>et al.</i> (1985)

* References not listed – see Kaksonen *et al.* (2004) for reference details.

Generally, active chemical treatment provides effective neutralisation of AMD, but has high operating costs and produces large sludge volumes with a mixture of metals (Johnson and Hallberg, 2005) that presents problems in disposal.

2.6.2.2 Active biological treatment processes

As supplement or alternative to the chemical/physical processes for AMD remediation, biological treatment would seem an attractive option. Biological treatment usually forms one unit process in a treatment train encompassing additional chemical and/or physical treatment (Rose *et al.*, 2002; Maree, 2002) but can sometimes stand alone (Luptakova and Kusnierova, 2005).

Several biological mechanisms have been used in the removal of metals from AMD waters and are summarised in Table 2.4 (for review, see Gadd, 1992; White *et al.*, 1995).

Table 2.4: Biological mechanisms for removal of metals from wastewaters (adapted from Kaksonen *et al.*, 2004).

Mechanism	Organisms/materials	Reference(s)*
Biosorption	Plants, algae, bacteria, fungi, yeast, peat, agricultural by-products, biopolymers	Peters <i>et al.</i> (1985); Brierley <i>et al.</i> (1989); Rossi (1990); Gadd (1992); Eccles (1995); Tsezos <i>et al.</i> (1995); Rubio <i>et al.</i> (1996); Scott and Karanjkar (1998); van Hille <i>et al.</i> (1999); Brown <i>et al.</i> (2000); Chen <i>et al.</i> (2000); Utgikar <i>et al.</i> (2000); Gázsó (2001); Mallick (2002); Ibeanusi <i>et al.</i> (2003)
Intracellular uptake and accumulation	Plants, algae, bacteria, fungi and yeast	Brierley <i>et al.</i> (1989); Rossi (1990); Gadd (1992); Ghosh and Bupp (1992); Brady <i>et al.</i> (1994); Eccles (1995); Evangelou and Zhang (1995); Scott and Karanjkar (1998); Gázsó (2001); Ibeanusi <i>et al.</i> (2003)
Complexation	Microorganisms, algae, peat, immobilised siderophores	Brierley <i>et al.</i> (1989); Gadd (1992); Gazea <i>et al.</i> (1996); van Hille <i>et al.</i> (1999); Brown <i>et al.</i> (2000); Gázsó (2001); Ibeanusi <i>et al.</i> (2003)
Oxidation	Fe ²⁺ and Mn ²⁺ oxidising microorganisms	Jianwei (1995); Gazea <i>et al.</i> (1996); Umita (1996); Diz and Novak (1998); Gázsó (2001)
Reduction	Fe ³⁺ , Hg ²⁺ , Cr ⁶⁺ , Mn ⁴⁺ , U ⁶⁺ , Tc ⁷⁺ and Co ³⁺ reducing microorganisms	Gadd (1992); Kashefi and Lovley (2000); Gázsó (2001); Chardrin <i>et al.</i> (2002)
Methylation and volatilisation	Hg ²⁺ , Cd ²⁺ , Pb ²⁺ , As, Se and Te methylating microorganisms, fungi	Brierley <i>et al.</i> (1989); Rossi (1990); Gadd (1992); Gázsó (2001)
Extracellular precipitation	Phosphate liberating micororganisms, sulphate-and sulphur-reducers, pH increasing microorganisms	Rossi (1990); Macaskie <i>et al.</i> (1995); Roig <i>et al.</i> (1997); Thomas and Macaskie (1998); Ibeanusi and Wilde (1998); Robb and Robinson (1995); White <i>et al.</i> (1997); Podda <i>et al.</i> (2000); Gázsó (2001); Boonstra <i>et al.</i> (2002)

* References not listed – see Kaksonen *et al.* (2004) for reference details.

In addition, various biological processes can generate alkalinity which can be used to neutralise the AMD. These include photosynthesis (van Hille *et al.*, 1999; Johnson, 2000),

denitrification (Kalin *et al.*, 1991; WRC, 1984; ammonification, methanogenesis, and iron and sulphate reduction (Kalin *et al.*, 1991; White *et al.*, 1997; Johnson, 2000). Among these, iron and sulphate reduction represent the most obvious and effective candidates for the bioremediation of AMD (Johnson, 2000).

For sulphate removal, the biological process makes use primarily of sulphate reducing bacteria (SRB) while iron oxidising bioreactors have also been implemented for iron removal (Johnson, 2000; Johnson and Hallberg, 2005). Since the focus of the present research is on the use of a cost-effective carbon source for anaerobic sulphate reduction, the following sections review the existing biological sulphate reduction systems.

2.7 BIOLOGICAL SULPHATE REDUCTION (BSR)

BSR processes have been implemented in both the passive systems (e.g. anaerobic wetlands) and active systems. The engineered active systems have potential advantages over the passive systems (Johnson and Hallberg, 2005) in that: (i) their performance is more readily controlled and optimised, (ii) they have the potential to allow metal recovery and re-use, and (iii) significant sulphate removal rate can be achieved. However, these advantages come at considerable economic costs. Compost beds and open pit reactors, fed organic waste materials, provide an intermediate position between active and passive systems (Kalin *et al.*, 1991; Devorak *et al.*, 1992; Béchard *et al.*, 1993; Kuyucak and St-Germain, 1994). These processes allow the control of active processes in the systems, and have lower operating costs.

Being heterotrophic, SRB require an organic carbon source and electron donor with sulphate as electron acceptor: If CH_2O represents a generic organic substrate, the catabolic reaction for BSR is given by (Herlithy *et al.*, 1987):



It is also known that hydrogen (H_2) causes sulphate reduction and may substitute as electron donor (Du Preez *et al.*, 1992):



From the reactions above, BSR removes sulphate (salinity), generates hydrogen sulphide (H_2S) and consumes protons thereby generating alkalinity. The sulphide produced can react with metal ions to form insoluble metal sulphide (MS) precipitants (Christensen *et al.*, 1996):



The alkalinity generated in BSR will increase the AMD pH, stimulating precipitation of metal hydroxides provided the pH is increased sufficiently. Thus, BSR offers significant potential for AMD remediation. Engineered active applications of BSR for AMD treatment includes Biosulfide[®] (Johnson, 2003), CSIR[®] (Maree *et al.*, 2004), BioSURE[®] (Rose *et al.*, 2002) and a variation of the Thiopaq[®] process (Johnson, 2003; Rein, 2005).

Due to the propriety nature of these systems, details in the open literature are limited. The Biosulfide[®] system has two independently operated components, one biological and one chemical (Johnson and Hallberg, 2005). Raw AMD enters the chemical component where it is contacted with H_2S generated in the biological component; by manipulating pH and sulphide concentration selective metal sulphide precipitation and separation is possible. Some of the chemically treated AMD passes to the biological component for BSR and generation of sulphide; this sulphide-rich recycle passes to the chemical component. Through the selective precipitation and separation of the metals, metal recovery is possible. A number of pilot- and full-scale systems appear to have been implemented and evaluated, but details are sparse, so also for the BSR reactor type and substrates used. In this system, since only the recycle passes to the BSR, sulphate removal is only partial.

The CSIR[®] system has sequential chemical and BSR stages (Maree *et al.*, 2004). In the chemical stage, powdered CaCO_3 or lime is used to raise the pH for AMD neutralisation. Simultaneous aeration causes ferrous (Fe^{2+}) oxidation with resultant hydroxide precipitation. The AMD then passes to a second chemical stage where lime is used to raise the pH to 12 for precipitation of the metals that are not removed in the first chemical stages (such as Mg). Partial sulphate removal due to gypsum (CaSO_4) precipitation is also achieved. The pH is reduced with CO_2 from that generated in the first chemical stages, and the AMD then flows to the BSR stage. This incorporates BSR, but additionally partial

oxidation of the resultant sulphide to elemental sulphur (S^0) by the action of sulphide oxidising bacteria (SOB), controlled by oxygen entering this single reactor:



Sulphide not converted to S^0 is stripped and converted to S^0 by contacting with ferric (Fe^{3+}) iron. Pilot-scale studies with completely mixed and column reactors for BSR with sucrose and/or ethanol as substrate have been demonstrated (Maree *et al.*, 2004), but the integrated system requires evaluation.

The Paques® Thiopaq® based system (Paques, 2002; Johnson, 2003; Rein, 2005) has sequential chemical pre-treatment for carbonate and hydroxide precipitation, followed by BSR, with the resultant sulphides used for metal sulphide precipitation. Where sulphide production exceeds the requirements for the precipitation, the excess sulphide is converted in a second aerated biological stage to elemental sulphur by SOB. Again details of this propriety system are not readily available, but a 3Mℓ/d pilot-plant at Anglo Coals Landan Colliery (South Africa) has been implemented to treat a gypsiferous AMD (Rein, 2005). The Thiopaq® technology applies to the removal and conversion of sulphide to elemental sulphur, the latter in a propriety gas-lift bioreactor called Circox® (Benschop *et al.*, 2004). Successful implementation of the principle to treat and recover zinc from a zinc contaminated ground water at the Budelco Zinc Refinery (Netherlands) has been reported (Scheeren *et al.*, 1993; Johnson, 2003). For the BSR stage, various electron donors such as H_2 gas, ethanol, methanol and waste products are suggested (Paques, 2002); no details on the substrate for the Anglo Coal application are available, but natural gas converted to H_2 in a reformer is used at Budelco.

One difficulty in applying selective metal removal via sulphide precipitation is due to the presence of iron in AMD which will form iron sulphide (FeS_2) which settles very poorly. Hence metal recovery from AMD via sulphide precipitation may be restricted to applications with low iron, such as at the Budelco Zinc Refinery.

Irrespective of the type of biological AMD processes technology used, the singular factors constraining the biological treatment approach are the reactor configuration used, the cost of construction, and particularly the cost and availability of a carbon source (electron donor) for the microbial reduction processes.

2.7.1 Bioreactor configuration

To be successful and effective, the specific organisms (e.g. sulphate reducing bacteria in AMD remediation) must be retained in the bioreactors and as such carry out the desired conversions (Lens *et al.*, 2002). This concern of efficient biomass retention in the system has been the major impetus for development of process configurations using immobilised cells. Figure 2.4 shows a schematic representation of various reactor configurations used in anaerobic wastewater treatment. Speece (1983) reported that each reactor configuration has implications for the ratio of sludge retention time/hydraulic retention time (SRT/HRT) in continuous flow reactors.

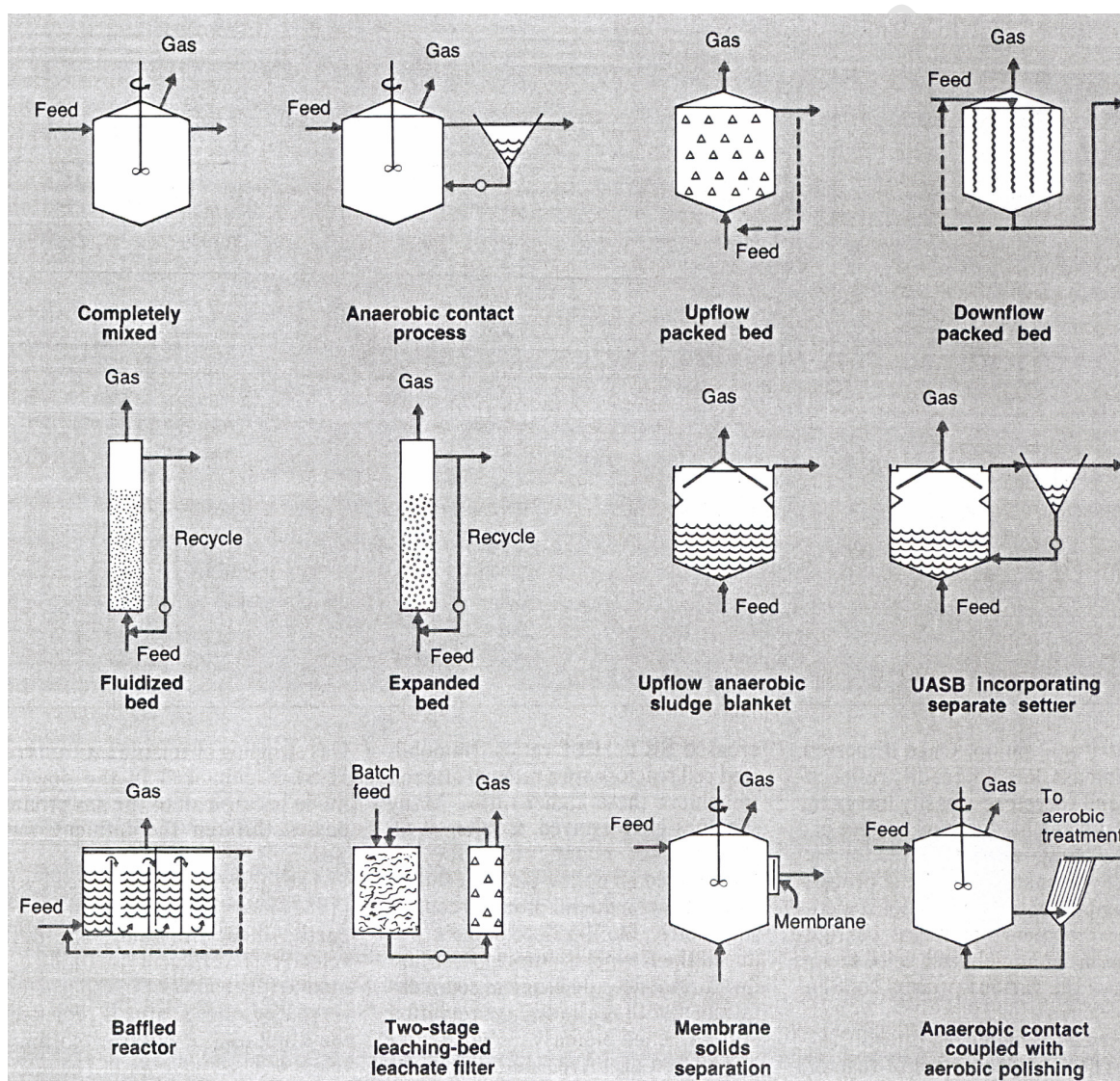


Figure 2.4: Reactor configurations used in anaerobic wastewater treatment (adapted from Speece, 1983).

For process stability and minimal sludge production, the sludge or biomass retention should be maximal. Therefore, SRT is the fundamental design parameter of biotechnology systems (Speece, 1983). This is in agreement with Lettinga *et al.* (1980) who reported that the biomass retention in the reactor largely dictates the loading rates of a process. On the other hand, the HRT should be kept at a minimum to minimise the reactor volume thus reducing capital costs. The advantages and disadvantages of various continuous flow reactors as reported by different researchers are listed in Table 2.5.

Table 2.5: Benefits and drawbacks of various reactor types (adapted from Kaksonen *et al.*, 2004).

Reactor type	Advantages (+) and disadvantages (-)	Reference(s)*
Continuously stirred tank reactor (CSTR)	+ Consistent reliable and rapid equilibrium conditions - Poor retention of biomass	Barnes <i>et al.</i> (1991a, 1991b) Speece (1983)
Anaerobic contact process (ACP)	+ Better retention of biomass as compared to CSTR - Pumping of biomass breaks down flocs and sludge	Speece (1983) Speece (1983)
Anaerobic filter reactor (AFR)	+ Low shear forces + Longer sludge retention time than in CSTR + Possibility to utilise gravitation in downflow mode + Stripping of H ₂ S effective in downflow mode - Channelling of the flow possible - Pressure gradients can be large	Barnes <i>et al.</i> (1991b) Barnes <i>et al.</i> (1991b) Speece (1983) Speece (1983) Barnes <i>et al.</i> (1991b) Anderson <i>et al.</i> (1990)
Fluidised-bed reactor (FBR)	+ Large surface area for biofilm formation due to fluidised carrier material + High retention of biomass on the carrier + Efficient mass transfer + Small pressure gradients + No channelling of flow + Influent concentrations diluted due to recycle flow + No clogging + Selects for microbes with low K _m values - Energy needed for carrier fluidisation - Shear forces can detach biomass - Less volume available for biomass compared to the UASB reactor due to the inert biomass carrier	Speece (1983); Anderson <i>et al.</i> (1990) Marin <i>et al.</i> (1999) Marin <i>et al.</i> (1999) Anderson <i>et al.</i> (1990) Anderson <i>et al.</i> (1990) Marin <i>et al.</i> (1999) Speece (1983) Melin <i>et al.</i> (1997); Melin <i>et al.</i> (1998) Speece (1983) Rittmann (1982) Yoda <i>et al.</i> (1989)
Upflow anaerobic sludge bed (UASB) reactor	+ No channelling of flow + No compacting of sludge + No cost due to biomass carrier + No clogging + Possibility to obtain high treatment rates - Biomass flush out common during process failures - More susceptible to changes in influent quality compared to AFR	Barnes <i>et al.</i> (1991b) Barnes <i>et al.</i> (1991b) Speece (1983) Speece (1983) Speece (1983) Speece (1983) Jhung and Choi (1995)
Anaerobic hybrid reactor (AHR)	+ Less susceptible to clogging compared to AFR + Sludge removal easier than in AFR + Biomass retention better than in UASB	Steed <i>et al.</i> (2000) Steed <i>et al.</i> (2000) Steed <i>et al.</i> (2000)
Anaerobic baffled reactor (ABR)	+ Long sludge retention time + No costs due to biomass carrier + Good tolerance for shocks of hydraulic and organic loading	Speece (1983) Speece (1983) Barber and Stuckey (2000)

* References not listed – see Kaksonen *et al.* (2004) for reference details.

In upflow anaerobic sludge bed (UASB) reactors, usually good biomass retention is achieved because of the good settling properties of the granular sludge (Lettinga *et al.*, 1980). The successful operation of UASB reactors depends on both physical parameters and biological processes which determine the removal efficiency and conversion of organic compounds. The biological processes whether in a methanogenic or sulphidogenic system are well documented. On the other hand, the physical parameters and the physical-chemical mechanisms of solids removal have rarely been reported (Mahmoud *et al.*, 2003). Since in this present investigation, BSR using PSS as carbon source was achieved in a UASB reactor, it was important to understand the physical parameter(s) causing sludge bed instability and progressive system failure. Accordingly, one of the objectives of this study was to determine whether sludge settleability or another cause (namely bed expansion) was the capacity limiting process at low HRT (i.e. high upflow velocity).

2.7.2 Use and availability of organic carbon sources

Carbon (and energy) sources which have been evaluated for active BSR include sewage sludge, animal waste slurries, lactate and cheese whey, molasses, ethanol and methanol and producer (or synthesis, CO + H₂ gas) (Ristow *et al.*, 2001).

In general, carbon sources (electron donors) which are available in sufficiently large quantities for BSR of AMD can be divided into two groups, namely organic waste materials and bulk chemicals. The use of organic waste materials, such as compost, sheep and poultry manure and oak leaf (Gilbert *et al.*, 2004) have been successfully evaluated, but are generally accompanied by additional pollution of the AMD and therefore a supplementary treatment process is needed to produce a clean effluent.

The use of relatively pure, fully degradable chemicals offers a number of advantages. Firstly, no remaining pollution exists and therefore no additional treatment is required. Secondly, pure chemicals have a well defined composition and concentration, making it easier to predict and describe the biodegradation and sulphate reduction. Possible compounds include ethanol, methanol and synthesis gas. Ethanol is a relatively cheaper substrate for small-scale plants, but synthesis gas becomes relatively cheaper at larger scales. All these pure substrates have proven effective for BSR but they are expensive thereby making AMD remediation costly. As a lower cost alternative, the BioSURE®

process has been proposed for the active treatment of AMD in which primary sewage sludge (PSS) serves as substrate (electron donor and carbon source) for the central BSR unit process (Rose *et al.*, 2002).

For the BioSURE[®] process to be sustainable, PSS should be readily available at the mine site from nearby municipal wastewater treatment works. Also a minimum population is required in the surrounding area to supply the required PSS. Taking a mine generating an average of 40ML of AMD per day with a sulphate concentration of 1500 mgSO₄²⁻/L and based on an average raw sewage production of 0.1 kgCOD/person/day (WRC, 1984) and with 40% COD removal in the primary settling tank, a minimum population of 1,875,000 people is required. Though the population size required appears high, it is still very practical to pump PSS from municipal wastewater treatment plants situated in nearby populated cities or towns to the mine water treatment plant, as is currently being done at the Ancor Works in Gauteng (South Africa).

2.7.3 The BioSURE[®] process

As mentioned earlier, the Rhodes BioSURE[®] Process has been developed as a low cost active treatment of AMD water (Rose *et al.*, 2002). The process flow diagram consists of a series of interconnected biological and chemical unit operations that allow for the removal of heavy metals and salinity (particularly sulphate) from AMD (see Figure 2.5).

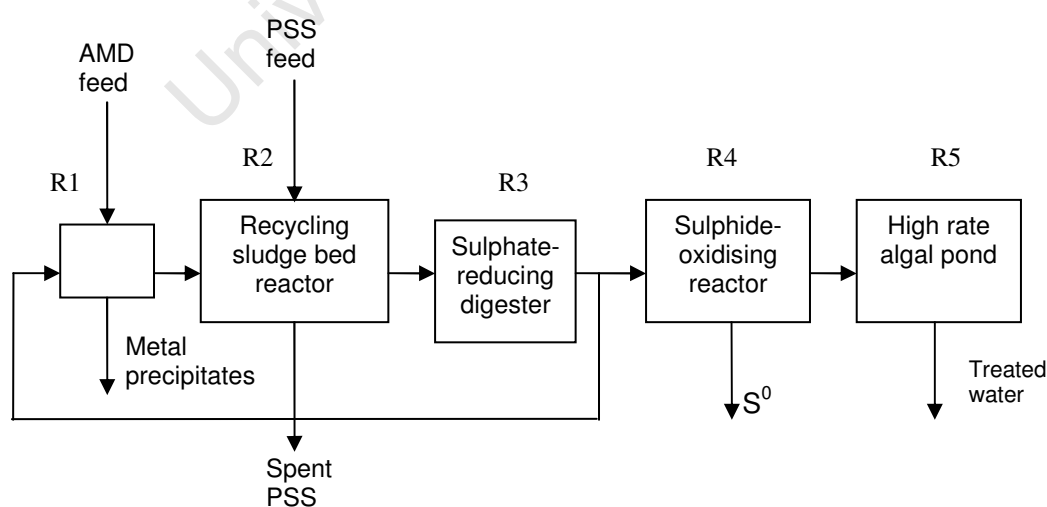


Figure 2.5: Process flow diagram of the Rhodes BioSURE[®] system applied to the treatment of acid mine drainage (AMD) wastewater (from Rose *et al.*, 2002).

The core unit process in the overall system is BSR. In the BioSURE[®] system BSR is achieved using PSS as the electron donor and organic carbon source, with the concomitant production of sulphide and carbonate alkalinities (Eq2.7). PSS is available as a by-product at municipal wastewater treatment plants, and this co-disposal proposes an elegant solution to biological sulphate reduction. Initially it was proposed that this reaction takes place in a recycling sludge bed reactor (RSBR) and a second sulphate-reducing digester (Figure 2.5).

The main aim of the RSBR is to solubilise the PSS to soluble organic matter such as short-chain fatty acids (SCFA, also called volatile fatty acids, VFA), which then are used by the sulphate-reducing bacteria in the second sulphate-reducing digester. The sulphide and carbonate alkalinities generated in this process (Reactor 3) are recycled and blended with the feed AMD, neutralising the pH and precipitating the heavy metals as metal sulphides, carbonates and hydroxides. The remaining effluent from the sulphate-reducing digester is discharged to a sulphide-oxidising reactor, where aqueous sulphide is oxidised to elemental sulphur (Equation 2.10) by a partial oxidation reaction. Finally, a high rate algal pond polishes this effluent. Based on the conceptual process design of the BioSURE[®] system, a technical pilot plant has been operated at the Ancor Works (East Rand Water Care Company (ERWAT) Gauteng, South Africa) to treat 2 ML/d of HDS pre-treated AMD (Neba and Rose, 2006) generated by Grootvlei Mines Ltd. The East Rand region represents the most immediate threat of a high volume, uncontrolled AMD discharge (Naicker *et al.*, 2003). It is estimated that about 80 ML of high total dissolved solids (TDS) water is being dewatered per day from the East Rand basin to prevent groundwater pollution. This water is thereafter treated on site using the HDS process to neutralise the pH and precipitate the iron from around 180 mg/L to 1 mg/L before it is discharged into the Blesbokspruit river (Rose *et al.*, 2002). A portion of this river downstream of the discharge point was declared a Wetland of International Significance under the Ramsar Convention because of the ecological character of this site.

However, this pre-treated HDS water still contains a significant sulphate concentration (~ 2300 mgSO₄²⁻/L) (Rose *et al.*, 2002) and therefore requires further treatment to bring down the sulphate concentration to an acceptable level (~ 250 mgSO₄²⁻/L). The successful implementation of the BioSURE[®] process to treat the 2 ML/d of pre-treated HDS AMD in the pilot plant highlighted the potential of PSS as a low-cost effective carbon source and

electron donor for BSR. A photograph of the pilot plant of the BioSURE[®] process using the RSBR configuration at the Ancor Works is shown below (Figure 2.6).



Figure 2.6: The 2 ML/d Recycling Sludge Bed Reactor (RSBR) in the BioSURE[®] sewage sludge solubilisation technical-scale plant constructed at ERWAT's Ancor Works in Springs, Gauteng, South Africa.

From the pilot scale project, it was found that the RSBR configuration proposed in the initial BioSURE[®] process resulted in some major drawbacks which might limit its full-scale application. The system requires a hydraulic retention time of approximately 48 h (Rose *et al.*, 2002) and this in turn requires a relatively large reactor size. Moreover, in the RSBR configuration, dissolved sulphate can “short-circuit” to the effluent requiring downstream BSR as proposed in the BioSURE[®] process. In addition, BSR systems with PSS tend to produce higher non-settleable solids concentrations than equivalent methanogenic systems (Ristow *et al.*, 2005), which in the RSBR configuration would cause high suspended solid concentrations in the effluent.

As alternative, it has been proposed to make use of an upflow configuration, based on the upflow anaerobic sludge bed (UASB) reactor (Ristow *et al.*, 2005). This scheme should facilitate improved contact between the PSS and the sulphate (all sulphate flows through the entire sludge bed). Furthermore, the UASB probably will have improved solids retention, allowing decoupling of the solid and liquid retention times, leading to higher sulphate loading rates and shorter hydraulic retention times, which would be of significant benefit.

2.7.4 Feasibility study of BSR using PSS in a UASB reactor

A laboratory-scale UASB-type reactor was operated to determine the feasibility of using this type of reactor configuration as the BSR digester in the Rhodes BioSURE[®] treatment scheme (see Ristow *et al.* (2005) for details). The UASB reactor had a total volume of 9.1L and an internal diameter of 93mm, and was heated to 35°C. The system was seeded with waste sulphate-reducing sludge from completely mixed sulphate-reducing digesters fed PSS, and waste from similar methanogenic digesters being fed waste activated sludge. The seed sludge thus contained acidogenic, methanogenic and sulphate-reducing biomass. The laboratory-scale UASB reactor feed consisted of 1200 mgSO₄²⁻/L, added as dissolved Na₂SO₄, and alkalinity (500 mgCaCO₃/L) added as NaHCO₃ powder. To this, 1600 mgCOD/L of PSS (Athlone Treatment Plant, Cape Town) was added. The feed COD:SO₄²⁻ ratio was based on the 0.8gCOD/gSO₄²⁻ utilisation ratio (1200 mgSO₄²⁻/L) requires 960mgCOD/L of biodegradable COD), and a total unbiodegradable COD fraction of 40% which is close to that determined by Ristow *et al.* (2005) for the PSS used (60% of total COD = 960mgCOD/L; total COD = 1600mgCOD/L). The PSS was macerated for 1min to break up the large particles.

The system hydraulic retention time (HRT) was initially set to above 5d, to allow for the biomass to acclimatise and for the sludge bed to accumulate. The sludge bed volume was allowed to increase from the initial volume of around 2L to between 4.5 and 5L, at which time sludge was wasted from a sample port along the length of the column. At regular intervals, the HRT was reduced stepwise by increasing the feed rate. The HRT was reduced to 12h, with a sludge bed retention time of 5h, and the system response monitored, see Table 2.6.

Table 2.6: Summary of preliminary results from BSR UASB system with PSS as influent substrate.

	Sample 1		Sample 2	
	Influent	Effluent	Influent	Effluent
Total COD (mgCOD/L)^a	1611	837	1666	853
Soluble organic COD (mgCOD/L)	221	56	214	89
Particulate organic COD (mgCOD/L)	1390	248	1452	236
Aqueous Sulphide (mgS/L)		266		264
Sulphate (mgSO₄/L)	1200	133	1200	86
Sulphate Conversion (%)		88.9		92.8
VFA (mgHAc/L)	96	0	88	31.9
Alkalinity (mgCaCO₃/L)	450	1883.2	680	1810.5

a: Total COD = organic + sulphide COD

From Table 2.6:

- The effluent sulphate concentration was below 135 mgSO₄²⁻/L and as low as 86 mgSO₄²⁻/L.
- The residual soluble organic COD (<90 mgCOD/L) and VFAs (<32 mgHAc/L) in the effluent were low, indicating that the PSS hydrolysis probably was the rate limiting step.
- Effluent particulate COD concentration was <250mgCOD/L, indicating successful solid-liquid separation and sludge retention in the system.

Particularly evident in the operation of the UASB system was the good solid-liquid separation, giving a well defined sludge bed and reasonably clear effluent.

Following the success in the brief study above, a preliminary study on the internal dynamics in the sludge bed was undertaken, to understand the processes operative. Concentration profiles were taken along the axis of flow through the sludge bed when the system was operating with a 6 h bed hydraulic retention time, see Figure 2.7.

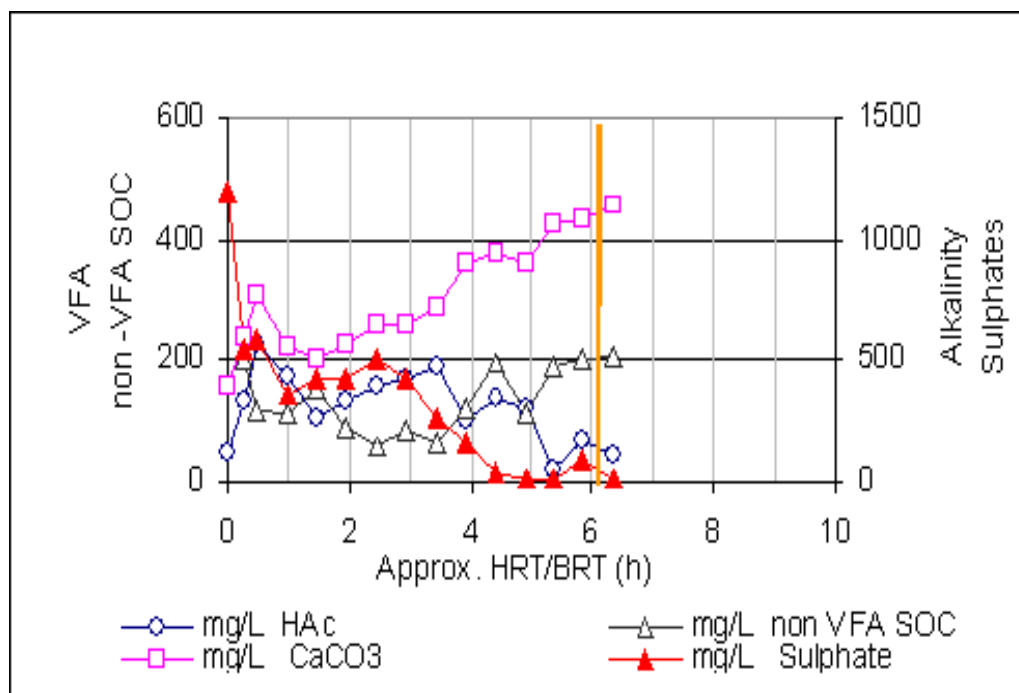


Figure 2.7: Profile taken along the axis of flow through the UASB reactor, receiving PSS as substrate and sulphate supplement; SOC = soluble organic carbon.

From Figure 2.7, two regions in the sludge bed can be identified:

- In the bottom half of the bed (<2.5h), sulphate concentrations (and alkalinities) remain relatively constant, whereas VFA concentrations increase. This indicates that sulphate reduction is rate limiting in this region.
- In the top half of the bed, sulphate and VFA concentrations decrease rapidly, to near zero at the exit from the sludge bed, while concomitantly alkalinity increases rapidly. This indicates that PSS hydrolysis is rate limiting in this region.

Again, encouraging results were obtained: Good bed separation and sulphate reductions were obtained. From this preliminary investigation, it was recommended that the sludge bed be recycled. This will seed SRB from the top half of the bed to the bottom, initiating BSR further down the bed profile and would consequently start the BSR process as soon as the feed enters the reactor.

This initial and brief feasibility study indicated that a more detailed investigation on sulphate reduction in UASB reactors with PSS as substrate was warranted, and this is the main aim of this present research.

2.8 SULPHATE REDUCING BACTERIA (SRB)

Sulphate reducing bacteria (SRB) are a unique physiological group of micro-organisms because they utilise sulphate as the terminal electron acceptor and an organic carbon source as an electron donor in anaerobic respiration. In anaerobic regions of sulphate-rich streams like acid mine drainage, different genera of SRB may exist with the principal ones being *Desulfovibrio*, *Desulfobacter*, *Desulfobulbus*, *Desulfomonas* and *Desulfotomaculum*. For a review on the taxonomy and physiology of the SRB, refer to Mori *et al.* (2003); Moussard *et al.* (2004). Although, these bacteria are strictly anaerobic, their presence has been detected in many ostensibly aerobic regions (Battersby *et al.*, 1985).

2.8.1 Anaerobic degradation of organic substrates

In an anaerobic environment and in the presence of sulphate, SRB have the ability to oxidise hydrogen and a wide variety of organic compounds ranging from simple carboxylic acids to more complex aromatic hydrocarbons (Akagi, 1995). Most of the substrates are typical fermentation products and intermediate breakdown products of larger molecules (Hansen, 1994), as illustrated in Figure 2.8.

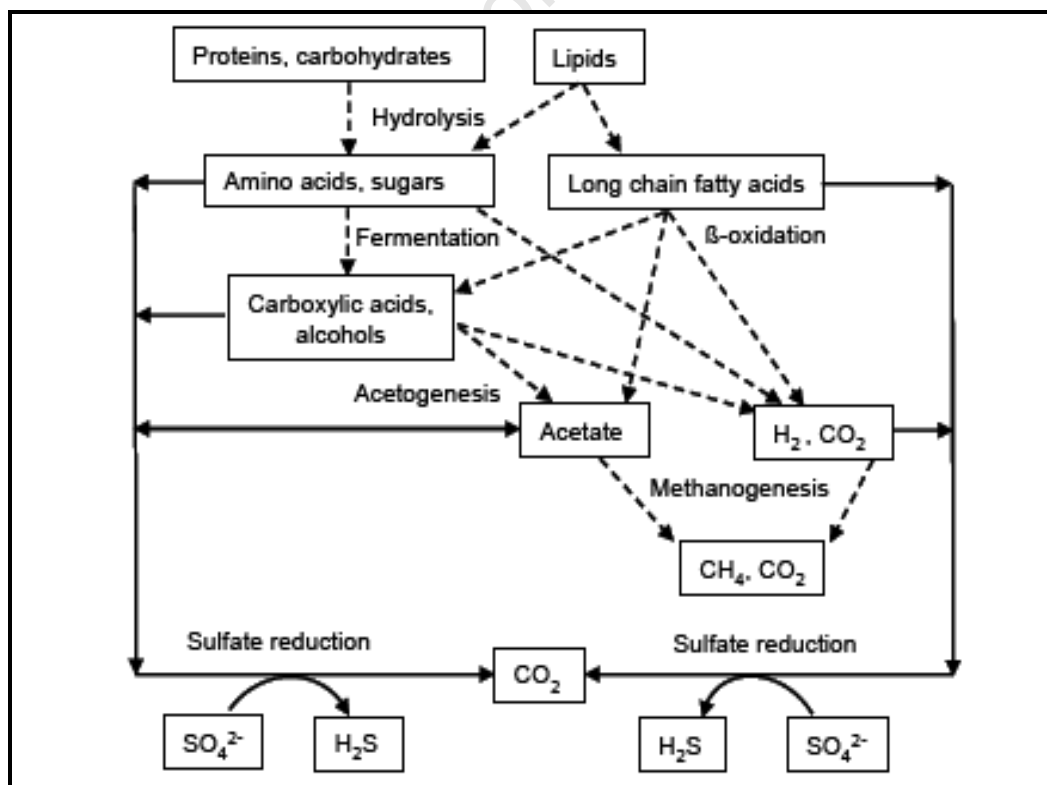


Figure 2.8: Anaerobic degradation of organic substrates by SRB using sulphate as electron acceptor (Visser, 1995).

2.8.2 Factors influencing the growth and activity of SRB

Beside anaerobic conditions, SRB have other specific environmental requirements that must be fulfilled in order for them to be effective. It is well known that parameters such as pH, temperature, heavy metals and sulphide concentrations affect the growth and activity of SRB. The effects of these environmental/operational factors on SRB are briefly reviewed in the following sections.

2.8.2.1 Effect of pH on SRB

The bioremediation of AMD represents a challenge because the acidic (pH = 2-3) nature of the water. This low pH may adversely affect the growth and activity of SRB. However, work from various researchers have shown that SRB can tolerate a wide range. Postgate (1984) reported that many species can tolerate pH values between 5 and 9.5, while Sen and Johnson (1999) isolated acidophilic SRB at pH 3.6 on solid growth medium. Though SRB (especially mixed SRB cultures) are acid-tolerant and are able to grow in low pH medium, there is a general consensus that the optimum pH for the growth of most known SRB is around 7 (Hao *et al.*, 1996).

2.8.2.2 Effect of sulphide concentration on SRB

Sulphide toxicity is dependent on the reactor pH. Sulphide can be present in different species namely as aqueous and gaseous hydrogen sulphide (H_2S), dissociated hydrogen sulphide (HS^-) and sulphide (S^{2-}). The state of these species is dictated by the pH in the reactor. At a pH of between 6 to 8, most of the sulphide concentration is in the H_2S and HS^- forms, whereas at a higher pH (>8), the HS^- and S^{2-} species predominate. The dissociation of hydrogen sulphide into HS^- and S^{2-} species follows the chemical equilibrium equations below.

$$K_1 = \frac{[HS^-][H^+]}{[H_2S]} \quad (2.11)$$

$$K_2 = \frac{[S^{2-}][H^+]}{[HS^-]} \quad (2.12)$$

The relationship between the sulphide species and pH is plotted using equations 2.11 and

2.12 as depicted in Figure 2.9.

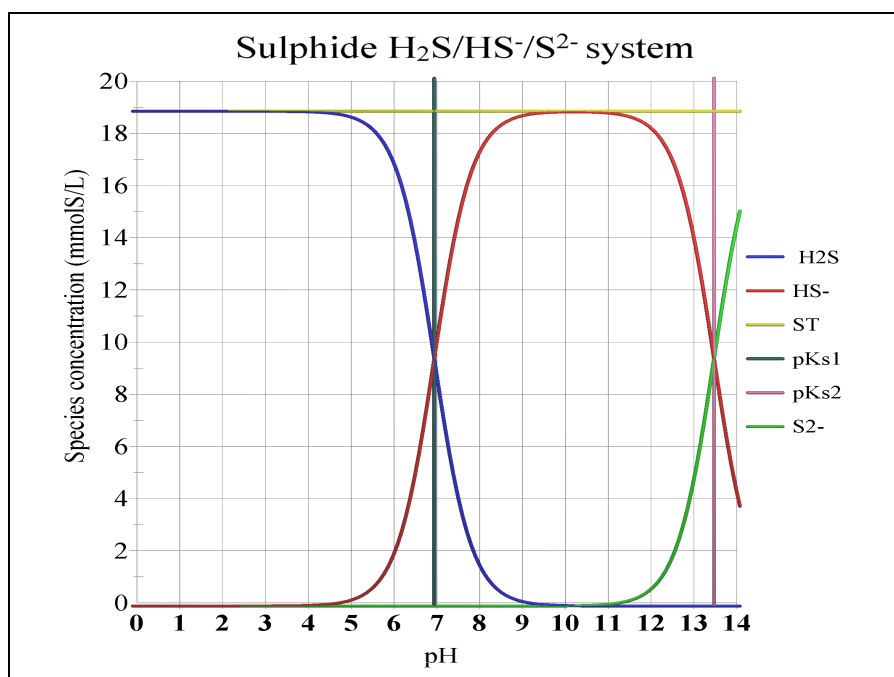


Figure 2.9: Distribution of sulphide species with pH at 25 °C.

Sulphide is strong toxicant for the majority of anaerobic bacteria including the Acetogenic, methanogenic and sulphidogenic bacteria. Because the pK value of the H₂S/HS⁻ subsystem is about 7 at mesophilic conditions, small pH variations can cause significant changes in the degree of inhibition. Sulphide inhibition on the activity and growth of SRB has been reported by various researchers. However, it is not easy to get a general consensus on the mechanism of sulphide toxicity, the inhibitory effects of the various forms of sulphide and their inhibition levels, as contradictory reports exist in the literature. With respect to the inhibitory mechanism, two hypotheses are stated. On the one hand, it has been reported that sulphide is absorbed into the cells and denatures the proteins thereby making the cell inactive (Postgate, 1984). If this is the case, the SRB should not be able to resume their activity once all the sulphide is stripped out, which is in contrast to the findings of Reis *et al.* (1992) who reported that the sulphide inhibition is reversible in SRB inoculated bioreactors. The second hypothesis is that the hydrogen sulphide in the reactor precipitates any metals present as metal sulphides. As a consequence, the SRB are deprived of essential trace element metals essential for their growth, thereby decreasing their activity (Bharathi *et al.*, 1990).

Further contradictions exist regarding the inhibitory concentration levels and also to whether

total sulphide (TS) or only undissociated H_2S is inhibitory (Visser, 1995). The inhibitory levels of sulphide on SRB growth, sulphate reduction and substrate degradation as reported by various researchers are summarised in Table 2.7.

Table 2.7: Inhibitory levels of sulphide (both TS and undissociated H_2S) as reported in the literature.

Bacterial group	Substrate	Reactor type and mode	Temperature (°C)	pH	TS (mgS/L)	H_2S (mgS/L)	Inhibition (%)	Reference
UASB sludge	Acetate	Batch reactor	30	7.5	569	107	50 ^a	Visser <i>et al.</i> (1996)
UASB sludge	Acetate	Serum bottle	-	7.2-7.4	615	161	50 ^b	Visser <i>et al.</i> (1996)
Anaerobic sludge	Acetate	Serum bottle	37	7.2	550	168	50 ^a	O'Flaherty <i>et al.</i> (1998)
				7.6	867	129		
Mixed SRB (granular)	Acetate	Shake flask batch	35	7.2-7.4	-	171	50 ^a	Visser (1995)
Mixed SRB (suspended)	Lactate	Shake flask batch	35	7.0	400	-	50 ^c	Hilton and Oleszkiewicz (1993)
Mixed SRB (suspended)	Lactate	Stirred tank reactor batch	35	7.2-7.6	-	80	50 ^c	Okabe <i>et al.</i> (1992)
Mixed SRB (suspended)	Lactate	Stirred tank reactor batch	35	8.0	-	185	50 ^c	McCartney and Oleszkiewicz (1993)
UASB sludge	Ethanol	UASB	35	7.1-8.0	1700-9951	570-610	50 ^c	Kalyuzhnyi <i>et al.</i> (1997)

2.8.2.3 Effect of temperature on SRB

Because of the biological nature of the anaerobic degradation of sulphate, there is a strong dependency of the process rate on the operating temperature. Based on their optimum growth temperature range, the SRB can be classified into mesophiles (growth temperature < 40 °C), moderate thermophiles (growth temperature: 40-60 °C) and extreme thermophiles (growth temperature > 60 °C).

In their experiments employing a mesophilic SRB, van Houten *et al.*, 1997; Weijma *et al.*, 2000, reported that sulphate reduction increased when the reaction temperature was increased from 20 to 32 °C. Rebac *et al.* (1996) reported that at a temperature ranging from 10 to 12 °C, organic loading rates of 10-12 kgCOD/m³/d can be achieved at hydraulic retention times of 1.6-2.5h in expanded granular bed reactors (with an upward velocity of 10 m/h). Thermophilic SRB may be an attractive alternative to mesophilic SRB for hot and

concentrated industrial wastewaters (Rintala *et al.*, 1991). The relationship between the reactor temperature and undissociated H₂S in the liquid is very important for successful treatment at high temperatures. Increased process temperature decreases the fraction of undissociated H₂S in the reactor liquid thereby shifting the gas-water partitioning towards the gas phase due to the lower solubility of H₂S. In thermophilic processes, the H₂S stripping effect caused by the high biogas production rates further decreases the liquid H₂S concentrations. This, therefore, allows for an increase in sulphate removal rate as reported by Visser *et al.* (1992); Rintala and Lettinga *et al.* (1992) who operated anaerobic reactors under thermophilic conditions with acetate at 55 °C. The optimum pH and temperature range together with the type of carbon sources for various genera of SRB are summarised in Table 2.8.

Table 2.8: Carbon source, pH and temperature range for growth of some SRB species (Widdel, 1988).

Genus	Carbon and energy source	pH		Temperature range (°C)
		Range	Optimum	
<i>Desulfobacter</i>	Acetate	6.2-8.5	7.3	28-32
<i>Desulfobulbus</i>	Propionate, lactate, pyruvate, ethanol, propanol	6.0-8.6	7.2	28-39
<i>Desulfococcus</i>	Formate, acetate, lactate, butyrate, pyruvate	-	-	30-36
<i>Desulfotomaculum</i>	Lactate, pyruvate, acetate, ethanol, hydrogen	-	-	-
<i>Desulfomonas</i>	-	6.5-8.5	7.2	30
<i>Desulfonema</i>	Acetate, malate, benzoate, pyruvate	-	-	-
<i>Desulfosarcina</i>	Formate, acetate, lactate, butyrate, propionate	6.9-7.0	7.4	33-38
<i>Desulfovibrio</i>	Lactate	7.5	-	25-35

2.8.2.4 Effect of heavy metals on SRB

The presence of high concentrations of heavy metals (such as lead, iron, zinc, copper and manganese) in AMD may be toxic or inhibitory to the activity of SRB. However, various studies have been reported where strains of SRB have been isolated that are capable of tolerating the presence of aluminium, lead, uranium, iron, chromium, copper, silver, nickel, manganese and cobalt at relatively high concentrations (Hard *et al.*, 1997; Garcia *et al.*, 2001). To alleviate the toxic effects of metals and increase the pH of AMD, some of the treated AMD can be recycled and mixed with the raw AMD (Glombitza, 2001; Rose *et al.*,

2002). As illustrated in the BioSURE[®] process design, the sulphide present in the treated AMD recycle stream will simultaneously precipitate any heavy metals present in the raw AMD and neutralise the pH ensuring suitable conditions for BSR in the subsequent reactor (refer to Figure 2.5).

2.9 MODELLING ANAEROBIC SYSTEMS

As mentioned earlier, the core unit process in the BioSURE[®] system is BSR with PSS. To aid the design, operation and control of (and research into) this unit process, a mathematical kinetic model would be an invaluable process evaluation tool. Mathematical models provide quantitative descriptions of the treatment system of interest that allow predictions of the system response and performance to be made. From these predictions, design and operational criteria can be identified to optimise the system performance. In addition, mathematical models are very useful as research tools. By evaluating the model predictions, it is possible to test hypotheses on the behaviour of the system (e.g. biological processes, their response to system constraints, etc.) in a consistent and integrated fashion. In essence, mathematical models provide an integrated mass balance based framework for the system which can give guidance to design, operation and research.

The development of a kinetic model describing the BSR unit process in the BioSURE[®] and similar systems has been undertaken by van Wageningen (2007) as the main objective of her research. This model will be updated in this present study to simulate the UASB BSR system taking due consideration of parameters such as undissociated H₂S inhibition and temperature.

The kinetic model UCTADM1-BSR is based on the UCTADM1 model developed by Sotemann *et al.* (2005a). Since the development, calibration and validation of UCTADM1-BSR are only recent, the model will be reviewed, fine-tuned and updated to improve its versatility. This exercise is conducted in Chapter 7 of this thesis where the model simulated results are also compared with the experimental UASB BSR data set.

To place the development and requirement of UCTADM1-BSR into context, an evaluation of existing kinetic models for anaerobic digestion with PSS would seem appropriate. These kinetic models are briefly described in the following sections with a particular focus on

UCTADM1 where appropriate mention will be made where this model differs from International Water Association (IWA) ADM1 (Batstone *et al.*, 2002).

2.9.1 Requirements for the kinetic model

The kinetic model for BSR with PSS, would need to incorporate the kinetics and stoichiometry for the two phase (aqueous-gas phase; the solid phase will be considered in future developments) chemical, physical and biological processes of importance in BSR with PSS. For the biologically mediated processes, the PSS first requires hydrolysis/solubilisation (usually the rate limiting step) and acidification, mediated by the acidogenic group of organisms. This rate limiting step generates the substrates for the subsequent processes and is common to sewage sludge methanogenic anaerobic digestion systems. Hence, the available kinetic models for methanogenic systems would seem a logical basis to start the development of the BSR model. The products of the hydrolysis and acidification processes, the volatile fatty acids (VFA), then can enter into the methanogenic or sulphidogenic processes, which essentially operate in competition. The end product of sulphate reduction is sulphide, which is inhibitory to the methanogens, requiring that this inhibition be included in the model. Further, the background weak acid/base chemistry would need to be included, since the biological processes consume and produce significant weak acid/base species, e.g. VFA, HCO_3^- and sulphide. The consumption and production of weak acid/base species will also influence the pH established in the reactor, which in turn will influence the rates of the biologically mediated processes. Hence, pH needs to be incorporated directly into the model, as a model predictive parameter, and its interaction with the biologically processes modelled. In addition, the gaseous equilibria of some of the end-products (sulphide, carbon dioxide and methane) need to be incorporated in the model.

2.9.2 Available anaerobic digestion models

Ristow *et al.* (2001) and Hansford (2004) developed a kinetic model for BSR in the RSBP reactor with PSS as substrate. In this model, the focus was on the biological processes and they excluded the chemical and physical processes which are of importance in BSR. They recognised that under steady state the hydrolysis of PSS was the rate-limiting step. However, they were not able to determine the most appropriate kinetic rate formulations for this rate controlling process (hydrolysis) since there was no consensus in the literature which was best. Due to these limitations, Ristow *et al.* (2005) undertook an extensive

investigation to describe and model the PSS hydrolysis step, under methanogenic, sulphidogenic and acidogenic conditions. They concluded that BSR does not affect the rate of PSS hydrolysis implying that the same methanogenic rate formulations and rate constants can be applied under BSR conditions. They also showed that for simple steady state models first order kinetics (which are analytically simpler to apply) for PSS hydrolysis are adequate, but that for more extensive kinetic models surface saturation (Contois) kinetics would be more suitable, in concordance with Vavilin *et al.* (2001) and later supported by Sötemann *et al.* (2005b)(see below).

The the IWA ADM1 (Batstone *et al.*, 2002), the substrate, in this case PSS, is characterised into carbohydrates, lipids and proteins. That is, in the characterisation of complex organics like PSS, the three organic types are generated in a disintegration step together with inert particulate and soluble compounds. The resultant carbohydrates, proteins and lipids are thereafter hydrolysed separately to their intermediate products (Figure 2.10). However, for PSS, measurements of carbohydrates, proteins and lipids and their COD equivalents are not routinely available, so a different approach was adopted for UCTADM1.

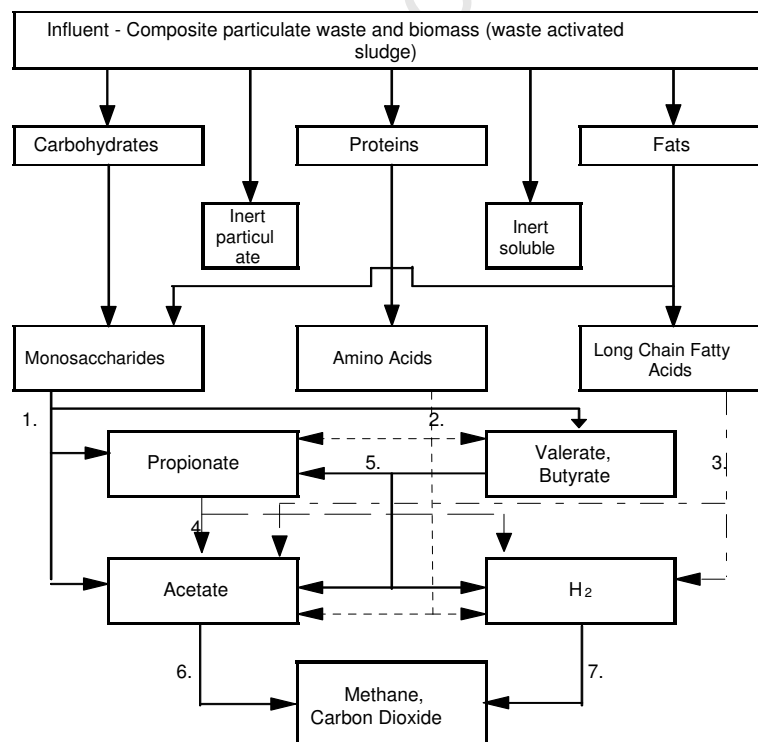


Figure 2.10: The ADM1 model (Batstone *et al.*, 2002) including biochemical processes: (1) Acidogenesis from sugars, (2) acidogenesis from amino acids, (3) acidogenesis from long chain fatty acids, (4) acetogenesis from propionate, (5) acetogenesis from butyrate and valerate, (6) acetoclastic methanogenesis, and (7) hydrogenotrophic methanogenesis.

In UCTADM1, initially developed by Van Rensburg *et al.* (2001) and extended and modified by Sötemann *et al.* (2005a) for methanogenic anaerobic digestion of sewage sludges, the influent PSS is characterised with the usual COD, TKN, TSS and VSS measurements and additional carbon, hydrogen and nitrogen (CHN) composition obtained from elemental analysis.

2.9.3 Development of the Univ. of Cape Town anaerobic digestion model No. 1 (UCTADM1)

Van Rensburg *et al.* (2001) and Sötemann *et al.* (2005a) integrated the biological kinetic processes for methanogenic anaerobic digestion (AD) into a two phase (aqueous-gas) subset of the three phase mixed weak acid/base chemistry kinetic model of Musvoto *et al.* (1997). The model, called UCTADM1, was implemented by Sötemann *et al.* (2005a) in the computer programme AQUASIM (Reichert, 1998). Thereafter, Sötemann *et al.* (2005a) calibrated and validated UCTADM1 with data from the laboratory mesophilic anaerobic digesters of Izzett *et al.* (1992) and O'Rourke (1968). The development of the model is briefly presented below with particular focus on its calibration and application.

2.9.3.1 Influent PSS organics characterisation

Sötemann *et al.* (2005a) followed the approach used for activated sludge simulation models (Wentzel *et al.*, 1990, 1992; Henze *et al.*, 1987) for characterising the PSS since the types of organics are common (Figure 2.11). This structure is based on COD units. Since the AD kinetic model by necessity was based on mole units (due to the requirement to include CO₂), conversion between the influent COD characterisation and the mole units was required to generate the input for the AD model.

For this conversion, Sötemann *et al.* (2005a) accepted that (i) the SCFA would be available from direct measurement and hence could be readily converted between mgHAc, mgCOD and mole units, (ii) the dissolved fermentable readily biodegradable COD would require quantification, but that its concentration relative to the biodegradable particulate organics is very small and hence with little error could be included with the biodegradable particulate organics, (iii) the unbiodegradable soluble COD concentration also was very low, and since it simply passes through the reactor, conversion to mole units is not required. Thus,

remaining are the unbiodegradable and biodegradable particulate organic fractions, which are the dominant ones in PSS. For these two fractions, Sötemann *et al.* accepted a generic organic composition $C_xH_yO_zN_a$ (McCarty, 1974) representing sewage sludge, with the stoichiometry determined from COD, TKN, FSA, TSS and VSS measurements on the PSS, C,H and N elemental analysis and product generation in the experimental systems. Because the unbiodegradable particulate organics remained unchanged through the digester, its composition does not need to be known. However, the division of the PSS particulates between the unbiodegradable and biodegradable fractions needed to be determined from analysis of experimental data from operating AD systems treating PSS.

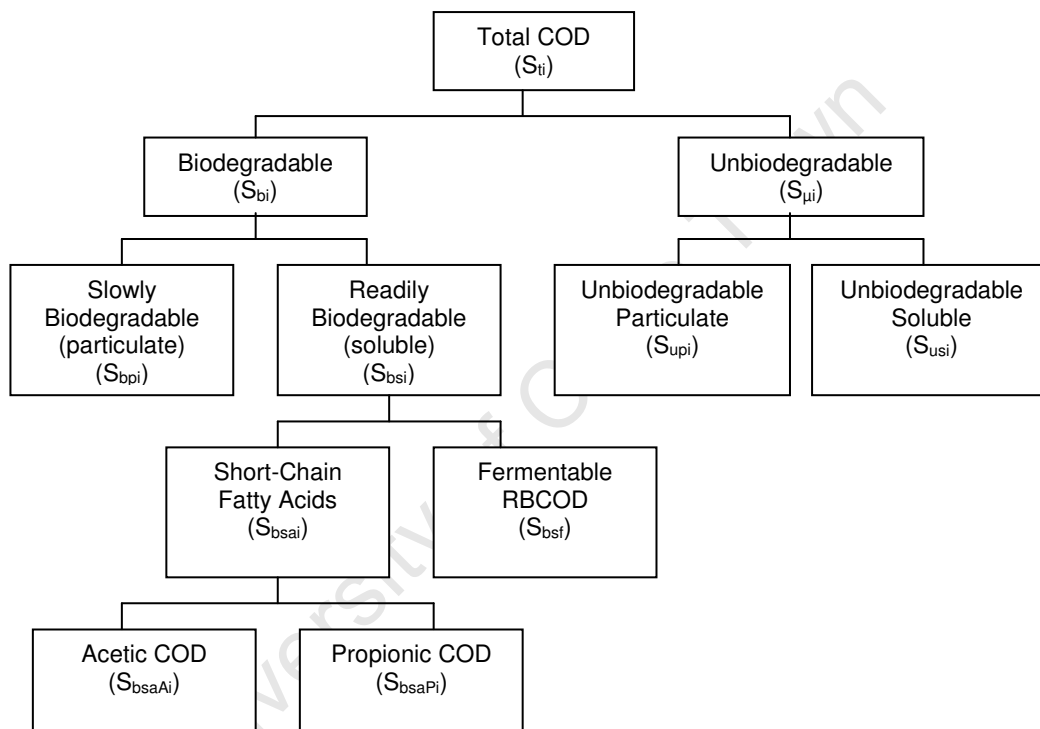


Figure 2.11: Schematic layout showing the characterisation of the influent sewage sludge organics, required as input to the model; the acetic and propionic acids require speciation from the influent pH.

2.9.3.2 Integrated chemical, physical and biological processes anaerobic digestion model

The integrated two phase (aqueous-gas) chemical, physical and biological processes anaerobic digestion model (UCTADM1) developed by Sotemann *et al.* (2005a) comprises:

- 1) the 16 forward and reverse chemical equilibrium dissociation (CED) processes (C1-C6, C9-C18) and their 13 associated compounds (C1-C2, C4-C14) – Table 1 in Musvoto *et al.* (1997). These are shown in Table 2.9.
- 2) the two forward and reverse CED processes for propionic acid (C46-C47) and their two associated compounds (C28-C29) (Table 2.10).
- 3) the three physical gas exchange processes of dissolution of CO₂ (P6) and its associated compound CO₂ gas (P1) and expulsion of CO₂ (P7) and expulsion of NH₃ (P8) and its associated compound NH₃ (C2) (Table 2.10).
- 4) the 10 biological processes for AD (D1-D10) and their 8 associated compounds (P4 and D1-D7) (Table 2.10).

Sotemann *et al.* (2005a) implemented the final model in the computer programme AQUASIM (Reichert, 1998).

Table 2.9: Matrix representation of the kinetic model for an aqueous mixture of weak acid/base systems. Exchange of CO_2 has also been included. (Note that the concentration of the compound CO_2 (g) is kept constant; It is included in the matrix only for continuity). Table 1 in Musvoto *et al.* (1997)

Compound → Process ↓	1 NH_4^+	2 NH_3	3 H_2CO_3^*	4 HCO_3^-	5 CO_3^{2-}	6 $\text{CO}_2(\text{g})$	7 H^+	8 OH^-	9 H_3PO_4	10 H_2PO_4^-	11 HPO_4^{2-}	12 PO_4^{3-}	13 HA	14 A^-	15 Ca^{2+}	Rate
Forward dissociation of NH_4^+	-1	1					1									$K'_{\text{fn}}[\text{NH}_4^+]$
Reverse dissociation of NH_4^+	1	-1					-1									$K'_{\text{rn}}[\text{NH}_3][\text{H}^+]$
Forward dissociation of H_2CO_3^*			-1	1			1									$K'_{\text{fc1}}[\text{H}_2\text{CO}_3^*]$
Reverse dissociation of H_2CO_3^*			1	-1			-1									$K'_{\text{rc1}}[\text{HCO}_3^-][\text{H}^+]$
Forward dissociation of HCO_3^-				-1	1		1									$K'_{\text{fc2}}[\text{HCO}_3^-]$
Reverse dissociation of HCO_3^-				1	-1		-1									$K'_{\text{rc2}}[\text{CO}_3^{2-}][\text{H}^+]$
Dissolution of CO_2			1			-1										$K'_{\text{fo2}}[\text{CO}_2(\text{g})]$
Expulsion of CO_2 from solution			-1			1										$K'_{\text{ro2}}[\text{H}_2\text{CO}_3^*]$
Forward dissociation of H_3PO_4							1		-1	1						$K'_{\text{fp1}}[\text{H}_3\text{PO}_4]$
Reverse dissociation of H_3PO_4							-1		1	-1						$K'_{\text{rp1}}[\text{H}_2\text{PO}_4^-][\text{H}^+]$
Forward dissociation of H_2PO_4^-							1			-1	1					$K'_{\text{fp2}}[\text{H}_2\text{PO}_4^-]$
Reverse dissociation of H_2PO_4^-							-1			1	-1					$K'_{\text{rp2}}[\text{HPO}_4^{2-}][\text{H}^+]$
Forward dissociation of HPO_4^{2-}							1				-1	1				$K'_{\text{fp3}}[\text{HPO}_4^{2-}]$
Reverse dissociation of HPO_4^{2-}							-1				1	-1				$K'_{\text{rp3}}[\text{PO}_4^{3-}][\text{H}^+]$
Forward dissociation of HA							1						-1	1		$K'_{\text{fa}}[\text{HA}]$
Reverse dissociation of HA							-1						1	-1		$K'_{\text{ra}}[\text{A}^-][\text{H}^+]$
Forward dissociation of water							1	1								K'_{fw}
Reverse dissociation of water							-1	-1								$K'_{\text{rw}}[\text{H}^+][\text{OH}^-]$
Units	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	

Table 2.10: Petersen matrix representation of the biological processes and associated compounds of the Univ. of Cape Town, Anaerobic Digestion Model No 1 (UCTADM1). Influent sewage sludge concentration is in mol/L; this concentration was calculated from the measured COD concentration of the sludge and the sludge composition formula $C_xH_yO_zN_a$ with measured values of x, y, z and a, Table 2.2 in Sötemann *et al.* (2005a).

	Number	C1	C2	C3	C7	C13	C28	C29	P1 ^a	P4	D1	D2	D3	D4	D5	D6	D7	
	Compounds	NH ₄ ⁺	NH ₃	H ₂ CO ₃ [*]	H ⁺	HAc	HPr	Pr ⁻	CO ₂	CH ₄	C _x H _y O _z N _a	C ₆ H ₁₂ O ₆	H ₂	Z _{AD}	Z _{AC}	Z _{AM}	Z _{HM}	
No	Processes		Dslvd	Dslvd					Gas	Gas	S _{bp}	S _{bsf}	Dslvd	Acido-gens	Aceto-gens	AMs	HMs	Process rates
C46	Forward dissociation of HPr				1		-1	1										K _{IPr} [HPr]
C47	Reverse dissociation of HPr				-1		1	-1										K _{Pr} [Pr ⁻][H ⁺]
P6 ^a	Dissolution of CO ₂ gas			1					-1									K _{CO2} (pCO ₂)(K _{HCO2})
P7 ^a	Expulsion of CO ₂ gas			-1					1									K _{CO2} [H ₂ CO ₃ [*]]
P8 ^a	Expulsion of NH ₃ gas		-1															K _{NH3} [NH ₃]
D1	Hydrolysis		S1	S2							-1	S3						Eq. 8d in Sötemann <i>et al.</i> (2005a)
D2	Acidogenesis (low pH ₂)	-1		S4	1	S5						-1/Y _{AD}	S6	1				Eq. 9 in Sötemann <i>et al.</i> (2005a)
D3	Acidogenesis (high pH ₂)	-1		S7	1	S8	S9					-1/Y _{AD}	S10	1				Eq. 10 in Sötemann <i>et al.</i> (2005a)
D4	Acidogen endogenous decay		S11	S12							S13			-1				b _{AD} [Z _{AD}]
D5	Acetogenesis	-1		S14	1	S15	-1/Y _{AC}						S16		1			Eq. 11 in Sötemann <i>et al.</i> (2005a)
D6	Acetogen endogenous decay		S11	S12							S13				-1			b _{AC} [Z _{AC}]
D7	Acetoclastic methanogenesis	-1		S17	1	-1/Y _{AM}				S18						1		Eq. 12 in Sötemann <i>et al.</i> (2005a)
D8	Acetoclastic methanogen endogenous decay		S11	S12							S13					-1		b _{AM} [Z _{AM}]
D9	Hydrogenotrophic methanogenesis	-1		S19	1					S20			-1/Y _{HM}				1	Eq. 13 in Sötemann <i>et al.</i> (2005a)
D10	Hydrogenotrophic methanogen endogenous decay		S11	S12							S13						-1	b _{HM} [Z _{HM}]
	Units	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	
	gCOD/mol	-	-	-	-	64	112	112	0	64	131.3 ^b	192	16	160	160	160	160	
	gN/mol	14	14	-	-	-	-	-	-	-	2.744	-	-	-	-	-	-	
	gH ₂ CO ₃ [*] as CaCO ₃ /mol	-	-	0	-50	-	-	-	-	-	-	-	-	-	-	-	-	

a: These processes and compound were included in the models of Musvoto *et al.* (1997, 2000) as follows: Processes P6 was C7, P7 was C8, and P8 was C46 and compound P1 was C6.

Because the matrix units are mol/L summing the stoichiometry across each process does not yield zero. However, if each stoichiometric value is multiplied by the compounds' gCOD/mol ratio and then summed across the process, zero is obtained, i.e. COD balances across each process. Also, C, N, O and H mass balances across each process.

b: This is the gCOD/mol for the primary sludge CHON content measured and predicted in this investigation, i.e. C_{3.5}H₇O₂N_{0.196}.

All the S coefficients (i.e. S1 to S20) are stoichiometric formulae in Sötemann *et al.* (2005a).

2.9.3.3 Model calibration

In calibrating the model, Sötemann *et al.* (2005a) noted that the kinetic constants required for the chemical and physical processes part of the model are the equilibrium constants (pK) of the six weak acid/base systems, Henry's law constant for CO₂ (K'_{H,CO_2}), and the apparent reverse dissociation and expulsion rate constants (K'_r) respectively for these processes. Sötemann *et al.* obtained the equilibrium constants (pK) and Henry's law constant for CO₂ (K'_{H,CO_2}), and their temperature sensitivity equations from the literature (from Table 2c of Musvoto *et al.*, 1997 – 1940s database). They accepted the pK value for propionic acid (pK_{Pr}) to be the same as for acetic acid, given by $pK_{Pr} = 1170.5/T_k - 3.165 + 0.0134T_k$, where T_k = temperature in Kelvin. The weak acid/base apparent reverse dissociation rate constants (K'_r) were obtained from Table 2a in Musvoto *et al.* (1997) and were set at very high values to ensure that aqueous chemical equilibrium conditions are established very rapidly at every time step of the simulation (<2 sec), e.g. ammonia $K'_{rN} = 10^{12}/d$.

In the biological processes part of the model, the kinetic and stoichiometric constants (Y , μ_{max} , K_S and b) for the four AD organism groups were required. Sötemann *et al.* (2005a) found that there is considerable variation and hence uncertainty in these values in the literature. Recognising this uncertainty, they accepted values for these constants from Sam-Soon *et al.* (1991), who obtained their values from a survey of the literature. Where specific weak acid/base species are included in the rate formulation (e.g. acetoclastic methanogenesis), Sötemann *et al.* appropriately adjusted the rate constants (e.g. Monod half saturation coefficients) to take into account weak acid/base speciation. This was done via the relevant pK values and pH. In application, the maximum specific growth rate of the acetoclastic methanogens ($\mu_{max,AM}$ in Equation (4.20) (in Sötemann *et al.*, 2005a)) was increased by Sötemann *et al.* from the range of 0.3 – 0.5/d used by Sam-Soon *et al.* (1991) to 4.39/d. This was necessary to reproduce the observed low HAc/Ac⁻ residual concentrations under stable steady state; they found that due to the low HAc/Ac⁻ concentrations, since the kinetic rates are formulated in terms of HAc, decreasing the half saturation constant ($K_{S,AM}$ in Equation (4.20) in Sötemann *et al.*, 2005a), which would have been an intuitively more satisfying alternative, caused instability in solution procedures. Thus, all the kinetic and stoichiometric constants in the model, except those for hydrolysis, were obtained from the literature so that the model calibration was reduced to determining (i) the unbiodegradable particulate COD fraction of the feed sewage sludge (f_{PSup}), (ii) the

hydrolysis kinetics formulation and associated constants and (iii) the sewage sludge CHON composition, i.e. the X, Y, Z and A values in $C_XH_YO_ZN_A$. These three components were determined interactively and iteratively through calculation and simulation of the data from experimental methanogenic AD systems.

2.9.3.4 Model application

The experimental data of Izzett *et al.* (1992) were identified as most appropriate for (i) identifying the hydrolysis kinetics and (ii) unbiodegradable fraction of the PSS (f_{PSup}) because the COD and N mass balances of the experimental data were good (107-109% and 91-99% respectively). The unbiodegradable particulate fraction of the sewage sludge was determined at 0.36 though the value varied from 0.32 to 0.36 depending on the kinetic formulation selected for hydrolysis. From influent sludge COD, TKN and C masses of the Izzett *et al.* data, and AD system product generation (Alk, FSA, CH_4 , CO_2) the stoichiometric composition of the influent biodegradable and unbiodegradable sewage sludge was estimated to be $C_{3.4}H_7O_2N_{0.192}$.

For the selected hydrolysis kinetics (surface mediated reaction (Contois)), with a single set of kinetic and stoichiometric constants, reasonable correlation was obtained between predicted and measured results for all retention times (7 to 20 days) for (i) COD (ii) free and saline ammonia (FSA), (iii) short chain fatty acids (SCFA), (iv) H_2CO_3 alkalinity and (v) pH of the effluent stream, and (vi) CO_2 and (vii) CH_4 gases in the gas stream (see Figure 2.12). Elemental analysis of PSS from two Cape Town wastewater treatment plants ranged between $C_{3.38}H_7O_{1.91}N_{0.21}$ and $C_{3.91}H_7O_{2.04}N_{0.16}$. The predicted PSS composition based on influent measurements and mass balances in model application was within 5 % of the average measured composition, providing persuasive validation of the model.

Because the system governing reaction was the hydrolysis process, a steady state model for AD of PSS was also developed (Sötemann *et al.* 2005b). This model comprises 3 parts (i) a COD based kinetic art from which the concentration of biodegradable PSS hydrolysed is calculated (ii) a C, H, O, N, COD and charge balanced stoichiometric part which transforms the AD reactant ($C_XH_YO_ZN_A$) of the biodegradable organics hydrolysed to AD products (biomass, dissolved CO_2 (HCO_3^-), gaseous CO_2 , CH_4 and ammonia), and (iii) an inorganic

carbon weak acid/base chemistry part from which the digester pH is calculated from the dissolved CO_2 and partial pressure of the headspace products.

This steady state model, once calibrated to the same unbiodegradable organics composition ($\text{C}_x\text{H}_y\text{O}_z\text{N}_a$), yields very similar results as the simulation model (Fig. 2.12). This steady state methanogenic AD model will form a basis to develop a BSR steady state model.

Similarly, Ristow *et al.* (2006) applied the kinetic model to the methanogenic experimental systems of Ristow *et al.* (2005), for example see Figure 2.13. For the hydrolysis kinetics, again Contois kinetics were found to be applicable, but the specific rate constants for hydrolysis had to be significantly increased compared with the value for the Izzett *et al.* (1992) systems. Sötemann *et al.* concluded that this was because the Ristow *et al.* systems were operated with “pure” PSS, whereas the Izzett *et al.* systems received a PSS and humus sludge mixture from the Potsdam trickling filter plant Milnerton, Cape Town. This was also found by Sötemann *et al.* (2005a) in their steady state methanogenic AD model development – the “pure” PSS of O’Rourke (1968) had a much higher hydrolysis rate than the Izzett *et al.* sludge. For the unbiodegradable fraction of the PSS, all three data sets gave closely the same value of 0.33 to 0.36. For the Ristow *et al.* data, this was found to be 0.335 from a 60 d retention time digester. Following the procedure described above for the Izzett *et al.* PSS characterisation, the average stoichiometric CHON composition for the Ristow *et al.* (2005) PSS was determined as $\text{C}_{4.17}\text{H}_7\text{O}_{2.63}\text{N}_{0.21}$ which is reasonably close to the value determined for the Izzett *et al.* data. From the above model applications, it was concluded that the COD, C, O, H, N and charge mass balance and continuity basis of the model fixes quantitatively, via the interrelated chemical, physical and biological processes, the relationship between all the reactants (inputs) and products (outputs) of the system. Hence, for a given sewage sludge biodegradation, the digester outputs (products i.e. effluent COD, TKN, FSA, SCFA, H_2CO_3 Alk, pH gaseous CO_2 and CH_4 production and partial pressures) are governed completely by the input sludge (and aqueous) characteristics (reactants).

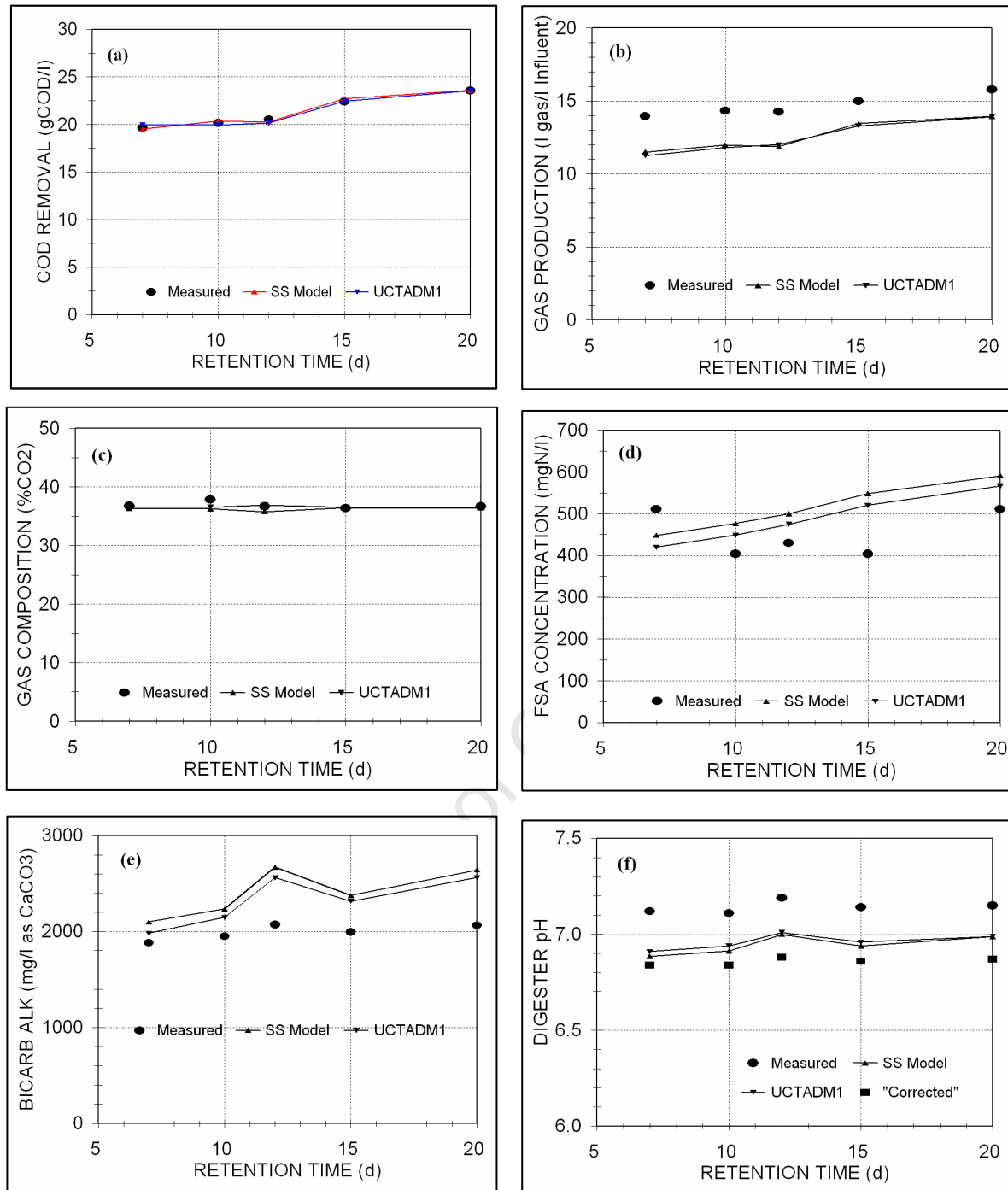


Figure 2.12: Comparison between kinetic simulation model (UCTADM1) predicted (lines) and measured (points) (a) COD removal, (b) gas production, (c) gas composition, (d) free and saline ammonia, (e) H_2CO_3^* alkalinity and (f) digester pH versus retention time for the Izzett *et al.* (1992) data set; also shown are the predictions of the steady state AD model.

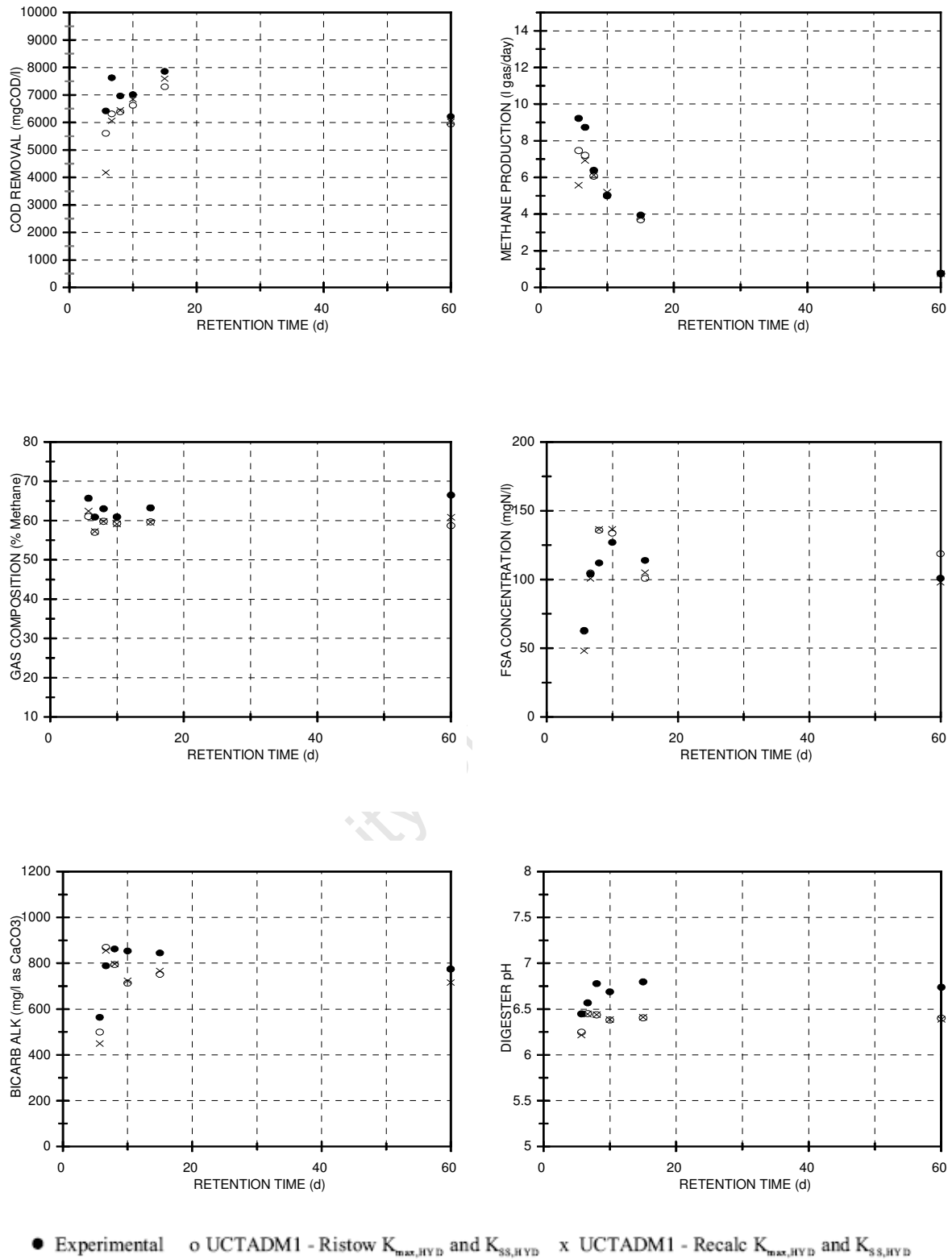


Figure 2.13: Comparison between kinetic simulation model (UCTADM1) predicted and measured (a) COD removal, (b) gas production, (c) gas composition, (d) free and saline ammonia, (e) $H_2CO_3^*$ alkalinity and (f) digester pH versus retention time for the Ristow *et al.* (2005) data set for feed COD concentrations between 9 and 13 gCOD/L.

Sötemann *et al.* (2005a) successfully integrated in a kinetic simulation model, the two phase mixed weak acid/base chemistry and biological processes for methanogenic AD and included the physical processes for gas exchange. This has provided a sound basis for further model development, and hence this model was selected for adding the BSR processes. This requires modelling the BSR processes with the same level of detail as the methanogenic processes.

Accordingly, the model of Sötemann *et al.* (2005a) (UCTADM1) was selected as the basis for the development of the kinetic model for BSR with PSS as substrate. This will require development of the kinetics and stoichiometry for the biological, chemical and physical processes in BSR in two phases (aqueous-gas), and integration of these with UCTADM1, taking due cognisance of any interactions introduced with the integration. Essentially, this will result in a two phase biological, chemical and physical processes model for the AD of PSS, with competitive methanogenesis and sulphidogenesis.

2.10 SULPHATE REDUCTION

Since UCTADM1 includes the processes common to methanogenic and sulphidogenic anaerobic digestion of sewage sludge, namely the biological processes of hydrolysis, acidogenesis and acetogenesis, the chemical processes for the weak acid/base chemistry and the physical processes for gas exchange, it was selected for the development of the kinetic model for BSR with PSS. In addition, the model which includes the biological methanogenesis processes would allow modelling of competitive methanogenesis and sulphidogenesis. In extending UCTADM1 for BSR, the BSR processes for inclusion needed to be identified. Moreover, the interactions of BSR with the weak acid/base chemistry and physical gas exchange processes, and with the methanogenic anaerobic digestion processes already in UCTADM1 needed to be included (van Wageningen, 2007). To identify the relevant BSR processes, available models for BSR in the literature were evaluated. The model set developed by Kalyuzhnyi and Fedorovich (1997) and Kalyuzhnyi *et al.* (1998) and that of Ristow *et al.* (2001) and Hansford (2004) appear suitable and appropriate. Both groups of researchers extensively reviewed and summarised previous models of BSR processes, adopting generally accepted principles from these preceding models and modifying and extending the processes, kinetics and stoichiometry where

appropriate. Therefore, only these models from the two research groups will be reviewed in this study.

Kalyuzhnyi, Fedorovich and co-workers developed a model for BSR in reactors fed with sucrose, butyrate, propionate and acetate as influent substrates. They focussed on modelling sulphide inhibition of the biological processes, and competition between methanogenesis and sulphidogenesis. In their review of the preceding models, they noted that only a few models for sulphidogenic systems had been developed, and identified the models of Gupta *et al.* (1994) and Vavilin *et al.* (2001) as of importance. Drawing information from these models and on BSR processes, kinetics and stoichiometry in the literature, they identified initially 7 (Kalyuzhnyi and Fedorovich, 1997) and later 9 (Kalyuzhnyi *et al.*, 1998) trophic groups of bacteria for inclusion in a competitive methanogenic and sulphidogenic model (1 fermentative, 2 acetogenic, 4 SRB, 2 methanogenic bacteria). The main features of the kinetic description for the processes mediated by these groups as noted by Kalyuzhnyi *et al.* (1998) are as follows:

1. Growth is according to Monod kinetics with inhibition by undissociated H_2S , and a Monod function for sulphate limitation for the SRB.
2. Effect of pH on the growth rates was included, by means of a bell-shaped pH function.
3. H_2S inhibition was according to first order inhibition kinetics.
4. Biomass production was directly linked to the substrate consumption.
5. Bacterial decay was via first order kinetics.
6. Maintenance substrate consumption was incorporated in a true yield.
7. Sulphate consumption for growth was considered negligible.
8. Diffusion effects were accepted to be constant and lumped into the constants.

For the weak acid/base chemistry, based on the work of Gupta *et al.* (1994) and Vavilin *et al.* (2001), equilibrium chemistry was used to speciate the weak acids/bases of importance and the charge balance used to determine H^+ and associated pH. The weak acid/base subsystems considered were water, phosphate, propionate, butyrate, HS^-/S^{2-} for the sulphide and HCO_3^-/CO_3^{2-} for the carbonate. For the physical processes, gas exchanges for H_2S , CH_4 and CO_2 were included via conventional gas-liquid mass transfers.

The above model processes were applied to completely mixed (Kalyuzhnyi and Fedorovich, 1997) and UASB (Kalyuzhnyi *et al.*, 1998) reactors, the latter application to simulate the concentration gradients that develop along the axis of flow in UASB type systems. Values for kinetic and stoichiometric constants were drawn from the literature. Model applications to experimental data from the literature indicated reasonable agreement between predicted and measured values.

Fedorovich *et al.* (2003) extended Anaerobic Digestion Model No. 1 (ADM1) (Batstone *et al.*, 2002) for methanogenic systems to systems with sulphate reduction. This extension maintained the structure of ADM1 and included additional blocks describing the sulphate reducing processes (multiple reaction stoichiometry, microbial growth kinetics, conventional material balances for ideally mixed reactor, liquid-gas interactions and liquid-phase equilibrium chemistry) drawn from their preceding model developments described above. Fedorovich *et al.* (2003) applied this extended model to describe a long term experiment on sulphate reduction in a volatile fatty acid-fed, UASB reactor. The model was generally able to predict the outcome of competition between acetogenic bacteria, methanogenic bacteria and sulphate reducing bacteria for these substrates. The computer simulations also showed that when the upward liquid velocity in the UASB reactor exceeds 1m/d, the structure of the sludge floc becomes critical due to bacterial detachment.

The models of Kalyuzhnyi, Fedorovich and co-workers form an extremely useful synthesis of the proceeding kinetics and stoichiometry of the processes acting in BSR systems, and address additionally the issues of sulphide and pH inhibition of the biological processes and accordingly have been used extensively for the BSR part of the UCTADM1-BSR model to be reviewed and updated in this study. However, the Kalyuzhnyi, Fedorovich and co-workers models do not address the situation where PSS serves as substrate, of particular importance here, and the use of the charge balance for solution of pH can present problems particularly if mineral precipitations are to be included in the model in future, which is an intention of the Water Research Group at the University of Cape Town. To resolve these difficulties, in these aspects the model of Sötemann *et al.* (2005a) appeared preferable (van Wageningen, 2007).

Ristow *et al.* (2001) drew substantially from the models of Kalyuzhnyi, Fedorovich and co-workers and the work of O'Rourke (1968), Eastman and Ferguson (1981), Gujer and

Zehnder (1983) and Costello *et al.* (1991) to develop a kinetic simulation model for the recycling sludge bed reactor (RSBR) with PSS as substrate. They selected the RSBR configuration since at the time it was proposed as the PSS hydrolysis / BSR core unit process in the BioSURE[®] system for AMD treatment developed at Rhodes University, South Africa (Rose *et al.*, 2002). The RSBR aimed principally to hydrolyse the PSS to generate substrates for the subsequent treatment in a downstream reactor of the sulphate component of AMD by means of BSR. However, some BSR was to be achieved in the RSBR due to the recycle implemented. In this system, Ristow and co-workers recognised that the PSS hydrolysis would be of considerable importance since this is the rate limiting step. Hence, they included PSS hydrolysis in their model, by dividing the PSS into carbohydrates, lipids and proteins with kinetics and stoichiometry included for the hydrolysis of each of these organic groups. For the hydrolysis kinetics, they used separate first order formulations with respect to the concentration of the specific organic group, in accordance with O'Rourke (1968). However, they noted that there was a variety of kinetic rate formulations for hydrolysis available in the literature and were not able to determine the most appropriate kinetic rate formulation for this crucial process.

Recognising the limitations and deficiencies in models describing PSS hydrolysis, Ristow *et al.* (2005) undertook an extensive investigation to describe and model the PSS hydrolysis step, under methanogenic, sulphidogenic and acidogenic conditions. The work of Ristow *et al.* (2005) is of significance in that it demonstrates that rate formulations and constants developed for PSS hydrolysis under methanogenic anaerobic digestion conditions can be applied under sulphidogenic conditions also.

2.11 INTRODUCTION TO THE UCTADM1-BSR MODEL

This current investigation forms part of a greater objective to treat AMD using cost-effective carbon sources. In parallel to this present study, van Wageningen (2007), undertook as the main objective of her Masters research, the task of developing a kinetic model for BSR (UCTADM1-BSR) using PSS. This model will be updated and applied to model the UASB BSR system performance as one of the objectives of this present research. The UCTADM1-BSR was developed by extending the UCTADM1 to incorporate BSR. The stoichiometry and kinetics for the bioprocesses (growth and death) mediated by the propionate degrading, acetotrophic and hydrogenotrophic sulphate reducing bacteria were

formulated. These bioprocesses produce and consume *inter alia* sulphate and sulphide acid/base species which were not present in the original UCTADM1 model. Accordingly, following the approach in the UCTADM1 model, chemical processes for these were included. Further, in the BSR model the end product sulphide has a gaseous equilibrium not included in the UCTADM1 model, to give a complete kinetic model for competitive methanogenic and sulphidogenic anaerobic digestion with sewage sludge as substrate. Van Wageningen (2007) calibrated and validated the model using the Ristow *et al.* (2005) sulphidogenic completely mixed reactor AD data set.

The kinetic model UCTADM1-BSR developed by van Wageningen (2007) will be updated in this investigation by including sulphide (namely undissociated H_2S) and pH inhibition. Moreover, a temperature function will also be included to simulate the effect of temperature on BSR. Thereafter, the model will be verified, calibrated and validated, after which, it will be used to model the UASB BSR system performance.

2.12 CLOSURE

Based on a literature survey, the formation and treatment of AMD have been described briefly. The existing treatment (physical, chemical and biological) technologies were reviewed in order to place into context the system of particular interest in this research, namely the BioSURE[®] system. It was found that among the various treatment processes, sulphate removal by biological sulphate reduction (BSR) is the most attractive and efficient. The major advantages of BSR are: (i) both sulphate and trace metals can be reduced to very low concentrations; (2) the amount of waste produced is minimal; (3) capital cost is relatively low and operating costs can be drastically reduced by the development of inexpensive carbon sources; (4) trace metals in mine drainage can be selectively recovered and sold for additional savings. These therefore highlighted the significant potential for BSR in AMD remediation and showed that the most significant factor driving the BSR process, both economically and technically, is the source and nature of the organic substrate. Conventionally, a variety of organic substrates such as molasses, ethanol, acetate, lactate (or cheese whey) and producer gas (CO_2 & H_2) have been successfully used for BSR. However, these organics are relatively expensive, making AMD remediation via BSR costly. To reduce overall cost, the BioSURE[®] process has been developed in which BSR is achieved using PSS as the organic carbon source and electron donor. In addition, this

process offers as option the use of the biogenerated sulphide (from sulphate reduction) for metal recovery via selective metal sulphide precipitation. PSS is freely available as a by-product at municipal wastewater treatment plants, and thus this co-disposal system proposes an elegant solution to BSR. Accordingly, attention has been focused on this system with the objective of changing the initial RSB configuration into the (upflow anaerobic sludge bed) UASB reactor configuration.

To aid the design, operation and control of the system, and improve understanding of the underlying processes, a mathematical simulation model would be an invaluable tool. To gather information for developing such a model, relevant available models have been reviewed. From this review, the models of Sötemann *et al.* (2005a), Kalyuzhnyi, Fedorovich and co-workers (Fedorovich *et al.*, 2003) and Ristow and co-workers (Ristow *et al.*, 2005) appear suitable. These models provide virtually all the necessary building blocks for development of an integrated two-phase (aqueous-gas), biological, chemical and physical processes kinetic model for competitive methanogenic and sulphidogenic anaerobic digestion with PSS as substrate. This model (called the UCTADM1-BSR) was recently developed by van Wageningen (2007) and will be reviewed, fine-tuned and updated to simulate the performance of the UASB BSR systems operated in this present investigation. This aspect is described in Chapter 7.

Chapter 3

Materials and Methods

3.1 INTRODUCTION

As highlighted in Chapter 1, one of the objectives of this investigation is to assess various operating parameters influencing biological sulphate reduction (BSR) using primary sewage sludge (PSS) as carbon source in order to optimise the system. These parameters are the reactor hydraulic retention time (HRT), bed hydraulic retention time (BRT), substrate loading rate (both feed COD and sulphate), influent pH, reactor temperature, sludge settleability and the effect of recycling biomass/sludge from top to bottom of the sludge bed. In order to evaluate the above, two upflow anaerobic sludge bed (UASB) reactors were operated at laboratory scale and the required experimental data were collected. This chapter describes the set-up, operation and monitoring of these reactors and the analytical procedures used to gather the experimental data.

3.2 REACTOR DESIGN AND EXPERIMENTAL SET-UP

Two identical lab-scale UASB reactors (designed R1 and R2) were constructed from Perspex tubes and fitted with Perspex lids and base-plates. Both UASB reactors had a total volume of 9.1 L with an internal diameter of 93mm and height 1330mm. The reactors were completely sealed so that any gas produced could be collected and channelled to the necessary gas collector. The reactors were fitted with a speed regulator base-mounted motor (0.1 kW) rotating a vertical stainless steel shaft with 2 adjacent stainless steel rods connected to it. The shafts were set to rotate together with the rods for 5 revolutions every 5 minutes, hence mixing and agitation inside the reactors were mild. This was desirable since the only purpose of internal mixing was to facilitate the hydrogen sulphide (H_2S) gas produced to escape without impeding the sludge bed. It was anticipated that hydrogen gas bubbles would lift the sludge and consequently break the sludge bed column into fractions and cause bed separation and instability. Effluent draw-off was subsurface via an inverted

'U'-tube which could be adjusted to control the reactor liquid volume. The effluent draw-off pipe was channelled into an effluent collection vessel. After some trials, the liquid volume for both reactors was eventually fixed to 8.4L while the effluent draw-off point was at 7.8L, leaving a head-space of 0.7L (total UASB reactor volume = 9.1L). This set-up was necessary to allow the gas bubbles formed in the reactor to go to the head space rather than escaping through the effluent draw-off point. Sampling ports were designed at 10cm height intervals from bottom to top of the reactors. The reactor R1 was heated to approximately 35 °C with heating wires wrapped around the column, with a thermocouple inserted into one of the sample ports of the reactor and connected to a temperature controller. The reactor R2 was not heated, but operated at 20 °C, the ambient temperature of the constant temperature laboratory. Figure 3.1 below shows a schematic diagram of the reactor lay-out as set up during the experimental investigation. Figures 3.2a & 3.2b illustrate the reactor lay-out as set up in the laboratory with and without heating coils.

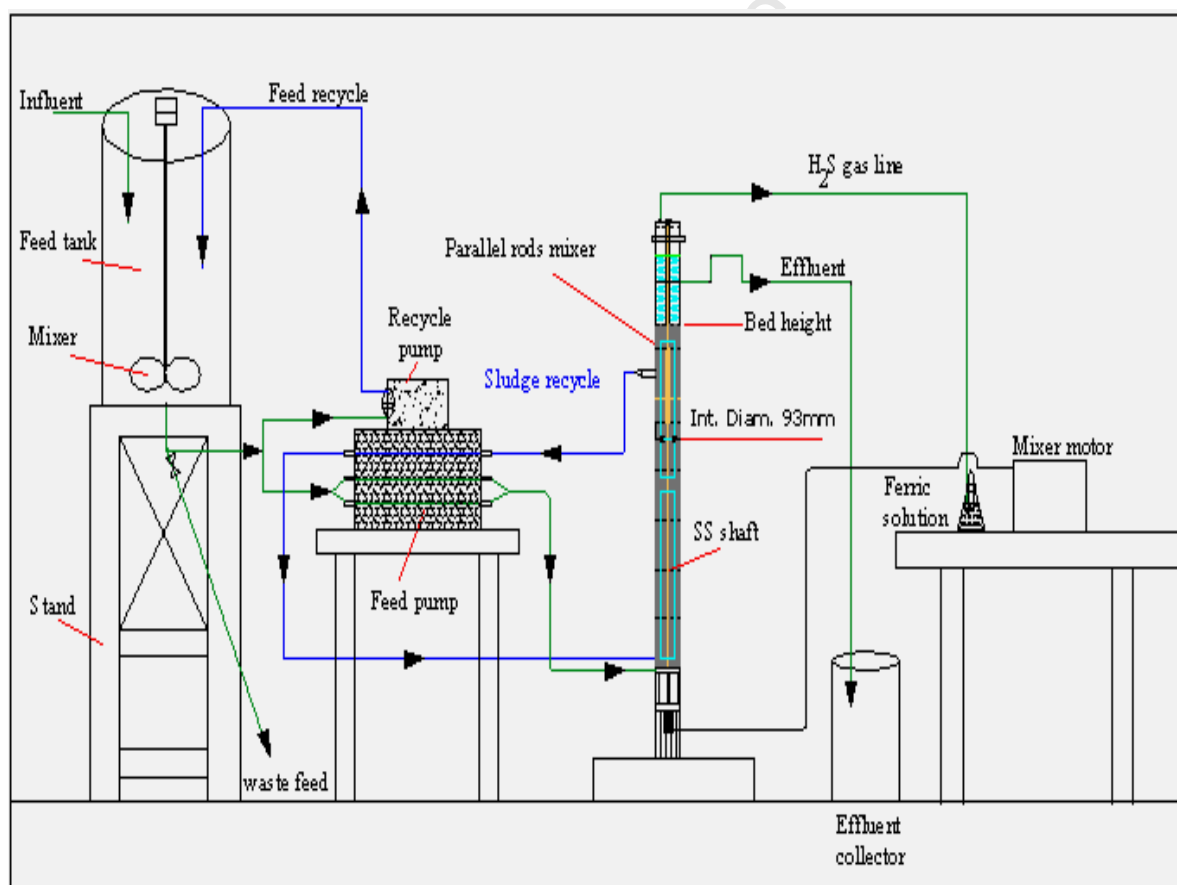


Figure 3.1: Schematic diagram of the lab-scale UASB reactor set-up.

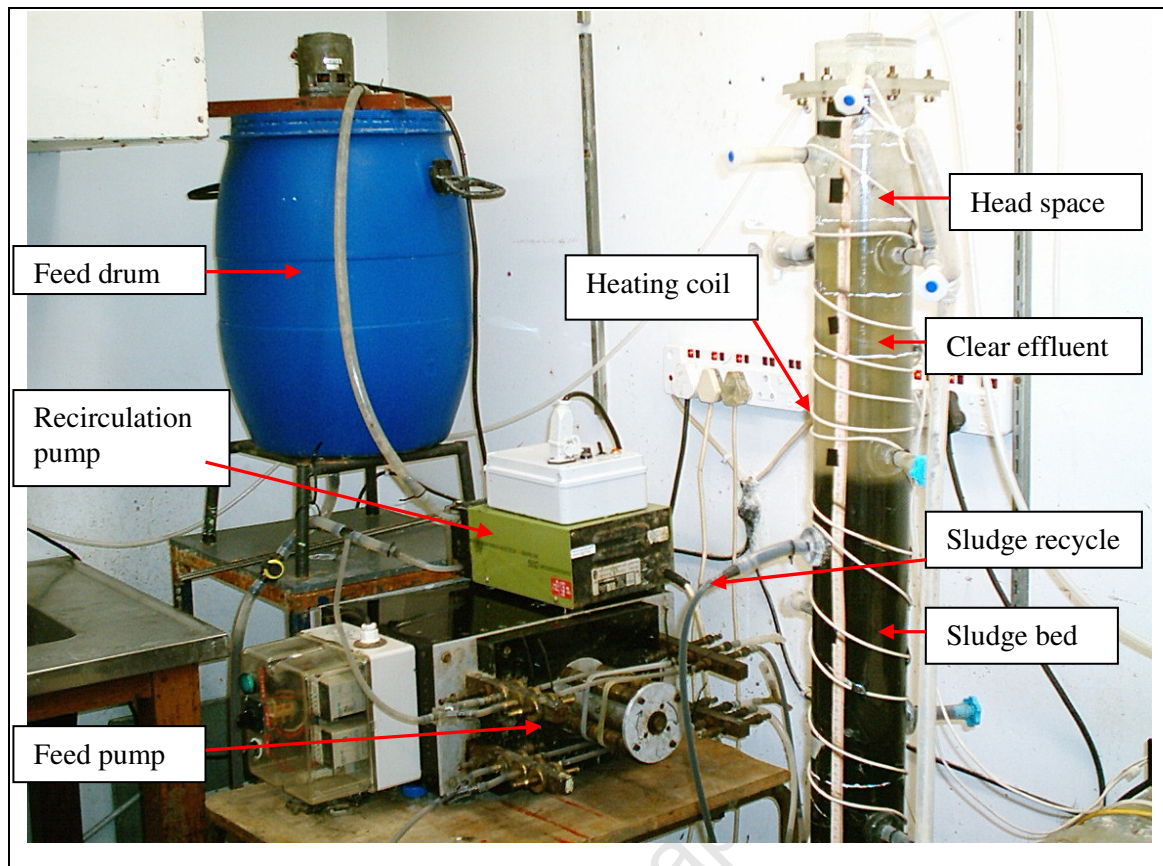


Figure 3.2a: Reactor R1 lay-out as set up in the laboratory with heating coils around the reactor.

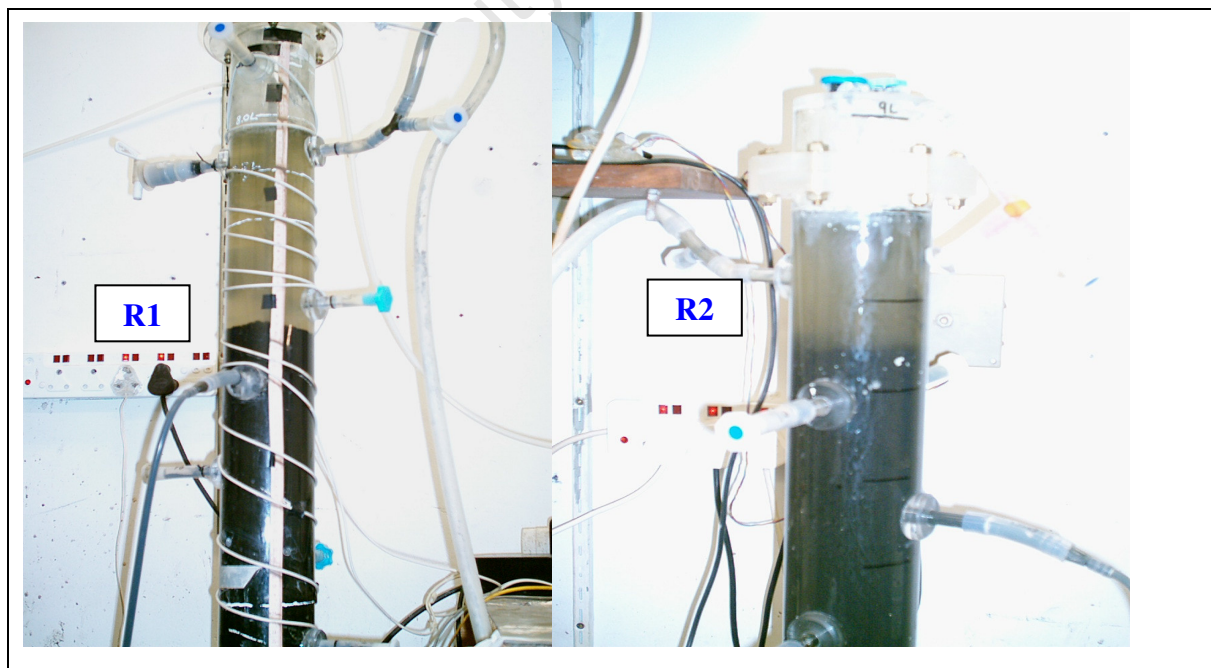


Figure 3.2b: Reactor R1 with heating coils around reactor and R2 with no heating coils.

The UASB reactors were inoculated with sulphate reducing bacteria, and operated with a sulphate rich feed similar to low sulphate AMD, except for the deliberate omission of heavy metals. PSS was added to the feed as substrate (carbon and electron) source for BSR. In order to close the sulphur loop and perform a sulphur mass balance around the system, the gas from the head space of the reactor was bubbled in ferric iron (Fe^{3+}) solution. In order to capture all the H_2S gas from the head space to the ferric iron solution, nitrogen carrier gas was blown into the head space for a reasonable period of time before changing the liquid level due to taking samples or harvesting sludge. Analyses of the ferric solution were conducted on a regular basis to determine the concentration of ferrous iron (Fe^{2+}) formed from the reduction of ferric iron (Fe^{3+}). (See Appendix 3A for the analytical procedure of Fe^{2+} using the Phenanthroline method).

The effluent pH was initially measured by fitting a pH probe (Metrohm 704pH meter model) to the top of the reactor through the lid leaving it to be immersed all the time in the liquid. However, this practice was very soon discontinued since some solids (organics and/or sulphur) deposited to the lower part of the probe sensor resulting in inaccurate pH measurements. Effluent pH was thereafter measured every day in situ by opening the cork situated on top of the reactor lid and immersing the pH probe 5-8 cm below the liquid level. As a rule, effluent pH was measured after blowing the nitrogen gas into the reactor head space to ensure that H_2S gas was not loss in the process of pH measurement.

3.3 PRIMARY SEWAGE SLUDGE (PSS)

3.3.1 Collection and storage

The PSS used for the whole research study was collected from the Athlone Wastewater Treatment Plant (Cape Town, South Africa), treating domestic wastewater but with a significant (~ 30%) industrial component as well. At the treatment plant, the PSS is pumped from the underflow of a series of primary settling tanks and transferred to the anaerobic digesters for sludge treatment. The PSS was collected prior to entering the anaerobic digesters in batches of 20L plastic drums. These drums were then brought to the Water Research Laboratory at UCT where they were stored at 4 °C in a refrigerated room. Prior to testing, each batch (drum) was sieved through a square mesh (6.5mm x 6.5mm) strainer to remove cigarette ends, plastic pieces, rags, pads, seeds, stones and other large debris.

However, care was taken to limit the removal of sludge lumps (organics) to the minimum thereby keeping the PSS composition more or less intact. The sieved PSS was then vigorously mixed to prevent settlement, thus ensuring homogeneity, before a sample was taken for the PSS COD analysis.

3.3.2 Analysis of PSS

The COD (total and soluble) concentrations of the PSS in the storage drums were analysed regularly because the systems were fed a constant mass of COD daily. The volume of PSS required daily depended on the PSS COD concentration. With the total PSS COD concentration of each 20L drum batch known, the daily PSS mass fed daily was estimated by volume based on a Total PSS COD:Feed sulphate ratio of 1.25 and bottled in 1L plastic bottles and stored at 4 °C in the refrigerated room. It was found that using pre-prepared volumes to quantify the feed COD mass was convenient and did not cause a great variation in the final diluted feed COD mass pumped to R1 and R2. Although the PSS was sometimes warmed to 20 °C, the large volume of tap water used to dilute the PSS (e.g. 9 to 13L tap water for 1L PSS) in the feed preparation did alleviate the effect of temperature difference, thereby preventing any potential temperature shocks to the system. After dilution, the feed temperature was in the range of 19-22 °C (lab temperature was maintained at 20 °C).

Based on the above feed preparation approach, the influent COD concentration was thereafter analysed on a regular basis and on average was found to be close to the target value therefore giving confidence in the approach adopted.

The total suspended solids (TSS) and volatile suspended solids (VSS) of the PSS were also measured in order to determine the PSS COD/VSS ratio.

3.4 SYSTEM FEED PREPARATION

The UASB digester feed consisted of 1500 mgSO₄²⁻/L added as Na₂SO₄ and 1875 mgCOD/L of PSS (total PSS COD:sulphate ratio of 1.25). From the stoichiometric COD utilisation for the sulphate reduced, a biodegradable COD:SO₄²⁻ ratio of 0.67 is required but some COD is also consumed for biomass production. So, a calculated COD:SO₄²⁻ ratio of 1g total PSS COD/0.8g SO₄²⁻ was used in which 1500 mgSO₄²⁻/L requires 1200 mg of biodegradable COD/L and the PSS was assumed to contain about 64% biodegradable COD.

This $\text{COD}:\text{SO}_4^{2-}$ ratio was slightly lower than that used by Ristow *et al.* (2005) in their study. Before dilution, the PSS was macerated in an electric blender (Braun MX2050 model) for about 1 minute to break up the larger particles in order to avoid pipe blockages in the UASB system and thereafter diluted with tap water in a calibrated 20L bucket. The mix was then augmented with sulphate before adjusting the pH. The sulphate stock solution was prepared by adding anhydrous sodium sulphate (Na_2SO_4) to distilled water so that a highly concentrated sulphate solution was obtained. As a routine practice, 355g of anhydrous Na_2SO_4 was added to 2L of distilled water and mixed thoroughly until all the salt dissolved. This concentrated stock solution therefore had a sulphate concentration of $120 \text{ gSO}_4^{2-}/\text{L}$. If a $1500 \text{ mgSO}_4^{2-}/\text{L}$ feed was required and the daily influent volume was 14L, then $(1500 \times 14)/120 = 175 \text{ ml}$ of the sulphate stock solution was needed.

Once the required sulphate stock solution was added to the concentrated PSS, the mixture was made up to the daily feed volume with tap water and the pH was adjusted. The feed pH was adjusted to between 7.1 and 7.4 with anhydrous sodium bicarbonate (NaHCO_3) powder ($\sim 450 \text{ mg/L}$ as CaCO_3) to optimise bacterial activity. The feed volume required for 1 day was then placed in the system feed drum ($\sim 30 \text{ L}$ capacity) at 20°C . Filling the system feed drum batchwise in this way allowed checking that all the feed had been pumped into the system over the 24h feeding period, an important aspect to achieve steady state and check COD, N and S mass balances over the system. The feed drum contents were mixed by paddle mixer (50 rpm) and a pumped recirculation flow was set up around the feed drum to prevent settlement. The feed was drawn at a constant rate and pumped via a peristaltic pump to an inlet at the bottom of the reactor (see Figure 3.1).

3.5 FEED ANALYSIS

Influent samples were taken on a regular basis and analysed for their COD (total, particulate and soluble COD), total volatile fatty acids (VFA), carbonate alkalinity (H_2CO_3^* alk.), total Kjeldahl nitrogen (TKN), free and saline ammonia (FSA), total and soluble phosphorous and pH. The feed COD was measured at least once a week to cross-check whether the measured values corresponded closely to the target values established for the systems. These feed COD concentration values were also needed for the COD mass balance over the system. The total COD concentration of the feed sample was diluted 5 times so that the final

concentration was within the range of the COD method. The influent COD concentration was tested in duplicate to obtain more reliable results.

The soluble parameters (soluble COD, VFA, H_2CO_3^* alk., FSA, filtered TKN, soluble P) were determined on filtered feed sample. In order to obtain enough filtrate for these measurements, three 50ml centrifuge tubes were filled with the feed sample and centrifuged for 10 minutes at 3500 rpm in a Kubota 5100 model centrifuge. After centrifugation, the quasi-clear supernatant was vacuum filtered through a glass fibre filter paper (S&S GF52 model) followed by a $0.45\ \mu\text{m}$ membrane filter (S&S ME 25/21 model). The total filtrate was then diluted as required for the analyses of the above relevant parameters.

The feed pH both before and after dosage with NaHCO_3 was measured in-situ using a manual pH meter (Metrohm 704 model) by immersing the pH probe in the feed drum.

The feed VFA and H_2CO_3^* alk. were analysed twice a week using the 5-pH point titration method by Moosbrugger *et al.*, 1992. The TKN and FSA were measured on a less frequent basis (monthly or so) in order to check the nitrogen mass balance. The total and soluble P were weekly measured only towards the end of the study because these parameters are not important in BSR.

3.6 REACTOR OPERATION

At the beginning of the investigation, only one reactor (R1 at $35\ ^\circ\text{C}$) was operated with the above-described feed procedure. The reactor R1 was seeded with 6L of old stored sulphate-reducing sludge and given an eight week start-up period to allow the SRB to develop and to accumulate a sludge bed. The sludge bed was then maintained at a constant volume of 6.7L in the reactor column by withdrawing excess sludge from the top of the sludge bed via a sampling port located at the 6.7L mark. Part of the reactor excess sludge was used for sludge analyses and the rest was stored in a 25L drum at $4\ ^\circ\text{C}$ for possible future use. From the feasibility study described in Section 2.7.4 of Chapter 2, a sludge recycle line was introduced to withdraw sludge from the UASB reactor just below the 6.7L volume and return it to the bottom of the reactor, at half the feed flow rate. It was expected that this recycle would initiate rapid BSR from the bottom of the bed by inoculating it with the high sulphate reducing bacteria sludge from the top of the bed. Moreover, it was envisaged that

the recycle would distribute the sulphate reducing biomass more evenly along the bed axis so that the sludge bed could be considered as a mixed digester.

After 205 days of operation, the second identical UASB reactor (R2 at 20 °C) was started in parallel to R1, to investigate system parameters that might influence the behaviour, such as temperature and loading rates (sulphate and organic). R2 was inoculated with 6L of the R1 wasted sulphidogenic sludge. It received the same influent feed as R1, that is 1500 mgSO₄²⁻/L, 1875 mgCOD/L and pH adjusted between 7.2-7.5 with Na₂CO₃. However, as noted above, the reactor temperature was maintained at a constant room temperature of 20 °C.

For both reactors, the hydraulic retention time (HRT) was reduced stepwise to obtain the minimum value for stable operation by increasing the feed flowrate. After each stepwise change, the systems were allowed to stabilise, indicated by measured effluent alkalinity, pH, VFA and sulphate remaining constant for a period of about 7-10 days. As a rule, it was accepted that an effluent VFA concentration of < 100 mgHAc/L would be regarded sufficiently low for the UASB reactor to be considered stable. The minimum stable HRT was accepted as the shortest HRT where the effluent VFA (<100 mgHAc/L) and effluent sulphate (<250 mgSO₄²⁻/L) were low, and the measured alkalinity and pH were almost constant. When the minimum stable HRT was reached, bed profiles through the sludge bed were done to gain insight into the process behaviour inside the reactor bed.

3.7 MONITORING

3.7.1 Effluent sampling

Daily, effluent samples were drawn from 10cm below the reactor liquid level (but above the sludge bed) via the effluent draw-off point to avoid any contact with the atmosphere and hence changes due to gas exchange. The effluent samples were then analysed for sulphate, VFA and alkalinities (total and H₂CO₃* alk.), COD (total, total soluble, organic soluble, total sulphide and particulate), TKN (unfiltered and filtered) and FSA. The effluent pH was measured in-situ by introducing a pH probe inside the liquid from the top of the reactor. Since this exercise required that the cork on top of the reactor lid be opened, nitrogen gas (~100% pure) was blown to purge the reactor head space and transfer all the head space H₂S

into the ferric iron solution (see Section 3.2). The effluent pH was thereafter measured and the reactor was then resealed by re-inserting the cork into the lid.

3.7.2 Analysis of waste sludge

Since the reactor sludge bed was maintained at a fixed volume of 6.7L, excess sludge had to be wasted daily. Excess sludge was removed from the sampling port located at the 6.7L mark. Before analysis, the waste sludge was well mixed so that a homogeneous sample could be taken and analysed for its COD components (total, organic soluble, sulphide and particulate), TSS and VSS concentrations on a weekly basis. The accurate analysis of the waste sludge characteristics and quantity was very important in the determination of the sludge COD/VSS ratio, the bed sludge age and in the mass balance checks. In addition, on a less regular basis (every 2 weeks or so) some of the waste sludge was oven dried at 105 °C for 24h and stored for sludge elemental analysis. Elemental analysis of the sludge was important to determine the concentration, if any, of elemental sulphur (S^0) stored in the biomass. At the same time, the sludge C, H, O, N and P contents were obtained from the analysis for stoichiometric modelling of the system.

3.7.3 Bed profiling

Once the optimum hydraulic retention time for both systems has been established and that sufficient steady state experimental data have been collected (2 to 3 sludge ages), bed profiling was undertaken in order to understand the process behaviour along the sludge bed. Profile tests were carried out by withdrawing a known volume of sludge (usually 100 ml) from the reactor bed via the sample ports at pre-determined bed heights (namely 10, 30, 50, 70 and 90 cm). The sludge sample at each bed height was analysed for its sulphate, VFA, alkalinity and COD (all components) concentrations.

3.8 ANALYTICAL PROCEDURES

3.8.1 Sample preparation for COD measurement

Effluent sample of 150ml were collected from the effluent draw-off port and analysed for the various parameters of interest. Part of the unfiltered effluent was directly used to measure the total COD, unfiltered TKN and total P with the necessary dilution. The

remainder was used to measure the soluble constituents. The sample was poured into 50ml centrifuge tubes and centrifuged for 10 minutes at 3500 rpm. The clear supernatant was then vacuum filtered through a glass fibre (S&S GF 52) and 0.45 μm membrane (S&S ME 25/21 ST) filter papers. The filtrate was thereafter diluted where necessary to analyse for total soluble COD, organic soluble COD, VFA, alkalinities (both total and H_2CO_3^* alk.), FSA and filtered TKN. Because the effluent of the UASB reactor was clear and contained little particulates, no flocculant (polyelectrolyte) was added to the samples prior to centrifugation. The total soluble COD comprised an organic component (organic soluble) and an aqueous total sulphide (TS or S_T) component. The total soluble COD concentration was measured on the filtrate obtained from the centrifuged and vacuum filtered sample.

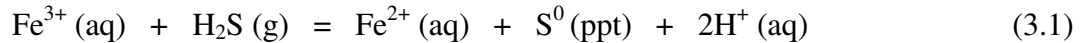
In order to analyse for the soluble organic COD, the aqueous sulphide needed to be removed prior to this COD test. Excess zinc sulphate (ZnSO_4) was added to the vacuum filtered sample in a 20ml centrifuge tube and shaken to precipitate the sulphide as zinc sulphide (ZnS). Any residual zinc ions (Zn^{2+}) were then precipitated by adding 3 drops of 10M NaOH to the sample. The solution was then centrifuged for 5 minutes at 3500 rpm and vacuum filtered through a 0.45 μm membrane filter paper and the resulting filtrate was tested for COD which is organic soluble COD concentration. The difference between the total soluble COD and the organic soluble COD is the total aqueous sulphide COD.

The analytical procedures of Standard Methods (1985) were used to determine the COD of the effluent, sludge bed and PSS.

The above analytical procedure resulted in poor COD and S mass balances around the R1 reactor (R2 had not been started yet). This prompted an investigation into the cause for the COD and S loss which was traced to sulphide loss mainly during vacuum filtration. The details of this investigation are given in Chapter 5. This investigation, in which standard solutions of sulphide, bicarbonate and acetic acid were tested by the different analytical methods and modifications to them to see where and how the loss occurred, yielded some interesting insights in particular in the mixed acid/base chemistry behaviour that need to be recognised when using only simple wet chemistry methods to monitor BSR systems and achieve 100% mass balances.

3.8.2 H₂S gas measurement

As mentioned above, H₂S gas generated in the BSR was collected by connecting a pipe from the head space of the reactor to a flask containing 1000 mgFe³⁺/L ferric iron (Fe³⁺) solution. The 1000 mgFe³⁺/L ferric iron solution was prepared by dissolving 2.905g ferric chloride (FeCl₃, MW=162.204g) in 1L distilled water. The H₂S gas reduces Fe³⁺ ions into ferrous iron (Fe²⁺) ions, as per the following equation.



After 24h, the ferrous iron (Fe²⁺) concentration present in the solution was analysed using the Phenanthroline method (see Appendix 3A for method description) to determine the concentration of Fe²⁺ ions formed from the generation of H₂S. The H₂S mass in the flask required to form the measured Fe²⁺ mass (concentration x volume) was then calculated from the above equation (Eq. 3.1). This H₂S mass was divided by the influent flow and was the H₂S gas produced in the reactor over a one day period.

3.8.3 Volatile fatty acids (VFA) and Alkalinity measurement

The VFA and alkalinity were measured using the 5-pH point titration method (Moosbrugger *et al.*, 1992). Since the system operated in the UASB reactor was a mixed weak acid/base one, total sulphide (S_T), phosphate (P_T) and ammonium (N_T) species needed to be included in the 5-pt titration calculation procedure. In this study, both the influent and effluent FSA and phosphorous concentrations were relatively low (60 mgN/L and 10 mgP/L). Therefore their effect on the VFA and alkalinity was negligible. Moreover, the ammonium system has a pK_n value of 9.04 (at 35 °C and adjusted for activity coefficient and ionic strength) which is close to that of the carbonate system (pK_{c2} HCO₃⁻/CO₃²⁻ is 9.98 at 35 °C and adjusted for activity coefficient and ionic strength), so its influence on the alkalinity is negligible (see Figure 3.4).

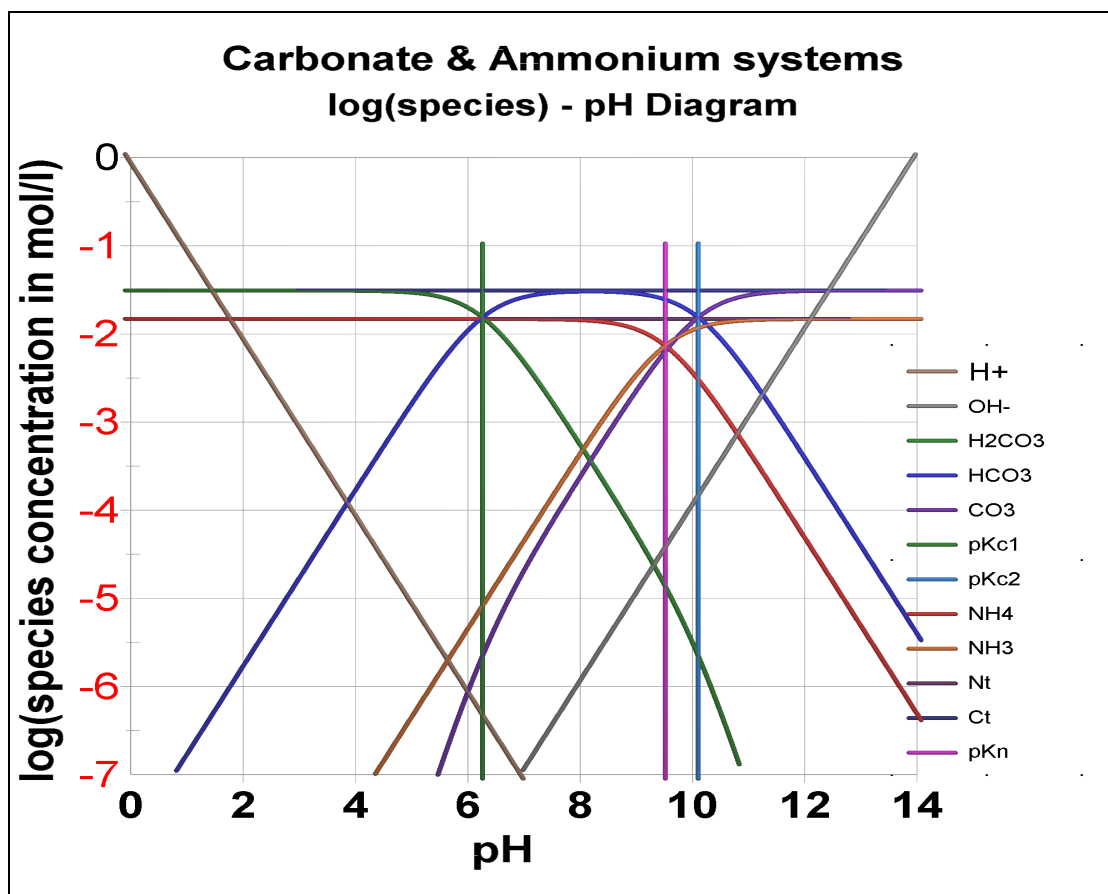


Figure 3.4: Log species-pH diagram for Carbonate and Ammonium systems.

The total sulphide species (S_T) in the effluent samples were high due to the sulphate reduction and these species do affect the $H_2CO_3^*$ alk. and the total alkalinity results obtained from the titration. In order to obtain the correct $H_2CO_3^*$ alk. and VFA concentrations from the titration procedure, it is essential that the correct sulphide concentration is entered into the programme – if the sulphide concentration is incorrect due to losses, e.g. in a vacuum filtration step before titration, the $H_2CO_3^*$ alk. and VFA concentrations obtained from the titration method will also be incorrect. However, the total alkalinity will be correct because this is not affected by H_2S or CO_2 losses. Because the effluent VFA concentration usually was low (< 100 mg HAc/L) relative to the effluent $H_2CO_3^*$ alkalinity concentration (~ 1500 mg/L as $CaCO_3$), the error in its result due to an incorrect sulphide concentration entry into the programme also is low (~ 5 mgHAc/L). In contrast, the error on the $H_2CO_3^*$ alk. concentration result is relatively high.

3.8.3.1 A brief description of the 5-pH point titration method

The 5 pH point titration method of Moosbrugger *et al.* (1992) calculates the H_2CO_3^* alk. and VFA only. A summary of the calculation procedures of the programme is outlined below:

- 10ml of the clear sample with no solids is made up to 50ml with distilled water.
- The 50 ml sample is very gently stirred to minimise H_2S and CO_2 losses.
- There are 5 pH points, the original sample pH (say 7.75) and four set pH points namely 6.70, 5.90, 5.20 and 4.30.
- The cumulative volumes of HCl acid with a known Normality added to reach each of the 4 pH points above are recorded.
- The temperatures of the original and final samples are also noted.
- The specific conductivity and total dissolved solids (TDS) of the sample are also required. Since only big variations in the conductivity and TDS concentrations would affect the H_2CO_3^* alk. and VFA, these parameters can be given a fixed value for convenience.
- The total ammonia, phosphate and sulphide system concentrations (N_T , P_T and S_T) need to be known – if these concentrations are very low in relation to the H_2CO_3^* alk. and VFA concentrations, they can be set to zero with negligible effect on the accuracy of the results.
- All the above values are then entered into the 5-pt titration programme (Titra5.exe) and the calculation procedure is run to determine the H_2CO_3^* alk. and VFA.
- A typical example of a 5-point titration result on one of R1 effluent samples is shown below (see Figure 3.5). In this example S_T is set to zero.
- The results are H_2CO_3^* alk. = 1803.7 mg/L as CaCO_3 and VFA = 31.4 mgHAc/L.

Y:\TITRA5.EXE

5 pH POINT TITRATION
TITRATION INPUT DATA

pH ₀ (initial pH)	7.75
pH ₁ (after adding U _{x1})	6.70
pH ₂ (after adding U _{x2})	5.91
pH ₃ (after adding U _{x3})	5.21
pH ₄ (after adding U _{x4})	4.30
U _{x1} (ml)	1.79
U _{x2} (ml)	3.89
U _{x3} (ml)	4.78
U _{x4} (ml)	5.11
Normality of titrant (mol/l)	0.0753
Sample size: undiluted (ml)	10
Sample size: diluted (ml)	50
Temperature (°C)	20
TDS (mg/l)	3300
Specific Conductivity (mS/m)	488
Inorganic Nitrogen (mgN/l)	0
Inorganic Phosphorus (mgP/l)	0
Inorganic Sulphide (mgS/l)	0

KEY	FUNCTION
↑↓	SELECT PARAMETER
<enter>	ERASE VALUE
<enter>	INSERT NEW VALUE
C	CALCULATION
Q	QUIT

Y:\TITRA5.EXE

OUTPUT DATA

H ₂ CO ₃ *alkalinity (undiluted sample) (mg/l as CaCO ₃)	1803.7
Short-chain fatty acids (undiluted sample) (mg/l as acetic acid)	31.4
Systematic pH error	-0.11
Do you wish to do a further calculation ?	Y/N
Do you wish to quit the program ?	Q

Figure 3.5: Results of H₂CO₃* alk. and VFA from a typical R1 effluent sample (Day 152).

Because a mixed weak acid/base system with a high sulphide concentration (S_T) was being tested, the measured S_T value needed to be entered into the calculation procedure. The results obtained when the measured S_T is entered into the programme are shown in Figure 3.6 below.

5 pH POINT TITRATION
TITRATION INPUT DATA

KEY	FUNCTION
↑↓	SELECT PARAMETER
<enter>	ERASE VALUE
<enter>	INSERT NEW VALUE
C	CALCULATION
Q	QUIT

OUTPUT DATA

H ₂ CO ₃ *alkalinity (undiluted sample) (mg/l as CaCO ₃)	1644.9
Short-chain fatty acids (undiluted sample) (mg/l as acetic acid)	33.1
Systematic pH error	-0.08
Do you wish to do a further calculation ?	Y/N
Do you wish to quit the program ?	Q

Figure 3.6: Results of H₂CO₃* alk. and VFA from a typical R1 effluent sample (Day 152) with measured S_T (186.5 mgS/L) entered into the programme.

When the effluent S_T (obtained from the COD test) for that particular operation day (Day 152) is entered, i.e. S_T = 186.5 mgS/L, the H₂CO₃* alk. is 1644.9 mg/L as CaCO₃ and the VFA is 33.1 mgHAc/L. From the results it can be seen that if for a mixed weak acid/base system containing sulphide species, S_T is left as zero in the calculation procedure, the

H_2CO_3^* alk. calculated is closely equal to the sum of H_2CO_3^* alk. and Alk H_2S . Note the nomenclature of the alkalities follows that of Loewenthal *et al.* (1989) namely H_2CO_3^* alk. is the alkalinity of the carbonate system with respect to the H_2CO_3^* reference species and includes the water species (OH^- and H^+) and Alk H_2S is the alkalinity of the sulphide system with respect to the H_2S equivalent solution and excludes the water species. Since the VFA is given separately, the total alkalinity therefore is given by:

$$\text{Total Alkalinity} = \text{H}_2\text{CO}_3^* \text{ alk.} + \text{Alk H}_2\text{S} + \text{Alk. HAc} \quad (3.2)$$

Alk H_2S and Alk. HAc are calculated from their pK values and the effluent sample pH and being monoprotic their alkalities are equal to the dissociated species concentrations. This error in the approximation of the actual H_2CO_3^* alk. as the sum of H_2CO_3^* alk. and Alk H_2S when S_T is left zero in the programme can be large where S_T is relatively high compared to the actual H_2CO_3^* alk.. The issue of alkalinity data interpretation and accuracy using the 5-pt titration method is in fact more complex than the above and is dealt with in more detail in Chapter 5.

3.8.4 Sulphate

The sulphate concentration was determined using the turbidimetric method as described in Standard Methods (1985, Method 426C). However, since soluble organics present in the sample would interfere with the turbidimetric test and lead to inaccurate absorbance readings in the spectrometer, the samples were subjected to a pre-treatment procedure. Ristow *et al.* (2005) developed the carbonate fusion test as a pre-treatment procedure to remove soluble organics present in a sample. In essence, in the carbonate fusion method, the sulphate samples were pre-treated with excess zinc acetate to precipitate the total sulphide as ZnS . Sulphide needed to be removed prior to the carbonate fusion since it would get converted to sulphate. Three drops of 10 M NaOH were then added to increase the pH and precipitate any residual zinc ions (Zn^{2+}) as $\text{Zn}(\text{OH})_2$ and the mix was centrifuged and vacuum filtered through a $0.45\mu\text{m}$ membrane filter paper. 10 ml of the filtrate was then poured into a platinum crucible and dried overnight in an oven at 110°C . Between half to two third of a teaspoon of sodium carbonate (Na_2CO_3) powder was added to the dried sample and the crucible was heated over a Bunsen burner until all the Na_2CO_3 melted and the soluble organics oxidised to CO_2 leaving a pale yellowish salt-like content. The crucible

and its content were allowed to cool and then a 33% concentrated HCl acid was added to dissolve the crystallised content. To avoid loss of sample during the acid addition, the crucible was covered with a glass cover to prevent any drops from fizzling out the platinum crucible. The resulting solution was then transferred to a 100 ml flask taking particular precautions to wash all residual solution into the flask. One drop of phenolphthalein indicator (made up from 1g phenolphthalein powder in 200ml distilled water) was added to the solution and neutralised dropwise with 10M NaOH until the pink end point was reached. The solution was then made up to the 100ml mark. Thereafter 50ml of the final solution was used in the barium test as outlined in the turbidimetric method. For accurate measurement, the sulphate concentration of the sample using the turbidimetric method should be between 10 to 45 mgSO₄/L.

3.8.5 Total and volatile suspended solids

The total suspended solids (TSS) concentration was measured on samples oven-dried at ~ 105 °C over 24h while the volatile suspended solids (VSS) concentration was measured by difference on sample incinerated at 600 °C for 25 minutes. Both methods are described in Standard Methods (1985, 2540(D) for TSS and 2540(E) for VSS).

$$\text{VSS} = \text{TSS (obtained from dried sample)} - \text{ISS (inert suspended solids obtained from incinerated sample)}$$

TSS and VSS measurements were done on both the primary sewage and UASB waste sludges.

3.8.6 TKN and FSA

The TKN (both filtered and unfiltered) and the FSA concentrations were determined by the micro-Kjeldahl method (4500-Norg (C)) and titrimetric method (4500-NH₃ (B), (E)) respectively as outlined in Standard Methods (1985, Method 420B).

3.8.7 Total phosphorous and ortho-phosphate (or soluble P)

The total phosphorous was measured using the sulphuric acid/persulphate digestion at 100°C (Standard Methods, 1985, Method 424C III) followed by molybdate-vanadate colour

development for ortho-phosphate (Standard Methods, 1985, vanadomolybdophosphoric acid colorimetric method).

3.9 MASS BALANCES

One of the objectives of this study was to develop a mass balance based steady state and dynamic simulation models for BSR with PSS and use the UASB system data to validate these models. For model validation to be reliable, the UASB experimental data also need to conform to mass balances. So to check data quality and reliability, mass balance checks were conducted on the system. The COD, nitrogen and sulphur mass balances were calculated as outlined below.

3.9.1 COD mass balance

$$(a) \text{ Mass COD}_{in} (\text{mgCOD/d}) = Q_i * S_{ti}$$

where Q_i = feed flow rate (L/d) and S_{ti} = feed COD (mgCOD/L)

(b) (i) Mass out based on sulphide produced

$$\begin{aligned} \text{Mass COD}_{out} (\text{mgCOD/d}) &= \text{Mass of total COD in the effluent} + \\ &\quad \text{Mass of total COD in the waste sludge} \\ &= (Q_e * S_{te}) + (Q_w * S_{tw}) \end{aligned}$$

$$\begin{aligned} \text{where } Q_e &= \text{Effluent flow rate (L/d)} \\ Q_w &= \text{Waste flow rate (L/d)} \\ S_{te} &= \text{Total effluent COD (total organic + aqueous sulphide)} \\ &\quad (\text{mgCOD/L}) \\ S_{tw} &= \text{Total waste COD (total organic + aqueous sulphide)} \\ &\quad (\text{mgCOD/L}) \end{aligned}$$

For a COD balance, Mass COD_{out} must equal Mass COD_{in} , and for this to be so, an S balance also must be achieved.

$$\% \text{ COD balance} = \text{Mass COD}_{out} / \text{Mass COD}_{in} * 100$$

(ii) Mass out based on sulphate reduced

$$\begin{aligned} \text{Mass COD}_{out} \text{ (mgCOD/d)} &= \text{Mass of total } \textbf{organic} \text{ COD in the effluent} + \text{Mass of} \\ &\quad \text{total } \textbf{organic} \text{ COD in the waste} + (64/96 * \text{Mass of} \\ &\quad \text{sulphate as SO}_4 \text{ reduced, because 1 mole of sulphate as} \\ &\quad \text{SO}_4 \text{ produces 1 mole of H}_2\text{S which has a COD of 64} \\ &\quad \text{gO/mole H}_2\text{S – see Appendix B)} \\ &= (Q_e * S_{te}') + (Q_w * S_{tw}') + [(Q_e + Q_w) * 64/96 * \text{SO}_4^{2-} \text{ red.}] \end{aligned}$$

$$\begin{aligned} \text{where } S_{te}' &= \text{Total organic COD in the effluent (no sulphide)} \\ &\quad \text{(mgCOD/L)} \\ S_{tw}' &= \text{Total organic COD in the waste (no sulphide)} \\ &\quad \text{(mgCOD/L)} \\ \text{SO}_4^{2-} \text{ red.} &= \text{Sulphate reduced (= feed sulphate – effluent} \\ &\quad \text{sulphate) (mgSO}_4\text{/L)} \\ Q_e + Q_w &= \text{Feed flow rate, } Q_i \text{ (L/d)} \end{aligned}$$

For a COD balance, Mass COD_{out} must equal Mass COD_{in} and for this approach an S balance is not required.

3.9.2 Nitrogen mass balance

$$\begin{aligned} \text{Mass TKN}_{in} \text{ (mgN/d)} &= Q_i * \text{TKN}_i \\ \text{where TKN}_i &= \text{Feed TKN concentration (i.e. TKN of the diluted PSS)} \\ &\quad \text{(mgN/L)} \end{aligned}$$

$$\begin{aligned} \text{Mass TKN}_{out} \text{ (mgN/d)} &= \text{Mass of effluent TKN} + \text{Mass of waste sludge TKN} \\ &= (Q_e * \text{TKN}_e) + (Q_w * \text{TKN}_w) \end{aligned}$$

$$\begin{aligned} \text{where TKN}_e &= \text{Effluent TKN concentration (mgN/L)} \\ \text{TKN}_w &= \text{Waste sludge TKN concentration (mgN/L)} \end{aligned}$$

$$\% \text{ N balance} = \text{Mass TKN}_{out} / \text{Mass TKN}_{in} * 100$$

3.9.3 Sulphur mass balance

Sulphur mass balance in a 3-phase biological system is relatively complex since quantifying the sulphide exiting the system (both gaseous and aqueous) and the elemental sulphur (S^0) species in the waste sludge could be problematic. In this study the S^0 content in the waste sludge needed to be measured in order to check all possible exit routes for S to close the sulphur loop. The sulphur mass balance was then performed as follows:

$$\text{Mass } S_{in} \text{ (mgS/d)} = Q_i * 32/96 * SO_{4i}$$

$$\text{where } SO_{4i} = \text{feed sulphate concentration (mgSO}_4\text{/L)}$$

$$\begin{aligned} \text{Mass } S_{out} \text{ (mgS/d)} &= \text{Mass S (sulphide and sulphate) in effluent} + \text{Mass S (sulphide and sulphate) in waste sludge} + \text{Mass S (elemental sulphur stored in waste sludge)} + \text{Mass S in H}_2\text{S gas produced (mgS/d)} \\ &= [(Q_e * S_{Te}) + (Q_e * 1/3 * SO_{4e})] + [(Q_w * S_{Tw}) + (Q_w * 1/3 * SO_{4w})] + (Q_w * S_w^0) + \text{Mass S in H}_2\text{S gas (mgS/d)} \end{aligned}$$

$$\text{where } S_w^0 = \text{Elemental sulphur concentration in the waste sludge (mgS/L)}$$

$$S_{Te} = \text{Total aqueous sulphide concentration in the effluent (mgS/L)}$$

$$S_{Tw} = \text{Total aqueous sulphide concentration in the waste sludge (mgS/L)}$$

$$H_2S = \text{Mass of S in H}_2\text{S gas calculated from Eq.1 (refer to Section 3.8.2) (mgS/d)}$$

$$\% \text{ S balance} = \text{Mass } S_{out} / \text{Mass } S_{in} * 100$$

Since the biological processes considered in this study involved measurements in a complex 3-phase system, a COD mass balance between 95 and 105% and a S mass balance between 90 and 110% were considered acceptable.

3.10 HYDRAULIC AND BED RETENTION TIMES

3.10.1 Hydraulic retention time (HRT)

The hydraulic retention time was determined with the equation below.

$$\text{HRT (d)} = \frac{V_r(L)}{Q_i(L/d)} \quad \text{or}$$

$$\text{HRT (h)} = \frac{24 * V_r(L)}{Q_i(L/d)}$$

where Q_i = Feed flow rate (L/d)

V_r = Effective liquid reactor volume (L)

The effective liquid reactor volume (V_r) was set to be the total volume up to the height of the liquid level, which was always maintained at the 7.8L mark. So, with V_r fixed, the HRT was only dependent on the feed flow rate. The HRT was therefore established by setting Q_i . At the start of the experiment, the HRT was set up as high as 3 days and then reduced gradually by increasing the feed flow rate until the optimum value was reached. This optimum HRT value was defined as the minimum HRT at which the effluent criteria (VFA < 100 mgHAc/L; SO_4^{2-} < 250 mg SO_4^{2-} /L) were met for at least 10 consecutive days. The reactor was then accepted to have reached its maximum capacity and lowest design parameters (such as HRT and BRT) for the specific substrate loading rates (COD and sulphate).

3.10.2 Bed hydraulic retention time (BRT)

The BRT is defined as the time taken for the liquid (feed soluble contents) to pass through the entire bed axis and was determined from the following equation.

$$\text{BRT (d)} = \frac{V_b(L)}{Q_i(L/d)} \quad \text{or}$$

$$\text{BRT (h)} = \frac{24 * V_b(L)}{Q_i(L/d)}$$

where Q_i = Feed flow rate (L/d)
 V_b = Sludge bed volume (L)

The sludge bed volume (V_b) was the volume of the reactor up to the top of the sludge bed, which was set up depending on the substrate loading rate. V_b was set by wasting sludge once daily to keep the bed height at the required level. The bed height was set at 6.7L and 7.1L when the UASB reactor was operated with a feed sulphate of 1500 mgSO₄²⁻/L and 1800 mgSO₄²⁻/L respectively.

3.11 CLOSURE

In this chapter, the experimental set-up and monitoring of the 2 lab-scale UASB reactors (R1 and R2) were described. Also, the analytical procedures to collect the experimental data from both reactors on BSR using PSS and methods ensuring reliable data quality have been set out. The operation and performance of UASB reactor R1 when fed with 1500 mgSO₄²⁻/L of sulphate and 1875 mgCOD/L of PSS are described in the next chapter (Chapter 4); performance of R1 when fed 1800 mgSO₄²⁻/L and that of UASB reactor R2 are respectively described in Chapter 6.

APPENDIX 3A

Phenanthroline Method for Ferrous Iron

General: Keep glassware and reagents free of iron, although theoretically ferric iron should not be a problem if the method is being used to measure ferrous iron only.

1. Reagents

Phenanthroline

Dissolve at concentration of 1mg/ml in distilled water by heating to ~ 80 degrees C while stirring. A stock solution of 1L can be prepared as it stable for several months. 20ml of the phenanthroline solution is required per measurement.

1. Ammonium acetate buffer

Dissolve 250g of NH_4 -acetate in 150ml distilled water and add 700 ml glacial acetic acid. If the pH is <3, then bring it to 3.2-3.4 with strong NaOH.

This recipe is clearly wrong as a large fraction of the acetate precipitates and much distilled water must be added to bring the final volume to over 2L. As far as the ammonia is concerned, it does nothing, so instead simply use a suitably strong concentration of glacial acetic acid whose pK is in the right region, and adjust to 3.2.

2. Standard ferrous solution

Prepare a stock iron solution from ferrous sulphate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (MW = 273,03g) of 1000mg ferrous per litre (dissolve 2.489 g in 500ml). Filter this solution to remove any ferric hydroxide and then **immediately** acidify the filtrate to approximately pH 2 by adding 0.5ml conc. HCl. This solution is stable for several months.

Standard iron solutions must be prepared daily from stock solution. Dilute 5 in 100 (1:20) twice to get 1:400 (2.5mg/L). Use 0.01M HCl* rather than water as diluent to keep pH low. Then dilute 5, 10, 20 and 40 ml in 100ml 0.01M HCl each to give 0.125, 0.25, 0.5 and 1.0 mg/L standards. Since only 50ml is needed, the other 50ml can be kept for the next day (but only if 0.01M HCl was used).

Blank consists of 50ml water + buffer + phenanthroline brought up to 100ml as below. On the spectrophotometer used in this research, the blank gives a zero reading (absorbance), so there was no need to repeat the measurement daily. [In fact distilled water can be used as the blank because the above-mentioned blank gives the same reading]. Plot calibration results to make a standard reference linear graph. R^2 should be > 99% for 4 points. The conversion factors are then taken from the coefficients of the equation.

3. Method

Add 50ml of sample (appropriately diluted to between 0 and 1 mg ferrous/L to a 100ml volumetric flask and add 5ml (10 is unnecessary) buffer and then 20ml phenanthroline, plus water to 100ml. Shake and allow to stand for 5 mins. Measure at 510nm wavelength. The measurement can be accurately taken up to 15 mins after final mix.

4. Range and comments

According to Standard Methods (1985), pH of final mix should be between 2.9 and 3.5. See Standard Methods for interfering agents.

*To make 0.01M HCl dilute 1.98ml 32% HCl in 2L of water.

In practice, it is not necessary to do the standards every day as the changes in the slope of the graph were minimal and didn't make a difference to the results. Occasionally, if the results looked out of range, a standard check is required. But in the beginning it is worth doing it regularly (say weekly or whenever one is unsure of the results) in order to get the experience and see how your spectrophotometer readings are performing.

Regarding the ammonia-acetate, the ammonia can be left out. Simply use a 1:1 (glacial acetic acid: distilled water) solution brought to pH 3.3 via the addition of concentrated NaOH (make a 5 molar solution = 200g/L).

Chapter 4

Operation and performance of UASB reactor R1 (fed 1500 mgSO₄²⁻/L at 35 °C)

4.1 INTRODUCTION

As described in Chapter 3, Section 3.6, only one lab-scale UASB reactor (R1 at 35 °C) was operated at the start of this investigation to confirm the feasibility study as well as study the effect of sludge recycle on the system. R1 was fed at two substrate (PSS and sulphate) loading rates. Initially, it was operated with a feed sulphate concentration of 1500 mgSO₄²⁻/L and PSS concentration of 1875 mgCOD/L (based on a PSS COD/SO₄²⁻ ratio of 1.25, see Chapter 3, Section 3.4) and this feed was maintained for a period of 280 days. Thereafter, the feed sulphate and PSS concentrations were increased to 1800 mgSO₄²⁻/L and 2592 mgCOD/L respectively, with a PSS COD/SO₄²⁻ ratio of 1.44. In this Chapter, the operation and performance of R1 for only the first 280 days are evaluated and discussed through detailed analysis of the measured data; subsequent performance is described in Chapter 6. The detailed day to day experimental data collected for R1 over this period are presented in Appendix 4A.

4.2 INVESTIGATION OBJECTIVES

This first part of the investigation focused mainly on the potential of PSS to serve as an energy source in BSR using the UASB reactor (R1 at 35 °C). In addition, the minimum values of the operating parameters (hydraulic retention time (HRT), bed hydraulic retention time (BRT) and sludge age) for maximum sulphate reduction were determined from the performance of the reactor. Further, the effect of introducing a sludge mass recycle line from the top to the bottom of the reactor bed was studied, by conducting profile tests along the axis of flow through the UASB reactor. Because of the disruptive nature of the profile tests, daily analyses of the effluent parameters were stopped from steady state period 9 (Day 190 onwards) but analyses were performed intermittently to check whether steady state was

maintained. In addition, preliminary attempts were also made to assess and remedy the COD, S and N mass balances.

4.3 UASB R1 EXPERIMENTAL PROGRAMME FOR FEED SULPHATE 1500 mgSO₄²⁻/L

As described in Chapter 3, UASB R1 was maintained at a constant temperature of 35 °C, and fed a constant (as far as possible) influent feed COD concentration. During this experimental programme the influent feed flow was varied to vary the hydraulic retention time (HRT), and system response monitored.

4.3.1 PSS characteristics

For the entire experimental programme (Days 1-500) in this research work (including that reported in Chapter 6), the total COD concentration of the undiluted raw PSS varied from 17408 to 69626 mgCOD/L. This large variation did not influence the feed to the UASB reactor since a pre-determined influent COD (1875 mgCOD/L) was prepared by diluting raw PSS with tap water.

4.3.2 UASB reactor R1 start-up period

Though UASB R1 was inoculated with 6L of stored sulphate-reducing sludge, the start-up of the BSR system was slow. This long start-up period could be ascribed to the fact that the sulphidogenic sludge may have become inactive during the prolonged storage period (~ 1 year) at 4 °C. The reactor required around 80 days to achieve a constant effluent quality, with low VFA (< 100 mgHAc/L) and sulphate (< 250 mgSO₄²⁻/L) concentrations, at a long HRT of 30h. This relatively long start-up period allowed the sulphate reducing bacteria (SRB) to acclimatise to the new environment, and the sludge bed to accumulate and then be maintained at 6.7L.

4.3.3 Feed flow rate (Q_i) and hydraulic retention time (HRT)

After the 80 days start-up period, the HRT was reduced stepwise to determine the minimum HRT of stable operation, by increasing the feed flow rate (Q_i, L/d). Accordingly, at each

HRT, steady state conditions (assessed by low effluent VFA and sulphate concentrations) were allowed to establish for about 4 to 7 days before the next reduction in HRT. The HRT was reduced stepwise from 30h down to 12h, usually in 1h steps. Each time the HRT was reduced by increasing the volumetric flow rate, major fluctuations in effluent parameters were observed. However, after about 3-4 days of operation, the biomass adapted to the new environment imposed, and the effluent quality improved consistently. The HRT was reduced stepwise until the effluent quality was not able to meet the specified requirements (VFA <100 mgHAc/L; sulphate <250 mgSO₄²⁻/L) for a period of 20 days. It was then accepted that the system had reached the limit of successful performance and that a further reduction in HRT would result in progressive system failure (unstable sludge bed and/or sludge wash-out with the effluent). Figure 4.1 shows the stepwise decrease of the HRT (i.e. stepwise increase of Q_i) as a function of time. The periods where steady state conditions were achieved are marked 1 to 9.

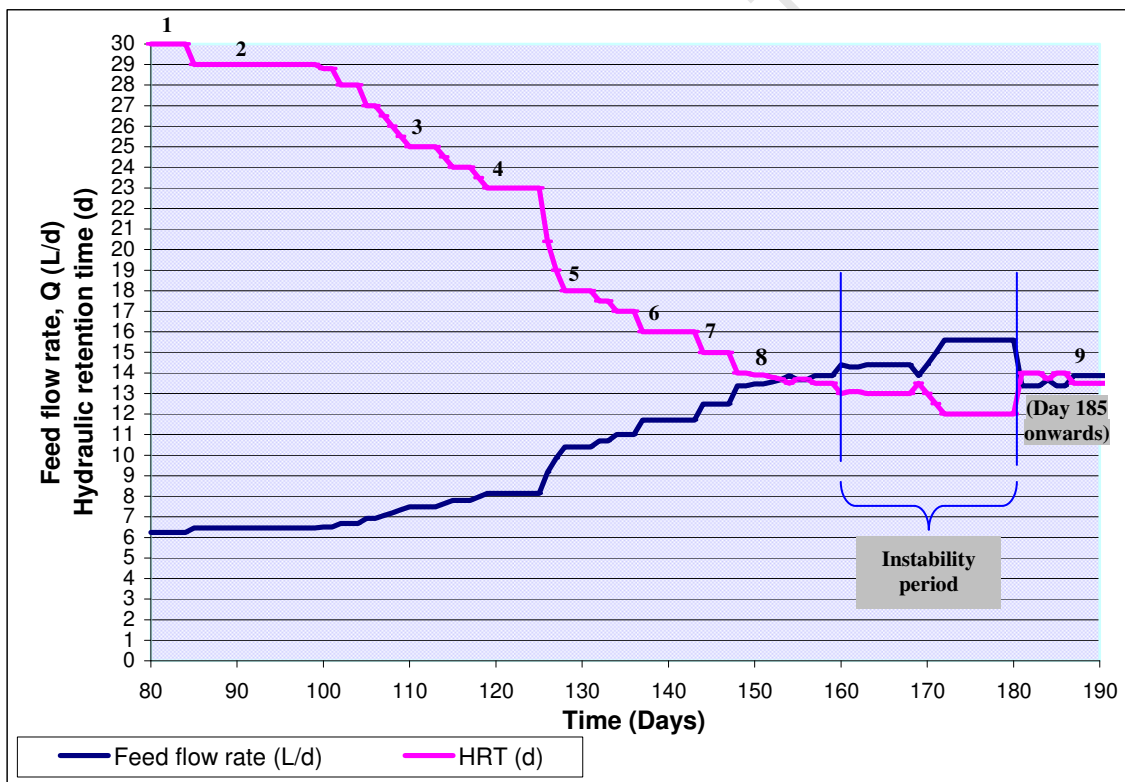


Figure 4.1: Variation in hydraulic retention time (HRT) and feed flow rate with operating time for the UASB reactor R1 (35 °C, 1500 mgSO₄²⁻/L); steady state periods are numbered 1 to 9 (see Table 4.1).

Days 160 to 180 in Figure 4.1 demonstrate the unstable period during which the reactor was deliberately operated at a HRT below the minimum value (< 13.5h) for performance

stability. The reason for this low HRT was to study the effects of high upflow velocity on the BSR system, and likewise determine the capacity limiting process. Results and discussion of this unstable period are detailed in Subsection 4.5.2.4 below. Following this failure condition, the HRT was restored to 13.5-14.0h for the remainder of the investigation, to allow examination of internal bed dynamics through profiling and assessment of mass balances and determination of sludge age.

4.3.4 Summary of operational conditions

To summarise the various stages in the experimental programme when R1 was fed 1500 mgSO₄²⁻/L and 1875 mgCOD/L during the first 280 days of operation, the operational conditions during that period are set out in Table 4.1: The different steady state periods with respect to operating HRT, the days at which bed profile tests were carried out and the mass balance determinations conducted are listed.

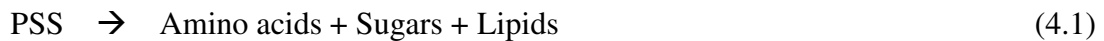
Table 4.1: Summary of operational conditions for UASB reactor R1 during the 280 days of operation.

Day of operation	Reactor status/activities performed	HRT (h)
1-79	SRB acclimatisation and bed accumulation	30.0
80-84	Steady state (SS) 1	30.0
94-104	SS 2	29.0
110-114	SS 3	25.0
122-125	SS 4	23.0
130-137	SS 5	17.0- 18.0
138-143	SS 6	16.0
144-147	SS7	15.0
148-159	SS 8	13.5-14.0
160-180	Unstable state	12.0-13.0
184-280	SS 9	13.5-14.0
157, 186, 198 and 205	Bed profile tests	14.0
187-280	H ₂ S gas capture in ferric solution and measurement*	13.5-14.0
187, 240 and 252	COD, S and N mass balances calculated	14.0
240 and 252	Determination of sludge age	14.0
* H ₂ S gas measurement done only when conducting sulphur mass balance over the system		

4.4 SEQUENCE OF REACTIONS FOR BSR WITH PSS

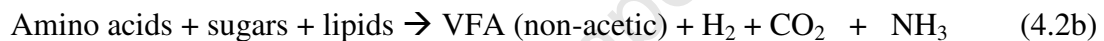
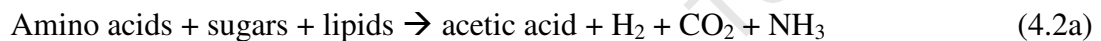
To assist with the interpretation of the data collected in the experimental investigation, the sequence of biologically mediated reactions expected in the BSR UASB reactor with PSS was extracted from the literature (Kalyuzhnyi *et al.*, 1998; Ristow *et al.*, 2005; Sotemann *et al.*, 2005a).

1. PSS hydrolysis (mediated by acidogens)

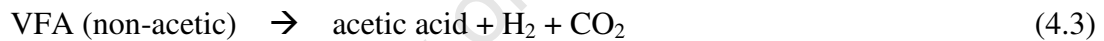


2. VFA production

(i) *Acidogenesis (mediated by acidogens)*



(ii) *Acetogenesis (mediated by acetogens)*



3. Sulphidogenesis (mediated by sulphidogens)

(i) *Hydrogenotrophic sulphidogenesis*



(ii) *Acetoclastic sulphidogenesis*



(iii) *Propionate degrading sulphidogenesis*



From the reaction sequence, in summary PSS hydrolysis Eq(4.1) and acidification Eq(4.2) mediated by acidogens produce VFA and H₂ which serve as substrates for the BSR processes Eqs(4.4) to (4.6), which consume VFA, H₂ and sulphate and produce sulphide and alkalinity. Thus, these produced and consumed parameters can be used to obtain an indication of the extent of the processes, and their relative rates.

4.5 DEVELOPMENT OF UASB R1 PERFORMANCE WITH TIME

4.5.1 Influent feed characteristics

The influent feed to the UASB reactor was regularly analysed to cross-check whether the desired concentration was fed to the system. For the set feed sulphate of $1500 \text{ mgSO}_4^{2-}/\text{L}$, $1875 \text{ mgCOD}/\text{L}$ of PSS was required to give the $\text{COD}:\text{SO}_4^{2-}$ ratio of 1.25. The diluted influent was analysed regularly for COD, TKN, FSA, VFA and H_2CO_3^* alkalinity concentrations and pH, while P concentrations were analysed only once during the 280 days experimental period. The variations in the diluted influent total and soluble (0.45 μm membrane filtered) COD concentrations with time are shown in Figure 4.2. The measured COD values were also plotted on a transformed rank probit plot in Figure 4.3 (see Muller *et al.*, 2003 for details on the construction and interpretation of these plots) to demonstrate the extent of the variations in the feed total COD concentrations. In addition, a summary of the results from the measurements of the above parameters are shown in Table 4.2.

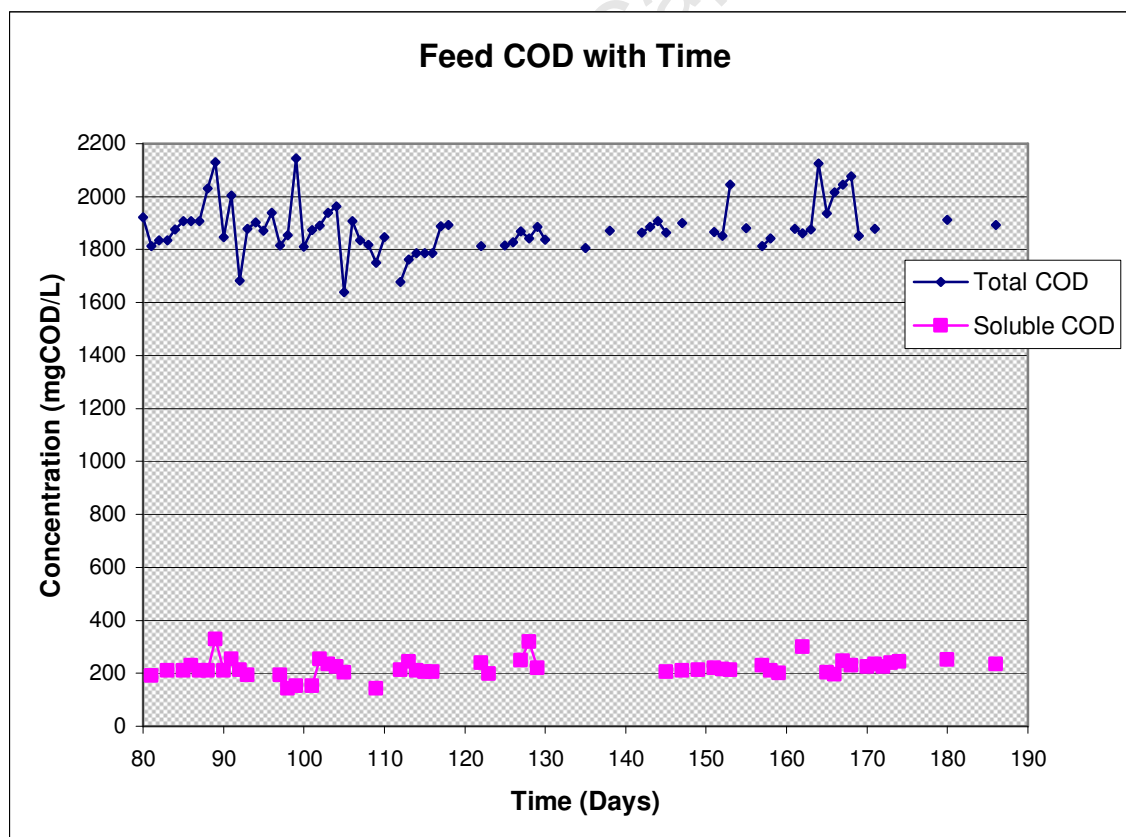


Figure 4.2: Influent total and soluble COD concentrations with time for UASB reactor R1 (feed sulphate $1500 \text{ mgSO}_4^{2-}/\text{L}$).

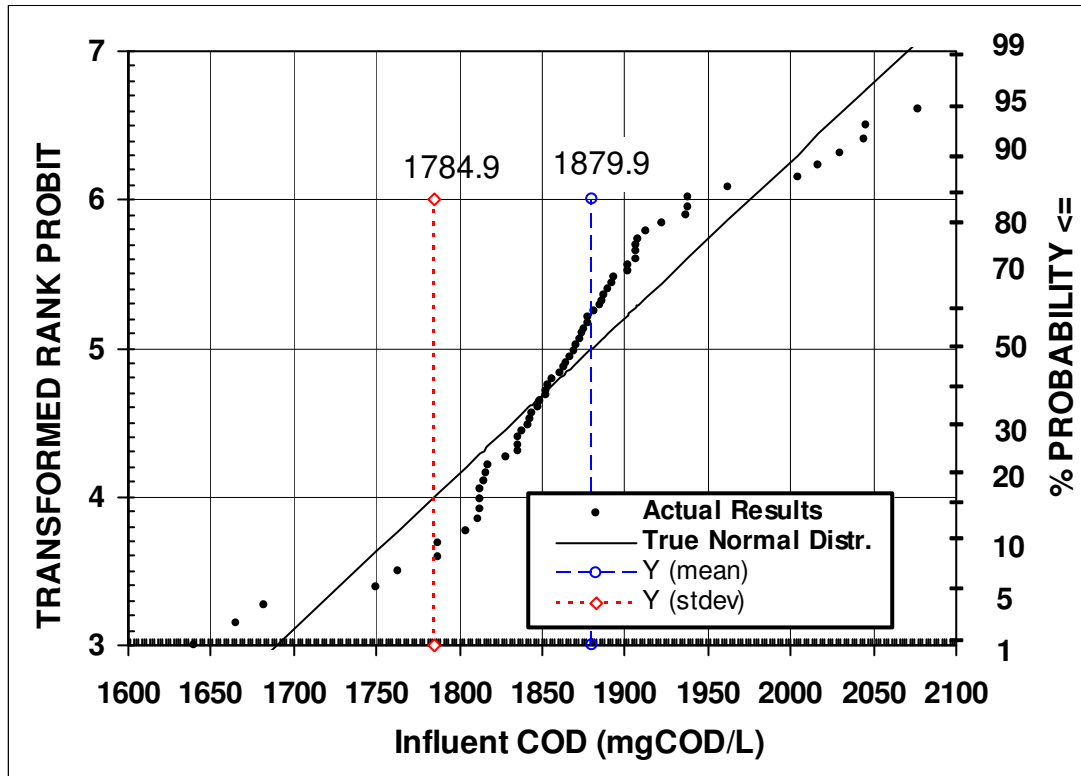


Figure 4.3: Statistical plot of the influent total COD concentration fed to UASB reactor R1 (feed sulphate $1500 \text{ mgSO}_4^{2-}/\text{L}$).

From Figure 4.2, it can be seen that in general the influent COD fed to the system remained virtually constant with time. This substantiated that the system was maintained under constant load as required for steady state conditions. From the statistical plot in Figure 4.3, the average feed COD was 1880 mgCOD/L with a sample standard deviation (SSD) of 95 mgCOD/L . This average COD value is close (0.3% higher) to the desired COD of 1875 mgCOD/L required for a system fed with a sulphate concentration of $1500 \text{ mgSO}_4^{2-}/\text{L}$ based on a feed PSS COD/ SO_4^{2-} ratio of 1.25.

The diluted influent TKN and FSA concentrations were less frequently measured than the COD, only when conducting N mass balance. Also, the total phosphorous and ortho-phosphate measurements were carried only once on the feed, since the P system not directly relevant to the aspects of BSR under investigation here.

The PSS particulate COD to VSS ratio (f_{cv}) was found to be $1.593 (\pm 0.087) \text{ mgCOD/mgVSS}$ and the TKN/VSS ratio (f_n) was $0.073 (\pm 0.005) \text{ mgN/mgVSS}$. These

ratios are typical for PSS generated at municipal wastewater treatment plants (Ristow *et al.* 2005).

Table 4.2: Summary of the influent characteristics for UASB reactor R1 when fed 1500 mgSO₄²⁻/L (SSD = sample standard deviation).

Parameter	Average value	SSD
Total COD (mgCOD/L)	1880	95
Total soluble COD (mgCOD/L)	226	34
Unbiodegradable particulate COD ($f_{up} = 0.36$) (mgCOD/L) ¹	677	
VFA (or SCFA) (mgHAc/L)	126	13
Fermentable readily biodegradable COD (mgCOD/L)	94	
Slowly biodegradable COD (mgCOD/L) ¹	977	
Unbiodegradable soluble (mgCOD/L) ¹	6	
TKN (mgN/L)	78	9
FSA (mgN/L)	10	2
H ₂ CO ₃ * alkalinity (mg/L as CaCO ₃) before dosage	22	3
H ₂ CO ₃ * alkalinity (mg/L as CaCO ₃) after dosage	450	25
Total phosphorous (mgP/L) ²	20	
Ortho-phosphate (mgP/L) ²	5.9	
pH before dosage	6.09	0.10
pH after dosage	7.20	0.15

¹ By calculation

² Only one measurement

4.5.2 Reactor performance

Since, during the initial period of this investigation the focus was on the feasibility and performance of the UASB reactor treating sulphate-rich water using PSS as organic substrate, the different effluent parameters measured are plotted and discussed below. Daily analyses of the effluent parameters were not conducted from steady state period 9 (Day 190 onwards) because of the disruptive nature of the profile tests. However, these analyses were performed intermittently to check whether steady state was maintained.

4.5.2.1 Effluent COD concentration

Figure 4.4 illustrates the performance of the UASB reactor R1 in terms of effluent COD (total COD, total soluble COD, organic soluble COD, sulphide COD and particulate COD).

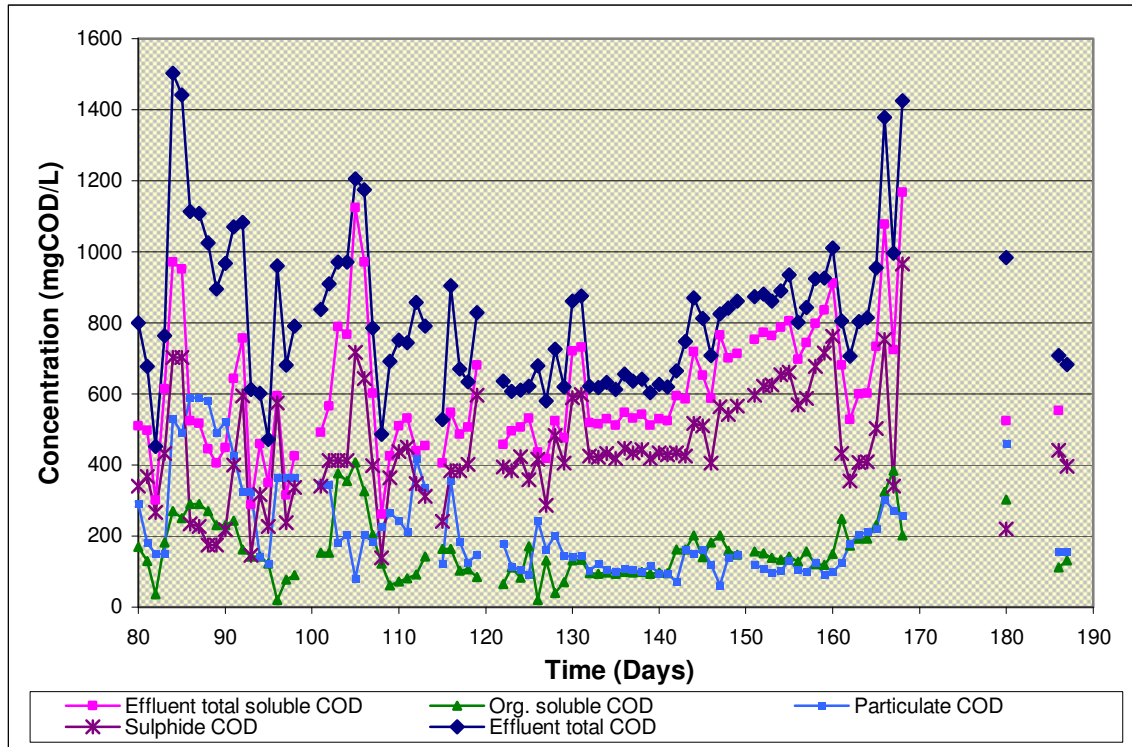


Figure 4.4: UASB reactor R1 effluent COD concentration-time profiles with PSS as substrate augmented with sulphate; Eff. Tot. COD = effluent total (soluble + particulate) COD (organic + sulphide); Organic soluble COD only = total soluble COD - sulphide COD; Part. COD = particulate organic COD.

After the initial start-up and sludge bed development phases (up to Day ~80), the effluent organic soluble and particulate COD concentrations decreased steadily while the sulphide COD concentration increased due to increased sulphate reduction. These observations indicate that BSR in the UASB reactor R1 was improving with time. The effect of HRT on effluent COD (namely the organic COD components) concentrations is discussed in Section 4.5.2.4.

4.5.2.2 Effluent sulphate concentration

The variation in UASB reactor R1 effluent sulphate concentration with time from Day 80 is presented in Figure 4.5. At each steady state period (see Figure 4.1), high sulphate removal

efficiencies (>82.5%) were obtained and the removal was more than 90% at the minimum HRT of 13.5-14.0 h (steady state period 9, >Day 185).

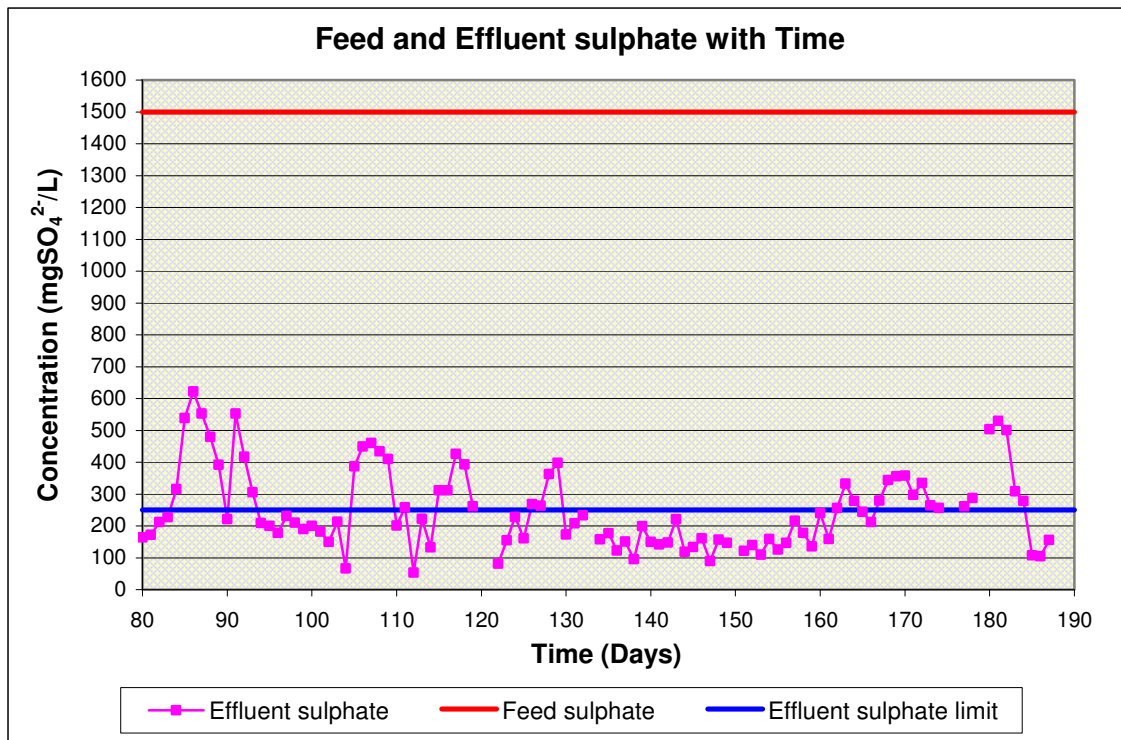


Figure 4.5: UASB reactor R1 effluent sulphate concentration-time profiles with PSS as substrate augmented with 1500 mgSO₄²⁻/L sulphate.

4.5.2.3 H₂CO₃* alkalinity, Alk H₂S and VFA concentrations

The UASB reactor R1 measured effluent H₂CO₃* alkalinity and VFA concentration with time are shown in Figure 4.6. Again, at each steady state period, high alkalinity production occurred (>1400 mg/L as CaCO₃) while the VFA concentration remained low (<100 mgHAc/L) indicating high sulphate reduction. The sum of the H₂CO₃* alk. and Alk H₂S is also plotted. For the various alkalinities, the nomenclature of Loewenthal *et al.* (1989) has been followed where Alkalinity preceding the reference species (Alk H₂S) excludes the water subsystem whereas alkalinity following the reference species (H₂CO₃* alk.) includes the water subsystem. For the sulphide subsystem, the system alkalinity (Alk H₂S) and total species concentration are related as follows:

$$\text{Alk H}_2\text{S (mg/L as CaCO}_3\text{)} = \frac{S_T (\text{mgS/L})}{\left(\frac{10^{(-pH)}}{10^{(-pK_s')}} + 1 \right)} * \frac{50}{32} \quad (4.7)$$

where $pK_s' = 6.833$ (adjusted for temperature 35 °C and ionic strength)

$pH = pH$ of sample

$S_T =$ sulphide subsystem total species concentration, i.e. $H_2S + HS^- + S^{2-}$ (mgS/L)

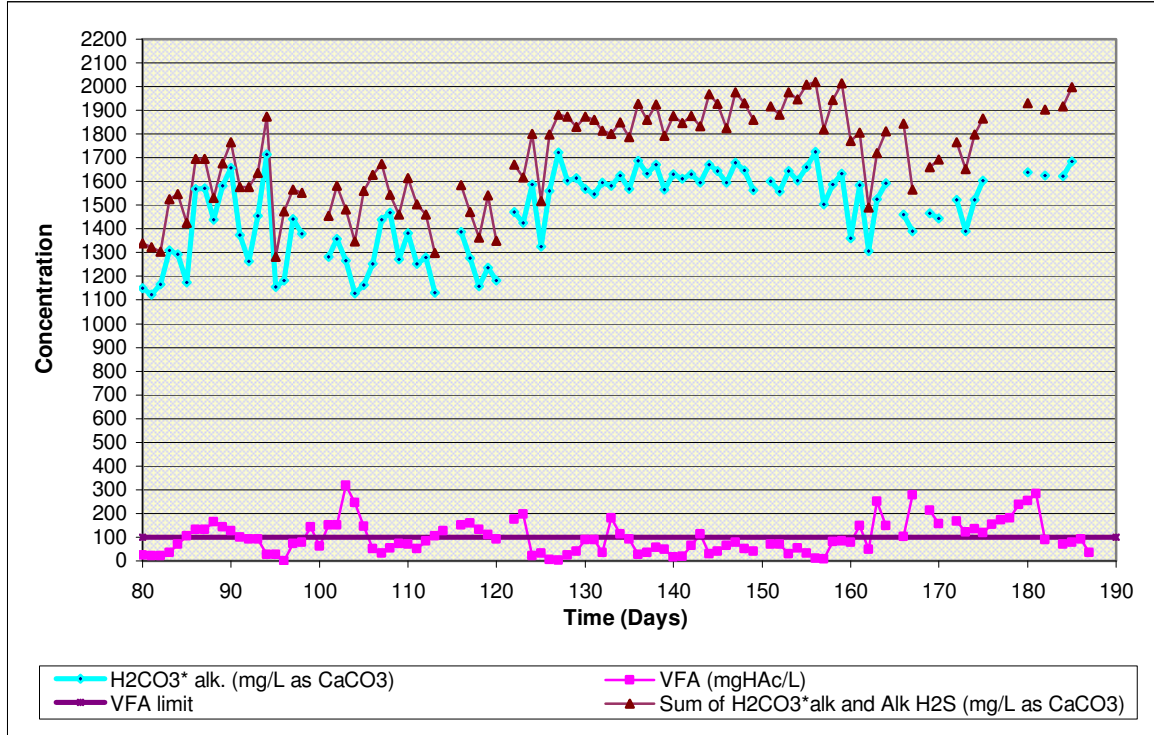


Figure 4.6: UASB reactor R1 effluent alkalinity and VFA concentration-time profiles with PSS as substrate augmented with 1500 mgSO₄²⁻/L sulphate.

As outlined in Chapter 3, Section 3.8.3, the 5-pH point titration method was used in this investigation to measure the $H_2CO_3^*$ alk. and VFA concentrations (Moosbrugger *et al.*, 1992). In a mixed weak acid/base system containing the sulphide subsystem, the correct subsystem sulphide total species concentration (S_T , mgS/L) must be entered into the 5-pH point titration programme to obtain the correct $H_2CO_3^*$ alk. and VFA concentrations. However, during this period of the investigation S_T was inaccurately measured due to the loss of H_2S during vacuum filtration and sample handling (this was later remedied with the development of new analytical procedures, as described in Chapter 5). Hence, the $H_2CO_3^*$ alk. given by the titration programme was incorrect, while the VFA concentration was marginally affected (<5%). However, the total system alkalinity is unaffected by errors in S_T and because VFA concentration and hence Alk HAc are only marginally affected, the sum of the $H_2CO_3^*$ alk. and Alk H_2S changes only marginally. Therefore, the variation of the sum of the $H_2CO_3^*$ alk. and Alk H_2S and the VFA concentrations with time plotted in Figure 4.8 are correct, while the $H_2CO_3^*$ alk. contains some errors. As noted above, during

sample handling H_2S was lost which decreases the measured S_T value thereby decreasing the Alk H_2S (Equation 4.7). As a result, when the low S_T is entered into the 5-pH point titration programme, the determined H_2CO_3^* alk. increases in order to keep the total alkalinity unchanged. Thus the determined H_2CO_3^* alk. is overestimated. The effects of H_2S (and CO_2) loss on subsystem species, total and subsystem alkalinities are discussed in detail in Chapter 5. Accepting the errors above, it should be noted that the influent sulphate concentration was kept constant throughout the investigation period, and the effluent sulphate concentration remained consistently low. This implies that with little error the effluent sulphide (S_T) concentration can be accepted as approximately constant. Hence, although the H_2CO_3^* alk. values in Figure 4.6 are in error, this error remains approximately constant as substantiated by the closely matching concentrations with time for H_2CO_3^* alk. and H_2CO_3^* alk. + Alk H_2S . Accordingly, the relative variation in H_2CO_3^* alk. in Figure 4.6 remains valid.

From Figure 4.6, as expected from Section 4.4, the UASB system generates significant alkalinity (1820 to 2018 mg/L CaCO_3), a significant advantage in the treatment of low pH and alkalinity AMD waters. Furthermore, even at a HRT as low as 13.5h, the effluent VFA remains low (< 84 mgHAc/L). Thus, in contrast to the RSBR configuration originally incorporated in the BioSURE[®] system, with the UASB reactor a downstream reactor is not required for sulphate reduction with effluent VFA. From Section 4.4, the low UASB reactor R1 effluent VFA concentration would indicate that the production of VFA is rate or mass limiting, rather than BSR with a high residual VFA. Thus, either of the processes 1. PSS hydrolysis or 2. VFA production is rate or mass limiting in the UASB system. To establish whether these processes are rate or mass limiting requires assessment of the residual biodegradability of the sludges wasted from the UASB system: If the biodegradability is high, the process rates are limiting, if low then the supply of PSS is limiting.

4.5.2.4 Effect of HRT on effluent parameters

With reference to the sequence of reactions for BSR with PSS illustrated in Section 4.4, Figures 4.4-4.6 are interpreted taking into consideration the effects of decreased HRT (i.e. increase in influent flow rate) with time. The intermittent concentration peaks, particularly evident in the effluent sulphate concentration (Fig. 4.5), are a direct consequence of the stepwise decreases in HRT. However, the UASB system adapted relatively rapidly to these

HRT decreases, indicated by the rapid decrease in effluent sulphate concentration. These results demonstrate that the system readily accommodated the decreases in HRT (increase in PSS loading), but required time to develop the relevant acidogenic and BSR biomasses. The significant presence of SRB is indicated by the low effluent sulphate and VFA concentrations, and the good sulphate removal achieved (~ 91%, see Table 4.3 later).

As a consequence of the BSR, significant alkalinity was generated in the system (Fig. 4.6) (influent alkalinity ~ 450 mg/L as CaCO_3). This high alkalinity production (Eqs (4.4) to (4.6)) maintained a relatively high effluent pH (7.05-7.25) (average pH = 7.15 ± 0.03 for a HRT of 13.5-14.0h) and resulted in a strong buffer capacity, and indicates that the system probably will maintain a near neutral pH by itself. The alkalinity generation is desirable in the overall process design for AMD remediation (Rose *et al.*, 2002), and can be recycled to blend with the raw AMD for metals precipitation and influent pH adjustment.

Throughout the investigation up to Day 160 (when the HRT >13.5h), the effluent VFA remained low (<100 mgHAc/L, except for intermittent spikes in response to HRT decreases). This, and the presence of residual sulphate would indicate that the VFA generation, i.e. PSS hydrolysis/acidification (Eqs (4.1) to (4.3)), was the rate limiting step, in agreement with Ristow *et al.* (2005). This was investigated further in the bed profiles, see below.

Following the initial start-up and sludge bed development phases (up to Day ~80), the effluent particulate COD concentration remained low, and continually decreased with time, to < 150 mgCOD/L by Day 130 (Fig. 4.3). This indicated good sludge bed separation substantiated by visual observations (Fig. 4.7). Significant sludge bed granulation (1.0 - 1.5 mm granules) was observed after 110 days, enhancing sludge bed separation. The effluent total organic COD (particulate + soluble but with sulphide removed) was as low as 200 mgCOD/L indicating an 89 % COD removal efficiency (average influent PSS COD 1880 mgCOD/L), even at a HRT as low as 14h.

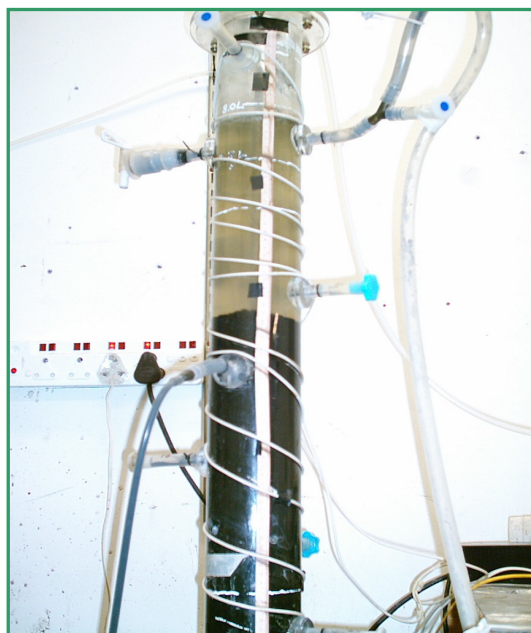


Figure 4.7: Photograph of the UASB reactor illustrating good sludge bed separation resulting in a clear effluent discharge.

In operation, the HRT was decreased stepwise to 16.0h by Day 138, and to 13.5h by Day 159 (Table 4.1). With the HRT in the 13.5-16.0h range, effluent COD, VFA and sulphate remained low and alkalinity high, indicating successful operation and performance of the system at these HRTs. However, when the HRT was reduced (Table 4.1) below 13.5h, to 13.0h on Day 160 to Day 167 and then to 12h from Day 168 to Day 180, progressive system failure was observed. This was indicated by the increase in the effluent sulphate concentration from 149 $\text{mgSO}_4^{2-}/\text{L}$ to 315 $\text{mgSO}_4^{2-}/\text{L}$ (Fig. 4.5) and VFA concentration from 48 to 172 mgHAc/L (Fig. 4.6), and decline in effluent alkalinity concentration from 2013 to 1594 mg/L as CaCO_3 (Fig. 4.6). During the 12h HRT period, the effluent organic COD concentration (Fig. 4.4) increased significantly from 250 to 626 mgCOD/L . This deterioration in system performance could be ascribed to two possible causes. Firstly, because the reduction in HRT was achieved by increasing the influent flow rate, the increase in upflow velocity caused expansion of the sludge bed. Since the bed volume was maintained constant at 6.7L, the mass of sludge removed from the system correspondingly increased, causing a reduced sludge bed mass (or sludge age) and concomitantly a reduced biomass available to mediate the reactions. Secondly, the increased upflow velocity resulted in a significant loss in the mass of sludge to the effluent (indicated by the increase in effluent particulate COD, Fig. 4.4), further reducing the sludge age and biomass available. These observations indicate a minimum stable HRT for the system would be about 13.5-

14.0h. This HRT appears to be determined by the upflow velocity in the sludge bed ($0.127 \text{ m}^3/\text{m}^2/\text{h}$ here) rather than by contact time between soluble substrate (VFA, sulphate) and biomass. The upflow velocity and bed volume are influenced by the reactor diameter and height, e.g. the bed volume can be kept the same with a lower bed height but an increased diameter, which would decrease the upflow velocity. Clearly, the relationship between HRT and upflow velocity needs to be investigated further - the effect of bed expansion on the UASB reactor performance will be further described in Chapter 6.

Following the observed system failure at $\text{HRT} < 13.5 \text{ h}$, on day 181 the HRT was restored to 14h (Table 4.1). Immediately a significant improvement in system performance was observed, to restabilise at the previously observed effluent concentrations as shown in Figures 4.4-4.6 for the effluent concentration with time graphs.

4.5.2.5 Effluent pH

Throughout the experimental period, the effluent pH remained within the range of 7.05 to 7.25. Later it will be shown that because the PSS is carbon (C) deficient, i.e. it can donate more electron than supply C for the required HCO_3^- alkalinity increase, the sulphide system governs the pH of the UASB system. Figure 4.8 shows the variation in UASB reactor R1 effluent pH with time. The influent pH is also shown for comparison. The influent pH was 7.2 because a measured mass of NaHCO_3 was added to the influent increasing its value to $\sim 450 \text{ mg/L}$ as CaCO_3 .

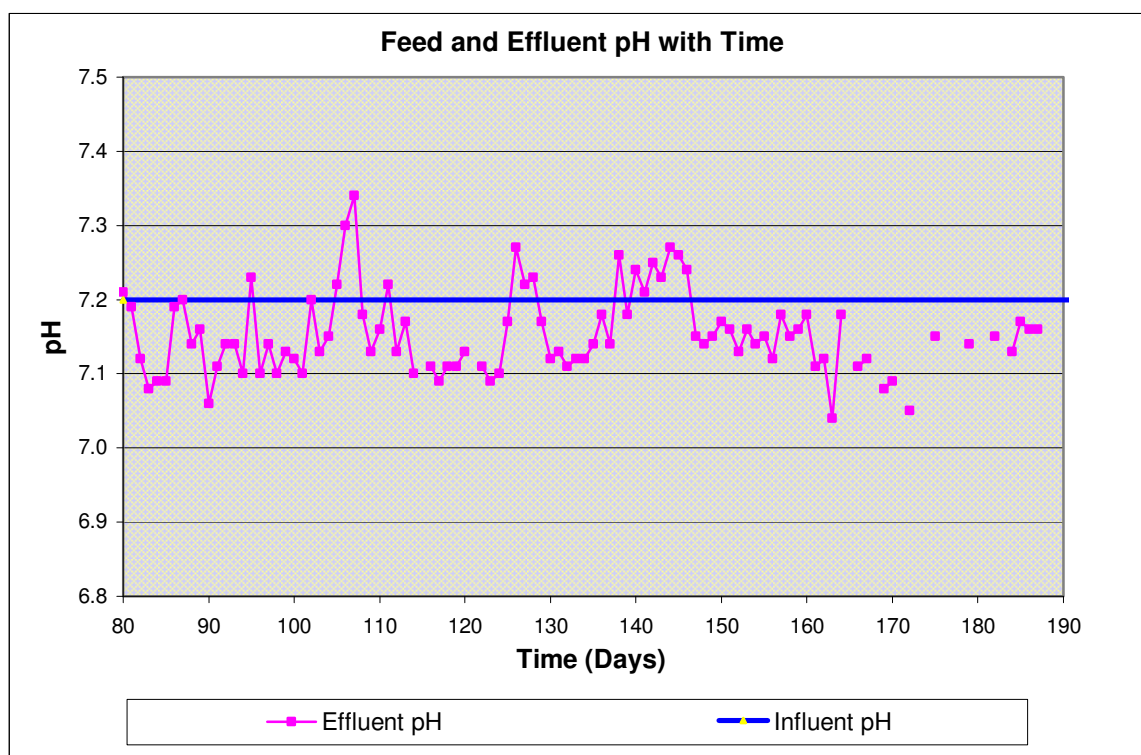


Figure 4.8: UASB reactor R1 influent and effluent pH-time profiles with PSS as substrate augmented with $1500 \text{ mgSO}_4^{2-}/\text{L}$ sulphate.

4.5.2.6 Summary of UASB R1 performance

A summary of the average experimental data at the different HRTs and bed retention times (BRTs) is listed in Table 4.3. The minimum HRT for which the specified effluent criteria were still met was found to be 13.5-14 h, where sulphate removal efficiency exceeded 90%. Reactor operation during Days 160-180 represents the period where the reactor was intentionally operated above its optimum capacity (HRT was reduced below 13.5h, namely to 12-13h), shown by the relatively low sulphate and organic COD removal efficiencies (66.4-82.9 % and 60.1-80.9% respectively).

Table 4.3: R1 Sulphate and organic COD removal (%) under steady state conditions at each HRT and BRT (see Fig. 4.1).

Days of operation	Steady state no. as on Fig 4.3	HRT (h) ^a	BRT (h) ^b	Feed flow rate (L/d)	Organic loading rate (gCOD/d)	Sulphate loading rate (gSO ₄ /d)	Sulphate removal (%)	Organic COD removal (%)
80-84	1	30.0	25.8	6.2	11.16	9.36	87.2	83.1
94-104	2	29.0	24.9	6.5	12.28	9.68	88.1	77.4
110-114	3	25.0	21.5	7.5	13.84	11.23	88.2	77.2
122-125	4	23.0	19.8	8.1	14.75	12.21	90.3	86.2
130-137	5	18.0	15.5	10.4	19.12	15.60	88.4	87.3
138-143	6	16.0	13.7	11.7	21.91	17.55	89.0	87.4
144-147	7	15.0	12.9	12.5	23.73	18.72	91.7	84.3
148-159	8	14.0	12.0	13.4	24.96	20.06	90.1	82.7
163-180	Unstable	13.0	11.2	14.4	29.47	21.60	79.2	73.1
184-187	9	13.8	12.1	13.6	25.67	20.35	89.4	86.2

a: HRT calculated at a liquid volume of 7.8L

b: BRT calculated at sludge bed volume of 6.7L

4.6 UASB R1 PERFORMANCE AT LOWEST OPTIMAL HRT

For the period Day 148-159, when the UASB reactor was operated under steady state conditions (steady state period 8, Table 4.3) at the minimum HRT of 13.5h, the values of the measured effluent parameters during this period are statistically analysed in this section. The average measured effluent concentrations and sample standard deviations (SSD) are evaluated.

4.6.1 Average effluent COD

The following averages were obtained for the various effluent COD concentrations:

Average total COD = 876 mgCOD/L (SSD 45)

Average total soluble COD = 761 mgCOD/L (SSD 41)

Average organic soluble COD = 141 mgCOD/L (SSD 32)

Average sulphide COD = 620 mgCOD/L (SSD 42)

Average particulate COD = 115 mgCOD/L (SSD 22)

The particulate COD removal was 93% (influent particulate COD = 1640 mgCOD/L) even at the HRT as low as 13.5h. The exceptionally good solid-liquid separation obtained in the UASB system is a major advantage of this configuration as opposed to the initial BioSURE[®] system with the RSBR configuration where significant solids loss to the effluent occurred (Rose *et al.*, 2002). This good solids retention and solids-liquid separation with low suspended solids in the UASB configuration obviates the need for including a post reactor for solids removal. A quasi-clear effluent was observed with low suspended solids, as can be seen in Figure 4.7.

4.6.2 Average effluent sulphate

For the period Day 148-159 (steady state no. 8) at the lowest HRT of 13.5 where performance remained stable, the effluent sulphate concentration is plotted statistically in Figure 4.9. The mean effluent sulphate concentration was 149 mgSO₄²⁻/L (SSD = 28).

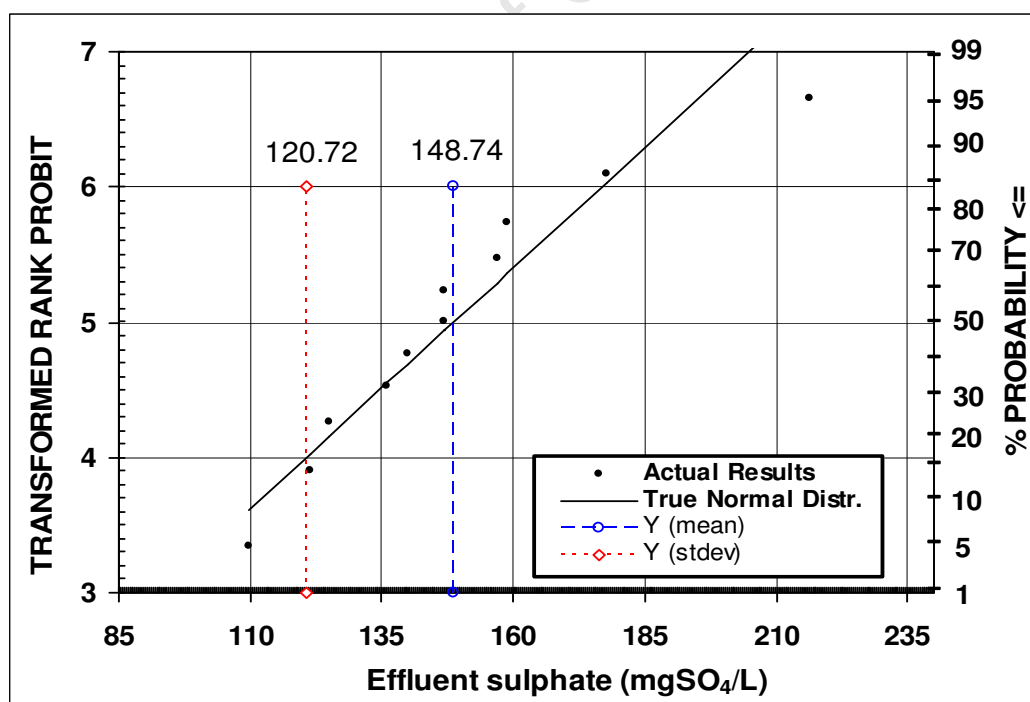


Figure 4.9: Statistical plot for effluent sulphate concentration in UASB reactor R1 (fed 1500 mgSO₄²⁻/L) for steady state 8 (days 148-159) with HRT = 13.5-14.0h.

4.6.3 Average effluent H_2CO_3^* alkalinity + Alk H_2S , H_2CO_3^* alkalinity and VFA

Statistical analyses for the sum of the H_2CO_3^* alk. and Alk H_2S , and for the VFA concentration during the period Day 148-159 (steady state 8) are plotted in Figures 4.10, 4.11 and 4.12 respectively.

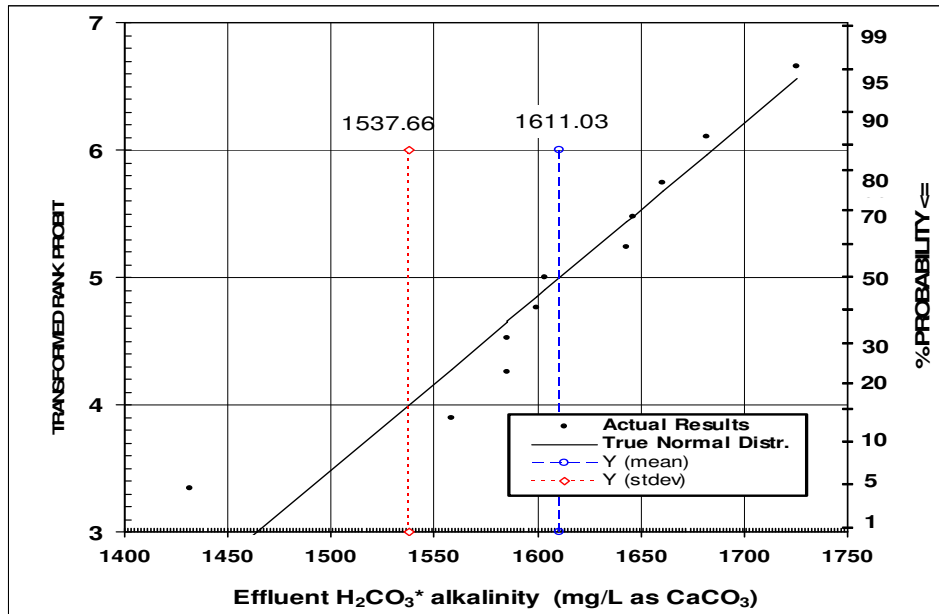


Figure 4.10: Statistical plot for effluent H_2CO_3^* alk. concentration in UASB reactor R1 (fed $1500 \text{ mgSO}_4^{2-}/\text{L}$) for steady state 8 (days 148-159) with HRT = 13.5-14.0h.

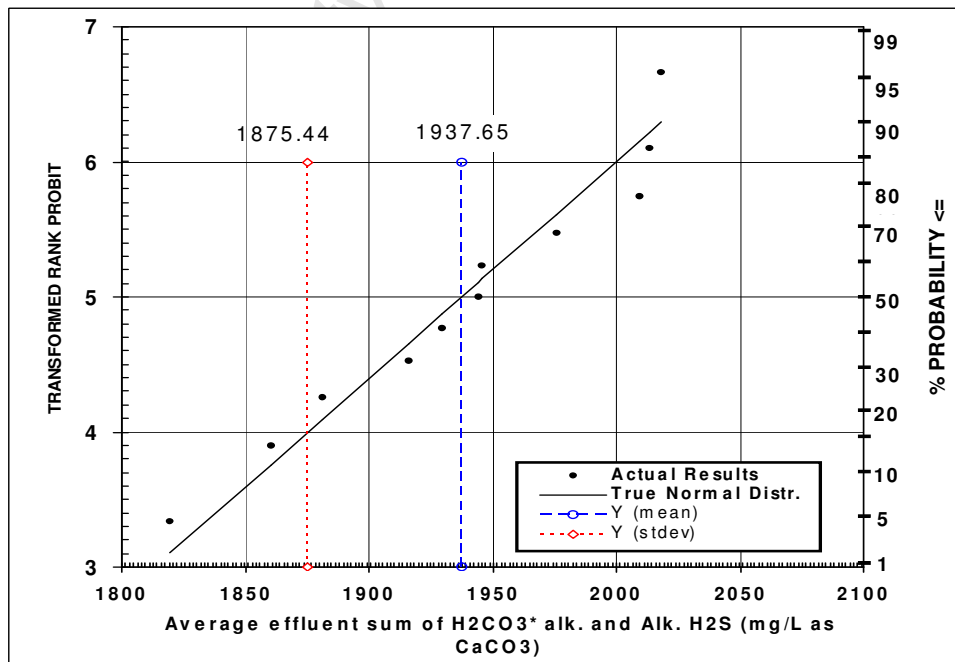


Figure 4.11: Statistical plot for effluent sum of H_2CO_3^* alk. and Alk H_2S concentration in UASB reactor R1 (fed $1500 \text{ mgSO}_4^{2-}/\text{L}$) for steady state 8 (days 148-159) with HRT = 13.5-14.0h.

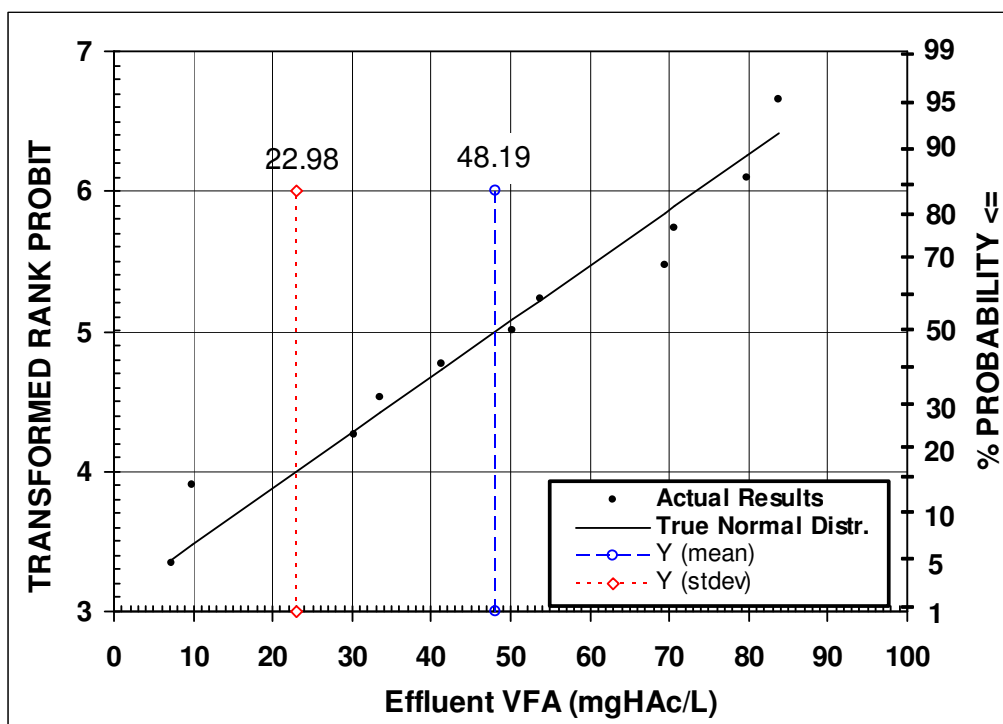


Figure 4.12: Statistical plot for effluent VFA concentration in UASB reactor R1 (fed 1500 mgSO₄²⁻/L) for steady state 8 (days 148-159) with HRT = 13.5-14.0h.

4.6.4 Average effluent pH

From the statistical plot depicted in Figure 4.13 for the period Day 148-159 (steady state 8), the average pH value was 7.15 with SSD 0.03. This pH falls within the optimum range for anaerobic digestion including BSR. This mean pH value is close to the pK value of the H₂S/HS⁻ subsystem which is 6.93 (at 35 °C) suggesting that the reactor pH was governed by the sulphide subsystem rather than the carbonate (CO₂) system. This observation is very important in the development of a steady state model for BSR to predict system performance and pH. Details of the development of such a model are described in Chapter 7.

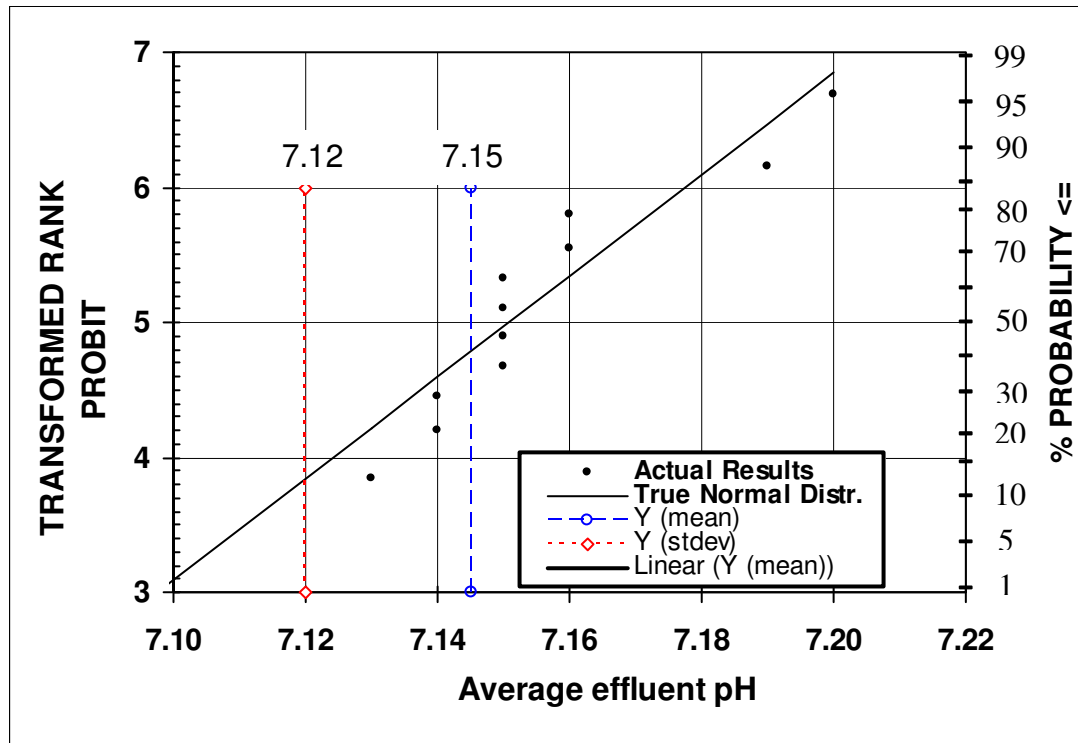


Figure 4.13: Statistical plot of effluent pH in UASB reactor R1 (fed $1500 \text{ mgSO}_4^{2-}/\text{L}$) for steady state 8 (days 148-159) with HRT = 13.5-14.0h.

4.7 BED PROFILING ALONG AXIS OF REACTOR R1

During periods of stable operation at 13.5 to 14.0h HRT, samples were taken from the intermediate sampling ports of the UASB reactor spaced at regular height intervals of 10, 30, 50, 70 and 90 cm. Samples were taken from the top to the bottom of the reactor column to minimise bed disruption during sampling. Bed profiles were conducted on days 157, 186, 198 and 205 (see Table 4.1 for steady state periods and operating conditions, and Figures 4.4-4.7 for steady state performance). Results of these bed profile tests are shown in Figures 4.14(a) and 4.14(b).

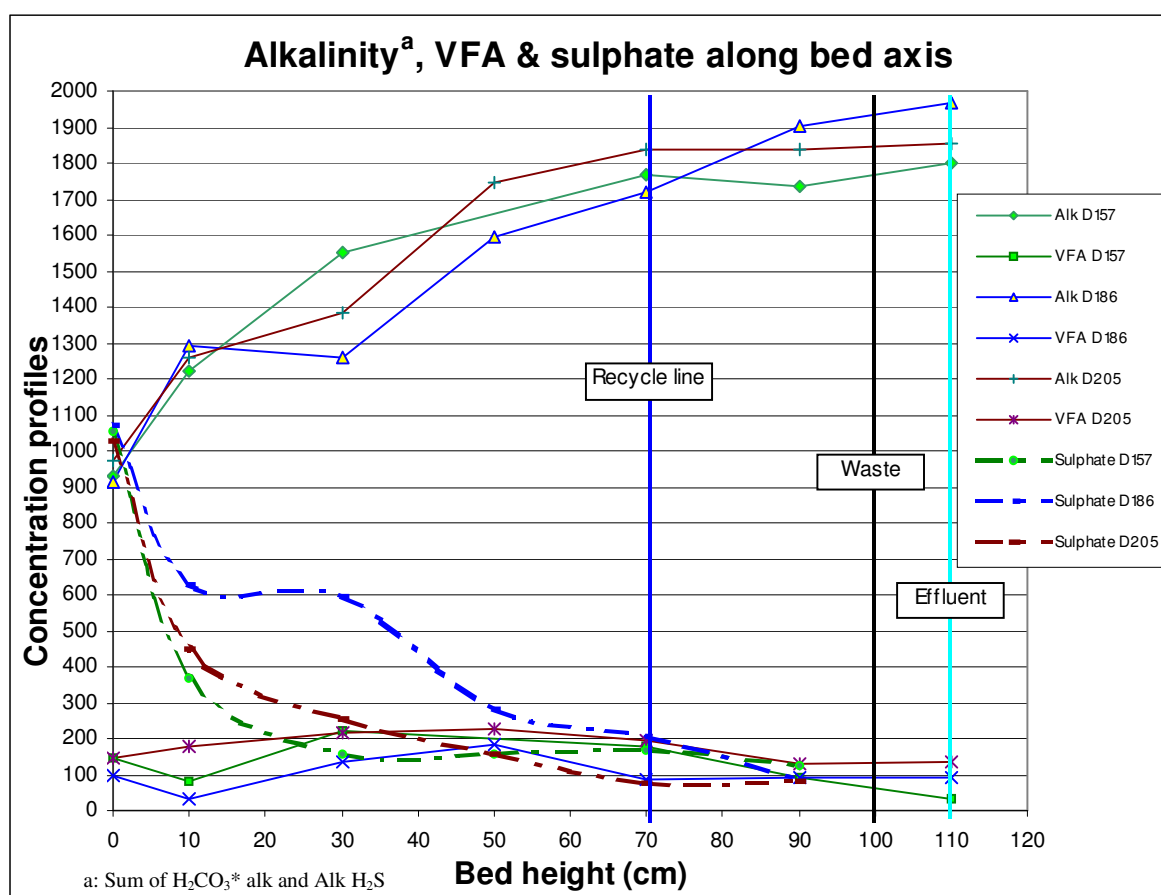


Figure 4.14(a): Reactor alkalinity, VFA and sulphate concentration profiles up the sludge bed height (98 cm) for a BRT of 12.0h.

From Figure 4.14(a), BSR, indicated by the decrease in sulphate and increase in alkalinity, commences immediately at the bottom of the bed and continues through the bed. Furthermore, through the 1st half of the bed there is only a very small increase in VFA (~200 mgHAc/L) followed by a decrease to the top half of the bed (>90 cm) where very little sulphate reduction takes place. These observations are different to those in the short feasibility study by Ristow *et al.* (2005) (refer to Chapter 2, Section 2.7.4) where it was observed that in the UASB system BSR only occurred in the top half of the bed. Thus, it appears that the sludge bed recycling implemented for R1 had a significant influence on the system behaviour, by seeding SRB to the bottom of the sludge bed and initiating BSR from the bottom of the bed. The better distribution of BSR through the UASB sludge bed offers considerable advantage to buffer fluctuations in influent loading and hence was strongly recommended in system implementation. Based on this preliminary investigation described in this Chapter, the 2 ML/d pilot scale BioSURE[®] system at the Ancor wastewater treatment plant (Springs, South Africa) was changed from a downflow RSBR system to an upflow UASB system with bed recycle from the top to the bottom.

In contrast to all other profiles, the Day 198 profile illustrates unusual profile characteristic Figure 4.14(b) in that the sulphate concentration increases and the alkalinity decreases at the 30 and 50 cm bed heights while the VFA concentration remained low. This indicates that the sludge recycling stopped temporarily at some point during the operation of the reactor preceding taking samples for the profile tests. This discontinuity in the sludge recycling was probably due to a recycle pipe blockage from the high organic particulate fraction of the bed sludge. Recycling highly settled sludge is often problematic in lab-scale experiments where small diameter pipes are used. This discontinuity was found to be more pronounced when R1 was operated at $1800 \text{ mgSO}_4^{2-}/\text{L}$ where a higher influent PSS COD concentration was fed resulting in higher particulate organics (see Appendix 6B for further results). It was envisaged to increase the pipe diameter to prevent blockage, but this decreased the velocity of the flow thereby causing the sludge to settle inside the pipes and eventually caused blockage. This observed impact of sludge recycle on system performance reinforced the recommendation to implement sludge bed recycling.

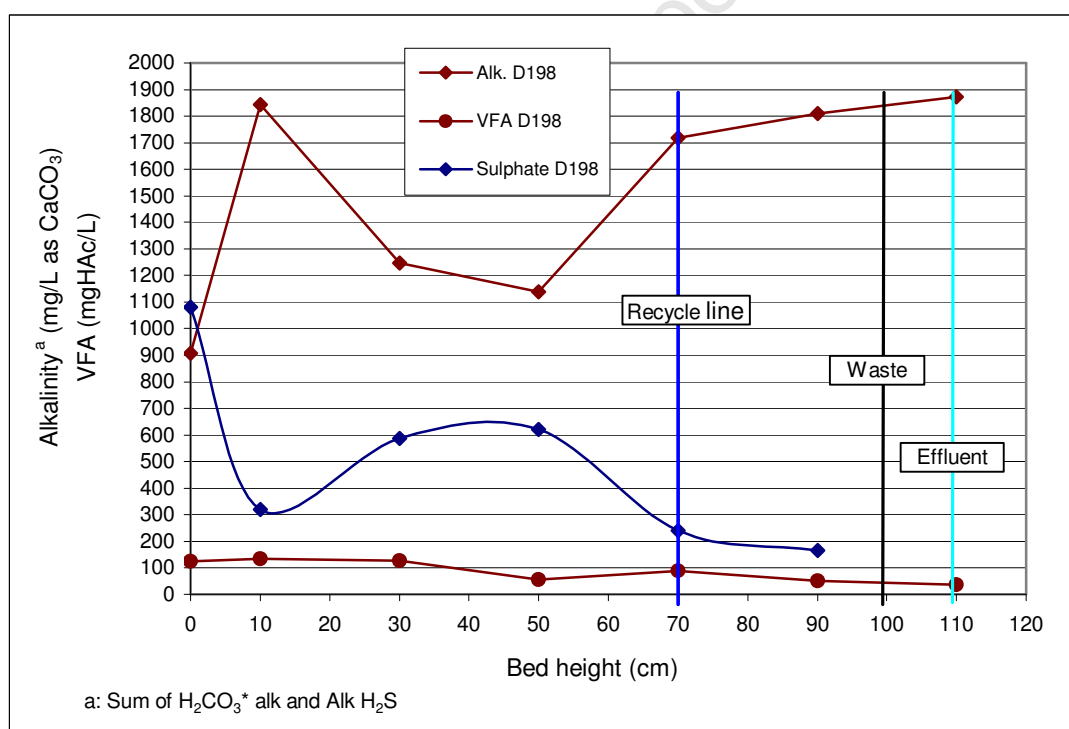


Figure 4.14(b): UASB reactor R1 alkalinity, VFA and sulphate concentration profiles up the sludge bed height (98 cm) for a BRT of 12.0h on Day 198.

Sporadic interruptions in the sludge recycling flow did not affect the steady state effluent quality at any stage as shown in Figure 4.14(b) because if blocked the sludge recycle was always reinstated the following day during system feeding and maintenance. The recycle

line was introduced to inoculate SRB biomass at the bottom of the bed to initiate BSR as soon as the feed enters the reactor and distribute the biomass more evenly along the bed. Consequently, modelling the sludge bed in the UASB system as a completely mixed reactor would be acceptable.

4.8 H₂S GAS MEASUREMENT

The H₂S gas produced by the BSR system was measured using the Phenanthroline method (see Appendix 3A). H₂S gas measurements started after the system was restored to a HRT of 14h on Day 181. The H₂S gas masses collected on operation Days 187, 240 and 252 were 0.010, 0.014 and 0.010 mgS/d respectively, with an average value of 0.011 mgS/d (SSD 0.002). These values are insignificant (~ 0.15%) when compared to the mass sulphate as S in the feed, and therefore can be ignored in the S mass balances.

4.9 TKN AND FSA CONCENTRATIONS

The average influent TKN, FSA and organic N concentrations were of 79, 10 and 69 mgN/L respectively. The effluent TKN, FSA and organic N values were 54, 31 and 23 mgN/L respectively. This therefore indicates a significant nitrogen release from the PSS organics to the effluent. The residual TKN and FSA are high and would require removal if effluent discharge to water courses is envisaged.

4.10 ANALYSIS OF WASTE SLUDGE

Every day, sludge was wasted from the top of the sludge bed to maintain the bed height constant at 6.7L. A sample of the waste sludge was dried at 105 °C and stored for elemental analysis while the rest was stored at 4 °C for future use. Waste sludge was analysed when conducting COD and N mass balances. Results of waste sludge analysis on Days 240 and 252 are shown in Table 4.4.

Table 4.4: Analysis of waste sludge from the UASB reactor R1 (fed 1500 mgSO₄²⁻/L).

Day of operation	Total COD (mgCOD/L)	Particulate COD (mgCOD/L)	TSS (mgTSS/L)	VSS (mgVSS/L)	Particulate TKN (mgN/L)	COD/VSS (f _{cv}) (mgCOD/mgVSS)	TKN/VSS (f _n) (mgN/mgVSS)
240	20400	19457	15056	12377	846	1.572	0.068
252	19850	18875	15104	13035	815	1.448	0.063
263	19632	18621	15318	12275	803	1.517	0.065

The COD/VSS (f_{cv}) and TKN/VSS (f_n) ratios were 1.512 (SSD 0.051) mgCOD/mgVSS and 0.065 (SSD 0.002) mgN/mgVSS respectively.

4.11 CALCULATION OF SLUDGE AGE (R_s)

The sludge age (R_s) in the UASB system was determined from the particulate COD of the sludge samples taken for profile tests from which the mass of sludge in the bed was calculated. The particulate COD concentration at bed height intervals 10, 30, 50, 70, and 90 cm was calculated from the measured total and soluble COD concentrations and plotted for operation Days 240 and 252 (Figure 4.15).

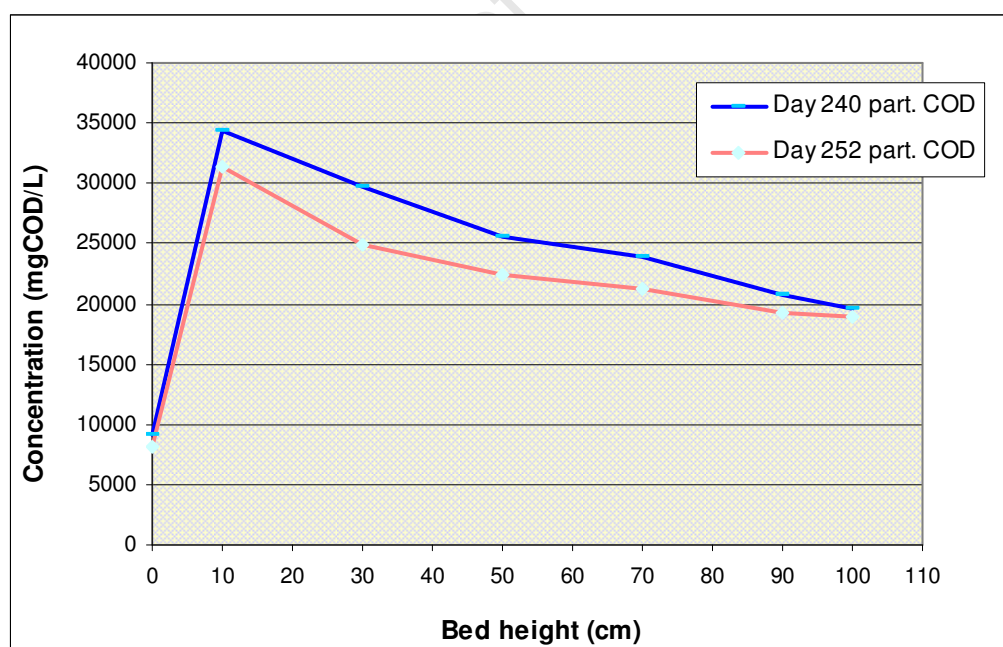


Figure 4.15: UASB reactor R1 particulate sludge COD concentration profiles up the sludge bed height (98 cm) for a BRT of 12.0h.

The particulate COD concentration at 0 cm height indicates the particulate COD concentration calculated via a mass balance on the measured influent and recycle sludge

particulate COD concentrations and the influent and recycle flow rates. The relatively high concentration of particulate COD at bed height 10 cm was due to better settling particulate organics accumulating at the bottom of the reactor and a decrease in the density of the sludge bed with bed height.

The sludge particulate COD concentration progressively decreased from the bottom of the bed to the top. This COD concentration variation along the bed axis gave no information whether the SRB biomass concentration is higher at the bottom or top of the bed, since high particulate COD does not necessarily mean high biomass concentration. However, from the profile test results in Figure 4.14(a), it was deduced that the biomass was evenly distributed along the axis of flow (made possible by the introduction of the sludge recycle line) and that BSR occurred at any bed height due to a continuously low VFA concentration.

Using the Trapezium rule, the area of the concentration curve for each sludge profile test in Figure 4.15 was determined. This area, divided by the length of the sludge bed, gave the average particulate COD concentration of the sludge bed. Though the concentration of the particulate COD of the effluent was very low with respect to the particulate COD in the sludge bed (and waste sludge) (approx. 1%), the mass of sludge in the effluent did influence the sludge age because of the high effluent flow rate (~ 13.0 L/d) compared to the waste flow rate (~ 0.4 L/d). Accordingly, the mass of solids loss with the effluent was incorporated in the calculation of the sludge age, defined as follows:

$$R_s = \frac{\text{Mass of sludge in the reactor bed}}{\text{Mass of sludge wasted/d} + \text{mass of sludge in effluent/d}}$$

$$= \frac{V_b' * S_{pb}}{Q_w * S_{pw} + Q_e * S_{pe}}$$

where:

- V_b' = sludge bed volume before wastage (L)
- S_{pb} = particulate COD concentration of sludge bed calculated from profile test (mgCOD/L)
- Q_w = waste flow rate (L/d)
- S_{pw} = particulate COD concentration of waste sludge (mgCOD/L)

Q_e	=	effluent flow rate (L/d)
S_{pe}	=	effluent particulate COD concentration (mgCOD/L)

The R_s calculated on Days 240 and 252 were 18.2d and 17.9d respectively, with an average value of 18.1d. As noted earlier, the sludge retention in the UASB reactor sludge bed, and hence R_s , is influenced by the upflow velocity which also establishes the HRT. The interrelationships between HRT, R_s and upflow velocity require further investigation. This investigation will have to be done at pilot- or full-scale due to the variability in hydraulic effects introduced with scale-up.

4.12 MASS BALANCES

The COD, S and N mass balances were calculated with the equations set out in Chapter 3, Sections 3.9.1 to 3.9.3. The mass balance were conducted at the end of the initial experimental programme for this period, namely on Days 187, 240 and 252.

4.12.1 COD mass balance

The COD mass leaving the UASB system was calculated from the unfiltered total COD in the effluent and waste sludge and their respective flow rates. As shown in Table 4.5, the COD mass balance for both Days 240 and 252 respectively was relatively low (average 88.7%). In tracing the discrepancy in the COD mass balance, the effluent total COD was fractionated into its various components as listed in Table 4.5. Comparing the measured sulphide with the theoretical sulphide calculated from the measured sulphate reduced, the measured sulphide was substantially lower. In examining the sulphide test method, it was suspected that sulphide was lost in sample handling (mixing, dilution and vacuum filtration) before conducting the COD test, causing an underestimate of the total effluent COD (S_{te}) concentration (organic + sulphide COD) and the waste sludge (S_{tw}) concentration (organic + sulphide COD). Since the COD mass out was calculated on unfiltered samples, it was deduced that H_2S gas might have escaped these unfiltered samples during handling (namely mixing and dilution) before conducting the COD test (~ 11%). It was therefore suspected that the low COD balance was due to error in analytical methods rather than in UASB system operation. This conclusion was supported by the low S mass balances achieved also.

Table 4.5: COD mass balance around UASB reactor R1 (35 °C).

Parameters	Units	Day 240	Day 252
Feed flow rate, Q_i	L/d	13.7	13.8
Influent total COD, S_{ti}	mgCOD/L	1905	1881
Influent sulphate in	mgSO ₄ /L	1500	1500
Effluent total COD, S_{te}	mgCOD/L	1070	1127
Effluent sulphide as COD	mgCOD/L	505	561
Sulphate reduced	mgSO ₄ /L	1303	1267
Effluent sulphide as COD (based on measured sulphate reduction)	mgCOD/L	869	845
Total COD of waste sludge, S_{tw}	mgCOD/L	20400	19850
Effluent flow rate, Q_e	L/d	13.3	13.4
Waste sludge flow rate, Q_w	L/d	0.4	0.4
Mass of COD in = $Q_i * S_{ti}$	mgCOD/d	26099	25963
Mass of COD out	mgCOD/d	22964	23230
Mass COD in waste sludge = $Q_w * S_{tw}$	mgCOD/d	8772	8139
Mass COD in effluent = $Q_e * S_{te}$	mgCOD/d	14192	15092
COD mass balance	%	88.0	89.5

4.12.2 Sulphur (S) mass balance

From Table 4.6, the S mass balance was found to be substantially lower in magnitude when compared to the COD mass balance. This discrepancy in the S mass balance was directly related to the error in measurement of sulphide. With the effluent sample pH varying between 7.05 and 7.25, a considerable fraction of the total sulphide (S_T) is in the undissociated hydrogen sulphide (H_2S) form. Since sulphide was measured via the COD test on vacuum filtered samples, a subsequent proportion of the H_2S was expelled during filtration resulting in a low sulphide (S_T) concentration. The average S mass balance over the system was 68.7% (SSD 3.4).

Table 4.6: Sulphur mass balance around UASB reactor R1 (35 °C).

Parameters	Units	Day 187	Day 240	Day 252
Influent flow rate, Q_i	L/d	13.50	13.70	13.80
Influent sulphate	$\text{mgSO}_4^{2-}/\text{L}$	1500	1500	1500
Mass S in	mgS/d	6750	6850	6900
Effluent flow rate, Q_e	L/d	13.12	13.28	13.39
Waste sludge, Q_w	L/d	0.38	0.42	0.41
Effluent sulphate	$\text{mgSO}_4^{2-}/\text{L}$	105	197	233
Sulphate in waste sludge	$\text{mgSO}_4^{2-}/\text{L}$	105	201	237
Effluent sulphide	mgS/L	316	253	281
Sulphide in waste sludge	mgS/L	316	273	281
H_2S gas produced	mgS/L influent	0.72	1.01	0.69
Mass S out	mgS/d	4749	4381	4961
S mass balance	%	70.4	64.0	71.9

A graphical representation of the concentrations of the total sulphide measured and the total theoretical sulphide produced from the measured sulphate reduction is shown in Figure 4.16 to visualise the discrepancy in S.

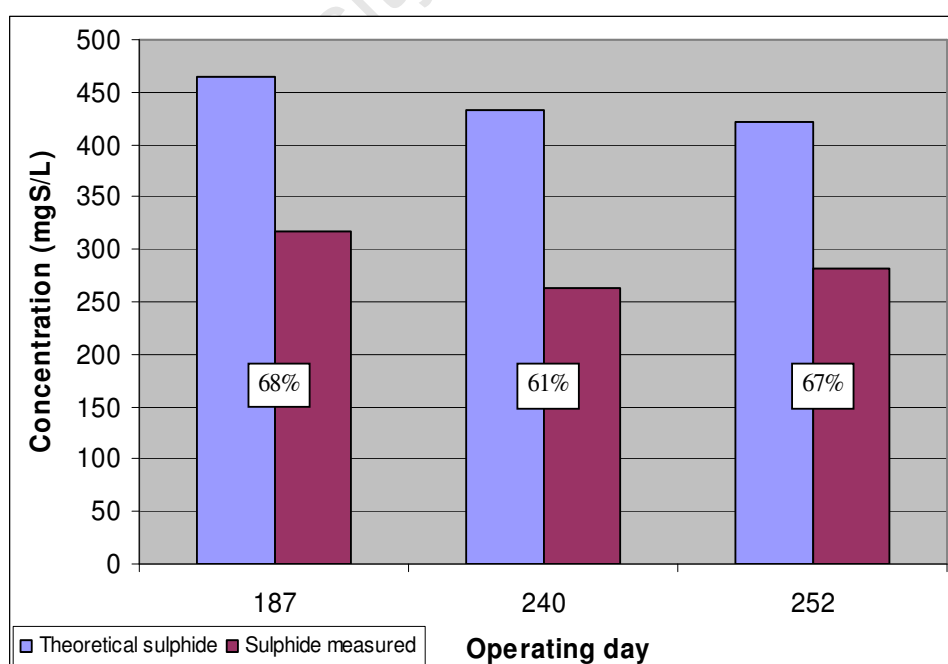


Figure 4.16: Graphical representation of concentrations of sulphide expected and sulphide measured for UASB reactor R1 (fed $1500 \text{ mgSO}_4^{2-}/\text{L}$).

Also shown in the same figure, is the % sulphide recovery over the theoretical value. Clearly, sulphide was inaccurately measured and was the parameter responsible for the low COD and S mass balances. Good operation of the UASB system was confirmed with the very good N mass balance achieved. The relatively low COD mass balance and poor S mass balance therefore prompted an investigation to prevent the loss of sulphide (namely H_2S) from the effluent sample by the development of simple wet chemistry analytical procedures thereby to accurately measure S_T using the COD test. This investigation is described in detail in Chapter 5.

4.12.3 Nitrogen (N) mass balance

The N mass balance was carried only once during this operating period on Day 240 and was found to be 97.1%. This good N mass balance confirms UASB system operation reliability.

4.13 LAB-SCALE REACTOR OPERATIONAL CONSIDERATIONS

During the experiment, some operational difficulties were encountered with the UASB system that had to be overcome. Firstly, although the PSS was thoroughly macerated prior to feed preparation, the peristaltic pump feed pipe burst on several occasions, especially at the start of the experiment, due to grit and/or sand particles in the PSS. To remedy this and prevent further pipe bursts, the silicon pipe was regularly changed, normally after every 4-5 days.

The second consideration was the removal of a relatively large volume of sludge in the profile tests. In order to carry out all the tests to determine the variation in the particulate and soluble organics along the bed axis, a considerable volume (~ 1L in total) of sludge was taken from the sampling ports of the reactor. The removal of this large volume of sludge removed decreased the bed height to considerably lower than 6.7L, hence creating a period of reactor performance instability. However, the system recovered rapidly over the subsequent 2 or 3 days and re-establishing the pre-set bed height. Accordingly, profile tests had to be carefully planned and spaced so as not to create unnecessary prolonged periods of instability in the sludge bed.

4.14 CLOSURE

In this Chapter, the experimental results of the UASB reactor R1 (35 °C) have been discussed. The results obtained show that sulphate was successfully reduced under sulphidogenic conditions in the UASB reactor to well below 200 mgSO₄²⁻/L (average 150 mgSO₄²⁻/L) using PSS as carbon source and electron donor. The UASB reactor was operated for 280 days with an influent sulphate concentration of 1500 mgSO₄²⁻/L and COD 1875 mgCOD/L. The minimum HRT was found to be about 14h (13.5-14.0h) with low effluent sulphate (< 250 mgSO₄²⁻/L) and VFA (< 100 mgHAc/L) concentrations. Solid-liquid separation in the system was excellent (unfiltered organic COD <200 mgCOD/L), achieved even at a HRT of 14h, with very low solids content in the effluent. The PSS and likewise the reactor sludge, which had a good settleability, appeared to enmesh and entrap fine solids arising from biodegradable particulate organic breakdown. Sludge bed granulation in the system was observed, which further enhanced solid/liquid separation. A summary of the operating and design parameters of BSR using PSS as substrate in a UASB reactor is given in Chapter 6 along with those of R2 (operated at T=20 °C and fed 1500 mgSO₄²⁻/L) and R1 (fed 1800 mgSO₄²⁻/L).

At HRT lower than 13.5h while maintaining the sludge bed height constant, effluent quality from the UASB reactor deteriorated. This deterioration could be ascribed to the reduced sludge bed biomass caused by sludge bed expansion and sludge loss with the effluent as a result of the increased upflow velocity. Since the upflow velocity is a function of the reactor aspect ratio (diameter to height), relationships between HRT, upflow velocity, sludge settleability and bed expansion needed to be established. An investigation of the sludge settleability and bed expansion was conducted on the UASB sludge and is discussed in Chapter 6. The introduction of a bed recycle flow from the top to the bottom of the reactor bed effectively distributed the SRB biomass throughout the bed, facilitating sulphate reduction as soon as the feed entered the reactor. This recycling of the sludge bed offered considerable advantages in BSR using the UASB configuration. Based on the preliminary results of this investigation, the pilot plant of the Grootvlei Mines Ltd (Springs, South Africa) was scaled up from 2 ML/d to 10 ML/d.

COD, S and N mass balances conducted over the system averaged 88.7%, 68.7% and 97.1% respectively. The relatively low COD mass balance was attributed to the loss of H₂S during

sample handling (mixing and dilution) in analysis, while the poor S mass balance was ascribed to the loss of H₂S during both sample handling and vacuum filtration. It was found that the measured total effluent sulphide was too low when compared with the sulphate reduced. This problem in S_T measurement using the COD test was addressed by developing new analytical procedures which are described and evaluated in the next Chapter.

University of Cape Town

APPENDIX 4A

UASB REACTOR 1 (fed 1500 mgSO₄²⁻/L)

Days	Inf. SO ₄	Feed total COD	Feed total soluble COD	Eff. SO ₄	SO ₄ rem. Effy (%)	SO ₄ removal (mg/l)	Eff. Tot. COD	Eff. Tot sol COD	Eff. Org sol COD	Eff. sulphide (mgCOD/L)	Eff. Part COD	Eff. Org. COD	Org. COD rem. Effy (%)	COD removal (mgCOD/l)	S _T (mgS/L)	Theor.S _T (mgS/L)	Eff. pH	Eff. VFA	Eff. Tot Alk.	Eff. H ₂ CO ₃ * alk.	Alk H ₂ S	BRT (h)	HRT	Flow rate (L/d)
80	1500	1922		164	89	1336	800	510	170	340	290	460	76	1462	170	445	7.21	23	1338	1151	187.0	26.9	30.0	6.2
81	1500	1812	190	172	89	1328	677	497	130	367	180	310	83	1502	184	443	7.19	21	1323	1124	199.3	26.9	30.0	6.2
82	1500	1836		212	86	1288	452	302	35	267	150	185	90	1651	133	429	7.12	21	1304	1166	137.3	26.9	30.0	6.2
83	1500	1836	210	228	85	1273	765	615	182	432	150	332	82	1504	216	424	7.08	34	1524	1309	215.6	26.9	30.0	6.2
84	1500	1875		316	79	1184	1302	772	270	502	530	800	57	1075	251	395	7.09	70	1545	1293	252.5	26.9	30.0	6.2
85	1500	1907	210	538	64	962	1242	752	250	502	490	740	61	1167	251	321	7.09	105	1426	1174	252.5	26.0	29.0	6.5
86	1500	1908	230	623	58	877	1114	524	290	234	590	880	54	1028	117	292	7.19	133	1696	1569	127.0	26.0	29.0	6.5
87	1500	1908	210	553	63	947	1108	518	290	228	590	880	54	1028	114	316	7.20	133	1696	1572	124.3	26.0	29.0	6.5
88	1500	2030	210	479	68	1021	1026	445	270	175	580	850	58	1180	88	340	7.14	164	1531	1439	91.8	26.0	29.0	6.5
89	1500	2130	330	392	74	1108	895	405	230	175	490	720	66	1410	88	369	7.16	142	1676	1583	93.2	26.0	29.0	6.5
90	1500	1848	210	222	85	1278	968	448	230	218	520	750	59	1098	109	426	7.06	126	1765	1658	106.8	26.0	29.0	6.5
91	1500	2004	254	553	63	947	1070	644	244	400	427	671	67	1333	200	316	7.11	100	1577	1373	204.3	26.0	29.0	6.5
92	1500	1682	213	417	72	1083	1082	757	163	595	325	488	71	1195	297	361	7.14	91	1575	1264	311.2	26.0	29.0	6.5
93	1500	1878	193	306	80	1194	813	488	142	346	325	467	75	1410	173	398	7.14	91	1636	1455	181.0	26.0	29.0	6.5
94	1500	1902		209	86	1291	601	459	142	317	142	284	85	1617	158	430	7.10	28	1874	1714	160.7	26.0	29.0	6.5
95	1500	1870		200	87	1300	472	350	122	228	122	244	87	1626	114	433	7.23	27	1281	1154	127.1	26.0	29.0	6.5
96	1500	1939		178	88	1322	961	595	20	575	366	386	80	1552	287	441	7.10	0	1474	1182	291.3	26.0	29.0	6.5
97	1500	1817	193	231	85	1269	682	316	78	238	366	444	76	1373	119	423	7.14	73	1565	1441	124.4	26.0	29.0	6.5
98	1500	1853	142	210	86	1290	792	426	89	337	366	455	75	1398	168	430	7.10	79	1551	1381	170.8	26.0	29.0	6.5
99	1500	2144	152	190	87	1310										437	7.13	143				26.0	29.0	6.5
100	1500	1811		200	87	1300										433	7.12	63				25.8	28.8	6.5
101	1500	1874	152	182	88	1318	838	493	152	340	345	498	73	1376	170	439	7.10	152	1455	1282	172.5	25.8	28.8	6.5
102	1500	1890	254	150	90	1350	911	565	152	413	345	498	74	1392	206	450	7.20	152	1582	1357	225.6	25.1	28.0	6.7
103	1500	1939	234	213	86	1287	972	789	376	413	183	559	71	1380	206	429	7.13	319	1481	1266	214.3	25.1	28.0	6.7
104	1500	1963	224	67	96	1433	972	768	356	413	203	559	72	1404	206	478	7.15	246	1346	1128	217.6	25.1	28.0	6.7
105	1500	1640	204	387	74	1113	1206	1125	408	717	82	490	70	1151	358	371	7.22	145	1560	1163	397.0	24.2	27.0	6.9
106	1500	1906		449	70	1051	1174	970	326	644	204	530	72	1376	322	350	7.30	51	1628	1253	375.1	24.2	27.0	6.9
107	1500	1836		460	69	1040	785	602	204	398	184	388	79	1448	199	347	7.34	33	1675	1438	237.0	23.8	26.5	7.1
108	1500	1818		434	71	1066	486	262	122	139	224	347	81	1471	70	355	7.18	55	1543	1468	75.0	23.3	26.0	7.2
109	1500	1750	143	410	73	1090	691	426	61	365	265	326	81	1424	182	363	7.13	73	1460	1271	189.3	22.9	25.5	7.3
110	1500	1848		201	87	1299	752	509	72	438	243	314	83	1534	219	433	7.16	70	1614	1382	232.4	22.4	25.0	7.5
111	1500			258	83	1242	745	532	81	451	213	294			225	414	7.22	53	1503	1253	249.8	22.4	25.0	7.5
112	1500	1679	212	53	96	1447	857	439	92	347	418	510	70	1169	174	482	7.13	85	1459	1279	180.4	22.4	25.0	7.5
113	1500	1763	243	222	85	1278	791	454	143	311	337	479	73	1283	156	426	7.17	105	1298	1132	166.6	22.4	25.0	7.5
114	1500	1787	210	132	91	1368										456	7.10	127				22.0	24.5	7.6
115	1500	1787	206	311	79	1189	528	405	163	242	122	286	84	1501		396						21.5	24.0	7.8
116	1500	1787	205	311	79	1189	905	548	163	385	357	520	71	1267	192	396	7.11	152	1585	1388	196.6	21.5	24.0	7.8
117	1500	1887		426	72	1074	670	487	102	385	184	286	85	1601	192	358	7.09	160	1470	1276	193.4	21.5	24.0	7.8
118	1500	1894		393	74	1107	633	507	106	401	126	232	88	1661	201	369	7.11	131	1362	1157	205.0	21.1	23.5	8.0
119	1500			261	83	1239	829	681	84	597	148	232			298	413	7.11	110	1541	1236	305.0	20.6	23.0	8.1
120	1500					1500									162	500	7.13	91	1349	1181	168.0	20.6	23.0	8.1
121	1500					1500										500						20.6	23.0	8.1
122	1500	1813	239	82	95	1418	636	458	64	394	178	242	87	1571	197	473	7.11	176	1672	1470	201.5	20.6	23.0	8.1
123	1500		199	155	90	1345	608	495	112	383	113	225			192	448	7.09	197	1617	1425	192.7	20.6	23.0	8.1
124	1500			228	85	1272	611	506	83	423	105	189			211	424	7.10	20	1801	1587	214.4	20.6	23.0	8.1
125	1500	1815		161	89	1339	622	531	172	359	91	263	85	1551	179	446	7.17	32	1517	1325	191.9	20.6	23.0	8.1
126	1500	1828		269	82	1231	679	436	20	416	243	263	86	1565	208	410	7.27	7	1798	1560	238.1	18.3	20.4	9.2
127	1500	1869	249	263	82	1237	580	418	132	286	162	293	84	1575	143	412	7.22	3	1881	1722	158.5	17.1	19.0	9.9
128	1500	1842	319	363	76	1137	726	524	40	483	202	243	87	1599	242	379	7.23	25	1874	1604	269.6	16.2	18.0	10.4
129	1500	1886	219	398	73	1102	620	475	71	405	144	215	89	1671	202	367	7.17	41	1831	1615	216.4	16.2	18.0	10.4
130	1500	1838		173	88	1327	862	720	132	589	142	273	85	1565	294	442	7.12	90	1873	1569	303.3	16.2	18.0	10.4
131	1500			208	86	1292	876	732	134	599	144	278			299	431	7.13	88	1859	1548	310.8	16.2	18.0	10.4
132	1500			233	84	1267	621	519	95	424	102	197			212	422	7.11	34	1813	1596	217.0	15.7	17.5	10.7
133	1500					1500	617	516	94	422	122	216			211	500	7.12	182	1799	1582	217.2	15.7	17.5	10.7
134	1500			158	89	1342	633	529	97	432	104	201			216	447	7.12	113	1849	1626	222.7	15.3	17.0	11.0
135	1500	1805		177	88	1323	612	511	93	418	101	194	89	1611	209	441	7.14	92	1786	1568	218.7	15.3	17.0	11.0
136	1500			122	92	1378	655	547	100	447	108	208			224	459	7.18	27	1929	1688	241.1	15.3	17.0	11.0
137	1500			150	90	1350	636	531	97	434	104	202			217	450	7.14	35	1861	1634	227.2	14.4	16.0	11.7

138	1500	1872		96	94	1404	641	543	99	443	98	197	89	1675	222	468	7.26	58	1924	1672	252.1	14.4	16.0	11.7	
139	1500			199	87	1301	604	511	93	418	116	210			209	434	7.18	50	1792	1567	225.2	14.4	16.0	11.7	
140	1500			150	90	1350	627	531	97	434	96	193			217	450	7.24	16	1875	1632	243.5	14.4	16.0	11.7	
141	1500			142	91	1358	619	525	96	429	95	191			214	453	7.21	18	1847	1611	235.9	14.4	16.0	11.7	
142	1500	1865		148	90	1352	666	595	161	434	71	232	88	1633	217	451	7.25	66	1877	1632	245.0	14.4	16.0	11.7	
143	1500	1885		221	85	1279	748	586	161	425	161	323	83	1562	213	426	7.23	112	1834	1597	237.1	14.4	16.0	11.7	
144	1500	1907		118	92	1382	871	719	202	518	151	353	81	1554	259	461	7.27	30	1967	1671	296.1	13.5	15.0	12.5	
145	1500	1863	206	133	91	1367	812	652	141	510	161	302	84	1561	249	456	7.26	39	1927	1643	283.1	13.5	15.0	12.5	
146	1500			161	89	1339	709	588	181	406	121	302			203	446	7.24	65	1824	1596	228.0	13.5	15.0	12.5	
147	1500	1901	210	90	94	1410	826	765	202	563	60	262	86	1639	282	470	7.15	78	1977	1680	297.0	13.5	15.0	12.5	
148	1500			157	90	1343	841	701	159	542	140	299			271	448	7.14	50	1930	1646	283.6	12.6	14.0	13.4	
149	1500		213	147	90	1353	861	714	148	566	147	295			283	451	7.15	41	1860	1562	298.4	12.6	14.0	13.4	
150	1500																7.17					12.5	13.9	13.5	
151	1500	1867	221	121	92	1379	874	753	157	596	121	278	85	1589	298	460	7.16	70	1916	1600	316.5	12.5	13.9	13.5	
152	1500	1852	214	140	91	1360	882	773	151	622	109	260	86	1592	311	453	7.13	71	1881	1558	323.0	12.4	13.8	13.6	
153	1500	2044	212	110	93	1390	862	764	138	626	98	236	88	1809	313	463	7.16	30	1976	1643	332.5	12.3	13.7	13.7	
154	1500			159	89	1341	890	788	134	654	102	236			327	447	7.14	54	1946	1604	342.2	12.1	13.5	13.9	
155	1500	1881		125	92	1375	936	805	143	662	131	274	85	1607	331	458	7.15	34	2009	1660	349.0	12.3	13.7	13.7	
156	1500			147	90	1353	802	697	128	569	105	233			284	451	7.12	10	2018	1725	293.0	12.3	13.7	13.7	
157	1500	1813	231	216	86	1284	843	744	157	587	99	256	86	1557	293	428	7.18	7	1820	1504	316.1	12.1	13.5	13.9	
158	1500	1842	211	178	88	1322	925	798	120	678	127	247	87	1595	339	441	7.15	80	1944	1587	357.3	12.1	13.5	13.9	
159	1500		200	136	91	1364	926	835	119	716	91	210			358	455	7.16	84	2013	1633	380.4	12.1	13.5	13.9	
160	1500			240	84.0	1260	1010	911	149	762	99	248			381	420	7.18	77	1770	1360	410.8	11.7	13.0	14.4	
161	1500	1878		259	82.7	1241	805	681	249	432	125	373	80	1504	216	414	7.11	149	1806	1585	220.8	11.8	13.1	14.3	
162	1500	1861	300	257	82.9	1243	706	527	173	354	179	351	81	1510	177	414	7.12	48	1490	1308	182.6	11.8	13.1	14.3	
163	1500	1877		333	77.8	1167	804	600	193	407	203	396	78.9	1481	204	389	7.04	250	1720	1524	196.3	11.7	13.0	14.4	
164	1500	2125		278	81.4	1222	815	601	192	409	213	405	80.9	1720	205	407	7.18	149	1812	1591	220.6	11.7	13.0	14.4	
165	1500	1937	202	244	83.7	1256	955	733	231	502	222	453	76.6	1484	251	419						11.7	13.0	14.4	
166	1500	2017	196			1379	1077	324	753	302	626	68.9	1391	376			7.11	103	1844	1460	384.8	11.7	13.0	14.4	
167	1500	2046	246	280	81.4	1220	997	725	384	341	272	656	67.9	1390	170	407	7.12	277	1565	1390	175.5	11.7	13.0	14.4	
168	1500	2076	231	344	77.1	1156	1425	1167	202	965	258	459	77.9	1617	483	385						11.7	13.0	14.4	
169	1500	1852		356	76.3	1144									196	381	7.08	213	1661	1465	196.0	12.1	13.5	13.9	
170	1500		226	358	76.1	1142									249	381	7.09	156	1693	1443	250.4	11.7	13.0	14.4	
171	1500	1879	235	298	80.2	1202									266	401						11.2	12.5	15.0	
172	1500		224	335	77.7	1165									251	388	7.05	167	1766	1522	244.0	10.8	12.0	15.6	
173	1500		239	264	82.4	1236									255	412	7.12	122	1652	1389	262.5	10.8	12.0	15.6	
174	1500		244	256	82.9	1244									264	415	7.13	135	1797	1523	274.5	10.8	12.0	15.6	
175	1500					1500									249	500	7.15	119	1867	1604	262.5	10.8	12.0	15.6	
176	1500					1500									260	500		155				10.8	12.0	15.6	
177	1500			261	82.6	1239										413		172				10.8	12.0	15.6	
178	1500			288	80.8	1213										404		180				10.8	12.0	15.6	
179	1500					1500												236				10.8	12.0	15.6	
180	1500	1913	251	503	66.4	997	985	524	303	221	461	764	60.1	1149	280	332	7.14	255	1931	1638	293.0	10.8	12.0	15.6	
181	1500			529	65	971										324		283				12.6	14.0	13.4	
182	1500			500	67	1000									265	333	7.15	90	1904	1625	279.4	12.6	14.0	13.4	
183	1500			308	79	1192										397						12.6	14.0	13.4	
184	1500			279	81	1221									284	407	7.13	70	1917	1622	294.9	12.3	13.7	13.7	
185	1500			107	93	1393									293	464	7.17	78	1998	1684	313.5	12.6	14.0	13.4	
186	1500	1892	234	104	93	1396	8	-146	111	-257	154	266	86	1627		465	7.16	93				12.6	14.0	13.4	
187	1500			156	90	1344	29		132	-257	154	287				448	7.16	35				12.1	13.5	13.9	
188	1500																					12.1	13.5	13.9	
189	1500																					12.1	13.5	13.9	
190	1500																					12.1	13.5	13.9	
191	1500																						13.5	13.9	
195	1500																							14.0	13.4
196	1500																							14.0	13.4
197	1500																							14.0	13.4
198	1500																							14.0	13.4
199	1500			171	89																			14.0	13.4
200	1500			66	96																			14.0	13.4
201	1500			166	89																			14.0	13.4
202	1500			219	85																			14.0	13.4
203	1500																							14.0	13.4
205	1500																								
206	1500			83	94																				
207	1500			78	95																				
208	1500			79	95																				
Steady State 8, Days 148-159	Mean	1880	220	149	90.1	1351	876	761	141	620	115	257	86	1625	310	450	7.15	48	1938	1611	327	12.3	13.7	13.6	
	SSD	94	35	28	2	28	39	43	14	51	18	27	1	84	26	9	0.02	25	62	57	28	0.2	0.2	0.2	

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Chapter 5

Measurement of aqueous hydrogen sulphide, alkalinities and volatile fatty acids in anaerobic digestion

5.1 INTRODUCTION

Chapter 4 describes the preliminary results of R1 (35 °C) with an attempt to fix the COD, sulphur (S) and nitrogen mass balances. Nitrogen mass balance was close to 100% (97.1%) while the COD and S mass balances were relatively poor. The COD and sulphur mass balances were affected since the measurements of the total aqueous hydrogen sulphide (both H_2S and HS^-) were problematic and inaccurate. The loss of undissociated hydrogen sulphide (H_2S) was suspected in sample preparation, namely during vacuum filtration and this was attributed to be the possible cause of incomplete COD and sulphur mass balances. This Chapter deals with one of the objectives of this research investigation which is to develop simple wet chemistry analytical procedures for the accurate measurement of parameters like sulphide, COD, alkalinities and VFA in order to monitor BSR systems and achieve 100% COD and S mass balances. In this Chapter, three different analytical approaches in the COD test for the determination of total aqueous hydrogen sulphide (S_T) produced in the biological sulphate reduction (BSR) are described and investigated. In addition, the effect of pH changes due to the loss of S_T on system alkalinities and VFA and species distribution is explained in terms of mixed weak acid/base chemistry to give insights to the effect of errors in the wet chemistry procedures.

5.2 HYDROGEN SULPHIDE AND SULPHUR MASS BALANCE

In the anaerobic digestion of sulphate-rich waters such as acid mine drainage (AMD), the accurate measurement of residual sulphate and sulphides produced is of utmost importance in order to close the sulphur loop and fix the sulphur mass balance over the system. The

measurement of both sulphate and total aqueous hydrogen sulphide (S_T) can be problematic. The issue of sulphate measurement in the presence of elevated concentrations of organic materials has been addressed by Ristow *et al.* (2005). They developed the carbonate fusion method in which the effluent sample is pre-treated to remove the dissolved organic matter present thereby eliminating its interference with the spectrometer absorbance reading. With this pre-treatment, excellent sulphate recoveries were obtained and rigorous testing of the method showed that reproducible and accurate results were obtained.

Quantifying the sulphide species in the sulphide system is fundamental in the biological reduction of sulphate-rich waters. Firstly, with the total hydrogen sulphide (S_T) known, the COD and sulphur mass balances can be completed on the system. Secondly, with S_T and pH measured, the undissociated and dissociated sulphide species can be calculated and used to assess the effect of undissociated H_2S inhibition (both in growth and activity) on the system. Thirdly, the alkalinity associated with the dissociated hydrogen sulphide (HS^-) can also be determined. Fourthly, for feed organics that are carbon limited, it is the HS^-/H_2S system that establishes the reactor pH.

The measurement of aqueous S_T is based on the COD measurement as outlined in Standard Methods (1985). The actual or conventional COD approach used has proved to be problematic due to the loss of hydrogen sulphide during sample preparation, namely vacuum filtration. Thus, the objective of this section of the research investigation is to bring about modifications to the actual COD method in order to address the issue of hydrogen sulphide losses during sample preparation. Three methods were investigated and they are described and evaluated below.

5.3 METHODOLOGY

As described in Chapter 3, two similar UASB reactors designed as R1 (T 35 °C) and R2 (T 20 °C), receiving sulphate-rich water blended with primary sewage sludge (PSS) were set-up to investigate biological sulphate reduction under various design conditions. Results of UASB R1 at 35 °C when fed 1500 $mgSO_4^{2-}/L$ and 1800 $mgSO_4^{2-}/L$ are described in Chapters 4 and 6 respectively, while those of UASB R2 at 20 °C (fed 1500 $mgSO_4^{2-}/L$) are reported in Chapter 6. For the purpose of this current study, only results of R1 are illustrated since the same principles were applied and hold true for the UASB reactor R2.

Three different approaches of S_T measurement were fully investigated namely:

- Method 1:** The actual or conventional COD method (as outlined in Standard Methods, 1985).
- Method 2:** Addition of 3 drops of 10M NaOH to the effluent sample before vacuum filtration.
- Method 3:** Addition of a polyelectrolyte to the effluent sample to coagulate the organic particles and use centrifugation for solid-liquid separation.

Effluent samples (approx. 100ml) were taken from the top of the UASB reactor and analysed for their total COD and their soluble COD constituents (total soluble COD and organic soluble COD and total sulphide COD), sulphate, alkalinities and VFA concentrations.

5.3.1 Method 1: Conventional COD method

Using the appropriate dilution, the effluent total COD was determined by the COD method outlined in Standard Methods (1985). The total soluble COD (soluble organic COD + sulphide COD) was determined on 0.45 μm filtered samples. To determine the total organic COD (sulphide removed), excess zinc sulphate (ZnSO_4) was added to a 50ml sample to precipitate the aqueous sulphide as zinc sulphide (ZnS). Thereafter, 3 drops of 10M NaOH were added to increase the pH to precipitate residual Zn^{2+} as $\text{Zn}(\text{OH})_2$. The solution was then centrifuged for 5 minutes at 3500 rpm and vacuum filtered through a 0.45 μm membrane filter paper and the resulting filtrate was tested for COD to measure its organic soluble concentration. The difference between the total soluble COD and the organic soluble COD was therefore the total aqueous sulphide COD.

5.3.2 Method 2: Addition of 3 drops of 10M NaOH to the effluent sample

It was suspected that hydrogen sulphide (H_2S) gas was lost during vacuum filtration, swirling or mixing (when conducting sample dilution) and also when samples were left standing for a long time (longer than 15 minutes). In order to prevent any undissociated H_2S from escaping the sample, 3 drops of 10M NaOH were added immediately after sample collection from the liquid phase of the UASB reactor. The NaOH increased the pH to

greater than 10 and allowed the sulphide to be retained in the sample. The H_2S changes to HS^- with the addition of NaOH . The $\text{H}_2\text{S}/\text{HS}^-$ system has a $\text{pK}_{\text{s}1}$ value of 7.05 at 25 °C (Lide, 2001) and at a pH of 10 almost all the sulphide is in the form of HS^- species with a very small proportion in the form of S^{2-} species ($\text{pK}_{\text{s}2} = 12.92$ at 25 °C) (Bjerrum, 1958) (see Figure 5.1). Neither HS^- nor S^{2-} species can escape from the sample since they are dissociated. Note that the NaOH added does not affect the COD test since it does not have a COD value. After the addition of the 10M NaOH , the same analytical and experimental procedures were carried out as outlined in Method 1 above. The total COD as well as the different soluble COD fractions of the effluent were likewise determined. The results of this approach are shown in Table 5.1.

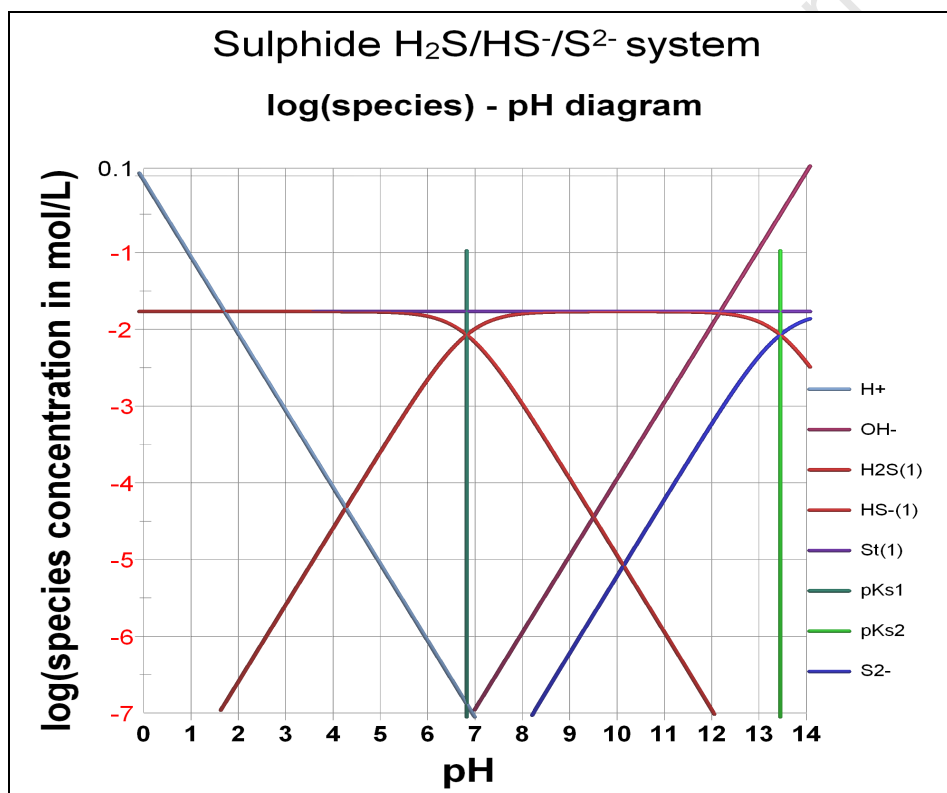


Figure 5.1: Log species – pH diagram of the sulphide system (at 35 °C).

5.3.3 Method 3: Addition of polyelectrolyte to the effluent sample

The third approach (Method 3) consisted of adding a polyelectrolyte coagulant to the effluent sample. This approach was undertaken in order to avoid vacuum filtering the samples and improve solid-liquid separation in centrifugation before measuring the effluent soluble COD fractions. While the polyelectrolyte is organic it would not add to the soluble

COD due to its removal with the particulate organics. A solution of the coagulant was prepared from 0.5g of the organic polyelectrolyte in 100ml of distilled water. The mixture was thoroughly mixed until a coagulant solution was obtained. Thereafter, 2 drops of this polyelectrolyte coagulant were added to a 50ml effluent sample and centrifuged for 10 minutes at 3500 rpm. After centrifugation, all the particulates/solids were coagulated onto the inner wall of the centrifugation tube leaving a quasi-clear effluent solution. This clear effluent was assumed to contain no suspended solids and was thus used to determine the various soluble COD fractions as described in Method 1. The results of Method 3 are demonstrated in Table 5.1.

5.4 RESULTS

5.4.1 Effluent soluble COD constituents

The total soluble (organic + sulphide) and sulphide COD concentrations on 3 different R1 experimental days for each of the 3 methods under study are shown below.

Table 5.1: Results of R1 effluent total soluble and sulphide COD from all three methods.

R1 effluent sample	Units	Method 1		Method 2		Method 3	
		Total soluble	Total sulphide (S _T)	Total soluble	Total sulphide (S _T)	Total soluble	Total sulphide (S _T)
Day 421	mgCOD/L	934	716	1159	940	1126	908
Day 473	mgCOD/L	910	696	1277	1063	1187	973
Day 498	mgCOD/L	926	671	1265	1010	1195	940

From Table 5.1, it can be seen that the total soluble COD concentration (and thus the sulphide COD) determined from Method 2 is higher than those from Methods 1 and 3. The difference between Methods 2 and 3 is not large on reactor operation Day 421 while it is more pronounced on Days 473 and 498. This is due to the fact that on these latter two days the effluent samples treated with polyelectrolyte (Method 3) were left standing for more than 20 minutes before the diluted samples were tested for COD. Solutions containing

undissociated H_2S at $\text{pH} < 9.0$ (reactor and effluent pH being ~ 7.1) are prone to H_2S losses on standing and mixing during analysis steps. This explains the lower sulphide concentrations recorded for Method 3 where no vacuum filtration was conducted prior to the effluent soluble COD measurement.

The total soluble and sulphide COD are the lowest with Method 1. These low values are due to H_2S losses during sample preparation, namely dilution, mixing and standing over (as experienced in Method 3) but more importantly during vacuum filtration to separate the particulate from the soluble organics. Vacuum filtration expelled almost all the H_2S present in the effluent sample since at a pH of 7.05-7.20 (as recorded for the effluent in the UASB reactors during the span of the experimentation) a considerable fraction of the total sulphide (S_T) is in the H_2S form. Therefore, S_T decreases accordingly by the same magnitude. Following these results, the next exercise is to calculate the mass of sulphur and COD leaving the reactor from each Method and determine the sulphur and COD mass balances.

5.4.2 Mass balances

The COD and sulphur (S) mass balance equations based on the S_T measured are given in Chapter 3, Section 3.9.1 and 3.9.3.

In the S balance, the H_2S gas concentrations in the headspace of the reactor measured with the Phenanthroline method (see Appendix 3A for method description) were found to be negligible with concentrations ranging from 0.4 to 1.0 mgS/L of influent (mean = 0.7 mgS/L) and masses between 0.003 and 0.01 mgS/d (mean 0.007 mgS/d). Moreover, from the sludge analysis, elemental sulphur concentration in the biomass was about 2% of the total sulphur mass (see Appendix 5A).

Since the biological processes considered in this study involved measurements in a complex 3-phase system, a COD mass balance between 95 and 105% and an S mass balance between 90 and 110% were considered acceptable. Based on the sulphide measurements shown in Table 5.1 and the mass balance equations (Chapter 3, Section 3.91), the COD and S mass balances were conducted and these are tabulated below (Tables 5.2 and 5.3).

Table 5.2: Comparison of COD mass balances from all 3 methods.

COD mass balance (%)			
Description	Method 1	Method 2	Method 3
R1 Day 421	95.5	97.1	95.5
R1 Day 473	91.8	95.4	91.8
R1 Day 498	93.5	97.0	93.5

Table 5.3: Comparison of S mass balances from all 3 methods.

Sulphur (S) mass balance (%)			
Description	Method 1	Method 2	Method 3
R1 Day 421	74.9	93.8	90.9
R1 Day 473	64.7	95.3	87.8
R1 Day 498	64.0	92.2	86.4

Table 5.2 shows the COD mass balance based on the total effluent COD of the UASB reactor R1 determined from all 3 methods under investigation. For Methods 1 and 3, the same effluent sample is used in the COD test (after the appropriate dilution) to calculate the total effluent COD. As expected, both methods resulted in the same total effluent COD and therefore the same COD mass balances. In Method 2, in which 3 drops of NaOH are immediately added to the sample to prevent H₂S loss, the COD mass balance is better (97.1%). The difference in COD mass balance between Method 2 and the others is due to the H₂S loss during dilution, mixing and standing of the effluent samples before testing. This is also reflected and confirmed in the sulphur mass balance (see Table 5.3).

In Table 5.3, the S mass balance in Method 2 is higher than that in Methods 1 and 3. These differences are a direct consequence of reducing H₂S losses in the analytical steps of the methods. Sulphide concentrations from each method were taken from Table 5.1 above to calculate the mass of sulphur leaving the system. It can be seen that the loss of H₂S during vacuum filtration is particularly significant. Moreover, the 92-95% S mass balance obtained in Method 2 shows that Method 2 is reliable in fixing the S mass balance close to 100%. It can therefore be concluded that Method 2 (i.e. the addition of drops of NaOH immediately after effluent sample collection) is a better analytical method to use when vacuum filtering samples prior to the measurement of total sulphide concentration at pH < 9.0.

Likewise, it can also be deduced that the loss of H_2S came only from the vacuum filtration and during sample preparation (swirling, mixing and standing over) and not in the COD test itself. In order to test this and further validate Method 2 (sample treated with NaOH), two standard hydrogen sulphide S_T solutions with known concentrations were made up using sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$). The two standard solutions were made up by dissolving in 1L distilled water 3.030 g and 4.503 g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (MW = 240g) respectively. These standard solutions were checked with independent Na analysis and found to conform within 1%. The solutions were gently mixed until the entire compound dissolved. These solutions had therefore a total sulphide (S_T) concentration of 404 mgS/L and 600 mgS/L respectively. The pHs of the solutions were as high as 11.93 and 12.16 respectively. At these high pH values, the sulphide species were in the HS^- and S^{2-} forms as illustrated in the log species-pH diagram for the sulphide system (refer to Figure 5.1).

A sample of each of the standard S_T solution was vacuum filtered through 0.45 μm membrane filter paper and S_T measured in the COD test. Since the pH was high (> 12), the H_2S species was negligible (0.003 mgS/L), so there was no need to add NaOH.

In another sample of the S_T standard solution ($\text{S}_\text{T} = 600$ mgS/L), relatively weak hydrochloric acid solution (Normality = 0.067) was added dropwise and very gently stirred until the pH was 7.13. The solution pH was therefore similar to that of the USB effluent samples. This solution was then subjected to the same analytical procedures as for the UASB reactor and effluent COD samples, i.e. its COD was measured with standard COD test (Method 1) and Method 2 (addition of 3 drops of NaOH). The results of the COD tests done on various concentrations of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ solution both at high and low pH values are tabulated below (Table 5.4).

Table 5.4: Concentrations of S_T from COD tests from a known solution of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$.

Theoretical S_T (mgS/L)	pH	H_2S (mgS/L)	HS^- & S^{2-} (mgS/L)	Measured S_T		Loss of H_2S and/or HS^- (mgS/L)	% Recovery (measured/theoretical)
				(mgCOD/L)	(mgS/L)		
404	11.83	0	404	796	398	6	98.6
600	12.16	0	600	1148	574	26	95.6
424 ^a	7.13	142	282	637 ^b	318 ^b	106	75.0

Note: H_2S and HS^- are calculated from the sample pH and $\text{pK}_{\text{s}1}$ of the $\text{H}_2\text{S}/\text{HS}^-$ system.

a: Measured with Method 2 (NaOH treated).

b: Measured with Method 1 (Conventional).

From Table 5.4, it can be seen that the measured S_T at high pH is very close to the standard S_T solution concentration (96-99% recovery) implying that no or negligible sulphide species are lost in the COD test itself even at S_T concentration as high as 600 mgS/L. This was checked by placing tissue paper moistened with ferric chloride ($FeCl_3$) solution over the outlets of the COD test condensers- should H_2S gas have escaped during the reflux step, black spots would have formed- none were noted. The absence of H_2S loss from the COD test is probably due to the very rapid reaction between the potassium dichromate and sulphide, complete virtually immediately after adding the sulphuric acid. For the standard solution at low pH, the measured S_T is only 75% of the theoretical S_T indicating a loss in vacuum filtration and during sample preparation. At low pH, the H_2S species is relatively high and prone to escape to the air resulting in a decrease in S_T . Hence, the importance of increasing the sample pH with NaOH to bring all the sulphide in the HS^- (and S^{2-}) forms.

From the above, it can be concluded that at high pH (≥ 10.0), there is no loss in S_T during vacuum filtration while at low pH (7.13), there is considerable loss ($\sim 25\%$) in S_T . Moreover, the 96-99% S_T recovery at high pH proves there is negligible sulphide ($\leq 4\%$) loss in the COD test itself.

The polyelectrolyte addition (Method 3) was shown to prevent loss of H_2S by eliminating the vacuum filtration step. However, the polyelectrolyte addition was not be sufficient to remove all the suspended solids with only centrifuging the sample. In order to test this, an effluent sample containing high total suspended solids (TSS) concentration (>400 mgCOD/L) was taken from a completely mixed reactor treating sulphate-rich water using a process water (a mixture of VFAs and alcohols) as carbon source. This effluent sample was treated with the polyelectrolyte mix and centrifuged for 10 minutes at 3500 rpm, and the COD of the supernatant was measured. The same sample was also analysed for its TSS concentration in COD units (mgCOD/L) by measuring the total COD and the total soluble COD using the NaOH approach (Method 2). The COD of the suspended solids (particulate) was then calculated as the difference between (1) the total COD (particulate + total soluble) (1121.4 mgCOD/L) and the total soluble COD with Method 2 (714 mgCOD/L) and (2) the total COD (1121.4 mgCOD/L) and the total soluble COD with Method 3 (905 mgCOD/L). It was found that the total soluble COD with Method 3 was always significantly higher than with Method 2.

This indicates that samples with high TSS concentrations leave residual solids (very fine organic particles) that are not removed by polyelectrolyte addition and would therefore require filtration to be removed. However, for this study, because the effluent TSS was low ($< 400\text{mgCOD/L}$) due to good solids-liquid separation in the UASB reactor, Method 3 gave reasonable results and could be considered a possible option if membrane filtration is not available.

5.5 ALKALINITY AND VOLATILE FATTY ACIDS (VFA) MEASUREMENT IN A MIXED WEAK ACID/BASE SYSTEM

The measurement of alkalinity and VFA in a mixed weak acid/base system with sulphide species present can also result in error if the usual methods are applied without due consideration. In this research, alkalinity (H_2CO_3^* alk.) and VFA were measured using the 5-point titration of Moosbrugger *et al.* (1992). As outlined earlier in Chapter 3, Section 3.8.3, the 5 pH point titration programme calculates the carbonate alkalinity (H_2CO_3^* alk.) and the VFA concentration as separate outputs. The calculation procedure does cater for the inclusion of the sample total sulphide (S_T as mgS/L). Should the sample contain S_T , this value needs to be entered into the calculation procedure in order to determine the H_2CO_3^* alk. (mg/L as CaCO_3) and the VFA concentration (mgHAc/L) correctly. Since S_T measurement was problematic and inaccurate (at the beginning of this investigation), it was expected that the alkalinity and VFA measurements would also be affected and inaccurate. This section therefore deals with the effect of H_2S losses in the vacuum filtration during sample handling on the total alkalinity, H_2CO_3^* alk., Alk. H_2S and VFA (and Alk. HAc).

5.5.1 Some basic aquatic chemistry concepts on alkalinity in a mixed weak acid/base system

The effluent under investigation was made up of a mixture of weak acid/bases subsystems. These subsystems were the carbonate (via the CO_2 production), the ammonium (via the NH_4^+ production from the N content of the PSS), the phosphate (via the total phosphorus, P_T present in the raw PSS), the acetate (via the VFA generated from the hydrolysis of the PSS), the sulphide (via the reduction of SO_4^{2-}) and the water systems. Because the total phosphorus (P_T) concentration of the feed and the effluent was very low ($\sim 10\text{ mgP/L}$) compared with the other weak acid/base species concentrations, its effect on the total

alkalinity, H_2CO_3^* alk. and VFA was negligible. Hence zero was entered for P_T in the 5pt titration programme – entering $P_T = 10 \text{ mgP/L}$ made negligible difference to the results. Because the pK value of the ammonia (N_T) at 9.1 is 2 pH units above the sample pH values, and the N_T concentration very low compared with C_T , S_T and A_T , the total inorganic nitrogen (ammonia) species concentration (N_T) has no influence on the calculation of the H_2CO_3^* alk. and VFA concentrations, i.e. the NH_4^+ alkalinity at pH 7.1 is zero (0). Therefore, the carbonate, sulphide and acetate subsystems largely dominated the weak acid/base chemistry and pH of the system and for simplicity, the phosphate and ammonium systems were not considered further in this investigation. The total alkalinity was therefore the sum of the H_2CO_3^* alk. (including the water system), the Alk. HAc and the Alk. H_2S (each excluding the water system). The theoretical alkalinity equation for the 3 above subsystem alkalinities can be formulated from a proton balance equation (Loewenthal *et al.*, 1989, 1991). Each subsystem forms a reference state (or equivalent solution) from which a reference level alkalinity equation can be developed, namely:

$$\text{H}_2\text{CO}_3^* \text{ alkalinity} = \{ [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \} + \{ [\text{OH}^-] - [\text{H}^+] \} \quad (5.1)$$

$$\text{Alk. HAc} = [\text{Ac}^-] \quad (5.2)$$

$$\text{Alk. H}_2\text{S} = 2[\text{S}^{2-}] + [\text{HS}^-] \quad (5.3)$$

The total alkalinity is therefore the sum of the individual subsystem alkalinities.

$$\text{Total Alkalinity} = \text{H}_2\text{CO}_3^* \text{ alk.} + \text{Alk. HAc} + \text{Alk. H}_2\text{S} \quad (5.4)$$

Rearranging with the individual species gives:

$$\text{Total Alkalinity} = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+] + [\text{Ac}^-] + 2[\text{S}^{2-}] + [\text{HS}^-] \quad (5.5)$$

Note in the equations above, the nomenclature of Loewenthal *et al.* (1989) has been followed where Alkalinity preceding the reference species (Alk. H_2S) excludes the water system whereas Alkalinity following the reference species (H_2CO_3^* alk.) includes the water subsystem.

5.5.2 Effect of H₂S loss on the total and subsystem alkalinities

Since by definition, $\text{Alk. H}_2\text{S} = 2[\text{S}^{2-}] + [\text{HS}^-]$, the $[\text{H}_2\text{S}]$ does not affect the alkalinity. Therefore, H₂S loss during vacuum filtration causes no effect on the Alk. H₂S. Similarly, the total alkalinity will not be affected. In order to demonstrate this, the UASB effluent samples and standard solutions were analysed for alkalinity concentrations of all 3 subsystems (H₂CO₃* alk., Alk. HAc and Alk H₂S).

Analytical Methods 1 and 3 were conducted to investigate the effect of H₂S loss during vacuum filtration and sample handling on the effluent VFA and alkalinity concentrations (total, H₂CO₃* alk. and Alk. H₂S). Method 2 was not used because the NaOH added increases the alkalinity and this additional complexity was avoided for the alkalinity measurement part. Effluent samples were again taken from the liquid phase of the UASB reactor R1 and analysed for their alkalinities and VFA concentrations using Methods 1 (vacuum filtration with no NaOH addition for solid-liquid separation) and 3 (centrifugation with polyelectrolyte addition for solid-liquid separation). The results of these analyses are shown below in Tables 5.5 and 5.6. These tests were also done with standard S_T, C_T and A_T solutions which are described later.

Table 5.5: VFA and total alkalinities from Methods 1 (conventional) and 3 (polyelectrolyte treated) with S_T=0 in the calculation procedure.

Parameters	Units	Method 1	Method 3
S _T	mgS/L	0	0
Sum of H ₂ CO ₃ * alk. and Alk. H ₂ S with S _T =0 in the programme	mg/L as CaCO ₃	2042.2	2122.2
VFA	mgHAc/L	181.3	174.1
Sample pH		7.68	7.07
Alk. HAc	mg/L as CaCO ₃	150.9	144.5
Total alkalinity (Sum of H ₂ CO ₃ * alk., Alk. H ₂ S and Alk. HAc)	mg/L as CaCO ₃	2193.1	2266.7

Table 5.6: VFA and total alkalinities from Methods 1 and 3 with measured S_T from COD method entered into the 5-pt titration calculation procedure.

Parameters	Units	Method 1	Method 3
S_T	mgS/L	348.0	531.5 ^a
H ₂ CO ₃ * alk. with S_T inserted in the programme	mg/L as CaCO ₃	1684.9	1628.6
Effluent pH		7.68	7.07
Alk. H ₂ S calculated from S_T and pH	mg/L as CaCO ₃	476.1	525.9
VFA with S_T in programme	mgHAc/L	170.0	165.0
Alk. HAc	mg/L as CaCO ₃	141.5	137.0
Total alkalinity (Sum of H ₂ CO ₃ * alk., Alk. H ₂ S and Alk. HAc)	mg/L as CaCO ₃	2302.5	2291.5

a: Measured from Method 2 (NaOH addition before vacuum filtration)

Table 5.5 shows that the total system alkalinity and VFA measured from samples prepared from either Method 1 or 3 are almost similar (3% difference). This confirms that H₂S loss during sample preparation (namely vacuum filtration) does not affect the total system alkalinity. However, from Table 5.6, the subsystem alkalinities are affected by the loss of H₂S. H₂S loss causes a decrease in the total sulphide (S_T) but increases the sample pH such that the loss of H₂S would result in a lower H₂S/HS⁻ ratio, as per the equations below.

$$[H^+] = K_s[H_2S]/[HS^-] \quad (5.6)$$

$$pH = -\log(K'_s[H_2S]/[HS^-]) \quad (5.7)$$

$$\text{where } K'_s = 10^{(-pK'_s)} \text{ calculated from } pK_s \text{ and } pK'_s \quad (5.8)$$

pK_s = equilibrium constant for H₂S/HS⁻ system = 7.05 at 25 °C (Lide, 2001)

pK'_s = pK_s adjusted for temperature, activity coefficients and ionic strength = 6.833 at 35 °C and 7.014 at 20 °C (refer to Appendix 5B for calculations).

This increase in pH does not change the total system alkalinity (i.e. the sum of H₂CO₃* alk., Alk. H₂S and Alk. HAc) but it does change the individual subsystems alkalinities, i.e.,

H_2CO_3^* alk., Alk. H_2S and Alk. HAc . This phenomenon is called ‘Re-speciation’ of the individual subsystem species and alkalinities and is described below.

With the loss of H_2S , the sample pH increases, for instance:

Before vacuum filtration, $S_{T1} = [\text{H}_2\text{S}]_{(1)} + [\text{HS}^-]_{(1)}$ and sample pH = 7.07

After vacuum filtration, $S_{T2} = [\text{H}_2\text{S}]_{(2)} + [\text{HS}^-]_{(2)}$ and sample pH = 7.68

$S_{T2} < S_{T1}$ ($S_{T1} - S_{T2}$ = loss of H_2S during vacuum filtration)

However, $[\text{HS}^-]_{(2)}$ is lower than $[\text{HS}^-]_{(1)}$, as illustrated in the log species-pH diagram at the two pHs established (Table 5.7 and Figure 5.2).

Table 5.7: Speciation of sulphide species before and after vacuum filtration.

	S_T (mgS/L)	pH	H_2S (mgS/L)	HS^- (mgS/L)
Before (1)	531.5	7.07	194.9	336.6
After (2)	348.0	7.68	43.3	304.7
Loss of H_2S or HS^- (mgS/L)	183.5 ^b		151.6	31.9

^b Loss of H_2S during vacuum filtration

Table 5.7 shows the pH and sulphide species distribution before and after vacuum filtration. Particularly striking here is the decrease in $[\text{HS}^-]$ concentration at the pH established after vacuum filtration. In other words, the total $[\text{HS}^-]$ concentration at pH 7.68 (after vacuum filtration) is slightly lower than that before vacuum filtration (at pH 7.07) (Figure 5.2). For simplicity, only the $\text{H}_2\text{S}/\text{HS}^-$ system is illustrated in Figure 5.2, since at a pH of 7.07 and 7.68, the $\text{HS}^-/\text{S}^{2-}$ system is not relevant because the $[\text{S}^{2-}]$ is negligible (Refer to the log sp-pH diagram in Figure 5.1).

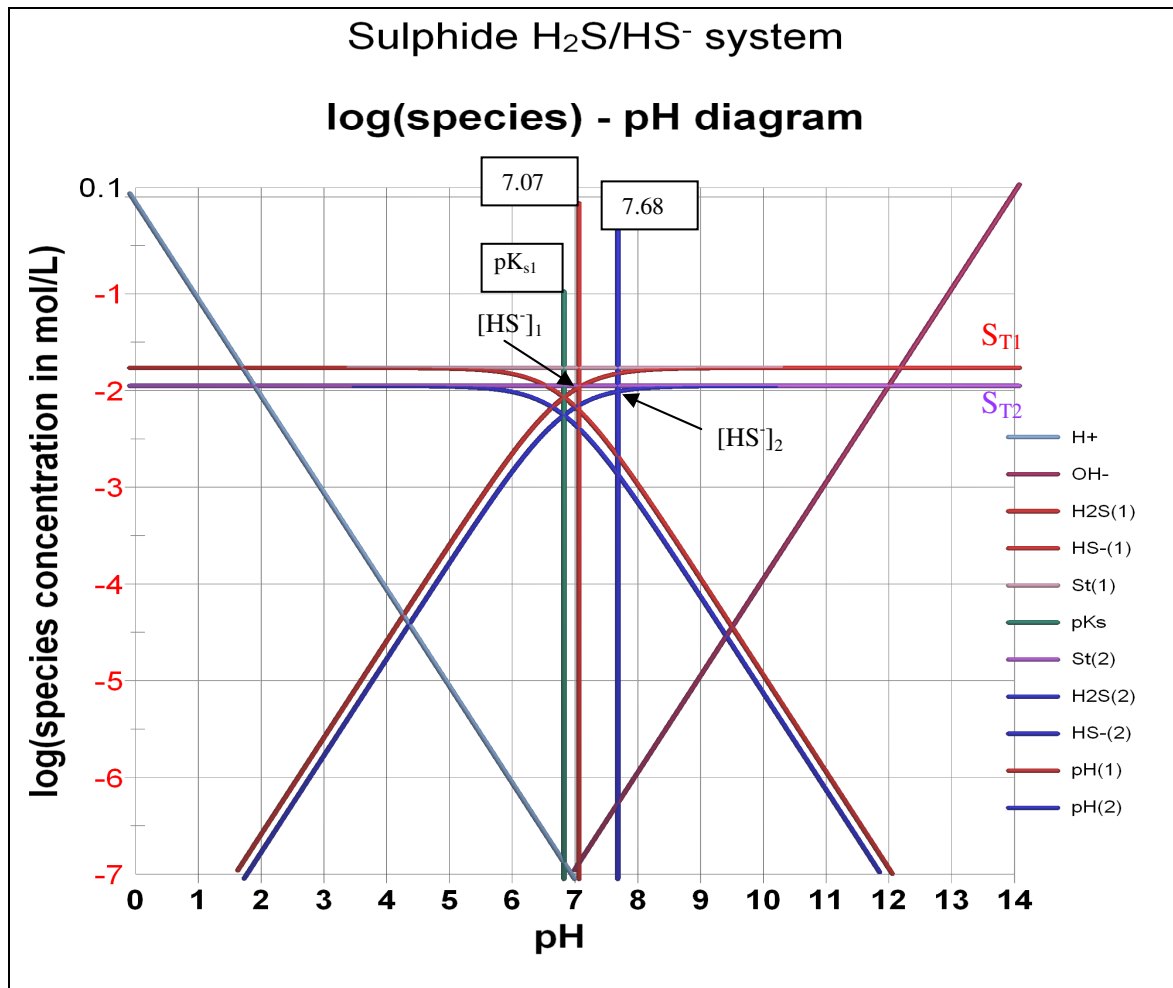


Figure 5.2: Log species-pH diagram of the sulphide system at the 2 pH values (7.07 and 7.68).

This decrease in Alk. H_2S in mixed weak acid/base systems is not obvious from the principle that H_2S (the reference species) loss does not change Alk. H_2S . However, this principle holds only if H_2S (or any other weak acid/base system) is the only weak acid/base system in water. For mixed weak acid/base systems, loss of one or more reference species does not change the total system alkalinity, but does change the individual subsystem alkalinities, including the alkalinities of the system(s) which have lost reference species. This is demonstrated below.

Considering a single weak acid/base system only such as the sulphide system in water, the total alkalinity is given by:

$$\text{H}_2\text{S alk.} = 2[\text{S}^{2-}] + [\text{HS}^-] + [\text{OH}^-] - [\text{H}^+] \quad (5.9)$$

The loss of H₂S gas from this system (only the sulphide system in water) does not affect the H₂S alk., which is equal to the total alkalinity of the system.

Similarly for only the carbonate system (H₂CO₃/HCO₃⁻/CO₃²⁻) in water, the total alkalinity is the same as the H₂CO₃* alk., given by:

$$\text{H}_2\text{CO}_3^* \text{ alk.} = 2[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{OH}^-] - [\text{H}^+] \quad (5.10)$$

Accordingly, the loss of CO₂ from the carbonate system does not affect the H₂CO₃* alk.. Now, considering the mixed weak acid/base system with all the subsystems (carbonate, sulphide, acetate and water) present in the UASB BSR system, the loss of H₂S and CO₂ should likewise not decrease the system total alkalinity since by definition, these species (i.e. [H₂S] and [CO₂]) do not appear in the equation (Refer to Equation 5.5). However, the loss of H₂S and CO₂ does change the subsystem alkalinities making up the total, and the sample pH. This change in pH will in turn affect the relative proportion of the various species of the individual subsystems. For instance, in this study, the loss of H₂S (and CO₂) during vacuum filtration causes the pH to increase from 7.07 to 7.68 thereby respeciating the H₂S/HS⁻ species of the sulphide subsystem, the H₂CO₃/HCO₃⁻/CO₃²⁻ species of the carbonate subsystem and the HAc/Ac⁻ species of the acetate subsystem. This respeciation of the individual subsystem species changes the individual subsystem alkalinities but the system total alkalinity remains unchanged.

Considering the sulphide subsystem and analysing the changes occurred with the loss of H₂S (and consequently to the sample pH) give more insight to the phenomenon of respeciation and its effect on subsystem alkalinity.

At pH 7.07 and S_T = 531.5 mgS/L, the [HS⁻] = 336.6 mgS/L and [H₂S] = 194.9 mgS/L;
Alk H₂S = [HS⁻] = 525.9 mg/L as CaCO₃.

After vacuum filtration and sample handling, the pH increases to 7.68 due to the loss of H₂S and S_T = 348.0 mgS/L. The new [HS⁻] = 304.7 mgS/L and [H₂S] = 43.3 mgS/L;
Alk. H₂S = 476.1 mg/L as CaCO₃.

From the above, there is a loss in Alk. H_2S when moving from pH 7.07 to 7.68 even though one expects the concentration $[\text{HS}^-]$ to increase at a higher pH (7.68) to keep the total alkalinity constant. However, in a mixed weak acid/base system, the other subsystems present (in this case the carbonate and acetate subsystems) compensate for the loss of one subsystem alkalinity by respeciation of their individual species to maintain the system total alkalinity unchanged. Accordingly, both the H_2CO_3^* alk. and Alk. HAc concentrations increase to compensate for the lower Alk. H_2S (Refer to Table 5.6).

To graphically illustrate these changes in subsystem alkalinities, the relevant Alkalinity-Acidity-pH equilibrium diagrams with the total species concentration are shown in Figures 5.3, 5.4 and 5.5.

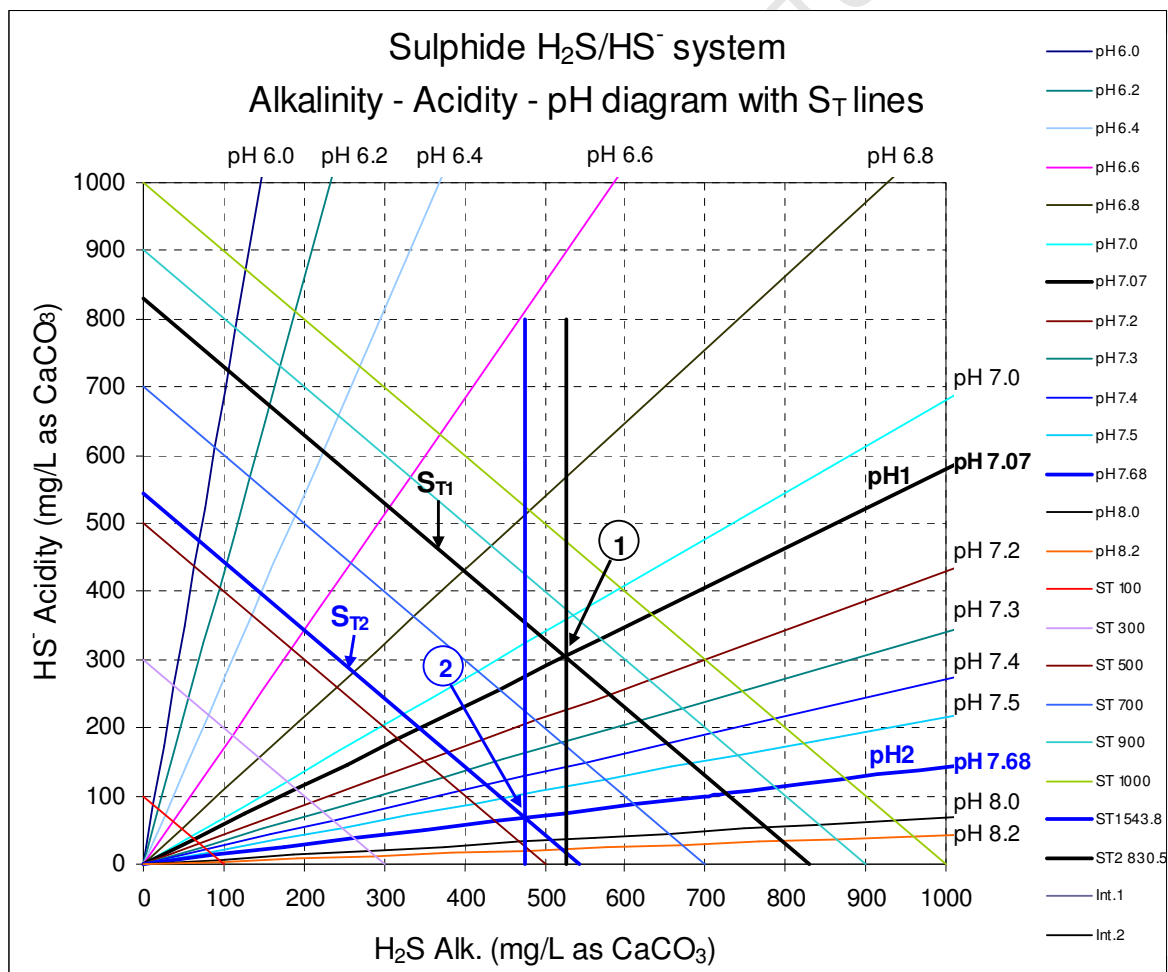


Figure 5.3: Alkalinity-Acidity-pH equilibrium diagram with total sulphide species (S_T) concentration lines.

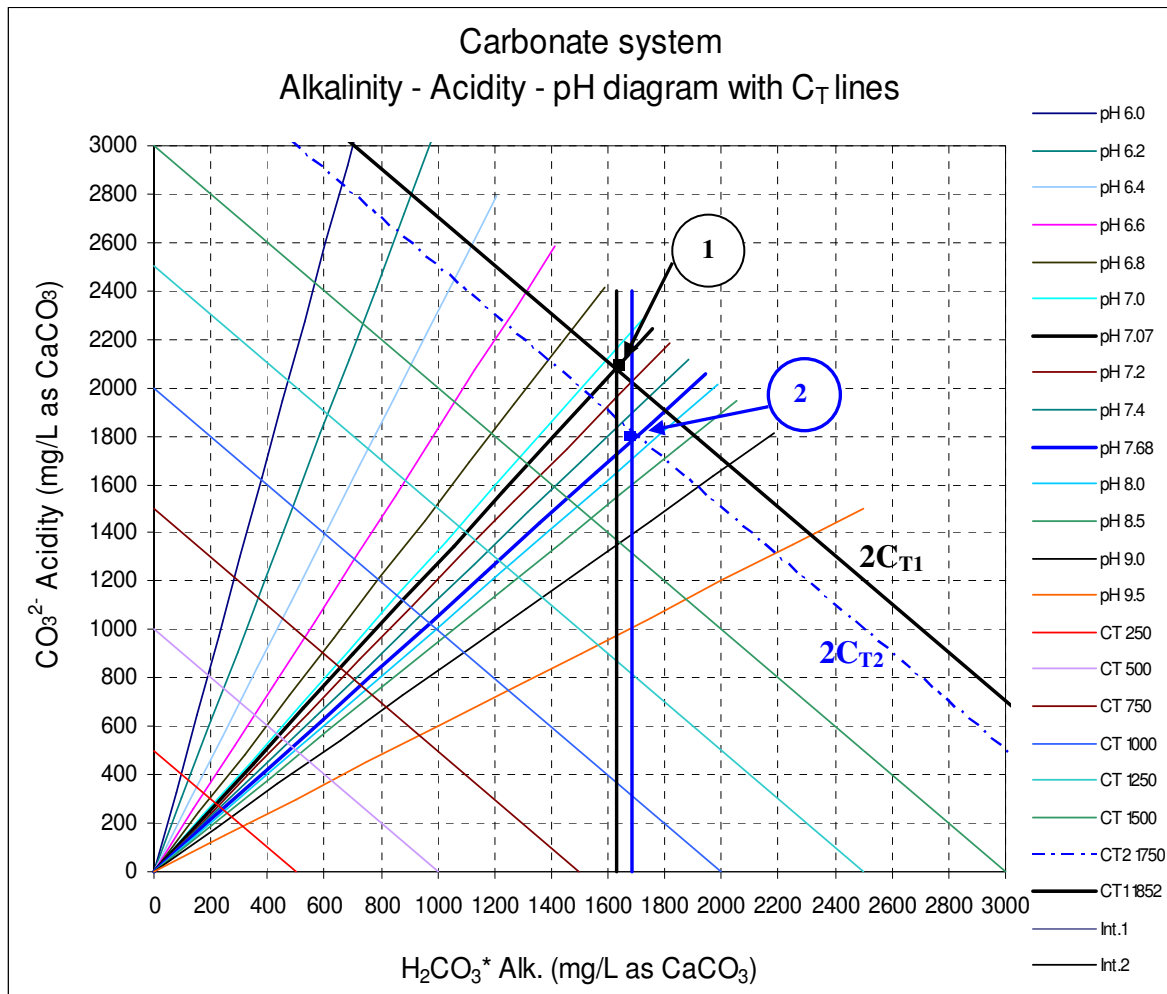


Figure 5.4: Alkalinity-Acidity-pH equilibrium diagram with total carbonate species (C_T) concentration lines.

Note: $\text{H}_2\text{CO}_3^* \text{ alk.} + \text{CO}_3^{2-} \text{ acidity} = 2 C_T$

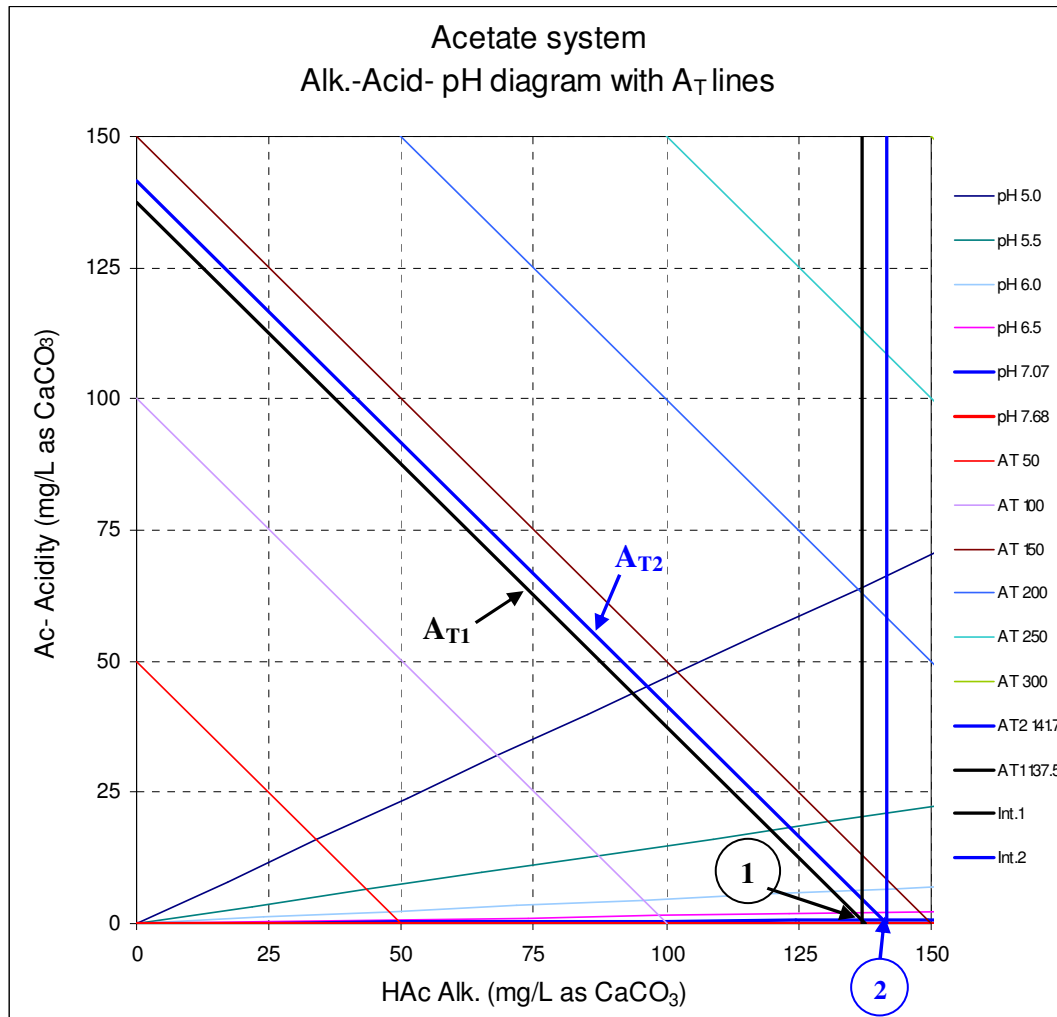


Figure 5.5: Alkalinity-Acidity-pH equilibrium diagram with total acetate species (A_T) concentration lines.

In Figures 5.3 to 5.5, the Point 1 indicates the concentrations of the subsystem alkalinity and acidity and the total subsystem species (all in mg/L as CaCO_3) for the pH 7.07, that is before vacuum filtration. Likewise, Point 2 indicates the new concentrations at the new pH 7.68 established after vacuum filtration. It can be seen that the subsystem alkalinities change with the change in pH after vacuum filtration, with H_2CO_3^* alk. and Alk. HAc increasing and Alk. H_2S decreasing. However, the net effect of these changes keeps the sum of the three subsystem alkalinities (= Total alkalinity) unchanged (see Table 5.6). This phenomenon of re-speciation of subsystem alkalinities is very common in mixed weak acid/base systems (Loewenthal *et al.*, 1989). Therefore, interpretation of subsystem alkalinities should be made with the correct understanding of subsystem species redistribution with changes in pH. This is in fact what the 5-pH point titration method is based on and shows the importance of entering the correct S_T value into the 5-pH point

titration programme to obtain the correct H_2CO_3^* alk. and VFA concentrations. This underlines the importance of obtaining accurate S_T values from the experimental systems in order to obtain accurate H_2CO_3^* alk. and VFA concentrations. The small change in A_T (from 137.5 to 141.7 mg/L as CaCO_3 in Figure 5.5) is due to experimental error in the titration procedure.

An observation from Figure 5.4 is that C_T (at Point 1 in Figure 5.4) also decreases due to loss of CO_2 during vacuum filtration. From the post filtration pH and H_2CO_3^* alk., the new C_T (C_T line at Point 2 in Figure 5.4) can be determined and the loss of CO_2 due to vacuum filtration quantified.

5.5.3 Respeciation effect on carbonate, sulphide and acetate standard solutions

The respeciation effect was further investigated on carbonate (C_T), acetate (A_T) and sulphide (S_T) standard solutions. It is expected that the addition of one of the above subsystem reference species to a solution with one or more of the other two subsystems will change the solution pH and accordingly respeciate the subsystem species. This changes the subsystem alkalinities but maintaining the total alkalinity unchanged. To verify this, a carbonate C_T solution with known concentration was made up from 3.630g sodium bicarbonate (NaHCO_3) in 2L distilled water. This C_T solution had an H_2CO_3^* alk. of 1080 mg/L as CaCO_3 and its pH was 8.18. A 50ml sample of this C_T standard solution was analysed for its H_2CO_3^* alk. concentration with the 5-pt titration method to cross-check the theoretical value.

To 1.04L of this standard C_T solution was added a 10ml volume of an A_T standard solution of concentration 10500 mgHAc/L (yielding an acetate concentration of 100 mgHAc/L in the mixed solution). The pure acetic acid solution had a pH of 3.2 and Alk. HAc = 0 because the reference species was added to pure water. On mixing the 2 standard solutions (C_T and A_T), the solution pH changes from 8.18 to 7.20. This new pH respeciates the subsystem species in such a way that now the $[\text{Ac}^-]$ largely dominates the A_T system gaining Alk. HAc = $[\text{Ac}^-]$ to the system. This Alk. HAc was “given up” by C_T system while keeping the total alkalinity unchanged. Again a 50 ml sample of this C_T - A_T solution was analysed for its H_2CO_3^* alk. and VFA concentrations. To the 1.0L (1.04L + 10ml – 50ml) mixed C_T - A_T solution left, 3.502g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was added and the final solution had an S_T

= 467 mgS/L and the final pH was 10.35. A 50ml sample of this mixed weak acid/base system (C_T , A_T and S_T) was again tested with the 5 point titration method. Measurements of $H_2CO_3^*$ alk., VFA, total alkalinity and pH were made before and after addition of each subsequent subsystem. These results are given in Table 5.8.

Table 5.8: Total and subsystem alkalinities and VFA after respeciation in a standard solution of mixed weak acid/base system.

Description	Theoretical	Measured	Units
Volume of distilled water		2	L
Mass of $NaHCO_3$ added		3.63	g
pH of solution		8.18	
$H_2CO_3^*$ alkalinity from 5-pH point titration	1080.4	1067.2	mg/L as $CaCO_3$
Volume of C_T standard solution used		1.04	L
Volume of 10500 mgHAc/L standard solution acetic acid added		10	ml
New volume of mixed C_T and A_T solution		1.05	L
Concentration of acetic acid added	100.0		mgHAc/L
New pH of solution (C_T and A_T)		7.20	
New $H_2CO_3^*$ alkalinity from 5-pH point titration	1070.1	995.0	mg/L as $CaCO_3$
VFA measured from 5-pH point titration		97.0	mgHAc/L
Alk. HAc	0.0	80.8	mg/L as $CaCO_3$
Total Alkalinity for C_T and A_T solution	1070.1	1075.8	mg/L as $CaCO_3$
Mass of $Na_2S \cdot 9H_2O$ added to 1L C_T and A_T solution		3.502	g
Total sulphide concentration, S_T		466.9	mgS/L
Theoretical Alk. H_2S from mass of $Na_2S \cdot 9H_2O$ added	1459.2		mg/L as $CaCO_3$
New pH of solution (C_T , A_T and S_T)		10.35	
New $H_2CO_3^*$ alkalinity from 5-pH point titration		1674.0	mg/L as $CaCO_3$
VFA measured from 5-pH point titration		102.5	mgHAc/L
Alk. HAc from pK_a and pH 10.35		85.4	mg/L as $CaCO_3$
Alk. H_2S from pK_s and pH 10.35		729.58	mg/L as $CaCO_3$
System Total Alkalinity	2529.2	2489.0	mg/L as $CaCO_3$
% Total Alkalinity Recovery		98.4	

From Table 5.8, it is noted that the individual subsystem species respeciate when mixed with another subsystem because of a change in pH. This respeciation changes the individual subsystem alkalinities but keeps the system total alkalinity unchanged. This is confirmed by comparing the theoretical (from known concentrations of C_T , A_T and S_T standard solutions) and measured data. The total alkalinity calculated from the measured $H_2CO_3^*$ alk. and VFA and the calculated Alk. H_2S and Alk. HAc from their respective pK values and the sample pH, was >98% of the theoretical total alkalinity (2489.0 v/s 2529.2 mg/L as $CaCO_3$).

Apart from validating that the total alkalinity remains constant when adding or losing a reference species to a mixed weak acid/base system, it also drew attention to specific points in the sample collection, handling and analyses procedures to obtain accurate results, namely:

- 1) Accurate sulphide (S_T) concentrations must be entered into the 5-pH point titration programme to obtain accurate $H_2CO_3^*$ alk. and VFA concentrations. The system total alkalinity is thereafter obtained by adding the $H_2CO_3^*$ alk., Alk H_2S (using accurate S_T and pH) and Alk HAc (using VFA and pH).
- 2) Sulphide loss in the sulphide determination with the COD test must be minimised by immediately raising the pH above 10 at sample collection. Then the sample can be vacuum membrane filtered.
- 3) CO_2 loss during vacuum filtration or other analysis steps does not affect the accuracy of the results.
- 4) Once S_T is accurately known, S_T loss does not affect the accuracy of the 5-point titration results. So, H_2S and CO_2 loss during the 5-point titration method does not affect the accuracy of the results.

From the above, it is only for the accuracy of the S_T determination with the COD test that H_2S loss has to be avoided. CO_2 loss at any stage of the analysis procedure does not affect the results because the 5-point titration is in fact conducted to characterise the carbonate system with the $H_2CO_3^*$ alk. (which is not affected by CO_2 loss) taking due consideration of the presence of the other weak acid/base systems.

5.5.4 Attempt to develop a 7-pH point titration procedure for estimating S_T in the titration programme

An attempt was made to estimate S_T from a 7-pH point titration method using a standard solution of sulphide prepared from $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. During the titration procedure, on addition of the HCl acid, hydrogen sulphide gas escaped from the sample even though maximum precaution was taken during gentle stirring of the sample and acid addition. It seems practically unfeasible to prevent the loss of H_2S from the sample because the acid added will decrease the pH to lower than the pK_s value of the sulphide system ($pK_s \text{ H}_2\text{S}/\text{HS}^- = 7.05$ at 25°C). Lowering the pH due to acid addition will increase the H_2S concentration with respect to the HS^- concentration and inevitably making the undissociated H_2S species to escape the sample even with very gentle stirring. As a consequence, S_T is reduced and will be therefore incorrectly estimated by the programme. The S_T concentration was also measured using the COD test (with Method 2 approach) and was found to be about 40% less at a pH of 6.7 (after acid addition) than the original S_T (S_T in the standard solutions prepared with initial pH 12.1) giving additional evidence of H_2S loss during the titration procedure.

To characterise a system with e.g. the phosphate, ammonium, sulphide, acetate, carbonate and water weak acid/base subsystems, 6 measurements need to be made, one for each subsystem. For the first four, they are the total species concentrations (P_T , N_T , S_T and A_T), for the carbonate system the H_2CO_3^* alk. and for the water the pH. The H_2CO_3^* alk. allows loss of CO_2 without affecting the accuracy of the results. If S_T is changing due to H_2S loss during the titration, then in effect one of the 6 measurements falls away. With the result that the system can no longer be characterised, one could change the 5-pH point titration programme to assume that no CO_2 loss takes place and obtain C_T from an inorganic carbon analyser. Then S_T could be determined with H_2S loss during the titration. Because one of the objectives of this research was to develop simple and inexpensive analytical procedures to monitor BSR systems, this approach was not pursued.

It was therefore accepted that S_T would have to be determined separately by the COD test as explained in Method 2 (NaOH treated) above. The Alkalinity and VFA concentrations can be determined on clear sample after polyelectrolyte treatment to remove solids using Method 3. The measure S_T (from the COD test) should be entered into the programme to

estimate the H_2CO_3^* alk. and VFA concentrations, while Alk. H_2S and Alk. VFA are calculated from the sample pH (reactor pH) and added to the H_2CO_3^* alk. to obtain the total system alkalinity.

5.6 CONCLUSION

This Chapter gives an assessment of the reasons of poor COD and sulphur mass balances due to sulphide loss during vacuum filtration of the UASB reactor effluent samples. Three analytical methods were investigated to minimise the loss of undissociated H_2S during sample preparation (namely vacuum filtration and mixing during dilution). Method 1 which is the recommended Standard Methods (1985) COD test method resulted in poor S mass balance (64-75%) due to loss of H_2S during sample preparation, mainly vacuum filtration because the sulphide concentration is measured without particulates present to improve accuracy. The total effluent COD concentration was on the other hand measured on unfiltered effluent sample (i.e. no vacuum filtration was required) but indicated a loss in H_2S during sample dilution, mixing and standing as shown by the relatively lower COD mass balance (~ 92%). Method 2, in which 3 drops of 10 M NaOH are added immediately upon effluent sample collection to raise the pH to > 10 retains all the sulphide by converting the undissociated H_2S species into the HS^- species. In so doing, minimal sulphide is lost during sample preparation (vacuum filtration, dilution, mixing and sample standing). Results of the COD and S concentrations obtained from the COD test based on Method 2 showed a marked improvement in the COD and S mass balances (97% and 92-95% respectively). Method 3, in which a polyelectrolyte is added to the effluent sample to improve solid-liquid separation with centrifugation and so avoid the vacuum filtration step did improve the S mass balance with respect to Method 1 (91% against 75% without long sample standing period and 88% against 65% with long sample standing period). However, S mass balance with Method 3 is still low when compared with Method 2 (86-91% against 92-95%). Method 2 (adding 3 drops of NaOH to the samples to prevent loss of H_2S) is therefore recommended to accurately measure S_T and achieve close to 100% COD and S mass balances.

In addition, attempts were also made to investigate the effects of pH changes due to sulphide loss on system alkalinities and species distribution as determined with the 5-pH point titration method. For this procedure, H_2S (and CO_2) loss does not influence the

accuracy of the results provided accurate S_T (from Method 2) concentration is entered into the titration calculation procedure. Entering inaccurate S_T concentrations will not affect the accuracy of the total alkalinity but the subsystem alkalinities and VFA concentrations will be incorrect.

Following the development of the simple wet chemistry analytical procedures for the accurate measurement of sulphide with the COD test, R1 and R2 COD and S mass balances were thereafter calculated based on Method 2 (addition of NaOH before vacuum filtration and sample handling) in order to achieve close to 100% recovery. These results together with the performance of UASB reactor R2 are discussed in the following Chapter (Chapter 6).

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APPENDIX 5A

Results from elemental analysis of dried primary sewage sludge (PSS) and waste sludge (WS).

	Waste sludge composition (% by mass on TSS)				
Parameters	R1 A	R1 B	R2 A	R2 B	PSS
Moisture	3.1	3.2	3.1	2.8	
Ash	33.9	33.1	29	28.9	
Volatile	55.4	55.4	59	59.2	
Fixed Carbon	7.6	8.3	8.9	9.1	
Carbon	34.65	35.28	38.58	38.5	43.01
Hydrogen	4.87	4.9	5.45	5.52	7.31
Nitrogen	3.35	3.36	3.91	3.91	6.61
Carbonates	3.21	3.22	1.93	1.93	
Total Sulphur	3.49	3.32	2.95	2.62	
Oxygen	13.43	13.62	15.08	15.82	
Phosphorus (P ₂ O ₅)	8.19	16.21	11.92	10.99	

Appendix 5B

1. Calculation of activity coefficient with the aid of the Davies equation

The calculation of the activity coefficient and the ionic strength (Loewenthal *et al.*, 1989) is described below. In salinity waters with TDS ~ 2800 mg/L, **activity coefficients** of ions can be determined from the Debye-Huckel theory or some modification of it. The most common and widely used modification of this theory is the one based on the Davies equation which is:

$$\log f_i = -AZ_i^2 \left(\frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.3 \mu \right) \quad (5.16)$$

where f_i = activity coefficient for ionic species i , written as f_m and f_d for mono and divalent ions respectively

μ = ionic strength = $\frac{1}{2} \sum C_i Z_i^2$

C_i = concentration of the i^{th} ionic species, mol/L

Z_i = charge of the i^{th} species, equal to 1 for mono and 2 for divalent ions

A = temperature dependent constant = $1.825 \times 10^6 \times (78.3T)^{-1.5}$
= 0.504 at 25°C

T = temperature in Kelvin

In the calculation of the **ionic strength**, μ , a complete analysis of the water is required and this is not often practical. However, the activity coefficients determined from the Davies equation above is not sensitive to ionic strength so that an approximate estimate of μ from the empirical methods is usually sufficient and acceptable. There are two empirical equations available (Kemp, 1971) namely,

$$1. \quad \mu \approx 2.5 \times 10^{-5} \times (\text{TDS} - 20)$$

where TDS = total inorganic dissolved solids, mg/L

$$2. \quad \mu \approx 1.68 \times 10^{-4} \times \text{SC}$$

where SC = specific conductance, in mS/m (1 mS/m = 10 μ mho/cm)

The ionic strength of the sample was found to be $\mu \approx 0.07$. For this ionic strength, the monovalent ion activity coefficient f_m at 35°C is:

$$\log f_m = -0.0919$$

$$\text{Hence } f_m = 0.8093$$

Once the activity coefficient is determined, the apparent dissociation constant pK'_s for the sulphide system (H_2S/HS^-) and pK'_w for the water system are calculated from Table 5.7.

Table 5.7: Weak acid dissociation constants at 25 °C (expressed as their negative log value pK) and their temperature dependency, for the carbonate, phosphate, short-chain fatty acids acetate and propionate, ammonium and hydrogen sulphide systems. $pK = A/T - B + CT$ where T is in Kelvin.

Weak acid		pK at 25 °C	A	B	C
Water	pK _w	14.000			
Carbonate	pK _{c1}	6.352	3404.7	14.8435	0.03279
	pK _{c2}	10.329	2902.4	6.498	0.02379
Henry's constant ^a	pK _{CO₂}	1.470	-1760	-9.619	-0.00753
Phosphate	pK _{p1}	2.148	799.3	4.5535	0.01349
	pK _{p2}	7.198	1979.5	5.3541	0.01984
	pK _{p3}	12.023	Not given		
Short chain fatty acids:					
Acetate	pK _{fa}	4.756	1170.5	3.165	0.0134
Propionate	pK _{fp}	4.874	1213.3	3.386	0.01406
Ammonium	pK _n	9.245	2835.8	0.6322	0.00123
Hydrogen sulphide (HS ⁻)	pK _{s1}	7.050 ^b	1351.9	-0.0992	0.00792
Hydrogen sulphide (S ²⁻)	pK _{s2}	12.920 ^c	Not given		
a [H ₂ CO ₃ *] = K _{CO2} . p _{CO2}					
b pK _{s1} from Lide (2001)					
c pK _{s2} from Bjerrum (1958)					

$$pK'_{s1} = pK_{s1} + \log f_m = 6.925 + (-0.0919) = 6.833$$

$$pK'_w = pK_w + \log f_m = 14.000 + (-0.0919) = 13.908$$

Chapter 6

Operation and performance of UASB reactors R1 and R2

6.1 INTRODUCTION AND INVESTIGATION OBJECTIVES

With the successful operation of the UASB reactor R1 at 35 °C (when fed 1500 mgSO₄²⁻/L for a period of 280 days), it was decided to study the performance of BSR using PSS in the second identical UASB reactor (R2) operated at ambient temperature, namely 20 °C. Accordingly, reactor R2 (T=20 °C) was run with feed sulphate and PSS concentrations of 1500 mgSO₄²⁻/L and 1995 mgCOD/L respectively representing a feed PSS COD to sulphate ratio of 1.33 mgCOD/mgSO₄²⁻ but this ratio was later increased to 1.75 to improve the system efficiency. R2 was started when R1 (fed 1500 mgSO₄²⁻/L) had been operated for 205 days. The operation and performance of R2 are assessed and evaluated in this Chapter.

When the experimental programme of R1 reached 280 days of operation with feed sulphate 1500 mgSO₄²⁻/L and all the necessary tests conducted (including profile tests) and also the optimum design and operating parameters (e.g. HRT, BRT and R_s) established, the influent sulphate was increased to 1800 mgSO₄²⁻/L. It was expected that high feed sulphate concentration would result in high sulphide concentration in the system. Though compared to other anaerobic micro-organisms (namely methanogenic archaea), the sulphate reducing bacteria (SRB) have the highest tolerance to sulphide, their activity is nevertheless affected by the presence of sulphide, especially undissociated hydrogen sulphide (H₂S). Undissociated H₂S is toxic to SRB and would consequently inhibit their growth and activity (Reis *et al.*, 1992; Maillacheruvu *et al.*, 1993; Konishi *et al.*, 1996; Kalyuzhnyi *et al.*, 1997; O'Flaherty *et al.* 1998). Investigating the effect of high feed sulphate concentration on the system performance was therefore worthwhile in order to have a preliminary assessment of

the extent of undissociated hydrogen sulphide (H_2S) inhibition on BSR system using PSS as substrate in a UASB reactor.

When UASB reactor R1 (fed $1800 \text{ mgSO}_4^{2-}/\text{L}$ at 35°C) was running at its maximum efficiency, sludge samples were taken and run in batch mode. Batch tests were conducted to study the production and utilisation of VFA and the consequent reduction in sulphate concentration. Details of these batch tests are reported in this Chapter.

Finally, the settling rate of the various solids fractions in the sludge particulates was also measured to determine if bed expansion or sludge settleability was the capacity limiting process of the UASB system. To determine this, a sludge settleability device, called a settleometer, was built and operated to test the 2 UASB sludges (R1 and R2 sludges) in it at different upflow velocities. This study on the settleability of the sludges is also reported in this Chapter.

In brief, this Chapter therefore deals with the following objectives:

- Part 1: Section 6.2 - Operation and performance of UASB reactor R2 (fed $1500 \text{ mgSO}_4^{2-}/\text{L}$ at 20°C)
- Part 2: Section 6.3 - Operation and performance of UASB reactor R1 (fed $1800 \text{ mgSO}_4^{2-}/\text{L}$ at 35°C)
- Part 3: Section 6.4 - Batch tests on UASB reactor R1 sludge
- Part 4: Section 6.5 - Measurement of the settling rate of solids fractions in the sludge particle of the UASB reactors

6.2 OPERATION AND PERFORMANCE OF UASB R2

6.2.1 R2 EXPERIMENTAL PROGRAMME FOR FEED SULPHATE $1500 \text{ mgSO}_4^{2-}/\text{L}$

During the 270 days experimental programme, the influent feed flow rate was varied to vary the HRT. To summarise the various stages in the experimental programme of UASB R2, the operational conditions during the 270 days are set out in Table 6.1. The different steady state periods with respect to the operating HRT with 2 PSS COD/ SO_4^{2-} ratios, the days at which bed profile tests were conducted, the period when alkalinity dosage was stopped and

the days on which mass balances were determined are listed. Towards the end of the programme, the settling rates of the bed particulates were determined (see Section 6.5 later).

Table 6.1: Summary of operational conditions for UASB reactor R2 during the 270 days of operation at 20 °C.

Day of operation	Reactor status/activities performed	HRT (h)	BRT (h)
1-70	Feed PSS COD to sulphate ratio 1.33 and sludge bed volume 7.1L		
1-50	SRB acclimatisation	28.0	21.8
51-70	Steady state (SS) 1	28.0	25.5
91-112	R2 SS 2	24.0	21.8
115-270	Feed PSS COD to sulphate ratio 1.75 and sludge bed volume 7.4L		
118-139	R2 SS 3	24.0	22.8
144-151	R2 SS 4	22.0	20.9
154-270	R2 SS 5	20.4-21.0	19.4-19.9
168 and 183	Bed profile tests (both on solubles and solids)		
126-155	CHON elemental analysis of waste sludge		
150-258	H ₂ S gas capture and measurement*	20.4-21.0	19.4
185-250	Stopped NaHCO ₃ dosage to feed	20.4-21.0	19.4
118-258	COD, S and N mass balances calculated		
168 and 183	Determination of sludge age	20.4-21.0	19.4
Sludge on days 260 and 261	Measurement of settling rates of bed particulates		
* H ₂ S gas measurement done only when conducting sulphur mass balance exercise over the system and was done only once since % mass H ₂ S gas was negligible			

6.2.2 REACTOR R2 START-UP PERIOD

Reactor R2 (T=20 °C) was inoculated with waste sludge from R1 (Day 0). Initially, R2 performance was not as good as R1, despite complete seeding with R1 sludge. The relatively short HRT (~28h) at which R2 was operated during the start-up period was probably too short. It was thought that R1 waste active sludge would result in a quick and effective start-up of R2 biological processes since R1 was at its maximum efficiency. However, it appeared that an adaptation period was required for the selected population group of sulphidogenesis to develop at the lower temperature. After 50 days of operation, granulation was observed and the system performance started to stabilise. The effluent

sulphate concentration remained stable from Day 56 to Day 118 with a sulphate removal of 80.7% and 79.8% respectively, even though the HRT was incrementally decreased from 28h to 24h (see Table 6.5 later), implying that the reactor was at steady state. However, the effluent sulphate concentration (303 mgSO₄²⁻/L) was still above the specified requirement (250 mg SO₄²⁻/L). In addition, during this period the VFA concentration was low suggesting that PSS hydrolysis was incomplete and remained the rate-limiting step under the lower temperature conditions.

6.2.3 DEVELOPMENT OF UASB R2 PERFORMANCE WITH TIME

6.2.3.1 Influent characteristics

Similar to R1, the prepared feed for R2 (from dilution of the PSS) augmented with 1500 mgSO₄²⁻/L was regularly analysed for its COD, TKN, FSA, VFA and H₂CO₃* alkalinity concentrations and pH. A summary of the results from the measurements of the above parameters are listed in Table 6.2.

It can be seen that two influent PSS COD/SO₄²⁻ ratios (namely 1.33 and 1.75 mgCOD/mgSO₄²⁻) were used. The reason was that at the start of the reactor R2, a slightly higher ratio than R1 (1.25) was used to take into account the slower hydrolysis rate at the lower temperature (20 °C). No information was available to indicate what PSS COD/SO₄²⁻ ratio was appropriate to supply the required VFA (from hydrolysis/acidogenesis of PSS) at 20°C. After a few trial ratios, it was found that a ratio of 1.75 seemed most favourable to supply enough VFA for BSR. The results obtained from the 1.33 and 1.75 ratios are discussed later. In addition, towards the end of the UASB R2 experimental programme, alkalinity dosage (~ 400 mg/L as CaCO₃) with NaHCO₃ was stopped in order to check that the pH of the system would adapt by itself.

Table 6.2: Summary of the influent characteristics of UASB reactor R2 (1500 mgSO₄²⁻/L at 20 °C) for steady state (SS) periods 2 and 5. (See Appendix 6A for the day to day data from which these averages were calculated).

Summary of the influent characteristics of UASB reactor R2 (fed 1500 mgSO ₄ ²⁻ /L at 20 °C)				
Feed PSS COD to sulphate ratio (mgCOD/mgSO ₄ ²⁻)	1.33		1.75	
Steady state period	SS2 (Days 91-112)		SS5 (Days 240-258)	
Parameter	Average value	SSD	Average value	SSD
Total COD (mgCOD/L)	1975	7	2596	78
Unbiodegradable particulate COD ($f_{pSup} = 0.36$) (mgCOD/L)	711	-	935	-
VFA (or SCFA) (mgHAc/L)	123	7	158	11
Fermentable readily biodegradable COD (mgCOD/L)	139	-	162	-
Slowly biodegradable COD (mgCOD/L)	987	-	1322	-
Unbiodegradable soluble (mgCOD/L)	7	-	8	-
TKN (mgN/L)	71	18	78	18
FSA (mgN/L)	8	5	10	4
H ₂ CO ₃ * alkalinity (mg/L as CaCO ₃) before dosage	18	3	23	3
H ₂ CO ₃ * alkalinity (mg/L as CaCO ₃) after dosage	423	6	429	15
Total phosphorous (mgP/L)	28	-	33	-
Ortho-phosphate (mgP/L)	8	-	10	-
pH before dosage	5.95	0.05	5.94	0.05

6.2.3.2 Effluent sulphate concentration with time

The variation in UASB R2 effluent sulphate concentration with time from Day 10 is presented in Figure 6.1 for the whole experimental period of R2 with the 2 PSS COD/SO₄²⁻ ratios. For the period Day 51-112 (comprising SS periods 1 and 2), on average the effluent sulphate was not reduced below 250 mgSO₄²⁻/L because of the low PSS COD/SO₄²⁻ ratio (1.33) and consequently low VFA generation from hydrolysis. However, from Day 115 onwards the ratio was increased to 1.75 which resulted in a marked decrease in the effluent sulphate concentration to around 100 mgSO₄²⁻/L. Clearly VFA generation via hydrolysis was the limiting rate for BSR.

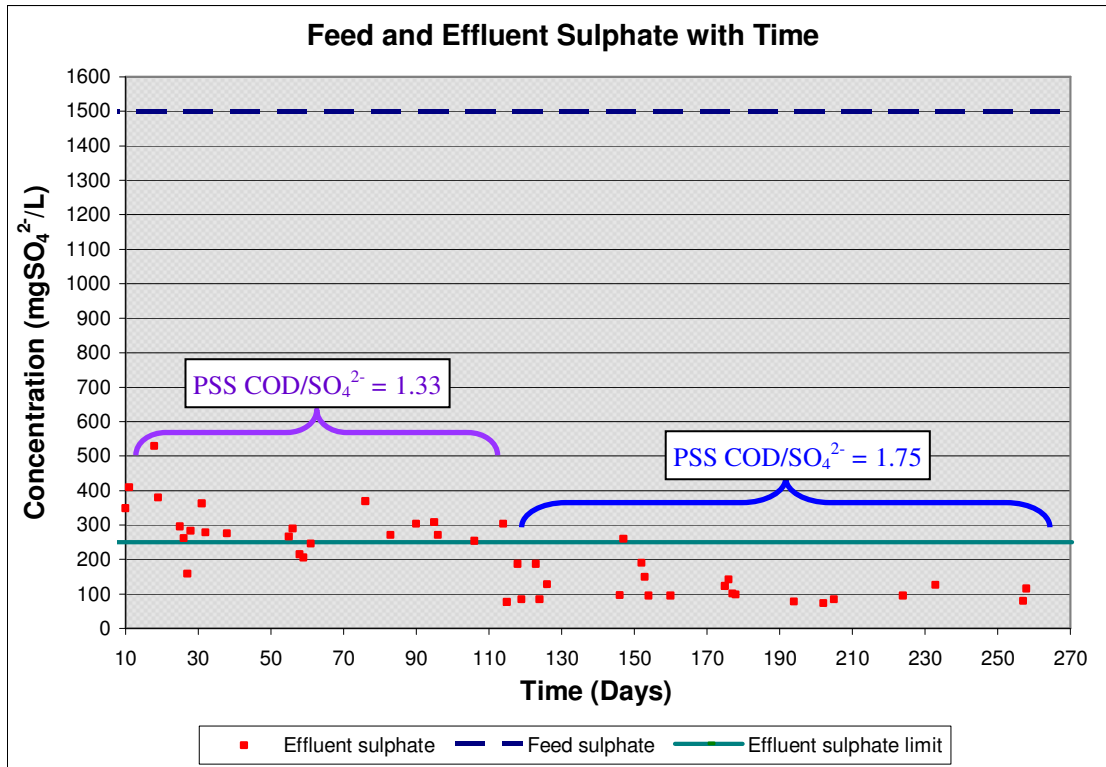


Figure 6.1: Effluent sulphate concentration-time profiles with PSS as substrate augmented with 1500 mgSO₄²⁻/L sulphate (R2).

6.2.3.3 Effluent H₂CO₃* alk, Alk H₂S and VFA concentrations with time

As expected, the effluent total Alk (sum of H₂CO₃* alk. and Alk H₂S) increased due to the increase in the PSS COD/SO₄²⁻ ratio (Days 115-170 in Figure 6.2) as a direct consequence of an increase in aqueous sulphide produced, hence, increasing the Alk H₂S.

The data points circled in Figure 6.2 represent the period (Day 195 onwards) at which the feed dosage with NaHCO₃ was progressively decreased to zero on Day 230. This reduction in feed alkalinity dosage did not affect the system performance as shown in Figs 6.2 and 6.1 by the low effluent VFA and sulphate concentrations. This is an important finding for the UASB R2 performance as it shows that BSR not only occurs successfully at low temperature (20 °C) but also that the system can be operated without alkalinity dosage because it is pH self-regulatory.

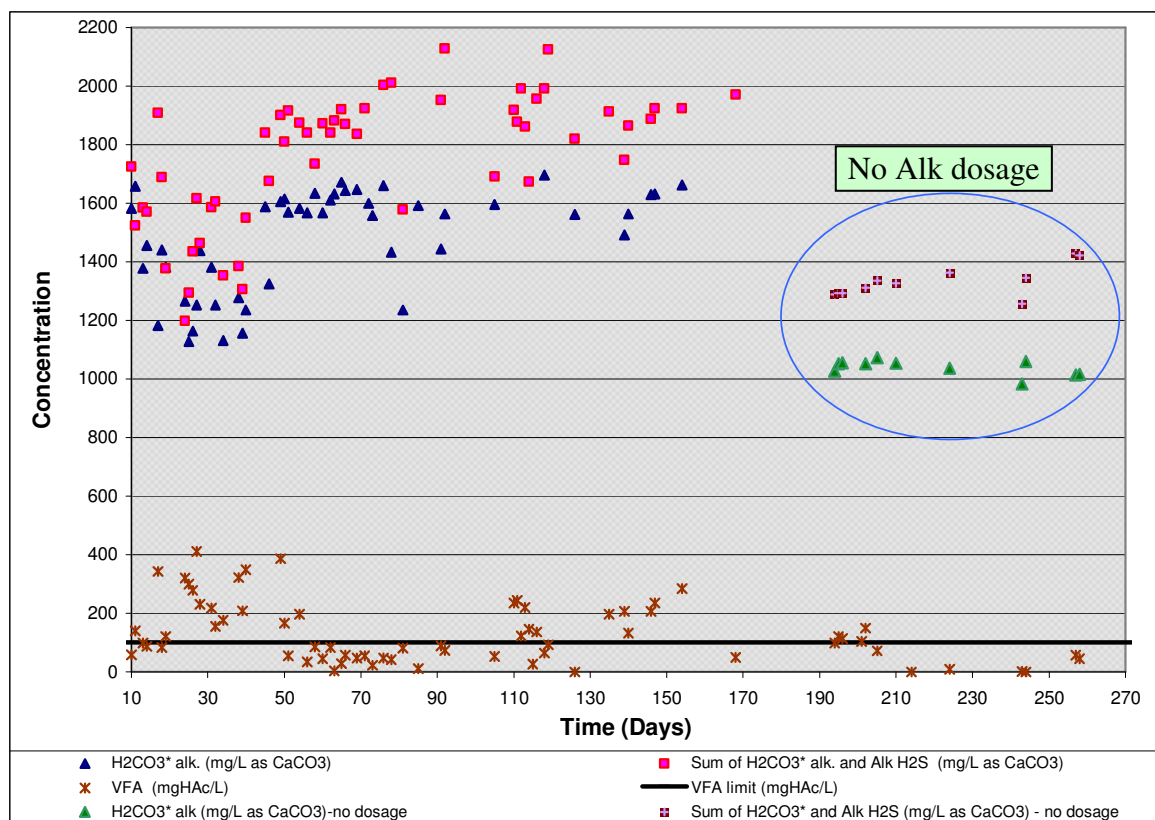


Figure 6.2: Effluent alkalinity and VFA concentration-time profiles with PSS as substrate augmented with 1500 mgSO₄²⁻/L sulphate (R2).

6.2.3.4 Reactor performance with PSS COD/SO₄²⁻ ratio of 1.33

Table 6.3 shows the performance of UASB reactor R2 when operated at a HRT of 24h. It can be seen that R2 performed satisfactorily because it achieved a sulphate removal efficiency of ~80% ($\pm 2\%$) and an organic removal efficiency of ~77% ($\pm 1\%$) (see Appendix 6A for calculations). However, despite the relatively high sulphate removal efficiency, the average effluent sulphate remained above the upper limit of 250 mgSO₄²⁻/L. The cause for this fairly high effluent sulphate concentration (~ 303 mgSO₄²⁻/L) was attributed to the unavailability of carbon source, namely VFA which remained very low in the effluent, despite the fact that the PSS COD/SO₄²⁻ ratio was 1.33 (biodegradable organics, $S_{bi} \sim 1230$ mgCOD/L). Accordingly, it was deduced that at low temperature, the hydrolysis rate of the PSS biodegradable organics was reduced thereby generating insufficient VFA and H₂ for sulphate reduction.

Table 6.3: Effluent characteristics of UASB reactor R2 with an influent PSS COD to sulphate ratio of 1.33 mgCOD/mgSO₄²⁻ at a HRT of 24h (Bed volume = 7.1L)

Steady state (SS) period 2 (Day 91-112)		Influent		Effluent	
Parameter		Average value	SSD	Average value	SSD
Total organic COD (mgCOD/L)		1975	7	453	13
Organic soluble COD (mgCOD/L)		277	7	146	8
Particulate COD (mgCOD/L)		1698	7	307	9
VFA (or SCFA) (mgCOD/L)		131	7	49	20
H ₂ CO ₃ * alkalinity (mg/L as CaCO ₃) after dosage		424	7	1553	25
pH		7.25 ^a	0.10	7.21	0.02
Sulphate (mgSO ₄ ²⁻ /L)		1500	-	303	30
Aqueous sulphide (mgS/L)		0	-	216	5
Theoretical aqueous sulphide from sulphate reduced (mgS/L)		-	-	399	11

a: Feed pH after dosage with NaHCO₃

In order to increase the production of VFA, the PSS COD/SO₄²⁻ ratio was increased which increased the feed biodegradable particulate COD concentration and consequently the concentration of biodegradable organics (S_{bp}) hydrolysed thereby generating sufficient VFA and H₂ for BSR. Increasing the PSS COD/SO₄²⁻ ratio also resulted in higher unbiodegradable particulate organics (S_{up}) and biodegradable particulate organics (S_{bp}) not hydrolysed. Hence more particulate organics needed to be wasted to maintain the bed volume. So to provide a larger bed volume (and concomitantly a longer sludge age), the reactor sludge bed volume (and height) was increased from 7.1 to 7.4L. The increased sludge age allowed more time for the S_{bp} to be hydrolysed as PSS hydrolysis is the rate limiting process.

6.2.3.5 R2 performance with a PSS COD/SO₄²⁻ ratio of 1.75 at lowest optimal HRT of 20.4-21.0h

As mentioned above, to decrease the effluent sulphate concentration below 250 mgSO₄²⁻/L, the PSS COD/SO₄²⁻ ratio was increased to 1.75. This allowed for more biodegradable COD to be fed into the reactor and consequently increase the percentage biodegradable organic

particulates hydrolysed. At this new ratio, the performance of R2 improved to the extent that the effluent quality concentrations were now met (i.e. sulphate $<250 \text{ mgSO}_4^{2-}/\text{L}$ and VFA $<100 \text{ mgHAc}/\text{L}$). The performance of UASB reactor R2 at the lowest optimal HRT of 20.4-21.0h with alkalinity dosage ($\sim 423 \text{ mg/L}$ as CaCO_3) from Day 154-184 (SS period 5a) was high with an average sulphate removal efficiency of $93.2 \pm 1.5\%$ (see Table 6.4a and Appendix 6A for details).

Table 6.4a: Effluent characteristics of UASB reactor R2 with an influent PSS COD to sulphate ratio of $1.75 \text{ mgCOD}/\text{mgSO}_4^{2-}$ at the lowest optimal HRT of 20.4-21.0h (Bed volume = 7.4L) with **alkalinity dosage** to feed (SS period 5a, Days 154-184).

Effluent parameters	Units	Average value	SSD
Sulphate	$\text{mgSO}_4^{2-}/\text{L}$	109	18
Total organic COD	mgCOD/L	664	102
Organic soluble COD	mgCOD/L	305	66
Particulate COD	mgCOD/L	358	42
VFA (or SCFA)	mgHAc/L	105	47
Sum of H_2CO_3^* alkalinity and Alk H_2S	mg/L as CaCO_3	1920	27
H_2CO_3^* alkalinity	mg/L as CaCO_3	1589	11
pH	-	7.22	0.02
TKN	mgN/L	63	9.0
FSA	mgN/L	37	12.0
Aqueous sulphide	mgS/L	344 ^a	39
H_2S gas	mgS/L	1.5	1
Theoretical aqueous sulphide from sulphate reduced (mgS/L)	mgS/L	464	6
a: H_2S measurement problem			

Alkalinity dosage with NaHCO_3 was discontinued as from Day 185 until the end of the experimental programme on Day 270. Table 6.4b lists the effluent parameter values when R2 was operated at a HRT of between 20.4-21.0h with no alkalinity dosage to the feed for the period Days 240-258. With the supply of additional carbon (i.e. more PSS), the sulphate removal efficiency increased from 80% ($\pm 2.0\%$) (when fed a PSS $\text{CO}/\text{SO}_4^{2-}$ ratio of 1.33) to $> 93\%$ ($\pm 1.3\%$) (with PSS $\text{COD}/\text{SO}_4^{2-}$ ratio of 1.75). From the high organic COD removal efficiency of 91% ($\pm 1.3\%$) it was found that the increase in PSS to meet the VFA demand did not impact the effluent quality in terms of suspended solids. In fact, the

particulate organic COD concentration remained low with an average value of 138 ($\pm$ 25) mgCOD/L.

The aqueous sulphide concentration was obtained from the modified wet chemistry analytical approach developed and described in Chapter 5. This aqueous sulphide concentration added to the measured H₂S gas and elemental S in the sludge matched very closely the theoretical sulphide produced from the sulphate reduced (see Section 6.2.7 for S mass balance). In addition, discontinuing the alkalinity dosage to the influent (from Days 188 to 270) did not affect the system performance. The alkalinity produced from BSR together with the increase in pH (from 5.94 to 7.21) suggests that the system is pH self-regulatory. This is a major advantage of this system to reduce the cost of acid mine drainage remediation.

Table 6.4b: Effluent characteristics of UASB reactor R2 with an influent PSS COD to sulphate ratio of 1.75 mgCOD/mgSO₄²⁻ at the lowest optimal HRT of 20.4-21.0h (Bed volume = 7.4L) with **no alkalinity dosage** to feed (SS period 5b, average values are from Days 240-258).

Steady state (SS) period 5 (Day 240-258)	Influent		Effluent	
Parameters	Average value	SSD	Average value	SSD
Total organic COD (mgCOD/L)	2596	44	234	27
Organic soluble COD (mgCOD/L)	339	17	96	8
Particulate COD (mgCOD/L)	2257	-	138	25
VFA (or SCFA) (mgCOD/L)	158	13	62	11
Sulphate (mgSO ₄ ²⁻ /L)	1500	-	101	19
Sum of H ₂ CO ₃ * alkalinity and Alk H ₂ S (mg/L as CaCO ₃)	23	3	1558	14
H ₂ CO ₃ * alkalinity (mg/L as CaCO ₃)	23	3	1144	10
TKN (mgN/L)	78	18	63	9
FSA (mgN/L)	9.6	4	38	5
pH	5.94	0.04	7.21	0.02
Aqueous sulphide (mgS/L)	0	-	427	5
H ₂ S gas in reactor head space (mgS/L influent)	0	-	2.1	0.3
Elemental sulphur in sludge (mgS/L sludge)	0	-	24.5	3
Theoretical sulphide from sulphate reduced (mgS/L)	0	-	466	6

Note: S_T was accurately measured from Days 240-258 using the modified wet chemistry analytical procedures described in Chapter 5.

6.2.3.6 Summary of UASB R2 performance

A summary of the average experimental data at the different HRTs and bed retention times (BRTs) is listed in Table 6.5. The minimum HRT for which the specified effluent criteria were still met was found to be between 20.4-21.0h, where sulphate removal efficiency was ~ 95% with a PSS COD/SO₄²⁻ ratio of 1.75.

Table 6.5: Sulphate and organic COD removal (%) under steady state conditions at each HRT and BRT.

Period of operation	SS period	HRT (h) ^a	BRT (h)	Feed flow rate (L/d)	Organic loading rate (g COD/d)	Sulphate loading rate (g SO ₄ /d)	Sulphate removal (%)	Organic COD removal (%)
Days 53-70	1	28.0	25.8 ^b	6.7	13.06	10.03	83.7	75.9
Days 91-112	2	24.0	22.1 ^c	7.8	19.88	11.70	79.8	76.8
Days 118-139	3	24.0	22.2 ^c	7.8	20.20	11.70	91.1	80.1
Days 144-151	4	20.8	19.2 ^c	9.0	23.28	13.48	88.2	74.6
Days 155-184	5a	20.5	19.4 ^c	9.1	24.14	13.70	92.7	75.2
Days 240-258 ^d	5b	20.4	19.4 ^c	9.2	24.71	13.76	93.3	91.2

a: HRT calculated at a liquid volume of 7.8L

b: BRT calculated at sludge volume of 7.1L with feed PSS COD to Sulphate ratio of 1.30

c: BRT calculated at sludge volume of 7.4L with feed PSS COD to Sulphate ratio of 1.75

d: No NaHCO₃ dosage to influent

6.2.4 BED PROFILING ALONG AXIS OF REACTOR R2

During the steady state period at 20.4-21.0h HRT (PSS COD/SO₄²⁻ ratio=1.75, bed volume=7.4L) (SS period 5a), sludge samples were taken from the intermediate sampling ports of R2 to construct concentration-depth profiles to examine the progress of the biological processes in the bed.

6.2.4.1 Profile of soluble parameters

Figure 6.3 depicts the profile characteristic of the sulphate, VFA and sum of H₂CO₃* alk and Alk H₂S concentrations (total Alk). The immediate sulphate reduction at the bottom of the sludge bed (with the concomitant generation/consumption of VFA and the high production of alkalinity) reinforces the prerequisite to recycle sludge from the top to the bottom of the reactor bed.

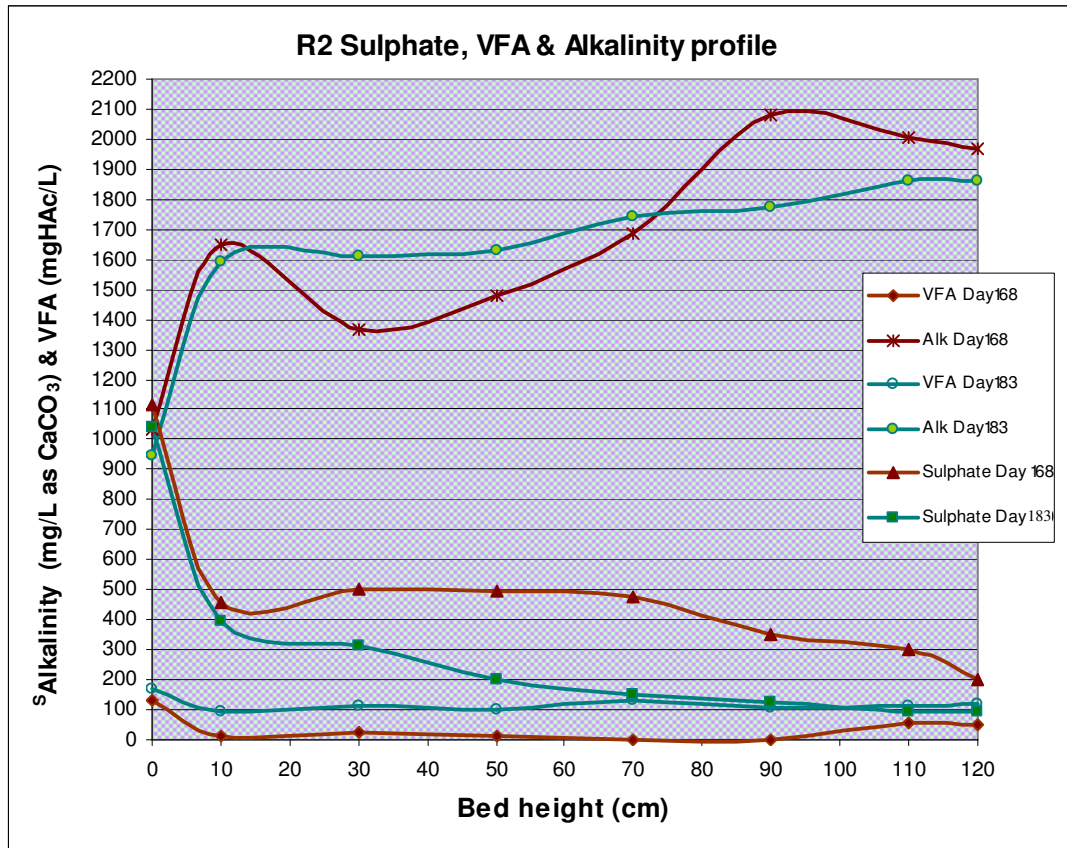


Figure 6.3: UASB R2 alkalinity, VFA and sulphate concentration profiles up the sludge bed height (110 cm) for a BRT of 19.3h on Days 168 & 183.

6.2.4.2 Profile of solids – Calculation of sludge age (R_s)

Figure 6.4 illustrates the variation of R2 solids along the bed axis. Above the 10cm height there is little difference in the solids concentration along the bed axis probably largely due to the sludge recycle. From these measurements, the mass of sludge in the bed was calculated, which in relation to the mass of sludge wasted (see below) and the mass of sludge in the effluent, yielded the sludge age (R_s) of the UASB reactor R2 at around 24.1d.

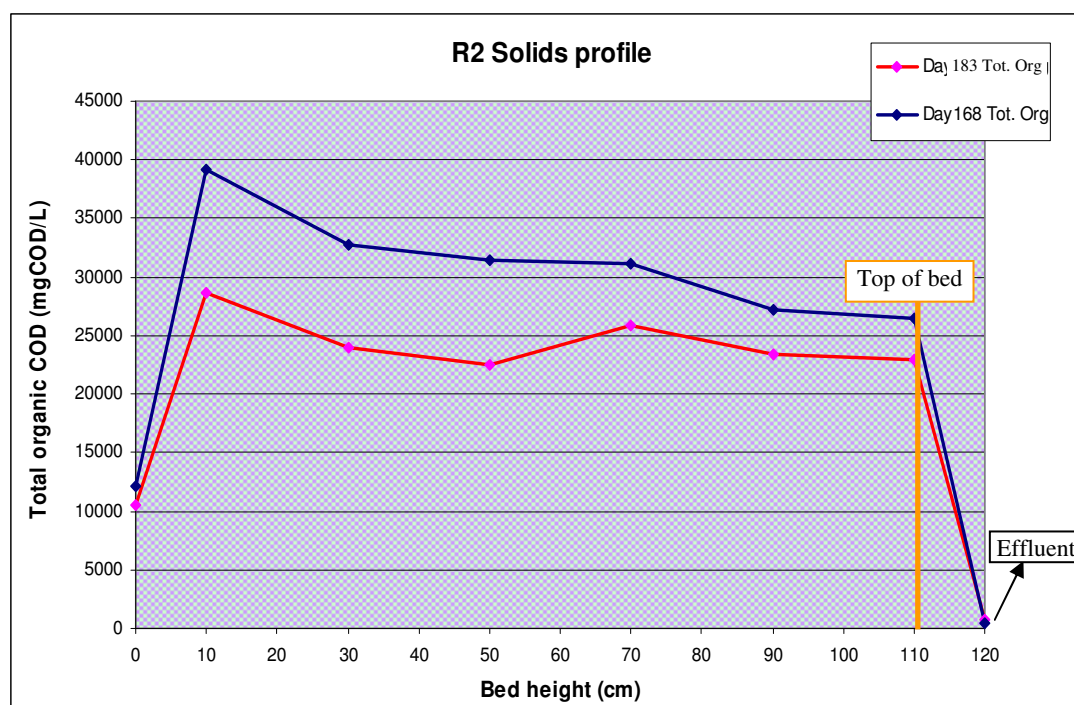


Figure 6.4: UASB reactor R2 sludge COD concentration profiles up the sludge bed height (110 cm) for a BRT of 19.3h on Days 168 & 183.

6.2.5 ANALYSIS OF WASTE SLUDGE

UASB reactor R2 waste sludge was analysed on 6 operational days (Table 6.6) and was found to have an average particulate organic COD/VSS (f_{cv}) and TKN/VSS (f_n) of 1.611 ± 0.041 and 0.068 ± 0.016 respectively.

Table 6.6: Analysis of waste sludge from the UASB reactor R2 (fed $1500 \text{ mgSO}_4^{2-}/\text{L}$).

Day of operation	Total COD (mgCOD/L)	Particulate COD (mgCOD/L)	TSS	VSS	TKN	COD/VSS (f_{cv})	TKN/VSS (f_n)	Volume wasted per day*, Q_w (L/d)
118	21336	20056	16120	12368	798	1.622	0.065	0.35
126	20117	18862	14798	11378	1113	1.658	0.098	0.35
139	28651	27174	22138	16906	1361	1.607	0.080	0.30
146	32458	30977	26398	20150	1005	1.537	0.050	0.32
147	27418	25745	21466	16220	980	1.587	0.060	0.40
154	37498	35832	28340	21648	1253	1.655	0.058	0.31
Mean	27913	26441	21543	16445	1085	1.611	0.068	0.34
SSD	6019	5888	4917	3727	185	0.041	0.016	0.03

* This was the volume of sludge wasted per day on these 6 analysis days. The average volume wasted daily over this operation period was 0.34 L/d to maintain the sludge bed volume at 7.4L.

6.2.6 MASS BALANCES

Mass balance exercise was conducted on R2 to check experimental data reliability. Similar to UASB R1 when fed $1500 \text{ mgSO}_4^{2-}/\text{L}$ during the first 280 days (Chapter 4), prior to the development of simple wet chemistry analytical procedures for the accurate measurement of aqueous sulphide, R2 COD mass balance was relatively low ($91.7 \pm 5.2\%$) while the S mass balance was poor ($69.4 \pm 6.4\%$). However, these mass balances, particularly the S mass balance, improved considerably with the new analytical method in H_2S measurement. The COD mass balance increased to 98.0% ($\pm 0.2\%$) while the S mass balance averaged 95.9% ($\pm 0.2\%$). These good mass balances confirm the reliability of the measured data and the new analytical approach in aqueous H_2S measurement reported in the previous Chapter. Nitrogen (N) mass balance was also very good and averaged 104.5 ($\pm 4.9\%$).

6.2.7 COMPARISON OF R1 (35 °C) AND R2 (20 °C) (both fed $1500 \text{ mgSO}_4^{2-}/\text{L}$)

Since the objective of operating the UASB reactor R2 was to study the performance of BSR using PSS at ambient temperature (namely 20°C), a comparison between R1 (fed $1500 \text{ mgSO}_4^{2-}/\text{L}$ at 35°C) and R2 was important since most full-scale systems are not likely to be heated to 35°C . Table 6.7 lists the performance of the 2 UASB reactors when they were both operated at their lowest optimal HRT. The influent characteristics for both R1 and R2 feeds are also compared for a closer assessment as this highlights the carbon requirement when operating BSR using PSS at the 2 reactor temperatures. With regard to the effluent quality, both reactors achieved excellent performance and successful BSR (Table 6.7). Nonetheless, in terms of the design and operating parameters, such as Q_i , HRT, BRT, R_s and V_b , reactor R1 outperforms R2. Because the hydrolysis rate of the PSS is strongly decreased by a temperature reduction of 15°C ($\sim 30\%$ reduction in S_{bp} hydrolysed), the feed PSS COD/ SO_4^{2-} ratio of R2 had to be increased to 1.75 to make up for the S_{bp} not hydrolysed. Moreover, R2 had a longer HRT and V_b in order to increase the BRT and sludge age (R_s) thereby improving the utilisation of S_{bp} . Economically these factors favour R1 as it has a more efficient use of S_{bp} ($\sim 90\%$) than R2 ($\sim 60\%$). However, in practical terms, this advantage might be offset as a UASB reactor would need to be heated to 35°C to achieve the R1 performance. A cost-benefit analysis of these 2 reactors' design and operating parameters would be required in order to assess the economics of the two systems. The successful operation of R2 asserts that sulphate reduction using PSS at ambient temperature

(20 °C) can be effectively achieved provided a higher feed PSS COD/SO₄²⁻ ratio and/or a longer R_s is used.

Table 6.7: Comparison of R1 and R2 performance at their respective lowest optimal HRTs.

Parameters	Units	R1 at 35°C (1500 mgSO ₄ ²⁻ /L)		R2 at 20°C (1500 mgSO ₄ ²⁻ /L)	
Effluent parameters		Influent	Effluent	Influent	Effluent
Total COD	mgCOD/L	1880	1165	2596	1141
Unbiodegradable particulate COD (f _{PS,up} =0.36)	mgCOD/L	677	-	935	-
Total soluble COD	mgCOD/L	226	761 ^b	339	948
SCFA COD	mgCOD/L	126	51	169	66
Unbiodegradable soluble COD	mgCOD/L	6	-	8	-
Biodegradable particulate COD	mgCOD/L	967	-	1322	-
Sulphate	mgSO ₄ ²⁻ /L	1500	149	1500	101
Free and saline ammonia (FSA)	mgN/L	10	32	10	38
pH	-	7.20 ^a	7.15	5.94	7.21
Sum of H ₂ CO ₃ * alkalinity and Alk H ₂ S	mg/L as CaCO ₃	456 ^a	1938 ^b	23	1558
H ₂ CO ₃ * alkalinity	mg/L as CaCO ₃	456 ^a	1611 ^b	23	1144
Design and operating parameters		R1 at 35°C (1500 mgSO ₄ ²⁻ /L)		R2 at 20°C (1500 mgSO ₄ ²⁻ /L)	
Volume of reactor bed/digester after wastage (V _r)	L	6.7		7.4	
Feed flow rate, Q _i	L/d	13.6		9.2	
Hydraulic retention time (HRT)	h	13.8		20.5	
Sludge age, R _s	d	18		24	
Waste flow rate, Q _w	L/d	0.37		0.32-0.34	
Upflow velocity, V _{up}	m/h	0.127		0.085	

a: Alkalinity dosage to R1 feed.

b: Problem in H₂S measurement during R1 first 280 days of operation.

6.3 OPERATION AND PERFORMANCE OF R1 FED 1800 mgSO₄²⁻/L

During the initial phase of this investigation, the design and operational parameters for UASB reactor R1 (T=35 °C) when fed with 1500 mgSO₄²⁻/L were established. Concentration profiles through the sludge bed were conducted to gain insight into the process behaviour inside the reactor bed. Solids profile tests were used to determine the sludge age of the system at the minimum HRT (13.5-14.0h) where effluent quality was met (i.e. effluent sulphate < 250 mgSO₄²⁻/L and effluent VFA < 100 mgHAc/L). Following the initial phase of R1, the influent sulphate was increased to 1800 mgSO₄²⁻/L to investigate the effect of high sulphate concentration on the system. Consequently, the PSS COD was also increased based on PSS COD/sulphate ratio of 1.44 mgCOD/mgSO₄²⁻. A slightly higher ratio than 1.25 (used in R1 at 1500 mgSO₄²⁻/L) was used in this case in order to ensure that the system is not organic carbon limited. In the BioSURE[®] process design for AMD remediation, the treated effluent is recycled to blend with the raw AMD. This high alkalinity (sulphide and carbonate alkalinities) recycle stream neutralises the pH, precipitates the heavy metals and almost halves the inflow sulphate concentration of the raw AMD. Therefore, in a situation where an effluent sulphate of 200 mgSO₄²⁻/L is recycled on a 1:1 effluent to incoming raw AMD flow rates, this can potentially treat a raw AMD of sulphate concentration of 3400 mgSO₄²⁻/L. It is well documented that the biological treatment of sulphate-rich wastewater involves the potential effect of sulphide inhibition on bacterial growth and activity. Operating R1 with a feed sulphate of 1800 mgSO₄²⁻/L gave insight in the extent of sulphide inhibition on the biological processes in the system. In the next section, the operation and performance of R1 at 1800 mgSO₄²⁻/L are described and analysed.

6.3.1 R1 EXPERIMENTAL PROGRAMME (fed 1800 mgSO₄²⁻/L)

R1 was fed 1800 mgSO₄²⁻/L on Day 281 until the end of the whole experimental programme for this study on Day 530. It took around 20 days for the reactor to reach the first steady state at which the effluent sulphate concentration (< 250 mgSO₄²⁻/L) was met at a HRT of 19h. Thereafter, the HRT was gradually decreased to establish the lowest optimal HRT. It was found that at a HRT below 18h, the effluent sulphate concentration could not be maintained below 250 mgSO₄²⁻/L either due to sludge bed expansion and/or insufficient

sulphate contact time with the biomass. Accordingly, the lowest HRT was set at 18.0-18.5h with a BRT of 16.4-16.8h based on a sludge bed volume of 7.1L (the upward velocity, $V_{up} = 0.093-0.096$ m/h) and the sludge age determined from bed profile test was 21d (see Appendix 6B for R1 concentration-depth profile tests). The various experimental stages and tests conducted on R1 (fed $1800 \text{ mgSO}_4^{2-}/\text{L}$) including batch tests during the experimental period from Day 281 to 530 are listed in Table 6.8.

Table 6.8: Summary of operational conditions for UASB reactor R1 fed $1800 \text{ mgSO}_4^{2-}/\text{L}$ during the 250 days of operation at 35°C .

Day of operation	Reactor status/activities performed	HRT (h)	BRT (h)
281-530	Feed PSS COD to sulphate ratio 1.44 and sludge bed volume 7.1L		
302-330	R1 Steady state (SS) 1	19.0	17.1
365-530	R1 SS 2	18.0-18.5	16.4-16.8
295, 297, 302, 304, 306, 326, 332, 389 and 478	Bed profile tests (both on solubles and solids)	18.0-19.0	16.4-17.1
362-478	H ₂ S gas capture and measurement*	18.0-19.0	16.4-17.1
400-473	Stopped NaHCO ₃ dosage to feed	18.0-18.5	16.4-16.8
475-530	Stopped sludge recycle line	18.0-18.5	16.4-16.8
362-478	COD, S and N mass balances calculated	18.0-18.5	16.4-16.8
295, 297, 304, 306, 332 and 389	Determination of sludge age	18.0-19.0	16.4-17.1
525-530	Batch tests on R1 sludge samples		
Sludge on days 460 and 461	Measurement of settling rates of solid particles in sludge		
* H ₂ S gas measurement done only when conducting sulphur mass balance exercise over the system and was done only once since % mass H ₂ S gas was negligible			

6.3.2 R1 PERFORMANCE (FED $1800 \text{ mgSO}_4^{2-}/\text{L}$) AT THE LOWEST OPTIMAL HRT OF 18.0-18.5H.

Table 6.9 summarises the concentrations of the effluent parameters of interest when R1 (fed $1800 \text{ mgSO}_4^{2-}/\text{L}$) was operated at its lowest optimal HRT of 18.0-18.5h (Day 420-473). For a more comparative assessment, the influent values are also listed with a particular interest in pH.

The low effluent organic COD, sulphate and VFA concentrations with the concomitant production of high alkalinity underline the very good performance of R1 even at a relatively low HRT and no alkalinity dosage to the feed. The system achieved ~ 92% sulphate removal efficiency implying that inhibition of undissociated hydrogen sulphide on the growth and activity of SRB was negligible. This is important in calibrating the value of hydrogen sulphide inhibition constant (K_I) to be used in the validation of the kinetic BSR model (UCTADM1-BSR) to be developed in the next Chapter. In addition, the reactor/effluent pH was very close to the pK value of the H_2S/HS^- system indicating that in the absence of gaseous CO_2 , the system pH is governed by the sulphide system. More importantly, the aqueous hydrogen sulphide recovery matches closely the theoretical sulphide from the sulphate reduced. COD, S and N mass balances were all very good averaging $96.5 (\pm 0.8)$, $95.8 (\pm 2.9)$ and $103.3 (\pm 8.3)$ respectively.

Table 6.9: Effluent characteristics of UASB reactor R1 at the lowest optimal HRT of 18.0-18.5h with **no alkalinity dosage** to feed.

Steady state (SS) period 2 (Day 420-473)	Influent		Effluent	
Parameter	Average value	SSD	Average value	SSD
Total organic COD (mgCOD/L)	2584	42	460	81
Organic soluble COD (mgCOD/L)	337	6	229	18
Particulate COD (mgCOD/L)	2249	54	231	72
VFA (or SCFA) (mgCOD/L)	158	10	72	36
Sulphate ($mgSO_4^{2-}/L$)	1800	-	146	51
Sum of $H_2CO_3^*$ alkalinity and Alk H_2S (mg/L as $CaCO_3$)	22	3	1855	73
$H_2CO_3^*$ alkalinity (mg/L as $CaCO_3$)	22	3	1358	6
TKN (mgN/L)	76	7	55	7
FSA (mgN/L)	9	6	46	12
pH	5.99	0.05	7.08	0.02
Aqueous sulphide (mgS/L)	0	-	502	25
H_2S gas (mgS/L)	0	-	1.1	0.4
Elemental sulphur in sludge (mgS/L sludge)	0	-	21	2
Theoretical aqueous sulphide from sulphate reduced (mgS/L)	0.0	-	539	23

With the highly encouraging performance of R1 from Day 280-400 when fed $1800 \text{ mgSO}_4^{2-}/\text{L}$ (Appendix 6B), NaHCO_3 dosage to the feed was ceased on Day 400. Figure 6.5 shows the variations in feed and effluent pH with time. Particularly striking is the unaffected effluent pH when alkalinity dosage to the feed was discontinued implying that the system is pH self-regulatory at $\text{pH} > 7.0$ even at the high sulphate feed concentration of $1800 \text{ mgSO}_4^{2-}/\text{L}$.

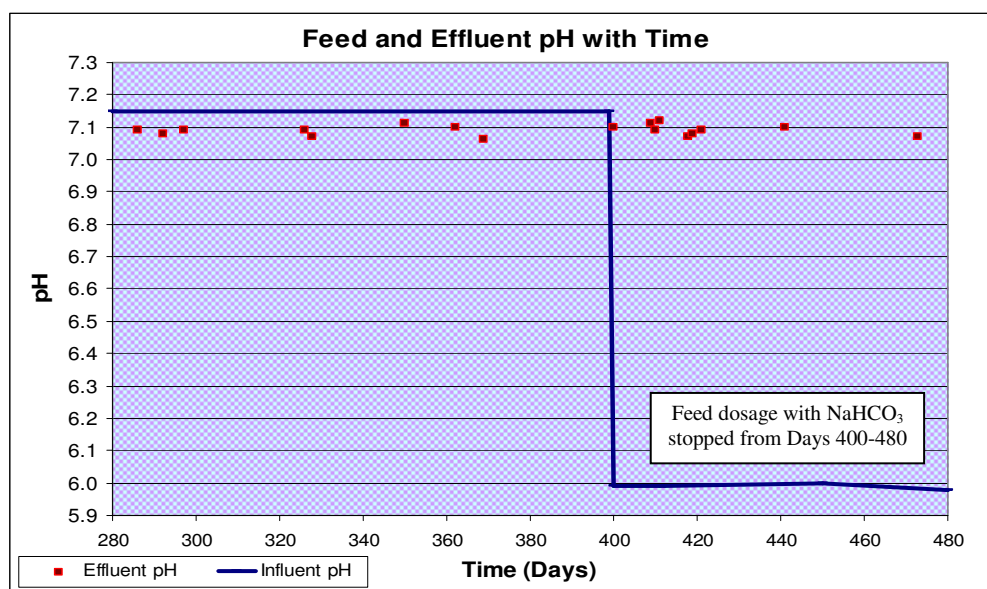


Figure 6.5: UASB reactor R1 influent and effluent pH-time profile with PSS as substrate augmented with $1800 \text{ mgSO}_4^{2-}/\text{L}$ sulphate.

6.3.3 COMPARISON OF OPERATING PARAMETERS AND PERFORMANCE WITH PREVIOUS STUDIES

A summary of the performance of the UASB reactors operated in this study along with the performance of various one-stage bioreactors for the treatment of sulphate-rich waters is listed in Table 6.10. Overall the use of PSS as carbon source (substrate) in UASB systems matches closely (and sometimes exceeds) the performance of systems fed with soluble substrates (namely ethanol, lactate and molasses). This further emphasises the benefits of PSS as a low cost-effective energy source for BSR.

Table 6.10: Performance of various bioreactors used for the biological reduction of sulphate-rich wastewaters.

Reactor and process type	Substrate(s) utilised	Temperature (°C)	Hydraulic retention time, HRT (h)	pH		Sulphate			Reference(s)
				Feed	Effluent	Feed (mgSO ₄ ²⁻ /L)	Volumetric reduction rate (g/m ³ /d)	Removal (%)	
UASB	PSS	35	13.5	7.2	7.2	1500	2792	90	Chapter 4
UASB	PSS	35	18.0	6.0	7.1	1800	2423	92	Chapter 6
UASB	PSS	20	20.5	5.9	7.2	1500	1737	93	Chapter 6
UASB	Lactate	35	16.0	3.0	7.7	1650	1860	75	Kaksonen <i>et al.</i> (2004)
UASB with a calm zone above sludge	Ethanol, nutrients (+ flocculant)	30	4.0	3.2	7.0	1480	7010	79	Barnes <i>et al.</i> (1991a)
FBR	Lactate	35	16.0	2.5	7.8	2290	2220	65	Kaksonen <i>et al.</i> (2004)
FBR	Ethanol	35	16.0	2.5	7.7	1920	2320	81	Kaksonen <i>et al.</i> (2004)
FBR	Ethanol	35	6.5	3.0	7.9	2080	4290	57	Kaksonen <i>et al.</i> (2004)
SBR	Molasses	31	15.0	-	7.0	2500	2712	68	Maree and Strydom (1987)
PBR	Molasses	31	20.0	-	7.0	900	525	58	Maree and Strydom (1987)

UASB = Upflow anaerobic sludge bed; FBR = Fluidised bed reactor; SBR = Sludge bed reactor; PBR = Packed bed reactor

6.4 BATCH TESTS

With UASB reactor R1 nearing the end of its experimental programme (Days 525-530), batch tests were conducted with the objectives of:

- (i) studying the macro-behaviour of the system, namely the effects of not recycling sludge from the top to the bottom of the reactor sludge bed. In fact, this will further give insight and understanding on the characteristics of the sludge at different bed heights, explicitly at the top and the bottom parts of the bed.
- (ii) gaining a preliminary quantitative assessment of the hydrolysis rate in the system in relation to the hydrolysis rate values reported in previous studies with PSS.

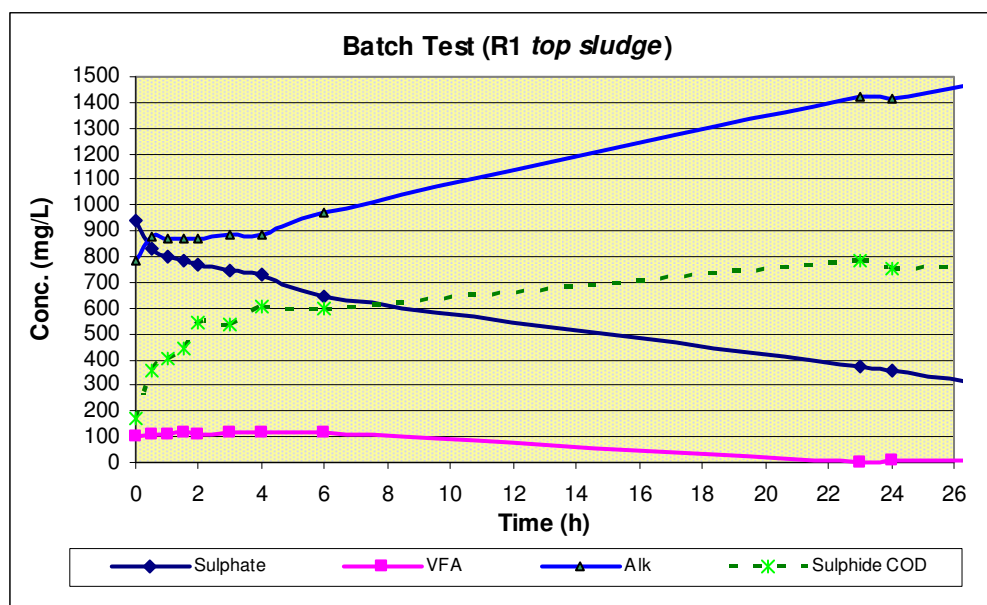
These tests were carried out when R1 was deliberately operated without the sludge recycle line for a period of more than 2 sludge ages (~50 days) from Day 475-530. This allowed the sludge particles (and consequently the biomass) to settle at different locations along the reactor bed height and develop a biomass concentration gradient as would be the case in a non-recycle sludge UASB system. Sludge samples were taken from UASB reactor R1 and put in a 3.0L batch reactor. PSS and sulphate were added as substrates.

A 0.5L reactor sludge volume was used for each batch test. 1.45L of the desired feed PSS and sulphate concentrations were then added before making up the total batch volume to 2.45L with 0.5L distilled water. The pH was adjusted to 7.1-7.2 with NaHCO_3 and the initial total alkalinity (sum of H_2CO_3^* alk. and Alk H_2S) was 775 mg/L as CaCO_3 . This alkalinity calculated on a mass balance basis includes the alkalinity in the sludge volume used and the H_2CO_3^* alk. from the NaHCO_3 dosage. A 50ml sample of the final content of the reactor was taken for analysis (to obtain the initial conditions of the parameters of interest) at time 0h. The batch reactor was heated to 35 °C to emulate the same conditions as in the lab-scale UASB reactor R1.

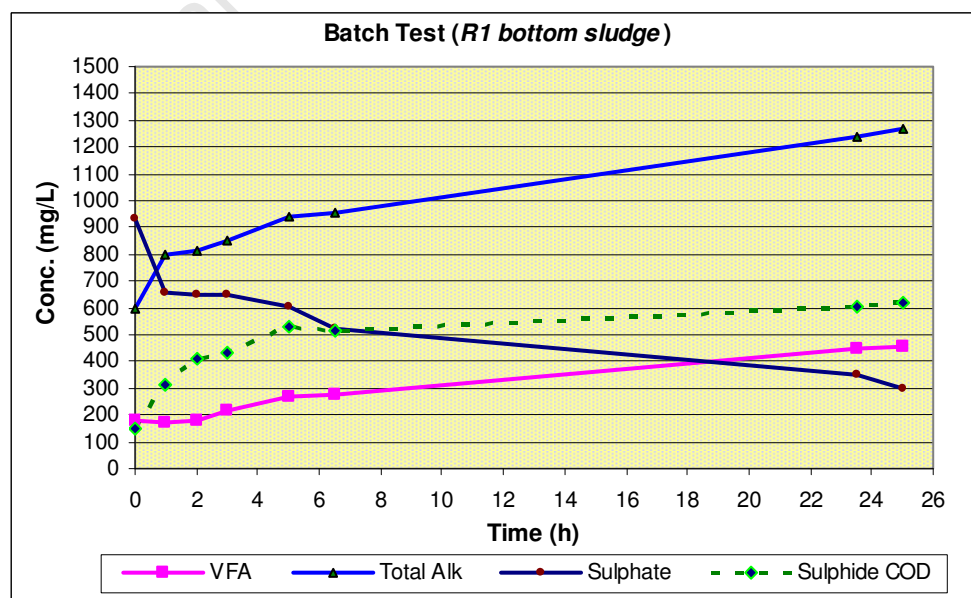
Batch tests were done on 3 types of sludge, namely:

- (i) top sludge (from top of the UASB reactor bed)
- (ii) bottom sludge (0-10 cm of the UASB reactor bed height)
- (iii) mixed sludge (prepared by draining and mixing all the sludge from the UASB reactor and taking the desired sample volume).

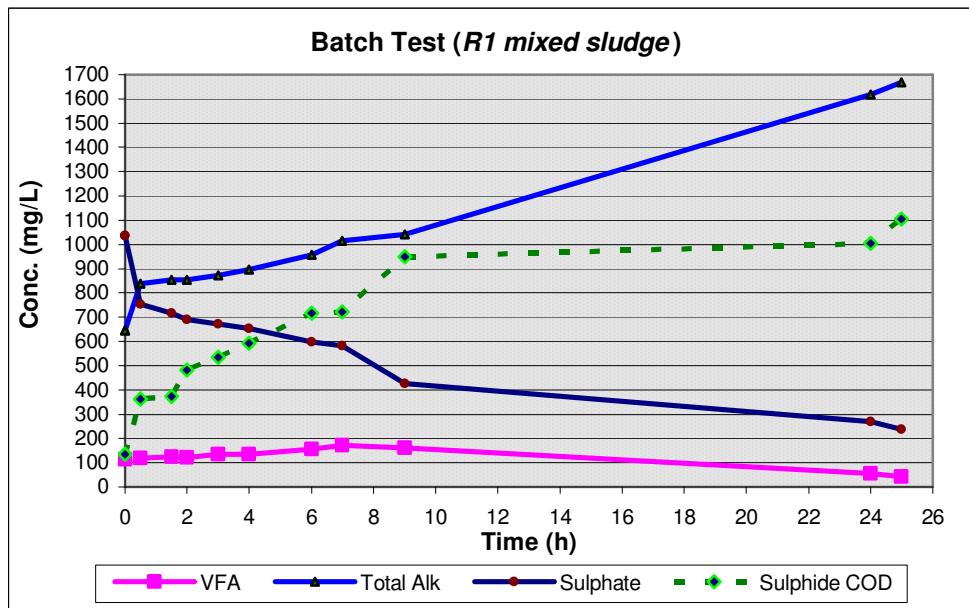
The initial sulphate, VFA, alkalinity and soluble COD constituents were measured at time 0h, that is, just after mixing the sulphidogenic sludge with the PSS and sulphate. Thereafter the parameters of interest (total COD, total soluble COD, organic soluble COD, sulphide COD, sulphate, pH, H_2CO_3^* alk., Alk H_2S and Total Alk) were measured at pre-set time intervals by each time taking a sludge sample from the batch reactor. The appearance and disappearance of VFA, the reduction of sulphate, production of alkalinity, the soluble COD constituents and pH were monitored over time. The time intervals were selected depending on the anticipated bioprocess rates. The concentration change of the total alkalinity, VFA, sulphate and sulphide with time is plotted for all 3 types of sludge (Figure 6.6a, b and c).



(a)



(b)



(c)

Figure 6.6: Batch test concentration-time profiles for R1 top, bottom and mixed sludges with PSS and sulphate as feed.

Each sludge type shows some unique features. As expected, the top sludge indicates that hydrolysis is the rate limiting step supported by the very low VFA concentration. In contrast, bottom sludge shows a VFA accumulation with time coupled with decreases in sulphate reduction rate and alkalinity production rate. The sulphate reduction rates with the top, bottom and mixed sludges were 1184, 595 and 929 $\text{mgSO}_4^{2-}/\text{L/d}$ respectively. These differences were to be expected because of the biomass concentration gradient along the sludge bed axis. The slower rate obtained with the bottom sludge confirms that without sludge recycle sulphidogenesis is the rate limiting step at the bottom of the sludge bed. The concentration of SRB at the bottom of the sludge bed (with no sludge recycling from the top) is very small compared with the acidogen concentration. This explains the high VFA production by acidogens in comparison with the low sulphate reduction by SRB. As far as the mixed sludge batch test results are concerned, the trend is very much similar to that of the top sludge implying that both sulphidogenic and acidogenic processes are occurring at a relatively fast rate resulting in a high sulphate reduction and the concomitant generation and utilisation of VFA.

Following the above observations, it was decided to use glacial acetic acid (CH_3COOH) as carbon source and electron donor instead of PSS in the batch tests, thereby by-passing the hydrolysis rate limiting process. As with PSS feed, the stoichiometric concentration of VFA

(~480 mgHAc/L) required to reduce a sulphate concentration of 750 mgSO₄²⁻/L was added to the batch reactor (V=2.45L). These were the concentrations to be expected at time 0h. The measured VFA and sulphate concentrations were 420 mgHAc/L and 734 mgSO₄²⁻/L respectively, close enough to the expected values. The batch reactor initial pH (at Time=0h) was adjusted to ~7.5 with NaHCO₃ and the initial H₂CO₃* alk. was ~3950 mg/L as CaCO₃. The VFA, total Alk, sulphate and sulphide COD concentration results are shown in Figure 6.7.

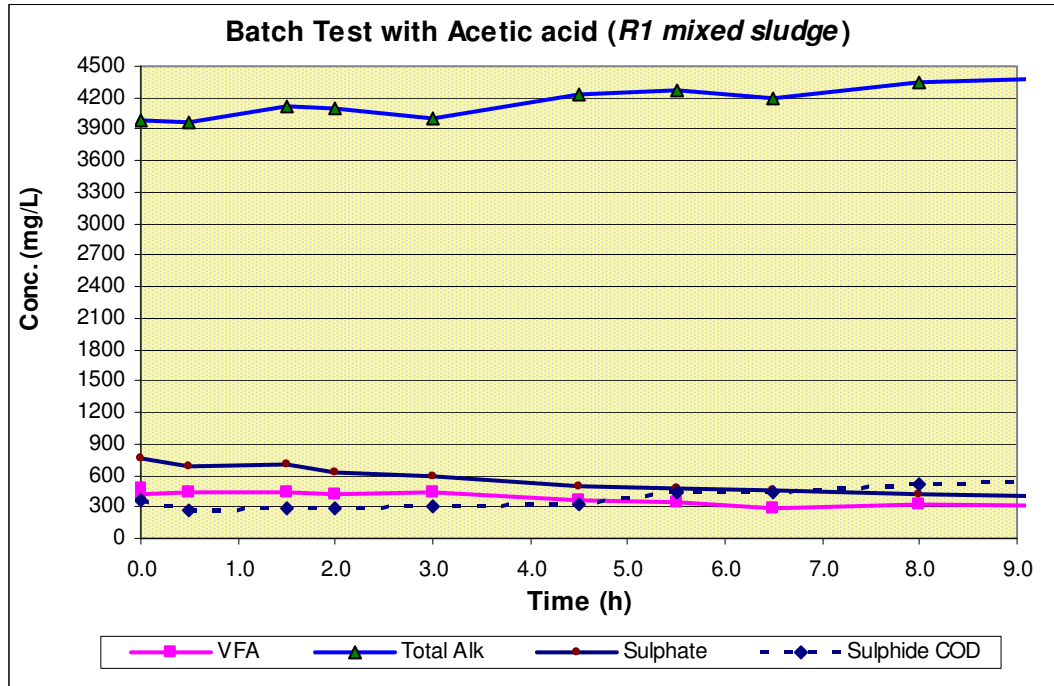


Figure 6.7: Batch test concentration-time profiles for R1 mixed sludge with acetic acid and sulphate as feed.

All four parameters plotted in Figure 6.7 follow the same trend as with PSS (Figure 6.6c), though the slope is less steep with acetic acid (HAc). The sulphate reduction rates calculated on the 2 acetic acid batch tests were 649.4 and 851.2 mgSO₄²⁻/L/d. These rates are unexpectedly slower than those obtained with PSS. A possible explanation could be that in the hydrolysis of PSS to VFA and H₂, 2 SRB population groups (acetotrophic (Z_{AS}) and hydrogenotrophic (Z_{HS}) SRB) mediate the sulphate reduction rate. Batch tests using HAc involves only the Z_{AS} population which uses ~2/3 of the energy available in PSS (i.e the HAc). The population of Z_{AS} is lower compared with the combined SRB population (Z_{AS} and Z_{HS}) mediating BSR with PSS. Another explanation could be that the Z_{AS} population is not accustomed to high HAc loads because in the UASB BSR systems, the production of HAc from PSS hydrolysis is rate limiting. This feature is also observed with other

organisms such as the Ammonia Nitrifiers which when batch fed with ammonia result in higher maximum specific growth rate compared with that in continuously fed systems (Still *et al.*, 1996). In this research, the UASB BSR reactors were continuously fed so the SRB populations present were not accustomed to high concentrations of HAc and H₂ (slowly produced from PSS hydrolysis).

From the batch tests results, a preliminary quantitative investigation on the hydrolysis rate of PSS in the system was carried out based on the rate of sulphate reduced. For this purpose, the saturation (Contois) maximum specific hydrolysis kinetic rate equation (Eq6.1) was applied.

$$r_h \text{ [gCOD/(L.d)]} = \frac{K_M (S_{bp} / Z_{AD})}{[K_S + (S_{bp} / Z_{AD})]} Z_{AD} \quad (6.1)$$

where:

K_M = the saturation maximum specific hydrolysis rate constant = 5.27 gCODorganics/(gCODbiomass.d) at 35 °C.

K_S = the half saturation coefficient = 7.98 (gCODorganics/gCODbiomass) at 35 °C.

S_{bp} = concentration of biodegradable organics (mgCOD/L)

Z_{AD} = concentration of acidogens (mgCODbiomass/L)

Relating r_h with the rate of sulphate reduction yields the following:

$$r_h = \frac{\Delta COD}{dt} = \frac{1}{0.67} * \frac{\Delta SO_4^{2-}}{dt} = \frac{K_M (S_{bp} / Z_{AD})}{[K_S + (S_{bp} / Z_{AD})]} Z_{AD} \quad (6.2)$$

$$K_M = \frac{1}{0.67} * \frac{\Delta SO_4^{2-}}{dt} * \frac{(K_S + S_{bp} / Z_{AD})}{Z_{AD} (S_{bp} / Z_{AD})} \quad (6.3)$$

A Z_{AD} concentration of 2140 mgCODbiomass/L, obtained from the prediction of the kinetic simulation model (UCTADM1-BSR) developed in Chapter 7, was accepted. The calculated values of K_M from the various batch tests conducted on R1 sludge are listed in Table 6.11.

Table 6.11: Calculated K_M values from batch test results on R1 sludge.

Sludge location	Time (d)	$SO_{4rem}/time$ (mg SO_4 /L/d)	$COD_{rem}/time$ (mgCOD/L/d)	Z_{AD} (mgCOD/L)	Infl. S_{bp} (mgCOD/L)	K_M (gCODorg/g CODbio/d)
Top	0.25	1184	793	2140	1004	6.678
Bottom	0.98	595	399	2140	913	3.673
Mixed	0.35	929	622	2140	1053	5.006

The K_M value ranges from 3.67 to 6.68 gCOD organics/(gCOD biomass.d) which are close to the value of 5.27 gCOD organics/(gCOD biomass.d) reported by Sötemann *et al.* (2005a) on Izzet *et al.* (1992) methanogenic PSS data. Since this is a preliminary assessment of the hydrolysis rate of the UASB system operated, further investigation is required to comprehensively determine the most appropriate and consistent value for the hydrolysis kinetic constant K_M .

From the batch test results using acetic acid as substrate, the value of the maximum specific acetic acid utilisation rate (μ_{max} or K_m) can be estimated from the following Monod kinetic rate equation.

$$r_h = \frac{\mu_{max} S_b}{K_s + S_b} Z_{AS} \quad (6.4)$$

where K_s = half saturation coefficient (mgCOD/L)
 S_b = concentration of acetic acid (mgCOD/L)
 Z_{AS} = concentration of acetotrophic sulphidogens (mgCODbiomass/L)

Since K_s value is very small in relation to S_b , the term $\frac{S_b}{K_s + S_b} \sim 1$.

Therefore,

$$r_h = \mu_{max} Z_{AS}$$

Similar to Z_{AD} , the concentration of Z_{AS} (867 mgCODbiomass/L) was taken from UCTADM1-BSR simulated value and used in the above equation to calculate the μ_{max} value with r_h being the change in acetic acid concentration with time, obtained from the stoichiometric conversion of sulphate reduced with time. μ_{max} value was 0.502-0.658 (mgCOD/mgCODbiomass)/d which corresponds closely to the μ_{max} value of 0.612 from Kalyuzhnyi *et al.* (1998) used in the UCTADM1-BSR model developed in the next Chapter. Again further investigation is required on this aspect which is beyond the scope of this research work.

6.5 MEASUREMENT OF THE SETTLING RATE OF SOLIDS FRACTIONS IN THE SLUDGE PARTICLE OF THE UASB REACTORS

6.5.1 INTRODUCTION

The application of the upflow anaerobic sludge bed (UASB) reactor in high rate anaerobic wastewater treatment systems (mainly from industrial sources) have gained considerable attention over the past three decades. The success of the UASB reactor depends largely on the settling properties and stability of the sludge bed which consists of active biomass. A stable sludge bed provides a long sludge retention time and a high sludge mass, and these are key features to ensure process stability and high substrate loading rates, thereby optimising the UASB system.

From the operation of the 2 lab-scale UASB reactors for biological sulphate reduction (BSR) using primary sewage sludge (PSS) as energy source, the hydraulic retention time (HRT) was decreased (by increasing the feed flow rate) to determine the minimum HRT (giving the smallest reactor volume) at which the effluent meets the effluent quality criteria (i.e. $\text{SO}_4^{2-} < 250 \text{ mgSO}_4/\text{L}$, $\text{VFA} < 100 \text{ mgHAc}/\text{L}$ and low particulate COD). For instance, reactor R1 had a minimum HRT of 13.5h when fed $1500 \text{ mgSO}_4/\text{L}$. A further reduction in HRT ($< 13\text{h}$) resulted in unstable sludge bed conditions and progressive system failure, indicated by poor effluent quality, i.e. high effluent VFA, SO_4^{2-} and particulate COD due to bed solids loss with the effluent. This prompted an investigation to measure the settling rate of the various solids fractions in the PSS bed to determine if bed expansion or sludge settleability is the capacity limiting process of the system. Accordingly, a sludge settleability device, called a settleometer, was built and operated to test the 2 UASB sulphidogenic sludges (R1 and R2 sludges) in it at different flow through rates. This settleometer was designed based on the method developed by Moosbrugger (1994).

6.5.2 MATERIALS AND METHODS

A series of 4 vertical transparent PVC columns of outer diameters (OD) 63, 75, 90 and 110 mm and internal diameters (ID) 57, 67.8, 86.4, 105.6 mm respectively, was interconnected by plastic tubing (20 mm inner diameter). Each PVC column was 500mm long and was

capped on both top and bottom ends with solid PVC lids with an outlet in the centre to attach the interconnecting plastic tubing. Stainless steel clamps were fitted to the bottom tubing for drainage. A collection vessel (20L) was connected to the last column (the largest pipe, i.e. OD 110mm) which was then fitted to a peristaltic pump (Watson Marlow Model 220). The pump was in turn connected to the first PVC column (the smallest pipe, i.e. OD 63mm) to close the water circuit. The 3rd and 4th columns were the ones representing the UASB column since their ID were close to the UASB reactor ID (93mm). A schematic flow diagram and a photograph of the settling device are shown below in Figures 6.8 and 6.9.

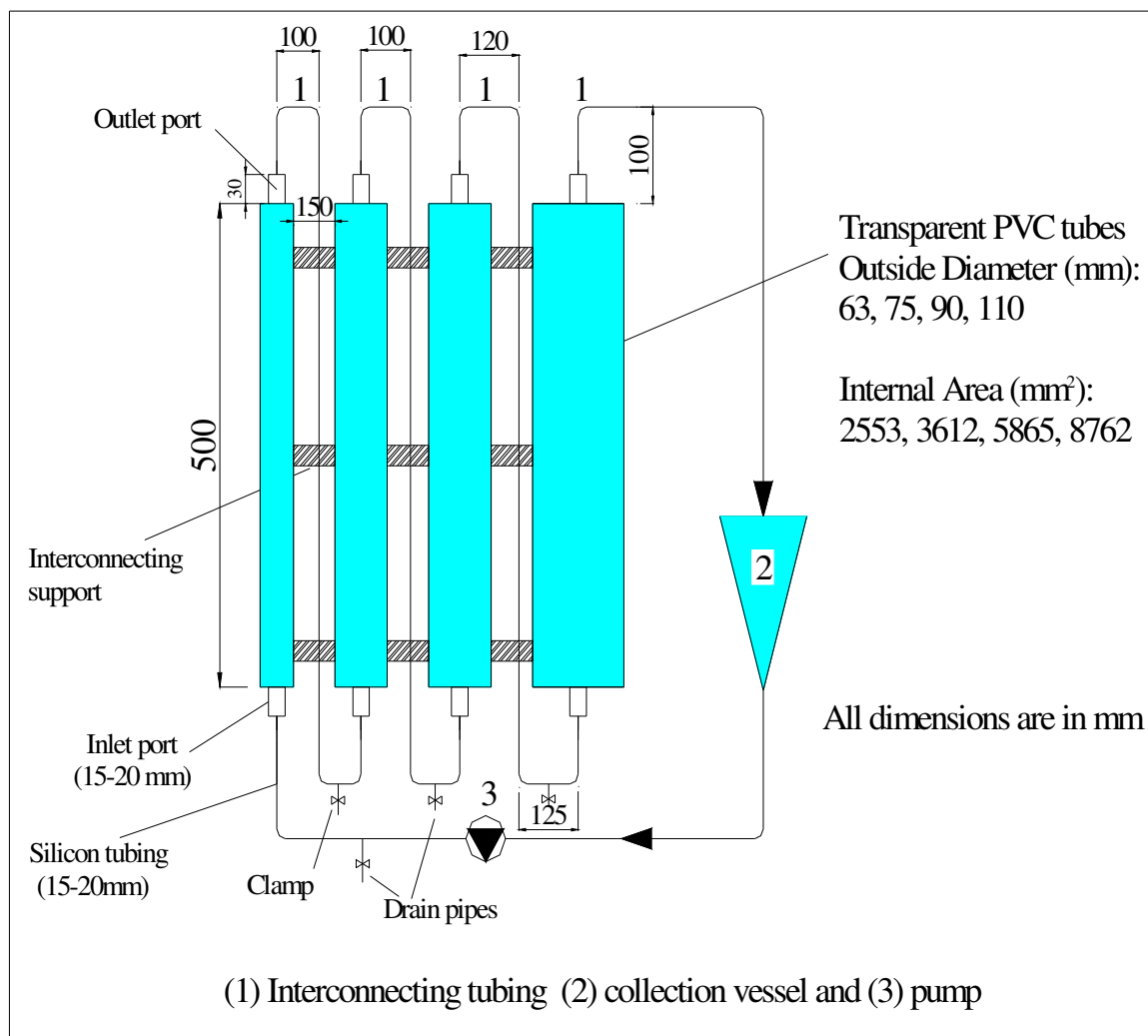


Figure 6.8: Schematic diagram of the settleometer.

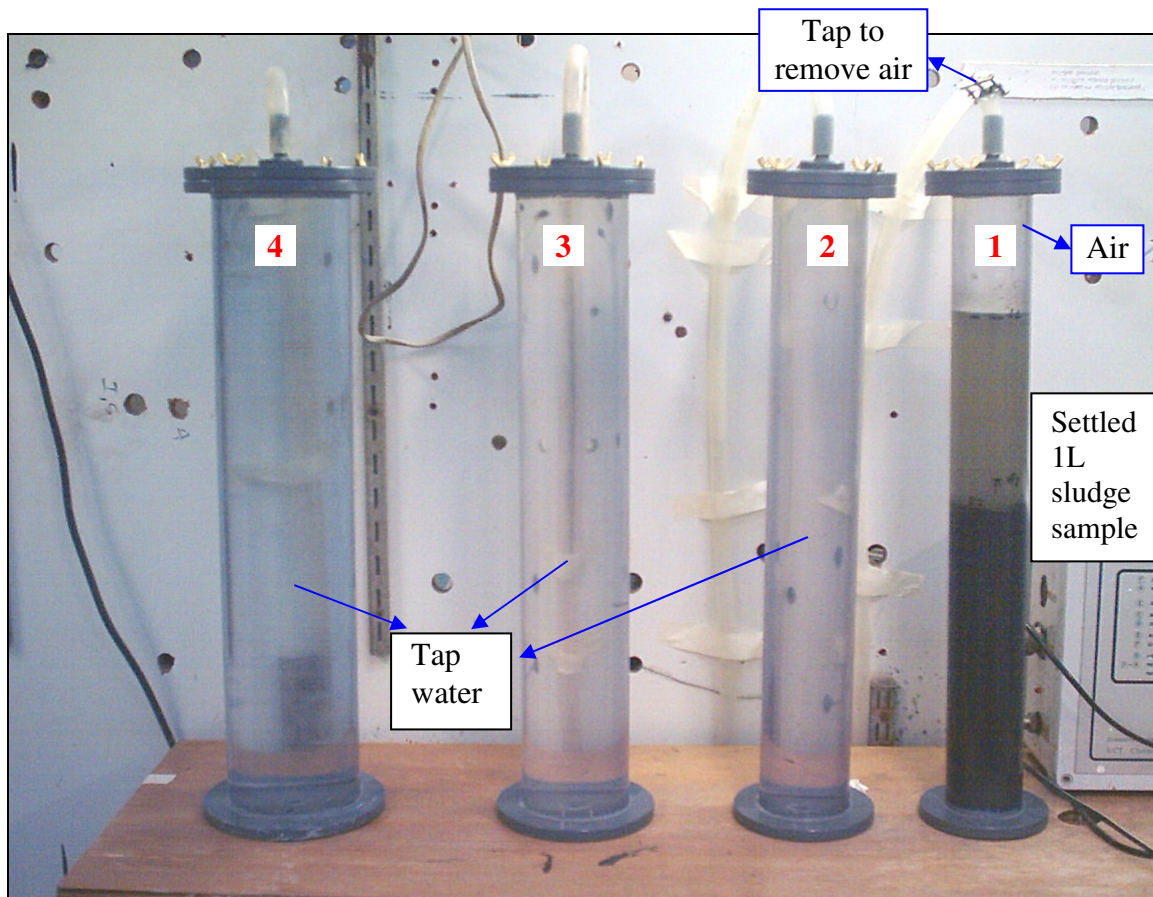


Figure 6.9: Picture of the settleometer with the 1L lab-scale UASB sludge after 5h settling time before the application of flow rate.

The principle of the settleometer is relatively simple: A pre-determined volume (say 1L) of sludge is taken from a UASB reactor and placed in the first column (smallest one). A constant flow rate (Q) was applied in an upflow mode similar to the UASB reactor (Figure 6.9). Since the upflow velocity (V_{up}) decreased incrementally in the subsequent columns (from smallest to largest), the sludge sample is fractionated according to particle size and density. The percentage sludge mass retained in each tube was determined by dividing the mass of sludge retained in each column by the mass of sludge of the original sample. The sludge concentration in each column was further determined by dividing the mass of sludge retained in each tube by the initial sludge sample volume. Both the percentage sludge masses and the sludge concentrations were plotted against the respective tube upflow velocities, resulting in a graph describing the settling profile of the sludge at different hydraulic upflow velocities.

6.5.3 OPERATING AND TESTING PROCEDURES

At the start of the experiment, it is necessary to fill the system with tap water and expel all air bubbles from the system - air bubbles, if not removed, impacts negatively on the results of the experiment because they attach to sludge particles and create turbulence inside the columns when the pump is running. First, all four columns are filled to the top with tap water before closing with the top lids (Figure 6.9). Then, tap water is added to the collection vessel and pumped through the system to fill all the interconnected tubing, expel the air bubbles and allow a smooth flow of water through the whole device. When all the air bubbles have been expelled from the system, the first column (smallest one) is emptied while the other three are left full. Then a UASB sludge sample is prepared in such a way that it represents the sludge bed and added carefully (to minimise sludge break-up) through a funnel to column one, ensuring there are no air bubbles in the system before closing the column with its lid.

Both UASB reactor R1 and R2 sludges were tested separately in the settleometer. The entire sludge bed was drained from either R1 or R2 and gently stirred before a 1L sample was collected. A further 50ml sample was taken to measure its Total Settleable Solids (TSS) concentration. The first column, which has volume of 1.276L, was filled with the 1L mixed sludge sample. Before starting the pump, the sludge was allowed to settle for a few hours (usually 5h were enough) so as to imitate the same condition as the UASB reactor bed. The collection vessel was filled with slightly more than the remaining volume ($> 0.276\text{L}$) to prevent the pump from drawing air into the system. The peristaltic pump, pre-calibrated to the desired flow rate, was then switched on. First, the first tube was allowed to fill up until all the air in the empty space (0.276L) above the 1L sludge sample was expelled via the air vent (tap). Thereafter, the tap was closed so that the water flowed into the second tube and the whole settleometer. The flow rate was set so that more than 90% of the sludge mass was retained within the columns. Two different pre-determined pumping flow rates (7.08 and 10.17 L/h respectively) were applied such that the upflow velocities (V_{up}) in the last column (largest pipe) were 0.81 and 1.16 m/h respectively. These upflow velocities were 6.4 and 9.1 times respectively higher than the maximum operated upflow velocity (0.127 m/h) at which the R1 sludge bed (when fed $1500 \text{ mgSO}_4/\text{L}$) was allowed to expand so as not to cause the system to fail. The same V_{up} values (i.e. 0.81 and 1.16 m/h) were applied to R2 sludge sample and were in this instance 9.5 and 13.7 times respectively higher than the maximum

upflow velocity (0.085 m/h) at which R2 sludge bed was allowed to expand to prevent system failure - R2 was operated at a longer HRT than R1 (20.5h against 13.5h) for the same sulphate concentration (1500 mgSO₄/L) because of slower biological activity at the lower (20 °C) temperature.

The settleometer was run for 15h to ensure steady state was established between the settling velocities of the sludge particles and the upflow velocities in the columns (Figure 6.10). The pump was then switched off. The sludge fractions present in each column were then allowed to settle for 1-2h and the bed height measured before drawing all the mixed liquor from the bottom of each column via its respective drain pipe. The sludge fraction collected from each column was then mixed thoroughly and a representative sample of 50ml was taken and analysed for its TSS concentration. The TSS was measured using the same analytical procedure described in Standard Methods (1985, 2540(D) for TSS).



Figure 6.10: Picture of the settleometer showing R1 sludge fraction retained in each column at steady state ($Q = 10.17$ L/h and $V_{up} = 1.16$ m/h in the largest column).

The above procedures were repeated for two different pump flow rates and the mass of TSS (volume x concentration) in each column and in the collection vessel calculated. This mass was compared with the initial sludge mass added to column 1 to check the accuracy of the results. Better than 96% mass balances was achieved in the tests. The results for R1 and R2 sludges are listed in Tables 6.12 and 6.13 respectively.

6.5.4 RESULTS AND DISCUSSION

6.5.4.1 R1 sludge sample

Since the 1L sludge sample was placed into the smallest column, it was expected that with an increase in the applied flow rate (Q) (hence high upflow velocity, V_{up}), solids will be transferred to the other three columns and the collection vessel as a result of sludge wash out. The sludge settleability profile depicted in Figure 6.11 shows the % mass of TSS retained in each column versus upflow velocity (m/h) of that column at the 2 different flow rates applied to the system.

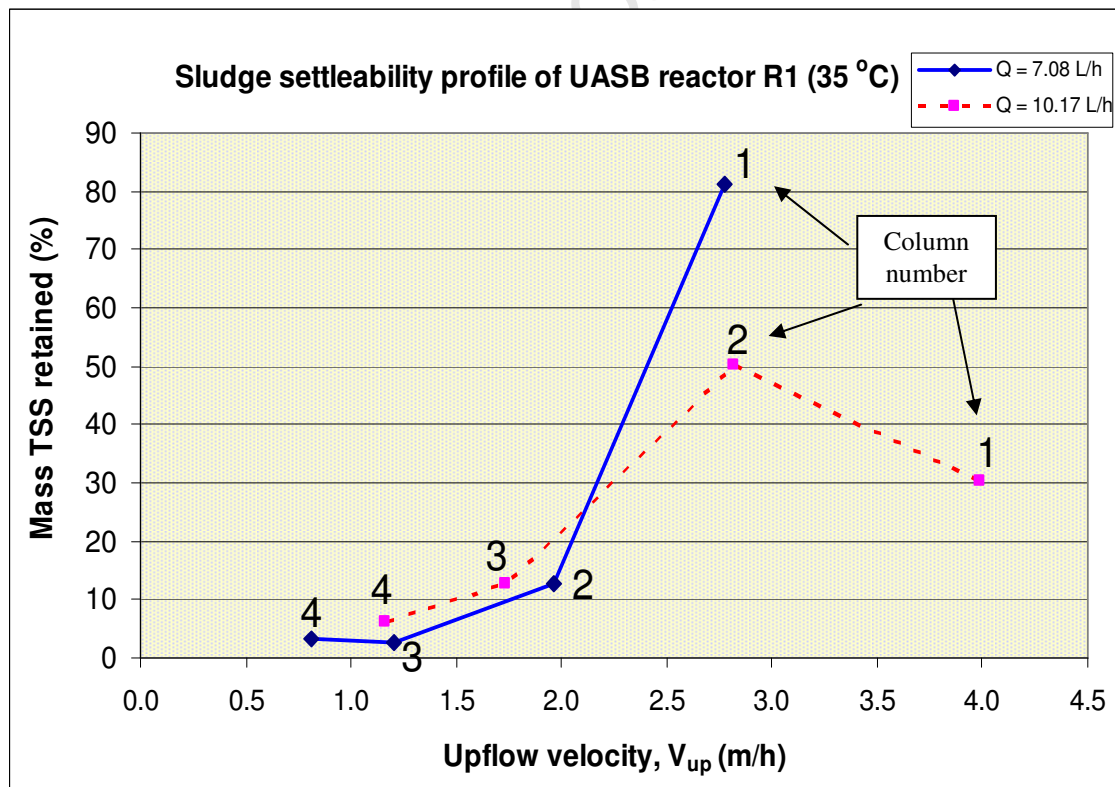


Figure 6.11: R1 sludge settleability profile with respect to the two applied flow rates.

At 7.08 L/h, ~ 81% of the total sludge mass settled fast enough at a V_{up} as high as 2.8 m/h to be retained in column 1. At $Q = 10.17$ L/h, only 30.5% was retained in column 1 due to the higher V_{up} in the first column (smallest one, thus highest V_{up}) and sludge transfer to the subsequent columns increased with 50% being retained in column 2. From the 10.17 L/h profile curve, it is observed that ~ 80.5% (30.5% in column 1 plus 50% in column 2) of the total sludge mass settled fast enough at a V_{up} of 2.8 m/h to be retained in columns 1 and 2, which is the same as that retained in column 1 (81%) at 7.08 L/h, giving confidence in the results obtained.

From the above, a cumulative sludge mass retained versus settling velocity gives greater insight into the settling behaviour of the sludge (Table 6.12 and Figure 6.12).

Table 6.12: Summary of results obtained with sludge from UASB reactor R1.

R1 sludge					
Applied flow rate, $Q = 7.08$ L/h	Pipe dia. (mm)	V_{up} (m/h)	Mass TSS (g)	% by Mass	% Retained (Cumulative)
	63	2.77	28.71	81.06	81.06
	75	1.96	4.55	12.85	93.91
	90	1.21	0.96	2.70	96.61
	110	0.81	1.12	3.17	99.78
	Collection vessel		0.08	0.22	
Total mass recovered over the whole system (g)			35.41		
Initial mass of the 1L sludge sample (g)			36.71		
Mass TSS recovered (%)			96.5		
Applied flow rate, $Q = 10.17$ L/h	Pipe dia. (mm)	V_{up} (m/h)	Mass TSS (g)	% by Mass	% Retained (Cumulative)
	63	3.98	9.83	30.37	30.37
	75	2.82	16.20	50.06	80.43
	90	1.73	4.08	12.60	93.03
	110	1.16	2.00	6.17	99.20
	Collection vessel		0.26	0.80	
Total mass recovered over the whole system (g)			32.36		
Initial mass of the 1L sludge sample (g)			31.94		
Mass TSS recovered (%)			101.3		

It can be seen from Table 6.12 (or Figure 6.12 below) that more than 99% of the total sludge mass was retained in the settleometer at a $V_{up} = 1.16$ m/h implying that almost all the solids in the sludge had a very good settleability. Since the maximum V_{up} at which R1 was operated was 0.127 m/h, it can be deduced that the cause for sludge bed instability when the reactor was operated at a $V_{up} > 0.127$ m/h was not due to poor sludge settleability.

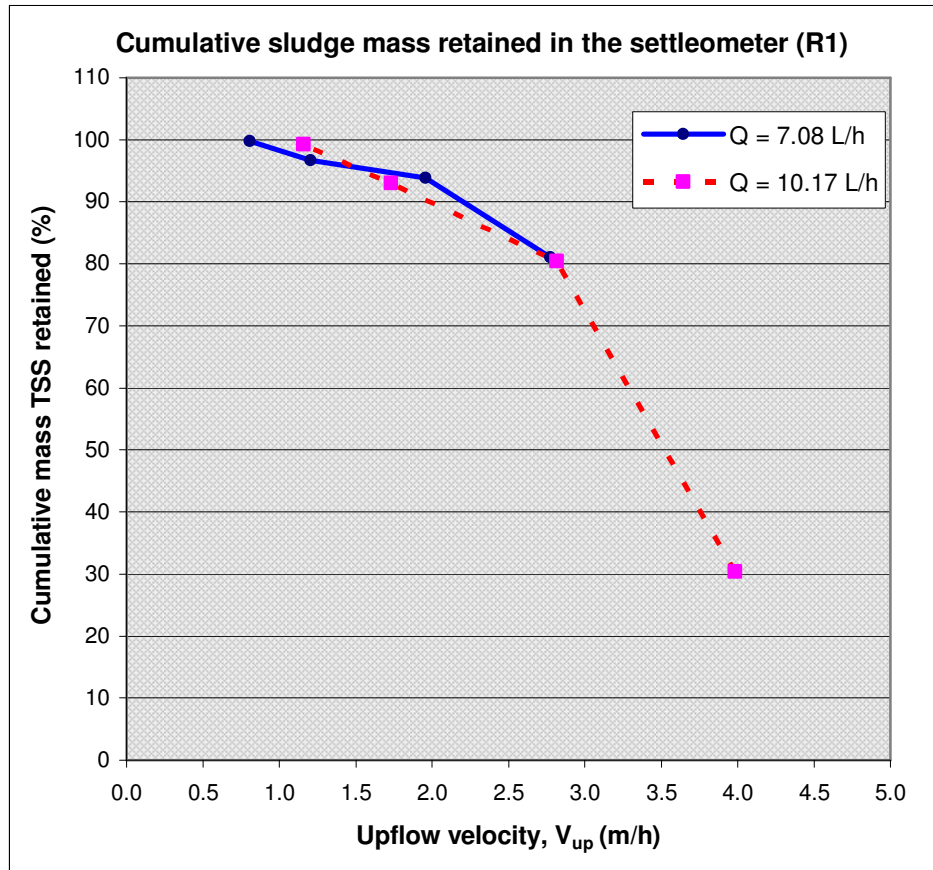


Figure 6.12: Percentage cumulative sludge mass retained with settling velocity (sludge from UASB reactor R1).

6.5.4.2 R2 sludge sample

Similarly, the sludge settleability profile for R2 sludge with respect to V_{up} was plotted (Figure 6.13). At $Q = 7.08$ L/h, only 22 % of the total sludge mass settled fast enough at a V_{up} as high as 2.8 m/h while at $Q = 10.17$ L/h an even smaller fraction (~9.7%) of the total sludge mass could settle at a V_{up} as high as 4.0 m/h. From the 10.17 L/h profile, it is observed that 31% of the total sludge mass settled fast enough at a V_{up} of 2.8 m/h to be

retained in column 1 (10%) and column 2 (21%) which is 10% more than retained in column 1 at the same V_{up} of 2.8 m/h at 7.08 L/h.

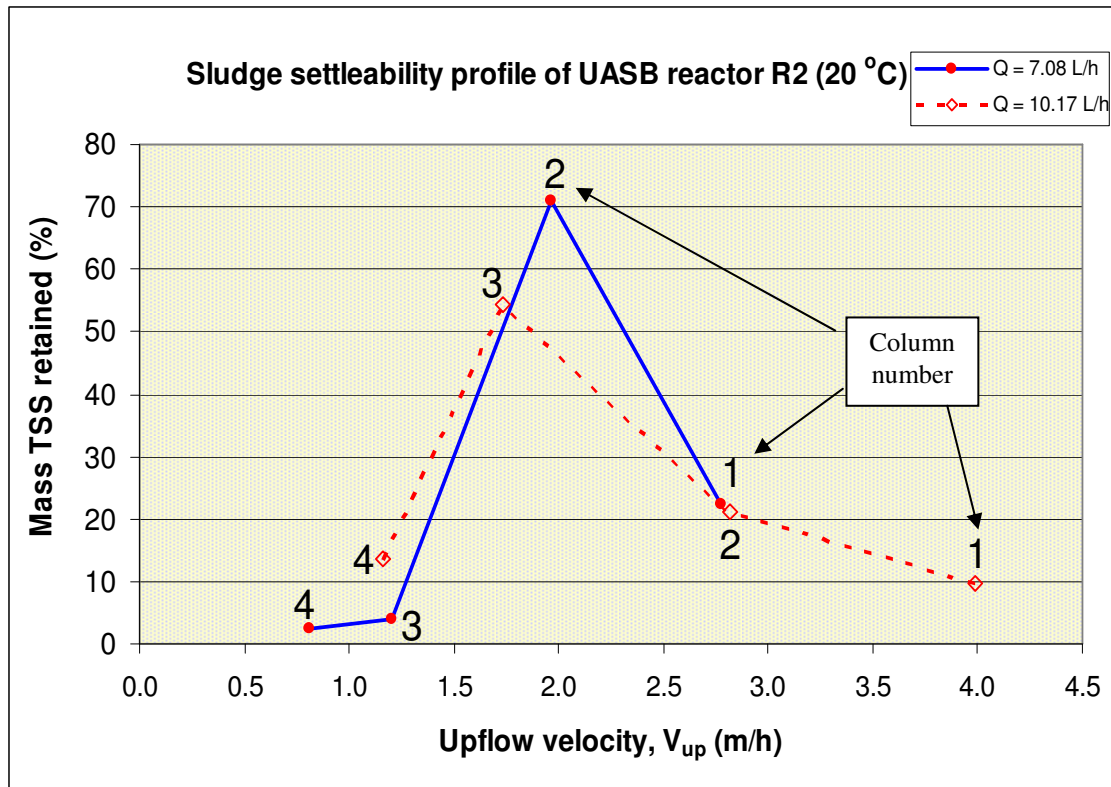
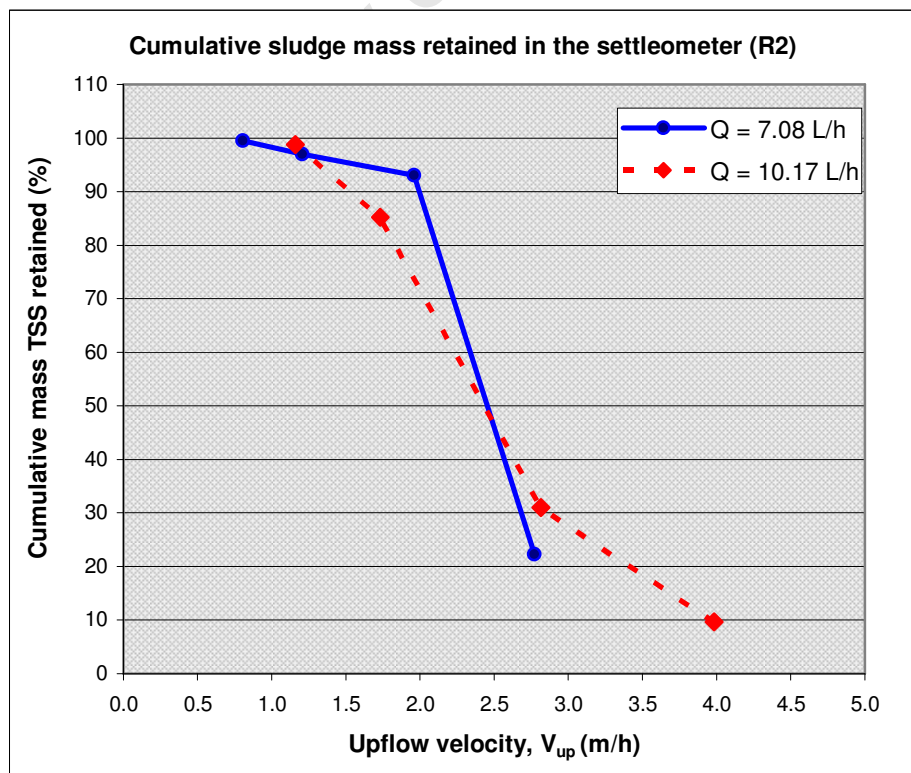


Figure 6.13: R2 sludge settleability profile with respect to the two applied flow rates.

From the Table or (plot) of the cumulative sludge mass retained in the settleometer (Table 6.13 or Figure 6.14 below), it is found that ~ 99% of the total sludge mass was also retained in the settleometer at a $V_{up} = 1.16$ m/h indicating that R2 sludge had good settling properties similar to the R1 sludge. The maximum V_{up} at which R2 was operated was 0.085 m/h, which is far less than 1.16 m/h. Accordingly, it was concluded also for the R2 sludge that sludge settleability was not the cause of unstable conditions and therefore not the capacity limiting process when both UASB reactors were operated at their respective minimum hydraulic retention times.

Table 6.13: Summary of results obtained with sludge from UASB reactor R2.

R 2 sludge					
Applied flow rate, Q = 7.08 L/h	Pipe dia. (mm)	V_{up} (m/h)	Mass TSS (g)	% by Mass	% Retained (Cumulative)
	63	2.77	7.30	22.23	22.23
	75	1.96	23.26	70.82	93.04
	90	1.21	1.27	3.87	96.92
	110	0.81	0.82	2.51	99.43
	Collection vessel		0.19	0.57	
Total mass recovered over the system (g)			32.85		
Initial mass of the 1L sludge sample (g)			33.41		
Mass TSS recovered (%)			98.3		
Applied flow rate, Q = 10.17 L/h	Pipe dia. (mm)	V_{up} (m/h)	Mass TSS (g)	% by Mass	% Retained (Cumulative)
	63	3.98	3.11	9.73	9.73
	75	2.82	6.78	21.24	30.96
	90	1.73	17.34	54.30	85.26
	110	1.16	4.29	13.44	98.71
	Collection vessel		0.41	1.29	
Total mass recovered over the system (g)			31.94		
Initial mass of the 1L sludge sample (g)			31.45		
Mass TSS recovered (%)			101.6		

**Figure 6.14:** Percentage cumulative sludge mass retained with settling velocity (sludge from UASB reactor R2).

6.5.5 BED EXPANSION RATIO

The HRT was reduced by increasing the feed flow rate: the higher than the feed (and recycle) flow rate the greater the sludge bed expansion. When the reactors were operated at a HRT lower than the minimum value (i.e. 13.5h and 18h for R1 when fed 1500 and 1800 mgSO₄/L respectively, and 20.5h for R2), the reactor sludge bed expanded to higher the pre-established bed height (corresponding to 6.7L for R1 fed 1500 mgSO₄/L, 7.1L for R1 fed 1800 mgSO₄/L and 7.4L for R2). Since the bed volume was maintained at a constant volume, the mass of sludge removed from the system correspondingly increased, causing a reduced sludge bed mass (and biomass sludge age) and concomitantly a reduced biomass available to mediate the BSR reactions. As a result, sulphate and VFA concentrations accumulated in the reactor until such time the system failed, indicated by a bed separation, sludge losses in the effluent and eventually deterioration in the effluent TSS and organic COD concentrations.

Based on the above, the effect of bed expansion on the UASB reactor performance was further investigated and is described below.

The bed expansion ratio is defined as the bed volume (or height) at zero flow through it over the bed volume (or height) when a flow rate is applied. A typical example of sludge bed expansion when R1 was fed 1500 mgSO₄/L at a HRT of 13.5h is illustrated below (Figure 6.15). The bed expansion ratios were 1.8 for R1 when fed both 1500 and 1800 mgSO₄/L and 2.0 for R2.

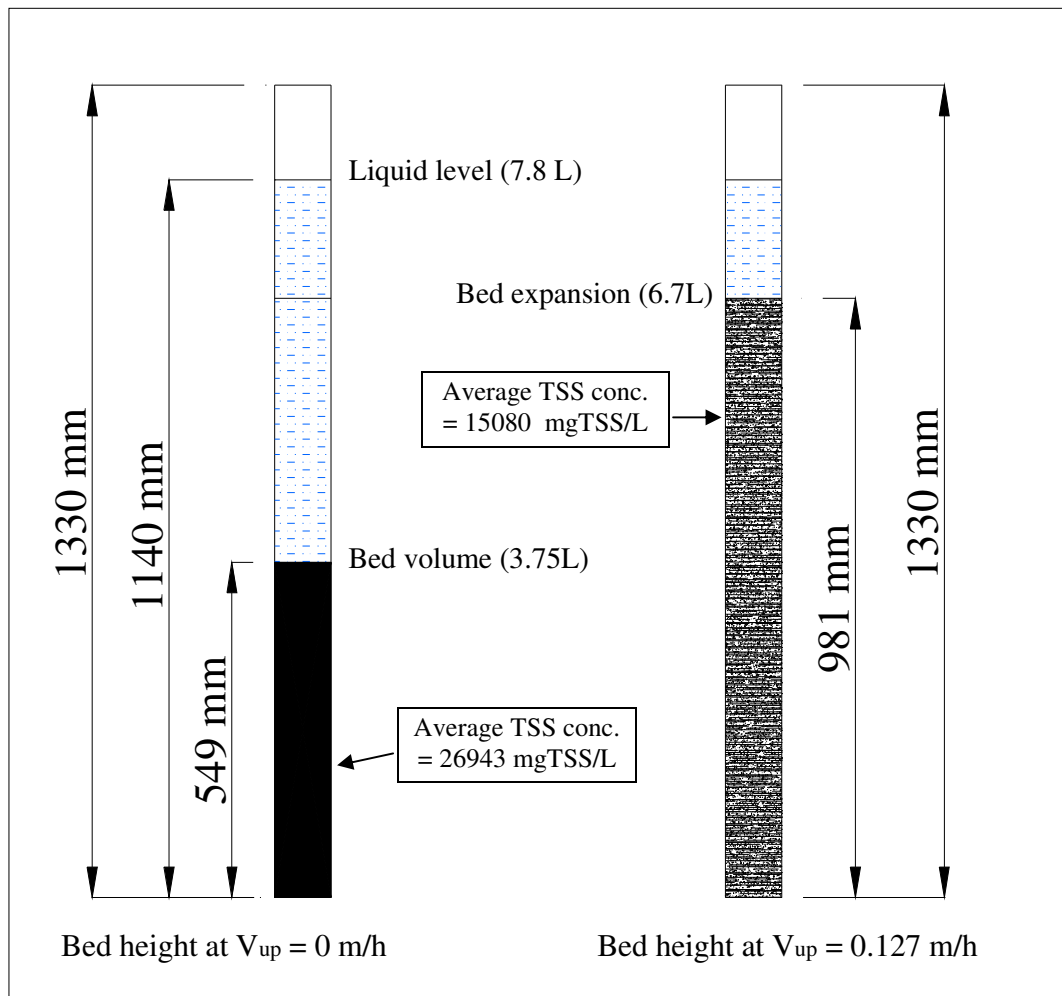


Figure 6.15: Illustration of R1 sludge bed expansion when operated with 1500 mgSO₄²⁻/L at a HRT of 13.5h.

$$\begin{aligned}
 \text{Bed expansion ratio} &= \frac{\text{Bed volume at } V_{up} = 0.127 \text{ m/h}}{\text{Bed volume at } V_{up} = 0 \text{ m/h}} \\
 &= \frac{6.7 \text{ L}}{3.75 \text{ L}} = 1.8
 \end{aligned}$$

With the aim of increasing the substrate loading rates (with a fixed feed PSS and sulphate concentrations), the feed flow rate was increased to its maximum value in order to optimise the system and establish the operational parameters. This increase in feed flow rate (therefore increase in V_{up}) caused the sludge bed to expand and since the reactor was operated with a recycle line at half the feed flow rate, this bed expansion was further increased. The relationship between bed expansion and upflow velocity was not measured

because this may be different for different primary sludges. The objective of this study was to determine whether it is sludge settleability or bed expansion that causes system failure – it clearly is the latter. A brief design procedure for BSR UASB systems using PSS as energy source is given in Section 6.6 below.

6.6 DESIGN AND OPERATING PARAMETERS

Taking into account the results and discussion of the various studies and tests conducted on both UASB reactors as reported in Chapter 4 and this Chapter, a summary of the different design and operating parameters to be considered for BSR UASB systems is listed in Table 6.14. Among them, 2 parameters are critical and govern the system performance and economics. The first one is the sludge age (R_s) which controls the sludge aspect ratio (bed height/diameter) and hence the reactor bed volume. This in turn will govern the biomass concentration for the optimum rate of the BSR processes. The second parameter is the hydraulic retention time (HRT) which controls the reactor volume comprising the bed and liquid parts. A short HRT is always desirable as it reduces the reactor investment cost. However, an excessive reduction in the HRT leads to disproportionate bed expansion and sludge wash out. Therefore, the optimum HRT should be established so as to- (i) allow sufficient contact time of the substrate with the sludge (biomass) and (ii) optimise the V_{up} which governs the bed expansion ratio which in turn dictates the sludge age if a constant bed height is required. The rest of the parameters will then be a consequence of how the R_s and HRT are optimised. As far as temperature is concerned, it was found that the feed PSS COD/SO₄²⁻ ratio has to be increased to 1.75 to cater for the incomplete hydrolysis (and consequently low VFA generation) due to the slow hydrolysis rate at a temperature of 20 °C. If a high % of biodegradable organics utilisation is required at the lower temperature, the sludge age of the UASB reactor needs to be increased by increasing the reactor area so that a higher sludge mass is retained in the reactor in relation to that wasted to maintain the bed height, i.e. in effect reducing the volumetric COD (and SO₄²⁻) loading rate.

Table 6.14: Design and operating parameters for BSR UASB system using PSS as carbon and energy source.

Design and operating parameters	Unit	Average values		
		R1 (35 °C)	R1 (35 °C)	R2 (20 °C)
Feed PSS COD based on f_{PSSup} of 0.36	mgCOD/L	1880	2584	2596
Feed sulphate	mgSO ₄ ²⁻ /L	1500	1800	1500
Influent pH	-	7.20 ^a	5.99	5.94
Influent flow rate, Q_i	L/d	13.6	10.4	9.2
Organic loading rate, OLR	g/m ³ /d	3806	3785	3224
Sulphate loading rate, SLR	g/m ³ /d	3037	2637	1863
Reactor liquid volume	L	7.8	7.8	7.8
Reactor bed volume	L	6.7	7.1	7.4
Sludge recycle ratio (w.r.t. Q_i)	-	0.5	0.5	0.5
Upflow velocity, V_{up}	m/h	0.125	0.096	0.085
Hydraulic retention time, HRT	h	13.8	18.0	20.4
Sludge aspect ratio (bed height/diameter)	-	10.5	11.2	11.6
Bed hydraulic retention time, BRT	h	11.9	16.4	19.3
Sludge retention time (Sludge age), R_s	d	18	21	24
Waste flow rate, Q_w	L/d	0.37	0.34	0.31
Expected sulphate removal rate	g/m ³ /d	2735	2423	1737
Expected sulphate reduction	%	90.1	91.9	93.3

a: Alkalinity dosage to feed but concluded not necessary since the system is pH self-regulatory.

6.7 CLOSURE TO CHAPTER 6

The successful operation of the UASB reactor R2 (fed 1500 mgSO₄²⁻/L) at 20 °C is of significant importance in this research as full-scale systems are not likely to be heated. Besides the 2 critical parameters (sludge age, R_s and hydraulic retention time, HRT), the other important parameter to consider in the operation of BSR system using PSS is the PSS COD/SO₄²⁻ ratio where at low temperature the PSS hydrolysis process rate is slowed down. By decreasing the temperature from 35 to 20 °C, less than 70% of the PSS is hydrolysed thereby generating inadequate VFA for BSR. Increasing the PSS COD/SO₄²⁻ from 1.25 (used in R1) to 1.75 (used in R2) increased the concentration of PSS hydrolysed to meet the VFA demand for sulphate reduction. Increasing the sludge age of the system by reducing

the volumetric COD and sulphate load would increase the % biodegradable PSS hydrolysed and reduced the PSS COD/SO₄²⁻ to 1.25.

In addition, UASB R1 was operated at a higher influent sulphate concentration (1800 mgSO₄²⁻/L) to study the inhibition effect by undissociated hydrogen sulphide generated from the reduction of this sulphate concentration level. It was found that high sulphate reduction (~ 92%) was achieved even at the relative low HRT of 18.5h. This observation is important in calibrating the value of the acetotrophic SRB inhibition constant (K_I) used in the kinetic simulation model (UCTADM1-BSR) developed in next Chapter.

Further, batch tests were conducted on R1 sludge to qualitatively and quantitatively assess the process rates taking place in the UASB reactor. The batch results confirmed the need to recycle sludge from the top to the bottom of the bed because sulphidogenesis is the rate limiting step at the bottom part of the sludge bed. Also, from the preliminary quantitative assessment, the value of the saturation maximum specific hydrolysis rate constant (K_M) was found to be 3.67-6.68 gCODorganics/(gCODbiomass.d). In addition, batch tests results using acetic acid as substrates yielded values of 0.502-0.658 (mgCOD/mgCODbiomass)/d for the maximum specific growth rate (μ_{max}).

In this Chapter, one of the main objectives of this research study which is to understand whether the settleability of the UASB reactor sludges (from R1 and R2) or the bed expansion is the capacity limiting process of the system was investigated. A settling device (settleometer) was designed following the principle outlined by Moosbrugger (1994) to test the sludge settleability of the two sludges. From the results above, it was deduced that both sludges settled well and 99% of the total sludge settled faster than 1.16 m/h. This upflow velocity was 9.1 and 13.7 times higher than the maximum operating upflow velocity (V_{up}) of R1 (0.127 m/h) and R2 (0.085 m/h). Tests were also done to demonstrate the effect of upflow velocity on the sludge bed expansion. It was found that R1 (35 °C) sludge had a bed expansion ratio of 1.8 at V_{up} of 0.127 m/h while R2 (20 °C) sludge had a bed expansion ratio of 2.0 at V_{up} 0.085 m/h. Since the bed volume was maintained at a constant volume, the mass of sludge removed from the system correspondingly increased with upflow velocity, causing a reduced sludge bed mass, sludge age and concomitantly a reduced biomass available to mediate the hydrolysis and BSR reactions. It was thus concluded that the cause and explanation for the system failure at an upflow velocity higher than the

optimum one was due to the sludge bed expansion rather than the sludge settleability problems. In addition, from the sludge settleability and bed expansion tests, it was deduced that R1 sludge (35°C) has a better settleability and expanded less compared to R2 sludge (20°C) at the same upflow velocity. Hence, this explains the shorter minimum HRT obtained in R1.

Lastly, based on the experimental data from this detailed investigation of BSR using PSS in a UASB reactor, the design and operating parameters to be considered have been established for the 3 systems operated.

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APPENDIX 6A

(UASB reactor R2 fed 1500 mgSO₄²⁻/L at 20 °C)

1. UASB R2 PERFORMANCE AT LOWEST OPTIMAL HRT

The performance of UASB reactor R2 when dosed with NaHCO₃ and operated at the lowest optimal HRT of 20.4-21.0h is summarised in Table 6A. With the excellent sulphate removal efficiency (93%) with the concomitant increase in alkalinity, it was decided to discontinue the dosage of NaHCO₃ to the feed to assess whether the system is pH self-regulatory. The statistical plots of the parameters of interest are shown below.

Table 6A: Summary of the UASB R2 effluent characteristics with an influent PSS COD to sulphate ratio of 1.75 at 20 °C with alkalinity dosage and HRT of 20.4-21.0h

Sulphate	mgSO ₄ ²⁻ /L	101	21
Total organic COD	mgCOD/L	582	88
Organic soluble COD	mgCOD/L	203	6
Particulate COD	mgCOD/L	379	10
VFA (or SCFA)	mgHAc/L	72	56
Sum of H ₂ CO ₃ * alkalinity and Alk H ₂ S	mg/L as CaCO ₃	1881	93
H ₂ CO ₃ * alkalinity	mg/L as CaCO ₃	1590	65
pH	-	7.21	0.02
TKN	mgN/L	63	9.0
FSA	mgN/L	37	12.0
Aqueous sulphide	mgS/L	266 ^a	11
H ₂ S gas	mgS/L	1.5	1
Theoretical aqueous sulphide from sulphate reduced (mgS/L)	mgS/L	467	8

a: H₂S measurement problem

2. Average effluent sulphate

For the steady state period Day 175-258 at the lowest HRT of 20.4-21.0h, the effluent sulphate concentration is plotted statistically in Figure 6A. The mean effluent sulphate concentration was 101 mgSO₄²⁻/L (SSD=22).

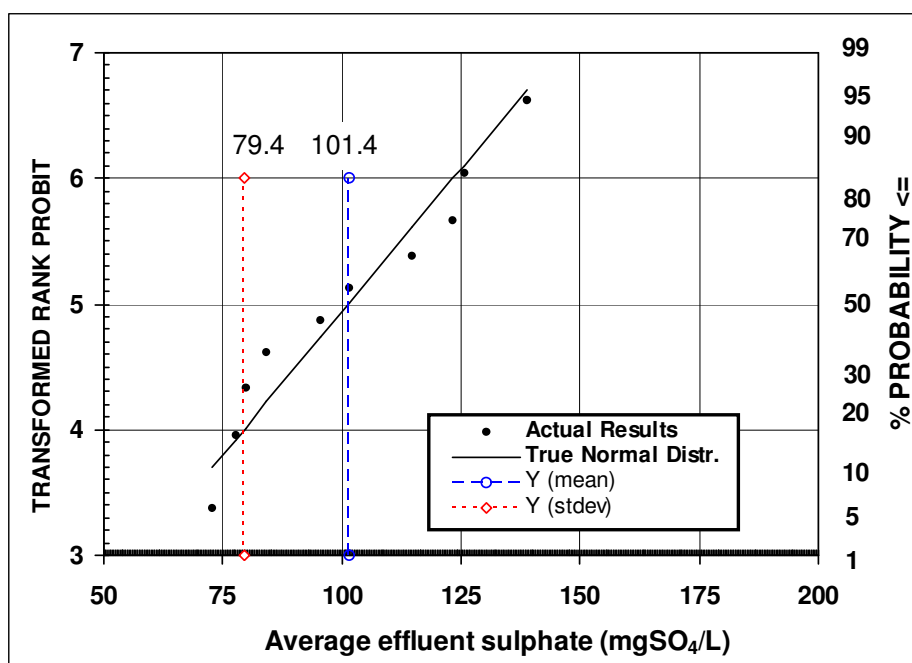


Figure 6A: Statistical plot for effluent sulphate concentration in UASB reactor R2 (fed 1500 mgSO₄²⁻/L) from Days 175-258 with HRT 20.4-21.0h.

3. Average effluent VFA

The statistical plot for UASB R2 effluent VFA concentration is plotted in Figure 6B.

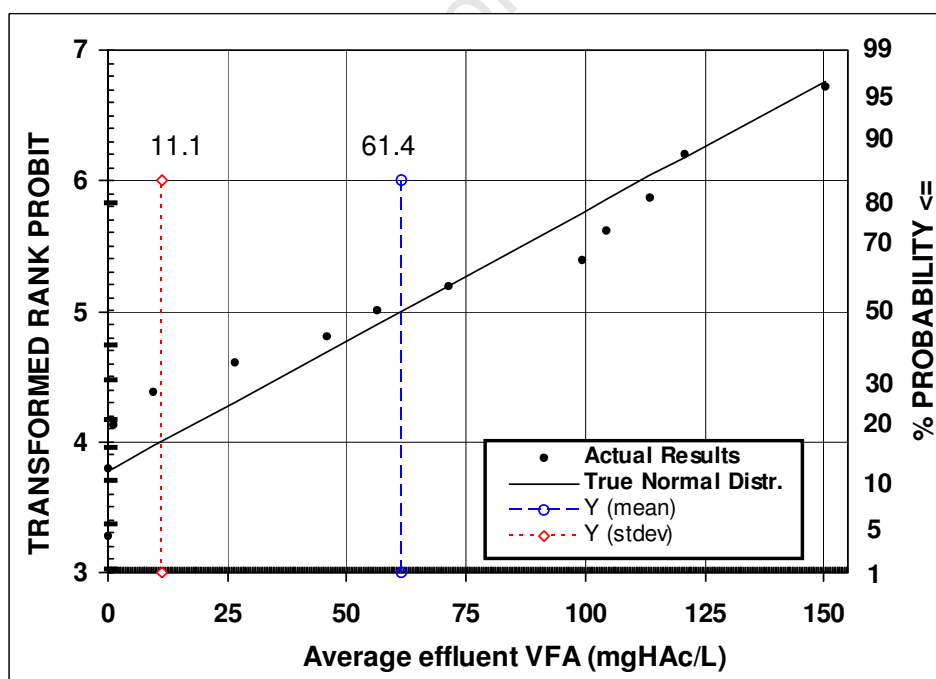


Figure 6B: Statistical plot for effluent VFA concentration in UASB reactor R2 (fed 1500 mgSO₄²⁻/L) from Days 194-258 with HRT 20.4-21.0h.

4. Average effluent pH

Figure 6C depicts the statistical plot for the effluent pH. The mean pH value of 7.21 (SSD = 0.01) confirms the statement that the reactor pH is governed by the sulphide ($\text{H}_2\text{S}/\text{HS}^-$) system which has a pK value of 7.014 (at 20 °C).

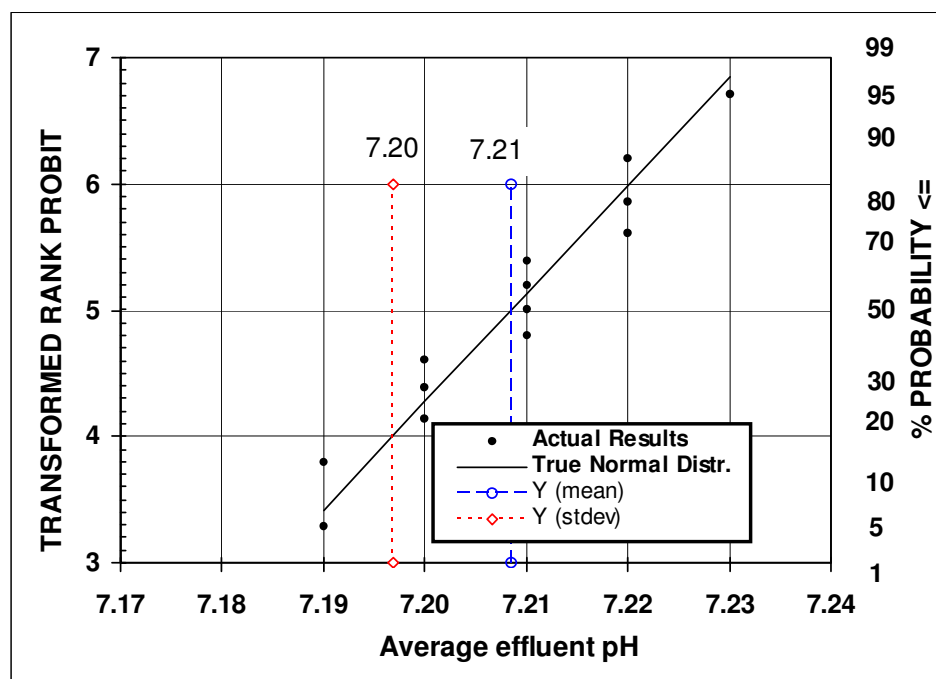


Figure 6C: Statistical plot for effluent pH in UASB reactor R2 (fed $1500 \text{ mgSO}_4^{2-}/\text{L}$) from Days 194-258 with HRT 20.4-21.0h.

APPENDIX 6B

(UASB reactor R1 fed 1800 mgSO₄²⁻/L)

1. DEVELOPMENT OF UASB R1 (FED 1800 mgSO₄²⁻/L) PERFORMANCE WITH TIME

1.1 Effluent sulphate

The variation in UASB R1 (fed 1800 mgSO₄²⁻/L) effluent sulphate concentration is illustrated in Figure 6D. Except for a few (5) data points, the effluent sulphate concentration was below 250 mgSO₄²⁻/L with values as low as 80 mgSO₄²⁻/L.

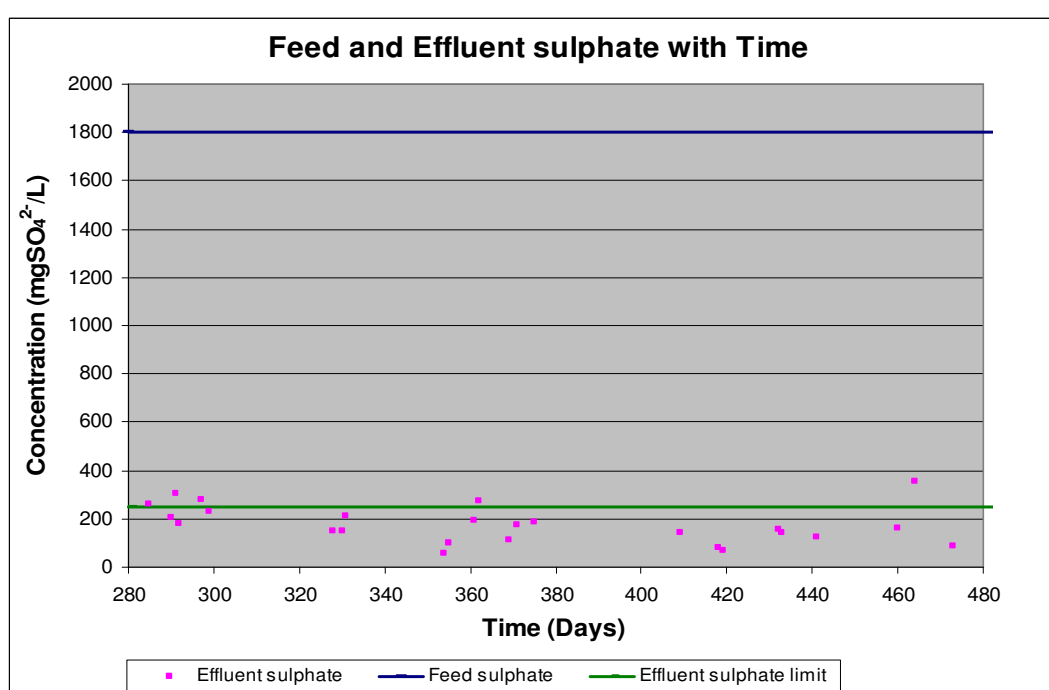


Figure 6D: Effluent sulphate concentration-time profiles with PSS as substrate augmented with 1800 mgSO₄²⁻/L sulphate (R1).

1.2 Effluent H₂CO₃* alk, Alk H₂S and VFA concentrations

Figure 6E plots the effluent alkalinities (Sum of H₂CO₃* alk + Alk H₂S, H₂CO₃* alk) and VFA concentrations. The data points circled represent the period (Day 400-465) on which the feed dosage with NaHCO₃ was discontinued. This did not affect the performance of the reactor as the effluent sulphate concentration remained under 250 mgSO₄²⁻/L (Figure 6D) and the effluent VFA in general was < 100 mgHAc/L.

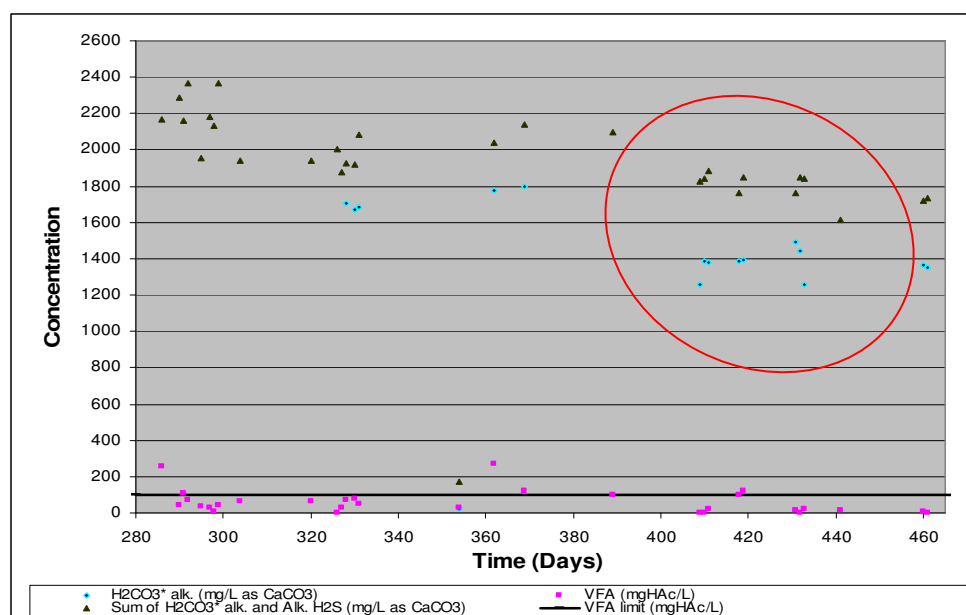


Figure 6E: Effluent alkalinities and VFA concentration-time profiles with PSS as substrate augmented with 1800 mgSO₄²⁻/L sulphate (R1).

2. BED PROFILE TESTS R1 1800

Profile of soluble parameters

Profile tests on the soluble parameters were conducted to study their variations along the bed axis. Figure 6F illustrates the profile characteristics of the sulphate, VFA and sum of H₂CO₃* alk and Alk H₂S concentrations. The immediate start up of the BSR processes at the bottom of the reactor sludge bed (with the concomitant generation/consumption of VFA and the high production of alkalinity) were a direct consequence of the recycling sludge from the top to the bottom of the reactor bed.

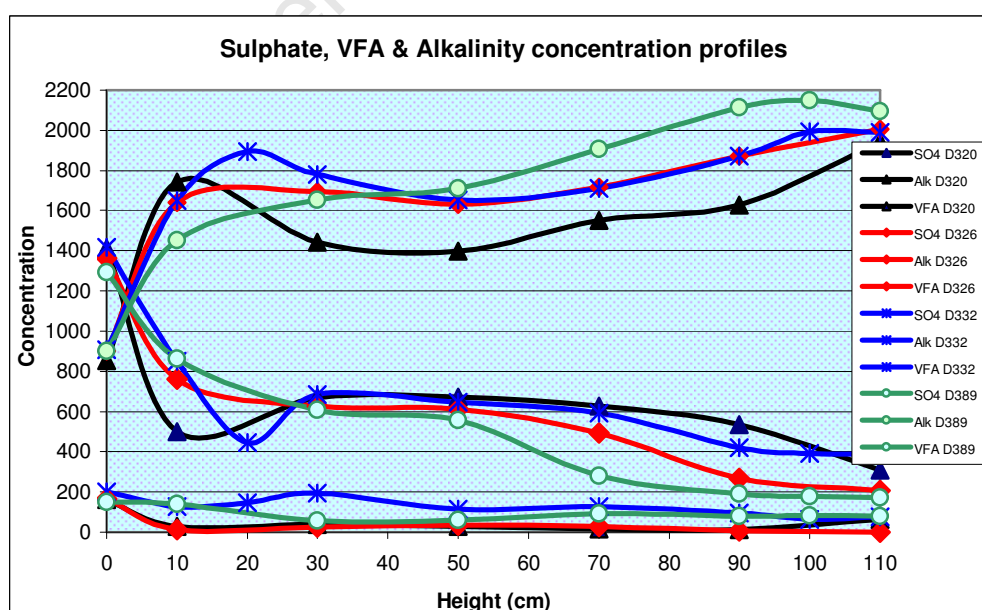


Figure 6F: UASB reactor R1 (fed 1800 mgSO₄²⁻/L) alkalinity, VFA and sulphate concentration profiles up the sludge bed height (104 cm) for a BRT of 16.4-16.8h.

2.2 Profile of solids along the bed axis– Calculation of sludge age (R_s)

Figure 6G depicts the variations of the particulate COD concentrations at different bed height intervals. It can be found that after the 10cm bed height, overall the particulate COD concentrations stayed more or less constant up to the bed height (~ 104cm). Using the method described in Section 4.11 in Chapter 4, the sludge age (R_s) was found to be $21.0 \pm 0.15d$.

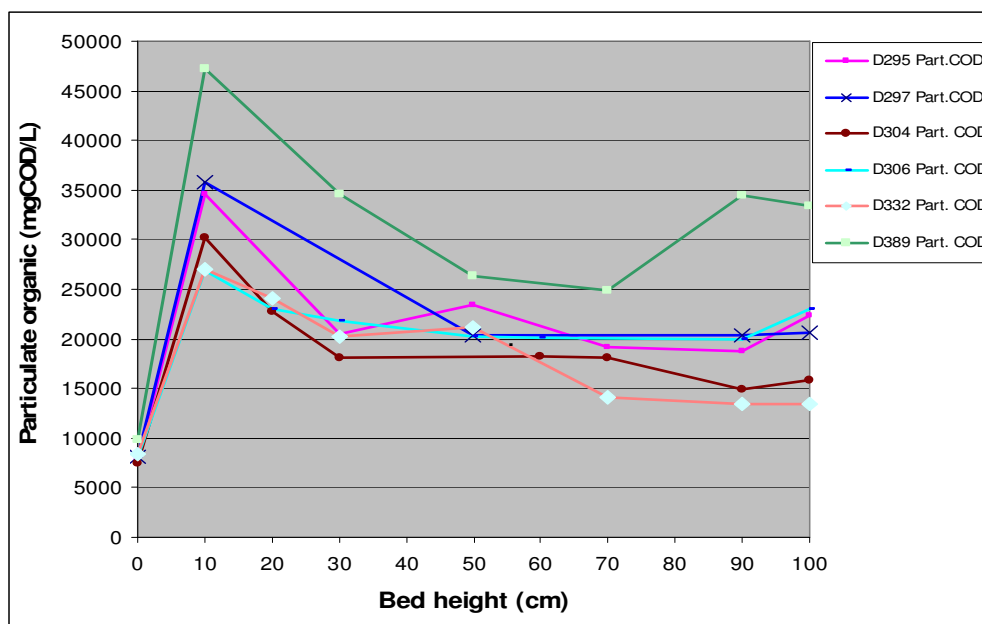


Figure 6G: UASB reactor R1 (fed $1800 \text{ mgSO}_4^{2-}/\text{L}$) particulate sludge COD concentration profiles up the sludge bed height (104cm) for a BRT of 16.4-16.8h.

3. ANALYSIS OF WASTE SLUDGE

The mean f_{cv} and f_c values calculated from the measured particulate COD, TKN and VSS for UASB R1 ($1800 \text{ mgSO}_4^{2-}/\text{L}$) were 1.52 ± 0.09 and 0.064 ± 0.013 respectively (Table 6B).

Table 6B: Analysis of waste sludge from the UASB R1 fed $1800 \text{ mgSO}_4^{2-}/\text{L}$.

Day of operation	Total COD (mgCOD/L)	Particulate COD (mgCOD/L)	TSS	VSS	TKN of particulate organic	COD/VSS (f_{cv})	TKN/VSS (f_n)
326	24336	23323	19686	14788	728	1.577	0.049
332	19063	18024	15096	11412	928	1.579	0.081
474	26928	25663	25210	18392	1125	1.395	0.061

4. EFFECTS OF STOPPING SLUDGE RECYCLE LINE

Sludge profile tests were conducted on R1 when the sludge recycle line was deliberately stopped for a period of 52 days towards the end of the experimental programme. Results of these profile tests are depicted in Figures 6H and 6I after 23 and 52 days respectively.

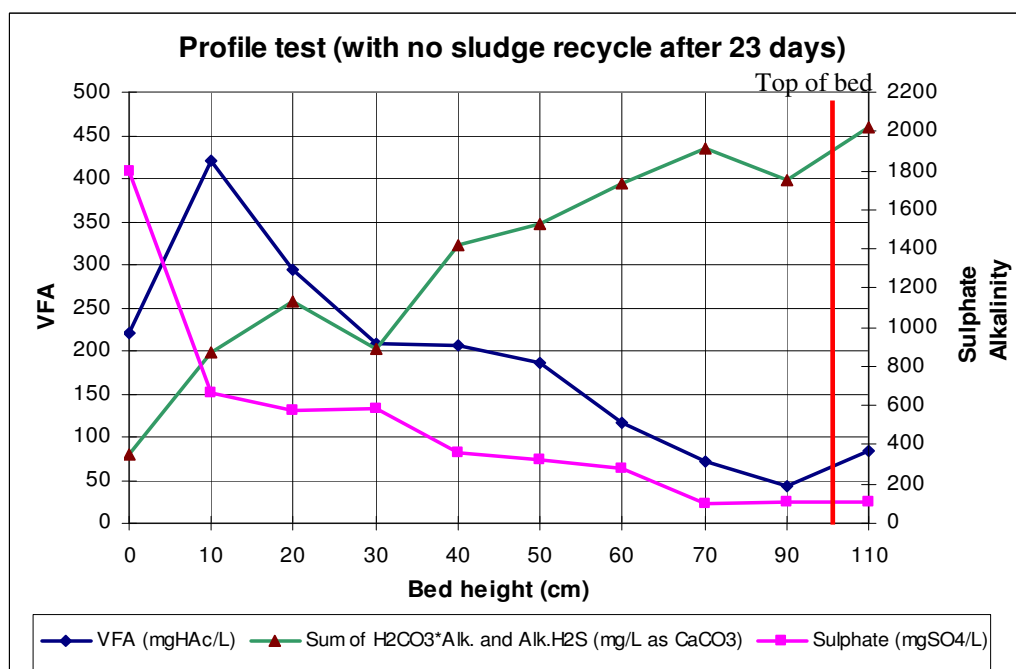


Figure 6H: Reactor alkalinity, VFA and sulphate concentration profiles up the sludge bed (104cm) after 23 days (with no sludge recycle line).

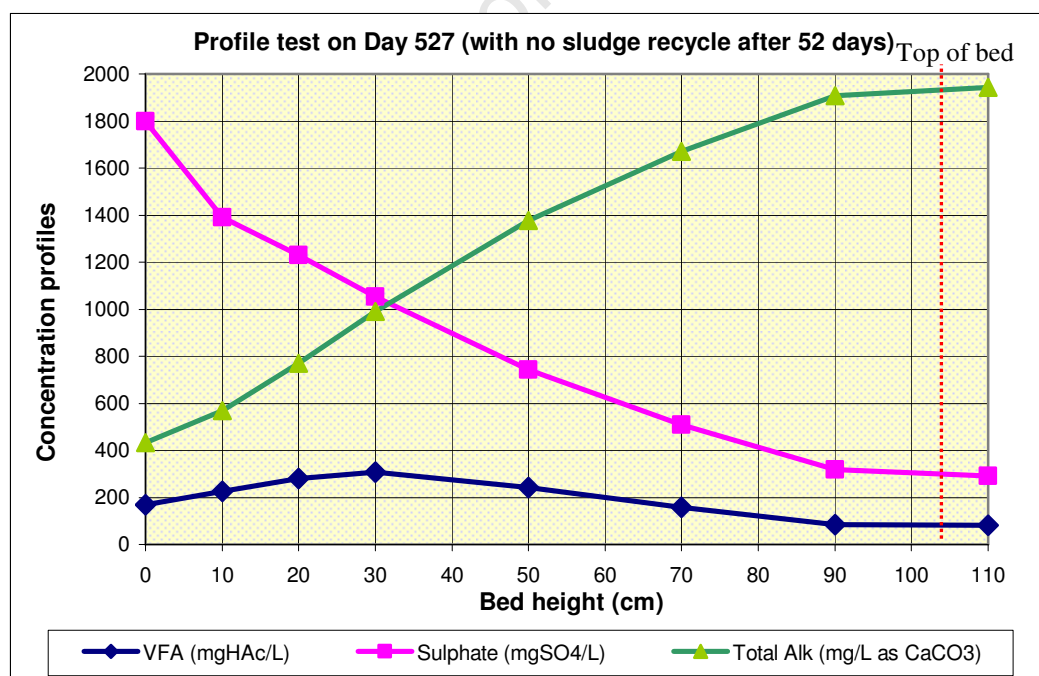


Figure 6I: Reactor alkalinity, VFA and sulphate concentration profiles up the sludge bed (104cm) after 52 days (with no sludge recycle line).

From the profile characteristics illustrated in Figures 6H and 6I, it is deduced that the recycling sludge from the top to the bottom of the reactor bed cannot be discontinued for a period of more than 23 days as afterwards the system performance starts to deteriorate.

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UASB REACTOR R2 (1500 mgSO₄²⁻/L at 20 °C)

Date	Days	Inf. SO4	Inf.sol.C OD	Inf. COD	Infl. Alk	Inf. VFA (mgHAc/L)	Eff. SO4	SO4 rem. Effy (%)	SO4 removal (mg/l)	Eff. Tot. COD	Eff. Tot sol COD	Eff. Part. COD	Eff. Org sol. COD	Eff. Sulphide COD	Eff. Org. COD	Org. COD rem. Effy (%)	COD removal (mgCOD/l)	S _T (mgS/L)	Alk H2S	Theor. S	Eff. pH	Sum of H2CO3 + Alk H2S	Eff VFA	Eff. H2CO3* alk.	BRT (h)	HRT (h)
11-Nov-05	1	1500																			7.24				24.1	28.0
12-Nov-05	2	1500																					56.5	1123.6	24.1	28.0
13-Nov-05	3	1500																			7.23		111.1	1166.4	24.1	28.0
14-Nov-05	4	1500																			7.25		147.6	1308.7	24.1	28.0
15-Nov-05	5	1500																			7.23		230.4	1293.0	24.1	28.0
16-Nov-05	6	1500																			7.22					
17-Nov-05	7	1500																								
18-Nov-05	8	1500																								
19-Nov-05	9	1500	250.6	1958.6			400.5	73.3	1099.5											366.5	7.21		57.9	1438.9	24.1	28.0
20-Nov-05	10	1500	260.4	1990.2	415.2	112.3	349.0	76.7	1151.0	879.5	602.8	276.7	126.4	476.4	403.1	79.7	1587.1	238.2	231.4	383.7	7.23	1814.1	58.2	1582.6	24.1	28.0
21-Nov-05	11	1500	244.9	1964.3			409.4	72.7	1090.6											363.5			139.3	1657.8	24.1	28.0
22-Nov-05	12	1500																			7.20				25.8	28.0
23-Nov-05	13	1500	269.5	1995.0						894.1	562.9	331.2	154.4	408.4	485.6	75.7	1509.4	204.2	191.4		7.19	1569.1	98.3	1377.7	25.8	28.0
24-Nov-05	14	1500																			7.18		87.4	1454.7	25.8	28.0
25-Nov-05	15	1500																							25.8	28.0
26-Nov-05	16	1500																							25.8	28.0
27-Nov-05	17	1500																					343.1	1182.2		
28-Nov-05	18	1500					528.2	64.8	971.8											323.9	7.16		83.0	1440.6		
29-Nov-05	19	1500					379.7	74.7	1120.3											373.4	7.15		121.4	1380.6		
30-Nov-05	20	1500																			7.22				25.8	28.0
1-Dec-05	21	1500																			7.18				25.8	28.0
2-Dec-05	22	1500																							25.8	28.0
3-Dec-05	23	1500																			7.19				25.8	28.0
4-Dec-05	24	1500																					319.9	1266.3	25.8	28.0
5-Dec-05	25	1500	239.1	1951.6	431.7	136.4	295.5	80.3	1204.5	911.2	625.6	285.6	159.2	466.4	444.8	77.2	1506.8			401.5	7.15		299.5	1128.1	25.8	28.0
6-Dec-05	26	1500					260.9	82.6	1239.1											413.0	7.22		279.0	1163.4	25.8	28.0
7-Dec-05	27	1500	263.5	1968.3			157.9	89.5	1342.1											447.4	7.30		410.6	1253.3	25.8	28.0
8-Dec-05	28	1500					282.7	81.2	1217.3											405.8	7.34		230.3	1437.9		
9-Dec-05	29	1500																			7.18					
10-Dec-05	30	1500																							25.8	28.0
11-Dec-05	31	1500	290.1	1980.2			362.9	75.8	1137.1											379.0	7.16		217.4	1382.1	25.8	28.0
12-Dec-05	32	1500	275.6	1965.6			278.7	81.4	1221.3											407.1	7.22		154.5	1253.5	25.8	28.0
13-Dec-05	33	1500																								
14-Dec-05	34	1500																			7.17		176.3	1131.8		
15-Dec-05	35	1500																			7.10					
16-Dec-05	36	1500																							25.8	28.0
17-Dec-05	37	1500																			7.11				25.8	28.0
18-Dec-05	38	1500	291.6	1986.5	422.9	124.6	275.7	81.6	1224.3	878.9	598.1	280.8	149.5	448.6	430.3	78.3	1556.2			408.1	7.09		323.0	1276.4	25.8	28.0
19-Dec-05	39	1500																			7.11		208.9	1156.8	25.8	28.0
20-Dec-05	40	1500																					349.5	1235.9	25.8	28.0
21-Dec-05	41	1500																			7.13				25.8	28.0
22-Dec-05	42	1500																							25.8	28.0
23-Dec-05	43	1500																			7.19				25.8	28.0
24-Dec-05	44	1500																							25.8	28.0
25-Dec-05	45	1500																			7.21			1587.1	25.8	28.0
26-Dec-05	46	1500																					1325.3	25.8	28.0	
27-Dec-05	47	1500																			7.27				25.8	28.0
28-Dec-05	48	1500																			7.22				25.8	28.0
29-Dec-05	49	1500																			7.23		387.2	1604.4	25.8	28.0
30-Dec-05	50	1500																			7.17		166.0	1614.5		
31-Dec-05	51	1500																					55.7	1569.2		

1-Jan-06	52	1500																			7.23					
2-Jan-06	53	1500																			7.18		196.9	1582.3	25.2	27.3
3-Jan-06	54	1500																						25.7	27.8	
4-Jan-06	55	1500					265.3	82.3	1234.7										411.6					25.9	28.1	
5-Jan-06	56	1500	281.0	1978.9			289.2	80.7	1210.8	894.1	569.8	324.3	156.4	413.4	480.7	75.7	1498.2	206.7	184.7	403.6	7.14	1752.4	33.8	1567.7	25.9	28.1
6-Jan-06	57	1500																		7.18				25.8	27.9	
7-Jan-06	58	1500	269.2	1964.3			215.3	85.6	1284.7											428.2			85.9	1633.9	25.9	28.1
8-Jan-06	59	1500					205.0	86.3	1295.0											431.7	7.26				25.8	28.0
9-Jan-06	60	1500																		7.18		45.3	1566.9	25.8	28.0	
10-Jan-06	61	1500	273.5	1965.4	420.6	120.2	245.3	83.6	1254.7	904.5	581.6	322.9	148.2	433.4	471.1	76.0	1494.3	216.7	212.4	418.2	7.24				25.8	28.0
11-Jan-06	62	1500																		7.21		83.4	1611.5	25.8	28.0	
12-Jan-06	63	1500																		7.25		3.0	1631.7			
13-Jan-06	64	1500																		7.23						
14-Jan-06	65	1500																		7.27		28.1	1671.1			
15-Jan-06	66	1500																		7.26		56.5	1643.4	25.8	27.9	
16-Jan-06	67	1500																		7.24				25.8	28.0	
17-Jan-06	68	1500																						25.8	28.0	
18-Jan-06	69	1500																		7.14		47.8	1646.3	25.9	28.1	
19-Jan-06	70	1500																		7.15				25.8	28.0	
Steady State period 1 (Days 51-70)		Average	275	1970	421	120	244	83.7	1256	899	576	324	152	423	476	75.9	1496	212	199	419	7.21	1752	99	1612	25.81	27.96
		SSD	4.9	6.6	0.0	0.0	31.1	2.1	31.1	5.2	5.9	0.7	4.1	10.0	4.8	0.2	2.0	5.0	13.8	10.4	0.04	0	102	33	0.17	0.19
20-Jan-06	71	1500																		7.17		54.9		22.2	24.0	
21-Jan-06	72	1500																						1599.7	22.2	24.0
22-Jan-06	73	1500																		7.23		23.1	1558.0	22.2	24.0	
23-Jan-06	74	1500																		7.16				22.2	24.1	
24-Jan-06	75	1500																						22.1	23.9	
25-Jan-06	76	1500	259.8	1945.0			368.8	75.4	1131.2	901.0	592.9	308.1	164.3	428.6	472.4	75.7	1472.6	214.3	211.8	377.1	7.25		47.1	1660.5	22.2	24.0
26-Jan-06	77	1500																		7.19				22.2	24.0	
27-Jan-06	78	1500																		7.20		41.0	1432.0	22.1	23.9	
28-Jan-06	79	1500																						22.1	23.9	
29-Jan-06	80	1500																		7.23				22.2	24.0	
30-Jan-06	81	1500																		7.18		81.8	1236.1	22.0	23.8	
31-Jan-06	82	1500																						22.2	24.0	
1-Feb-06	83	1500	292.3	1982.0			270.8	81.9	1229.2										409.7	7.21				22.2	24.0	
2-Feb-06	84	1500																						22.2	24.0	
3-Feb-06	85	1500																		7.18		11.7	1591.4	22.2	24.0	
4-Feb-06	86	1500																						22.2	24.0	
5-Feb-06	87	1500																						22.2	24.0	
6-Feb-06	88	1500																						22.2	24.1	
7-Feb-06	89	1500																						22.2	24.0	
8-Feb-06	90	1500																	399.2					22.2	24.0	
9-Feb-06	91	1500	269.1	1969.2	431.2	129.8	302.5	79.8	1197.5	888.2	594.4	293.8	158.2	436.2	452.0	77.0	1517.2	218.1	204.5		7.19	1703.1	89.4	1498.6	21.7	23.5
10-Feb-06	92	1500																		7.19		73.3	1563.2	22.2	24.0	
11-Feb-06	93	1500																		7.21				22.2	24.0	
12-Feb-06	94	1500																	397.2	7.22				22.2	24.0	
13-Feb-06	95	1500	274.5	1968.2	421.2		308.4	79.4	1191.6	881.8	557.2	324.6	138.6	418.6	463.2	76.5	1505.0	209.3	198.0	409.7	7.20	1759.2	34.7	1561.2	22.1	23.9
14-Feb-06	96	1500					270.8	81.9	1229.2	851.0	557.0	294.0	134.5	422.5	428.5			211.3	201.7		7.21	1750.3	43.6	1548.6	22.2	24.0
15-Feb-06	97	1500																		7.18				22.1	23.9	
16-Feb-06	98	1500																						22.2	24.0	
17-Feb-06	99	1500																		7.20				22.2	24.0	
18-Feb-06	100	1500																	383.5	7.17				22.2	24.0	
19-Feb-06	101	1500		1972.0			349.6	76.7	1150.4	923.8	592.8	331.0	141.6	451.2	472.6	76.0	1499.4	225.6	213.4		7.20			22.1	23.9	
20-Feb-06	102	1500																		7.23				22.2	24.0	
21-Feb-06	103	1500																		7.22				22.1	23.9	
22-Feb-06	104	1500																						22.1	23.9	
23-Feb-06	105	1500																		7.22				22.2	24.0	
24-Feb-06	106	1500	286.5	1986.5	417.2	115.2	254.0	83.1	1246.0	876.5	578.7	297.8	148.9	429.8	446.7	77.5	1539.8	214.9	210.6	415.3	7.24	1804.7	39.4	1594.1	22.2	24.0
25-Feb-06	107	1500																		7.19				22.2	24.0	
26-Feb-06	108	1500																						22.2	24.0	
27-Feb-06	109	1500																						22.2	24.0	
28-Feb-06	110	1500																	390.7	7.19		34.3	1552.1	22.2	24.0	
1-Mar-06	111	1500		1981.3			327.8	78.1	1172.2	894.0	590.0	304.0	147.4	442.6	451.4			221.3	211.3	396.6	7.21	1760.9	45.0	1549.6	22.2	24.0
2-Mar-06	112	1500					310.2	79.3	1189.8	882.8	580.2	302.6	152.4	427.8	455.0			213.9	206.0		7.22	1763.0	23.9	1557.0	22.2	24.0

[illegible]

2-May-06	173	1500																							19.4	21.0
3-May-06	174	1500																								
4-May-06	175	1500	333.6	2598.6	429.6	151.2	123.4	91.8	1376.6	1322	1006.2	315.8	213.2	793.0	529.0	79.6	2069.6	396.5	381.9	458.9	7.22	1956.5	48.9	1574.6	19.4	21.0
5-May-06	176	1500					141.7	90.6	1358.3											452.8					18.8	20.4
6-May-06	177	1500	341.7	2604.2	453.6	152.3	101.5	93.2	1398.5											466.2					19.4	21.0
7-May-06	178	1500					98.6	93.4	1401.4											467.1					18.9	20.5
13-May-06	184	1500																							19.4	21.0
Steady State period 5a (Days 154-184)- Aik dosage to feed		Average	338	2651	435	151	109	92.7	1391	1353	994	358	305	689	664	75.2	2003	344	332	464	7.22	1920	105	1589	19.2	20.8
		SSD	6.1	93.0	12.8	4.6	17.6	1.2	17.6	24.1	20.6	42.2	65.7	78.3	102.3	3.2	71.0	39.1	38.4	5.9	0.01	27.4	46.9	11.1	0.2	0.2
17-May-06	188	1500	328.5	2546.8	21.3																				19.4	21.0
18-May-06	189	1500	328.5	2546.8	21.3																				19.4	21.0
19-May-06	190	1500																							19.4	21.0
20-May-06	191	1500																							19.4	21.0
21-May-06	192	1500																							18.9	20.5
22-May-06	193	1500																							18.9	20.5
23-May-06	194	1500	372.6	2563.72	22.3	151.2	77.7228	94.8	1422.3					550.0				275.0		474.1	7.21	1272.2	99.3	1026.4	18.9	20.5
24-May-06	195	1500	372.6	2563.7	22.3									504.0				252.0			7.21	1231.1	120.8	1051.2	18.9	20.5
25-May-06	196	1500												500.0				250.0			7.20	1297.8	113.7	1056.3	18.9	20.5
26-May-06	197	1500																		7.19						
27-May-06	198	1500																		7.22					19.9	21.0
28-May-06	199	1500																		7.21					19.7	20.8
29-May-06	200	1500																		7.23					19.7	20.8
30-May-06	201	1500																		7.21	1248	104.6			19.7	20.8
31-May-06	202	1500		2590.72			72.7723	95.1	1427.2					540.4				270.2		475.7	7.22	1241	150.1	1050.8	19.7	20.8
1-Jun-06	203	1500																							19.7	20.8
2-Jun-06	204	1500																							19.4	20.4
3-Jun-06	205	1500																							19.4	20.4
4-Jun-06	206	1500																							19.4	20.4
5-Jun-06	207	1500																							19.4	20.4
6-Jun-06	208	1500	329.4	2543.1	20.1																			1054.3	19.4	20.4
7-Jun-06	209	1500	329.4	2543.1	20.1																				19.4	20.4
8-Jun-06	210	1500																							19.7	20.8
9-Jun-06	211	1500																							19.7	20.8
10-Jun-06	212	1500																		7.23	1219.9	0			19.7	20.8
11-Jun-06	213	1500																							19.7	20.8
12-Jun-06	214	1500																							19.7	20.8
13-Jun-06	215	1500																							19.7	20.8
14-Jun-06	216	1500																							19.7	20.8
15-Jun-06	217	1500																							19.7	20.8
16-Jun-06	218	1500																							19.7	20.8
17-Jun-06	219	1500																							19.4	20.4
18-Jun-06	220	1500																							19.4	20.4
19-Jun-06	221	1500																							19.4	20.4
20-Jun-06	222	1500	364.2	2613.0			95.6	93.6	1404.4											7.22		9.4	1037.0		19.4	20.4
21-Jun-06	223	1500																							19.4	20.4
22-Jun-06	224	1500																							19.4	20.4
23-Jun-06	225	1500																							19.4	20.4
24-Jun-06	226	1500																							19.4	20.4
25-Jun-06	227	1500																							19.4	20.4
26-Jun-06	228	1500																							19.4	20.4
27-Jun-06	229	1500																							19.4	20.4
28-Jun-06	230	1500																							19.4	20.5
29-Jun-06	231	1500	335.4	2546.9	28.2		125.6	91.6	1374.4																19.4	20.5
30-Jun-06	232	1500	335.4	2546.9	28.2																				19.4	20.5
1-Jul-06	233	1500																							19.4	20.5
2-Jul-06	234	1500																							19.4	20.5
3-Jul-06	235	1500																							19.4	20.5
4-Jul-06	236	1500																							19.4	20.5
5-Jul-06	237	1500																							19.4	20.5
6-Jul-06	238	1500																							19.4	20.5
7-Jul-06	239	1500																							19.4	20.5
8-Jul-06	240	1500	367.4	2544.2	20.1	147.5	124.8	91.7	1375.2	1127.6	948.4	179.2	101.5	846.9	280.7	89.0	2263.5	423.5	411.4	458.4	7.23	1544.6	54.8	1133.2	19.4	20.4
9-Jul-06	241	1500	334.0	2562.1	20.1	151.6	84.3	94.4	1415.7	1088.6	958.1	130.5	92.3	865.8	222.8	91.3	2339.3	432.9	420.6	471.9	7.23	1570.0	74.2	1149.4	19.4	20.4

10-Jul-06	242	1500																								
11-Jul-06	243	1500																		7.19					19.3	20.3
12-Jul-06	244	1500																		7.19						
																									19.4	20.5
23-Jun-06	257	1500	329.8	2627.3	27.6	150.2	79.7	94.7	1420.3	1077.1	948.6	128.5	85.7	862.9	214.2	91.8	2413.1	431.5	415.6	473.4	7.22	1573.4	56.3	1157.8	19.4	20.4
23-Jun-06	257	1500																								
24-Jun-06	258	1500	324.6	2651.6	24.4	143.1	114.8	92.3	1385.2	1060.8	948.2	112.6	106.1	842.1	218.7	91.8	2432.9	421.1	405.5	461.7	7.22	1542.3	45.9	1136.7	19.4	20.4
Steady State period 5b (Days 188-258)- No Alk dosage to feed	Mean		338.9	2596.3	23.1	148.1	100.9	93.3	1399.1	1088.5	950.8	137.7	96.4	854.4	234.1	91.0	2362.2	427.2	413.3	466.4	7.21	1557.6	57.8	1144.3	19.4	20.4
	SSD		16.8	44.4	3.2	3.2	19.3	1.3	19.3	24.6	4.2	24.9	7.9	10.1	27.1	1.2	66.8	5.1	5.5	6.4	0.02	14.2	10.3	9.9	0.1	0.1

Note that the averages for the influent and effluent parameters are from Days 240-258. This is so because the sulphide COD was calculated from the modified wet chemistry analytical procedures as from Day 240.

UASB REACTOR 1 (1800 mgSO₄²⁻/L) at 35 °C

Days	Inf. SO4	Inf. Sol COD	Inf. COD	Inf. VFA	Inf. H2CO3 alk.	Eff. SO4	SO4 rem. Effy (%)	SO4 removal (mg/l)	Eff. VFA	Eff. Tot Alk.	Eff. H2CO3* alk.	Eff. Tot. COD	Eff. Tot sol COD	Eff. Org sol COD	Eff. sulphide COD	Eff. Part COD	Eff. Org. COD	Org. COD rem. Effy (%)	COD removal (mgCOD/l)	S _T (mgS/L)	Alk H2S	Theor. S	Eff. pH	BRT (h)	HRT	Flow rate (L/d)	
285	1800					261.9																					
286	1800								257.2										2212.0				7.09	17.5	19.5	9.60	
287	1800																							17.9	20.0	9.36	
288	1800																							17.9	20.0	9.36	
289	1800																							18.8	21.0	8.91	
290	1800		2278.0			204.5	88.6	1595.5	45.2													531.8		17.9	20.0	9.36	
291	1800	249.5	2212.0	122.3	564.3	302.5	83.2	1497.5	107.7													499.2		17.9	20.0	9.36	
292	1800		2304.6			177.7	90.1	1622.3	67.5													540.8	7.08	17.5	19.5	9.60	
293	1800																							17.5	19.5	9.60	
295	1800								38.2															17.5	19.5	9.60	
296	1800																							17.5	19.5	9.60	
297	1800		2205.4			277.7	84.6	1522.3	28.4													507.4	7.09	17.5	19.5	9.60	
298	1800								8.4															17.1	19.0	9.85	
299	1800		2276.5			229.5	87.3	1570.5	39.3													523.5		17.2	19.2	9.75	
304	1800								62.7															17.1	19.1	9.80	
320	1800								62.7															17.1	19.0	9.85	
326	1800								0.0														7.09	17.1	19.0	9.85	
327	1800								25.7															17.2	19.2	9.75	
328	1800	287.6	2394.0	122.4	565.6	152.0	91.6	1648.0	68.9	1948.6	1705.3	865.6	562.9	71.1	491.7	302.8	373.9	84.4	2020.1	245.9	243.2	549.3	7.07	17.1	19.0	9.85	
330	1800								77.5	1936.1	1666.3	1016.0	699.0	144.3	554.7	317.0	461.3			277.4	269.7		7.05	17.1	19.0	9.85	
330	1800	329.4	2425.0	141.2	541.3	150.2	91.7	1649.8														549.9		17.1	19.0	9.85	
																								17.1	19.0	9.85	
SS 1 (Days 302-330)	Mean	308.5	2409.5	131.8	553.5	151.1	91.6	1648.9	49.6	1942.3	1685.8	940.8	630.9	107.7	523.2	309.9	417.6	84.4	2020.1	261.6	256.5	549.6	7.07	17.1	19.0	9.83	
	SSD	20.9	15.5	9.4	12.1	0.9	0.0	0.9	27.5	6.3	19.5	75.2	68.1	36.6	31.5	7.1	43.7	0.0	0.0	15.7	13.2	0.3	0.02	0.1	0.1	0.04	
	355	1800		2445.0		96.5	94.6	1703.5											2445.0			567.8		16.8	18.5	10.12	
	361	1800		2498.6		190.6	89.4	1609.4											2498.6			536.5		16.8	18.5	10.12	
	362	1800	266.1	2630.9		274.8	84.7	1525.2	269.4	2040.5	1776.2	1459.6	893.1	314.5	578.6	566.5	881.0	66.5	1749.9	289.3	281.3	508.4	7.05	16.8	18.5	10.12	
	367	1800																						16.8	18.5	10.12	
	368	1800																						16.8	18.5	10.12	
	369	1800		2671.2	132.6	581.2	110.4	93.9	1689.6	118.8	2135.4	1796.5	1643.0	971.7	243.9	727.8	671.3	915.3	65.7	1755.9	363.9	356.9	563.2	7.06	16.9	18.6	10.06
	371	1800		2569.3		175.6	90.2	1624.4														541.5		16.9	18.6	10.06	
	375	1800	285.4	2580.6	147.5	542.7	184.0	89.8	1616.0													538.7		17.0	18.7	10.01	
	389	1800		2562.5					99.3	2095.4														16.8	18.5	10.12	
SS 2a (Days 365-399) Alk dosage	Mean	275.7	2613.0	140.1	562.0	186.2	89.7	1613.8	194.1	2088.0	1786.4	1551.3	932.4	279.2	653.2	618.9	898.1	66.1	1752.9	326.6	319.1	537.9	7.1	16.9	18.6	10.1	
	SSD	9.6	40.8	7.4	19.3	58.5	3.3	58.5	75.3	47.5	10.2	91.7	39.3	35.3	74.6	52.4	17.1	0.4	3.0	37.3	37.8	19.5	0.0	0.1	0.1	0.0	
400	1800	Stop dosing																				7.10		7.10	16.8	18.5	10.12
409	1800	348.1	2586.1	148.4	25.3	144.1	92.0	1655.9	42.3	1707.7	1360.8	1512.3	922.2	243.5	678.7	590.1	833.6	67.8	1752.5	339.4	346.9	552.0	7.11	16.8	18.5	10.12	
410	1800																						7.09	16.8	18.5	10.12	
411	1800								51.5	1786.5	1356.8	1654.8	1046.2	212.1	834.1					417.1	429.7		7.12	16.8	18.5	10.12	
418	1800	325.6	2545.18			82.7	95.4	1717.3	43.6	1722.1	1324.2	1781.1	1041.2	236.8	804.4	739.9	976.7	61.6	1568.5	402.2	397.9	572.4	7.07	16.4	18	10.40	
419	1800	336.0	2615.008			68.8	96.2	1731.2	78.5	1703.4	1402.3	1497.8	830.0	226.3	603.7	667.8	894.1	65.8	1720.9	301.9	301.1	577.1	7.08	16.4	18	10.40	
420	1800																							16.4	18	10.40	
421	1800		2656.6			238.8			41.2	1824.8	1351.8	1458.6	1158.7	218.3	940.4	299.9	518.2	80.5	2138.4	470.2	473.0	520.4	7.09	16.4	18	10.40	
424	1800	334.5	2586.2																				7.10	16.4	18.0	10.40	
425	1800	336.2	2596.92	163.4	25.2	108.5																		16.4	18.0	10.40	
431	1800																							16.4	18.0	10.40	
432	1800					121.4																	7.05	16.4	18.0	10.40	
433	1800	330.2	2541.3	141.6	20.8	140.1			27.6	1860.9	1356.6	1526.3	1264.6	253.6	1011.0	261.7	515.3	79.7	2026.0	505.5	504.3		7.08	16.4	18.0	10.40	
441	1800	330.2	2541.3	141.6	20.8	122.2																		16.4	18.0	10.40	
460	1800					164.0																		16.4	18.0	10.40	
461	1800																							16.4	18.0	10.40	
464	1800	341.3	2553.8			226.9	87.4	1573.1														524.4	7.10	16.4	18.0	10.40	
	1800																										
468	1800	341.3	2553.8	147.2	26.6	111.2			103															16.4	18.0	10.40	
473	1800	346.8	2641.2			84.7	95.3																				

Chapter 7

Steady state and kinetic models for biological sulphate reduction

7.1 INTRODUCTION

As described in Chapter 2, the core unit process in the BioSURE[®] system is biological sulphate reduction (BSR) with primary sewage sludge (PSS). To assist in and optimise the design, operation of and research into this unit process, mathematical models (both steady state and kinetic) represent very useful process evaluation tools. Mathematical models provide quantitative descriptions of the treatment system of interest that allow predictions of the system response and performance to be made. Based on the predictions, design and operation criteria can be identified to optimise the system performance. The model predictions can be evaluated and as such make it possible to test hypotheses on the system behaviour, such as biological processes and their response to system constraints, in a consistent and integrated fashion.

Therefore, mathematical models constitute valuable research tools to improve the understanding of the underlying fundamental processes and their interactions. In essence, they provide an integrated mass balance based framework for the system which can give guidance to design, operation and research.

In this Chapter, a steady state (SS) anaerobic digestion model for BSR using PSS as energy source will be developed and calibrated. After which, the SS BSR model results will be compared with experimental data from the 2 lab-scale UASB reactors, R1 at 35 °C (when fed 1500 and 1800 mgSO₄²⁻/L) and R2 at 20 °C (fed 1500 mgSO₄²⁻/L). This SS model is presented in Section 7.2 of this Chapter. In Section 7.3, the integrated two phase (aqueous-gas) biological, chemical and physical processes kinetic model (UCTADM1-BSR) for

competitive methanogenic and sulphidogenic anaerobic digestion with PSS as substrate developed by van Wageningen (2007) is reviewed, refined and updated to simulate the performance of the 2 lab-scale UASB BSR reactors (R1 and R2). Finally, in Section 7.4, the kinetic model predictions are compared with the SS BSR results and the experimental data and appropriate conclusions will be drawn from the validation of these models.

7.2 DEVELOPMENT OF A STEADY STATE MODEL FOR BIOLOGICAL SULPHATE REDUCTION WITH PRIMARY SEWAGE SLUDGE AS ENERGY SOURCE

7.2.1 IMPORTANCE OF STEADY STATE MODELS

In contrast to complex dynamic simulation models, steady state models are comparatively simple stoichiometric models that require constant flows and loads as input to determine the system design parameters. They are based on the slowest process kinetic rate governing the overall behaviour of the system and relate this process to the system design and operating parameters. These design and operating parameters such as reactor volume, recycle ratios and retention time, can be estimated in a relatively simple and quick approach from the system performance measures, for instance effluent quality. Usually, steady state models constitute the initial step to estimate the design and operating parameters of a system. These parameters then serve as input to the more complex kinetic simulation models to explore the dynamic behaviour of the system and refine the design and operating parameters.

7.2.2 CHARACTERISATION OF PRIMARY SEWAGE SLUDGE

From the PSS COD removal, the effluent parameters (COD (all constituents), TKN, FSA, SCFA, H_2CO_3^* alk., Alk H_2S , $\text{H}_2\text{S}/\text{HS}^-$ and pH) are determined from the influent sludge constituents. Thus, in the development of the steady state (SS) model for BSR, the PSS is fully characterised based on the COD (total and unbiodegradable particulate fraction, $f_{\text{PS,up}}$), short chain fatty acids (SCFA) COD, TKN and FSA and the PSS $\text{C}_x\text{H}_y\text{O}_z\text{N}_a$ composition of the particulate solids. This approach is similar to that used by Sötemann *et al.* (2005b) and characterises the PSS in terms of the measurable parameters used in calculating the COD, C, H, O, N, S and charge mass balances.

7.2.3 ANAEROBIC DIGESTION (AD) STEADY STATE (SS) MODEL FOR METHANOGENESIS

Söttemann *et al.* (2005b) developed a SS model for AD of PSS under methanogenic conditions. This model consists of three sequential parts, namely:

- a COD based kinetic part from which the influent COD concentration hydrolysed, methane gas COD, biomass COD production and the effluent COD concentrations are determined for a given sludge age,
- a $C_xH_yO_zN_a$ charge and COD mass balance based stoichiometry part from which the gas composition (or partial pressure of CO_2), ammonia released and alkalinity generated are calculated from the COD concentration hydrolysed and its x, y, z and a composition in $C_xH_yO_zN_a$ of the biodegradable organics,
- a carbonate system weak/acid base chemistry part from which the pH of the digester is obtained from the partial pressure of CO_2 and alkalinity generated.

Based on the above, a steady state model for BSR of sulphate-rich waters using a generic biodegradable organic $C_xH_yO_zN_a$ as carbon source was developed. This SS BSR model will be useful to:

- 1) estimate product generation from influent organic C, H, O and N composition and establish whether or not a particular organic type is C deficient, i.e. generates insufficient inorganic C to supply the alkalinity (HCO_3^-) required for the SO_4^{2-} reduction,
- 2) estimate reactor volume and retention time for a required substrate COD loading and sulphate removal rate,
- 3) estimate product concentrations (such as hydrogen sulphide) and their sensitivity on system performance
- 4) provide a basis for cross-checking BSR kinetic simulation model results.

In the development of the SS model using PSS as organic, it is assumed that the hydrolysis/acidogenesis process generates directly the BSR end-products which are H_2S , HS^- , HCO_3^- , CO_2 , NH_4^+ and biomass. Thus, the SS BSR model includes the same three aspects as the methanogenesis SS AD model of Söttemann *et al.* (2005b) namely:

1. COD based kinetics of the hydrolysis/acidogenesis process (same as Söttemann *et al.*, 2005b)

2. C,H,O,N,S, charge and COD mass balance based stoichiometric conversion of the reactants from (1) to BSR end-products
3. effect of the end-products on the digester pH by applying mixed weak acid/base chemistry.

7.2.4 STEADY STATE (SS) AD MODEL FOR BSR

With the modified UASB configuration operated in this research, the sludge recycle line from the top to the bottom of the reactor bed ensured that the biomass was fairly evenly distributed along the bed axis. This biomass recycle line offered two advantages:

- (i) it initiates BSR at the bottom of the bed thus maximising the system performance, and
- (ii) it allows the UASB reactor bed to be modelled as a completely mixed digester. The latter avoids the necessity of evaluating uncertain and complex granular sludge dynamics along the reactor bed height in UASB reactors caused by dispersion, sedimentation and convection.

7.2.4.1 Hydrolysis of primary sewage sludge

Consider a UASB reactor of bed volume V_b (L) and influent flow rate Q_i (L/d). The UASB reactor configuration has the benefit of uncoupling the solids and liquid (hydraulic) retention time as compared with a flow through digester. For this reason, the fundamental design parameter, sludge age, (R_s in days) is considered in this case (Figure 7.1). However, should it be a flow through digester, either the hydraulic retention time or sludge age is accepted since they are the same.

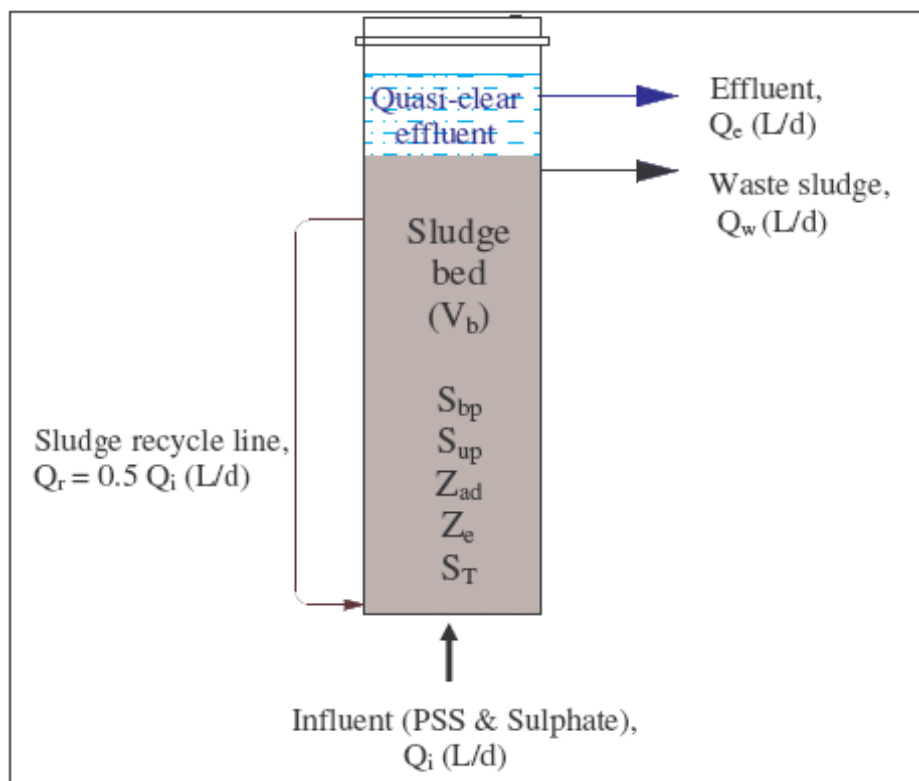


Figure 7.1: Schematic diagram of the UASB reactor used in this research.

The influent PSS COD is characterised in terms of measurable parameters (Figure 7.2).

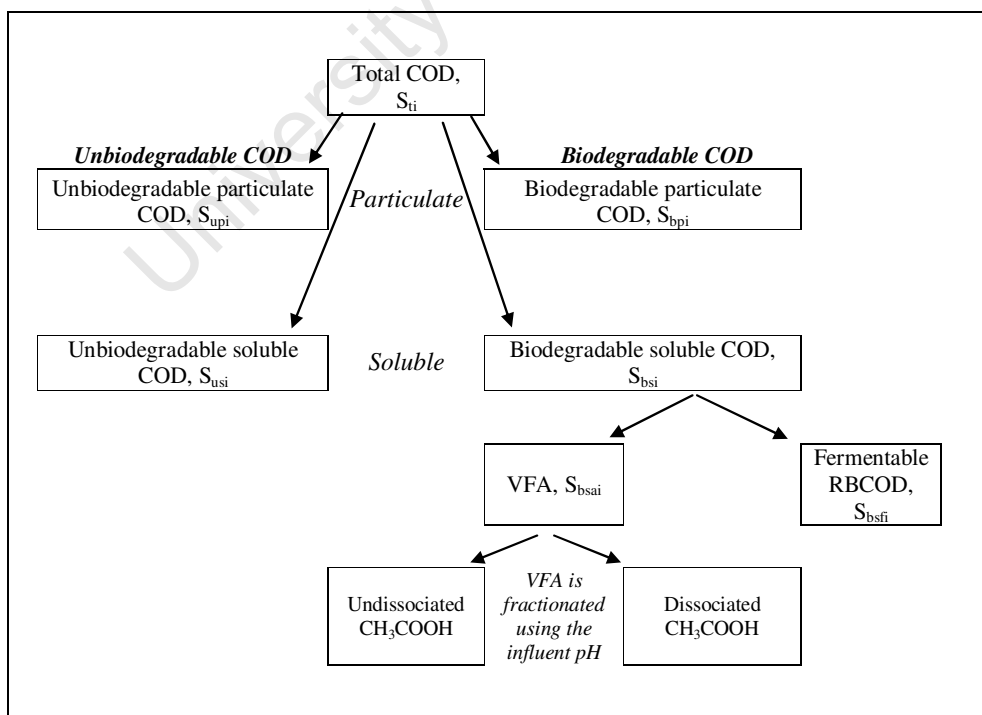


Figure 7.2: Influent primary sewage sludge COD fractionation for the steady state anaerobic digestion model for biological sulphate reduction.

The influent parameters are as follows (see Fig. 7.2):

- Total influent PSS COD, S_{ti} (mgCOD/L)
- Total soluble COD (membrane filtered), $S_{bsi} + S_{usi}$ (mgCOD/L)
- Volatile fatty acids (VFA), S_{bsai} (mgHAc/L, then converted to mgCOD/L)

With a known (or assumed) value of the unbiodegradable particulate fraction ($f_{PS,up}$) of the influent total PSS COD (S_{ti}), the biodegradable particulate COD (S_{bpi}) concentration in the influent is defined. The unbiodegradable soluble COD (S_{usi}) concentration forms part of the total soluble COD. Since the S_{usi} concentration is very low in relation to the S_{bsi} , it can be given an approximate value based on previous research. Usually S_{usi} is about 75 mgCOD/L in PSS. With the above, the influent PSS COD can be fully characterised (Figure 7.2). Knowing S_{usi} and S_{bsai} , the fermentable readily biodegradable soluble COD (F-RBCOD, S_{bsfi}) concentration can be quantified. The S_{bsfi} also undergoes the same hydrolysis/acidogenesis processes as the S_{bpi} and are both converted to VFA which then get utilised in BSR to generate hydrogen sulphide (H_2S/HS^-), bicarbonate (HCO_3^-), NH_4^+ and biomass.

In contrast, the influent VFA (S_{bsai}) is not included in the hydrolysis process but it does generate H_2S and HCO_3^- with no biomass production. So, S_{bsai} is included in the stoichiometry part of the steady state model. The zero sludge production for the utilisation of influent VFA is accepted in the SS model because the yield of acetoclastic sulphidogens is very low compared with that of the acetogens.

Ristow *et al.* (2005) concluded that the rate of PSS hydrolysis is the same under both methanogenic and sulphidogenic conditions. Since BSR does not affect the rate of PSS hydrolysis, the same hydrolysis kinetics (rate formulations and rate constants) for methanogenic AD can be applied to sulphidogenic AD conditions.

As outlined by Sötemann *et al.* (2005b), the acidogens have the highest yield coefficient ($Y_{AD} = 0.089$ gCOD biomass/gCOD organics hydrolysed) and constitute more than 77% of the total biomass formed. By increasing the Y_{AD} value from 0.089 to 0.113, the biomass formation of the other organism groups is taken into account. This adjustment in the Y_{AD} value resulted in similar % COD removal predictions and so was accepted. The SS model

for BSR derived here also uses the COD to quantify the organics and biomass concentrations and the saturation equation for the hydrolysis/acidogenesis rate.

The steady state anaerobic digester equations for the hydrolysis part of the SS BSR model applied to the UASB system (Fig. 7.1) were derived and are listed below.

- (i) Hydrolysis rate equation – saturation (Contois) kinetics:

$$r_h \text{ [gCOD/(L.d)]} = \frac{K_M (S_{bp} / Z_{AD})}{[K_S + (S_{bp} / Z_{AD})]} Z_{AD} \quad (7.1)$$

- (ii) Residual biodegradable organics concentration in reactor and waste flow:

$$S_{bp} \text{ (gCOD / L)} = \frac{S_{bpi} R_s / R_h}{\left\{ 1 + \frac{[Y_{AD} K_M - (1/R_s + b_{AD})][1 + b_{AD} R_s (1 - Y_{AD} (1 - f_{AD}))]}{Y_{AD} K_S (1/R_s + b_{AD})} \right\}} \quad (7.2)$$

- (iii) Acidogen biomass concentration in reactor and waste flow:

$$Z_{BAD} \text{ (gCOD/L)} = \frac{Y_{AD} (S_{bpi} R_s / R_h - S_{bp})}{[1 + b_{AD} R_s (1 - Y_{AD} (1 - f_{AD}))]} \quad (7.3)$$

- (iv) Unbiodegradable organics concentration in reactor and waste flow, $S_{up} = S_{upi} R_s / R_h$ (7.4)

- (v) The acidogen endogenous residue concentration:

$$Z_{EAD} \text{ (gCOD/L)} = f_{AD} b_{AD} R_s Z_{BAD} \quad (7.5)$$

where:

K_M = the saturation maximum specific hydrolysis rate constant = 5.27 gCOD organics/(gCOD biomass.d) at 35 °C.

K_S = the half saturation coefficient = 7.98 gCOD organics/gCOD biomass at 35 °C.

Y_{AD} = pseudo acidogen yield coefficient = 0.113 gCOD biomass/gCOD organics hydrolysed.

b_{AD} = acidogen endogenous respiration rate (/d).

R_s = sludge age (d).

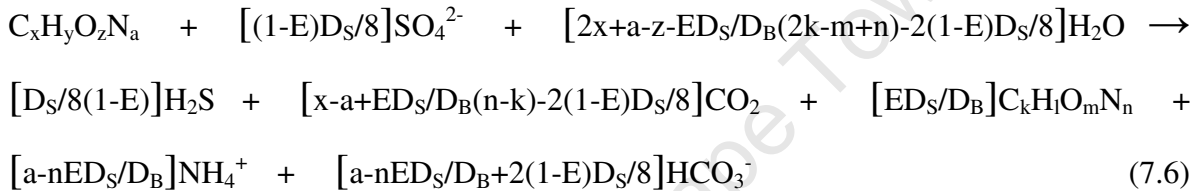
R_h = bed hydraulic retention time (d).

f_{AD} = endogenous residue of acidogens

From the hydrolysis kinetics, the COD concentration of the biodegradable particulate organics utilised in the BSR AD ($S_{bpi} R_s/R_h - S_{bp}$) is known. Following the hydrolysis process, the stoichiometry of BSR needs to be established taking into account the utilisation of the influent volatile fatty acids (VFA, undissociated and dissociated) which also affect alkalinity generation and hence digester pH.

7.2.4.2 Stoichiometry of BSR

The general stoichiometry of BSR with a biodegradable organic compound of composition $C_xH_yO_zN_a$ and generating sludge mass of composition $C_kH_lO_mN_n$ and CO_2 gas (i.e. C sufficiency) is given by:



where

$$D_S = 4x + y - 2z - 3a = \text{electrons per mole biodegradable organics } C_xH_yO_zN_a \quad (7.7a)$$

$$D_B = 4k + l - 2m - 3n = \text{electrons per mole biomass } C_kH_lO_mN_n \quad (7.7b)$$

$$M_S = \text{molar mass of organics } 12x+y+16z+14a \text{ g/mol} \quad (7.7c)$$

$$M_B = \text{molar mass of biomass } 12k+l+16m+14n \text{ g/mol} \quad (7.7d)$$

E = the mass of COD exiting the digester as active (Z_{BAD}) and endogenous (Z_{EAD}) sludge mass per day as a fraction of the mass of biodegradable organics (COD) utilized in the digester per day at steady state (note the unbiodegradable sludge mass is not included because it does not originate from the influent biodegradable organics), i.e. from the COD based kinetic model:

$$E = V_d(Z_{BAD} + Z_{EAD})/[Q_w(S_{bi} R_s/R_h - S_{be})R_s] = \\ Y_{AD}(1+f_{AD}b_{AD}R_s)/[1+b_{AD}R_s(1-Y_{AD}\{1-f_{AD}\})] \quad (7.8) \\ (\text{sludge COD produced/COD utilised})$$

where

Z_{BAD}, Z_{EAD} = COD concentration of the anaerobic biomass and endogenous residue respectively (mgCOD/L).

V_d	=	Volume of the digester (L) = UASB Sludge bed volume (L)
Q_i	=	Influent flow to digester (L/d)
Q_w	=	Bed waste flow from the digester (L/d)
S_{bi}, S_{be}	=	Influent and waste flow (bed) COD concentration to and from digester (mgCOD/L)
R_s	=	Sludge age of digester (d)
Y_{AD}	=	Yield coefficient of anaerobic biomass (mgCOD biomass/mgCOD utilised)
	=	0.113
b_{AD}	=	Endogenous respiration rate of anaerobic biomass (mgCOD/mgCOD/d)
	=	0.041
f_{AD}	=	Endogenous residue fraction = 0

From D_S and D_B , the COD of the biodegradable organics and sludge mass (accepting the live biomass and endogenous residue have the same composition) is $8D_S$ and $8D_B$ gCOD/mol respectively. Also, from known values of the COD/VSS (f_{cv}), TOC/VSS (f_c) and OrgN/VSS (f_n) ratios, the composition of the biodegradable organics (x, y, z and a) can be calculated from Eq(7.9), which also apply to the biomass (k, l, m and n).

$$y = 7 \quad (7.9a); \quad z = y/2[(1-f_{cv}/8-8f_c/12-17f_n/14)/(1+f_{cv}-44f_c/12+10f_n/14)] \quad (7.9b);$$

$$x = f_c/12[(y+16z)/(1-f_c-f_n)] \quad (7.9c); \quad a = f_n/14[(y+16z)/(1-f_c-f_n)] \quad (7.9d) \quad (7.9)$$

Alternatively, if the composition of the biodegradable influent organics (x, y, z, a) and biomass (k, l, m, n) are known, the COD/VSS (f_{cv}), TOC/VSS (f_c) and OrgN/VSS (f_n) ratios of the influent organics and biomass can be calculated from Eq(7.10).

$$\begin{aligned} f_{cv} &= 8[4x+y-2z-3a]/[12x+y+16z+14a]; & f_c &= [12x]/[12x+y+16z+14a]; \\ f_n &= [14a]/[12x+y+16z+14a] \end{aligned} \quad (7.10)$$

The influent VFA is assumed to be acetate. The split between the undissociated and dissociated acetate (HAc and Ac^- respectively) species is governed by the influent pH and since the influent pH was always greater than 5.9, almost all the influent VFA was in the acetate (Ac^-) species (Figure 7.3).

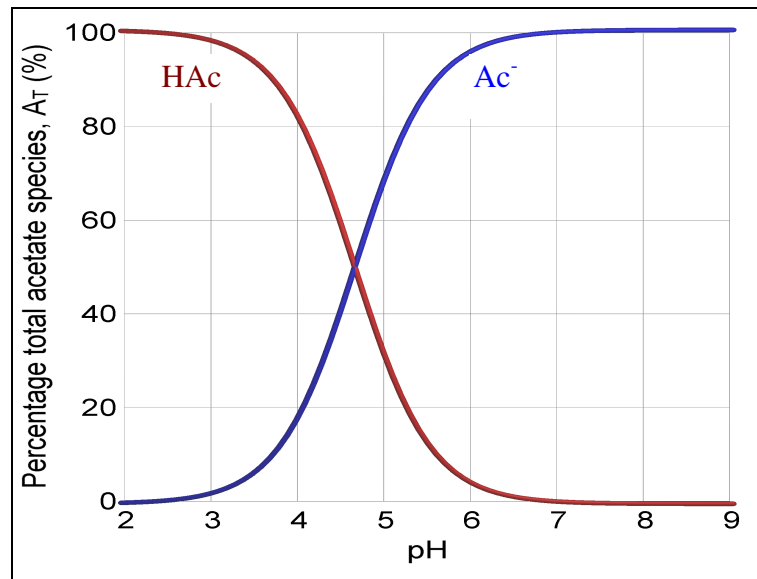
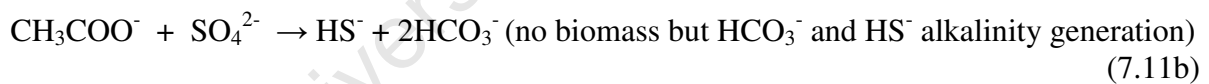
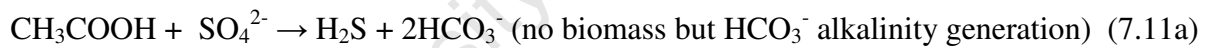


Figure 7.3: Percentage (%) of undissociated and dissociated acetate species versus pH.

Eq(7.6) holds also for acetate, both associated (HAc) and undissociated (Ac⁻) provided the correct composition $x(=2)$, $y(=4$ for HAc, $=3$ Ac⁻), $z(=2)$ and charge ($=0$ for HAc, $=-1$ for Ac⁻) are inserted. Because the yield of sulphidogens is very low, $E=0$ when applying Eq(7.6) to acetate, which yields,



From Eqs(7.11a & 7.11b), it can be seen that the influent VFA (both undissociated and dissociated) concentration is important for establishing the digester pH because its utilisation makes a significant contribution to the alkalinity generated.

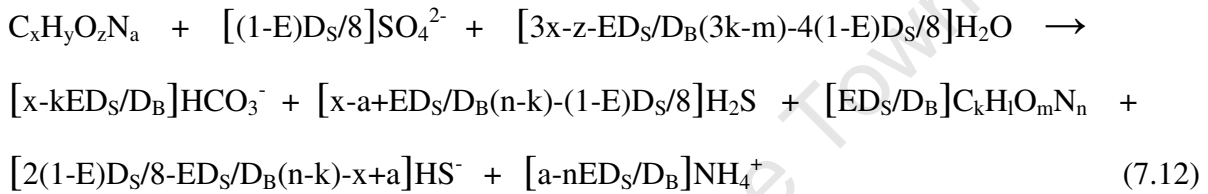
Eq(7.6) is valid for organics that generate sufficient CO₂ for the required alkalinity increase. This will be the case if the CO₂ term in Eq(7.6) is positive, i.e.

$$x-a + ED_S/D_B(n-k) - 2(1-E) D_S/8 > 0$$

Accepting zero biomass production ($E=0$) and substituting $4x+y-2z-3a$ for D_S yields $2z > y+a$. So organics with a composition that conforms to $2z > y+a$ are carbon sufficient.

Most organics do not conform to this, e.g. the amino acids, alcohols, all of the fatty acids except formic and acetic acids, and PSS. The mono-, di- and polysaccharides and acetic acid conform exactly, i.e. $2z=y$ for $a=0$, but with biomass growth ($E>0$) they become carbon deficient also. The COD/C ratio of these organics is 2.67, so organics with a COD/C ratio >2.67 are C deficient for BSR in the sense that they can donate more electrons for BSR than supply CO_2 for the alkalinity increase.

So for most organics, the gaseous CO_2 term in Eq(7.6) is negative. In this event the sulphide system produces the alkalinity shortfall in the form of HS^- . Re-arranging Eq(7.6) for C deficiency becomes:



The PSS with its determined composition from this investigation (see below) of $\text{C}_{3.35}\text{H}_7\text{O}_{1.45}\text{N}_{0.45}$ is C deficient.

7.2.4.3 Mixed weak acid/base chemistry

Once the products are known from the stoichiometry above, the digester pH is predicted using the weak acid/base chemistry. For C deficient systems, the $\text{H}_2\text{S}/\text{HS}^-$ system establishes the pH because a gaseous CO_2 phase is absent, namely:

$$[\text{H}^+] = K_s[\text{H}_2\text{S}]/[\text{HS}^-] \quad (7.13a)$$

$$\text{pH} = -\log(K'_s[\text{H}_2\text{S}]/[\text{HS}^-]) \quad (7.13b)$$

$$\text{where } K'_s = 10^{(-\text{pK}'_s)} \text{ calculated from } \text{pK}_s \text{ and } \text{pK}'_s \quad (7.13c)$$

$$\text{pK}_s = \text{equilibrium constant for } \text{H}_2\text{S}/\text{HS}^- \text{ system} = 7.05 \text{ at } 25^\circ\text{C} \text{ (Lide, 2001)}$$

$$\text{pK}'_s = \text{pK}_s \text{ adjusted for temperature and ionic strength}$$

$$= 6.833 \text{ at } 35^\circ\text{C} \text{ and } 7.014 \text{ at } 20^\circ\text{C}.$$

7.2.5 STEADY STATE BSR MODEL VALIDATION

Figure 7.4 illustrates the characterisation of the different components of the influent (PSS) and the waste sludge (WS) and determination their respective compositions. The superscripts 1 to 4 marked in the Figure are described below.

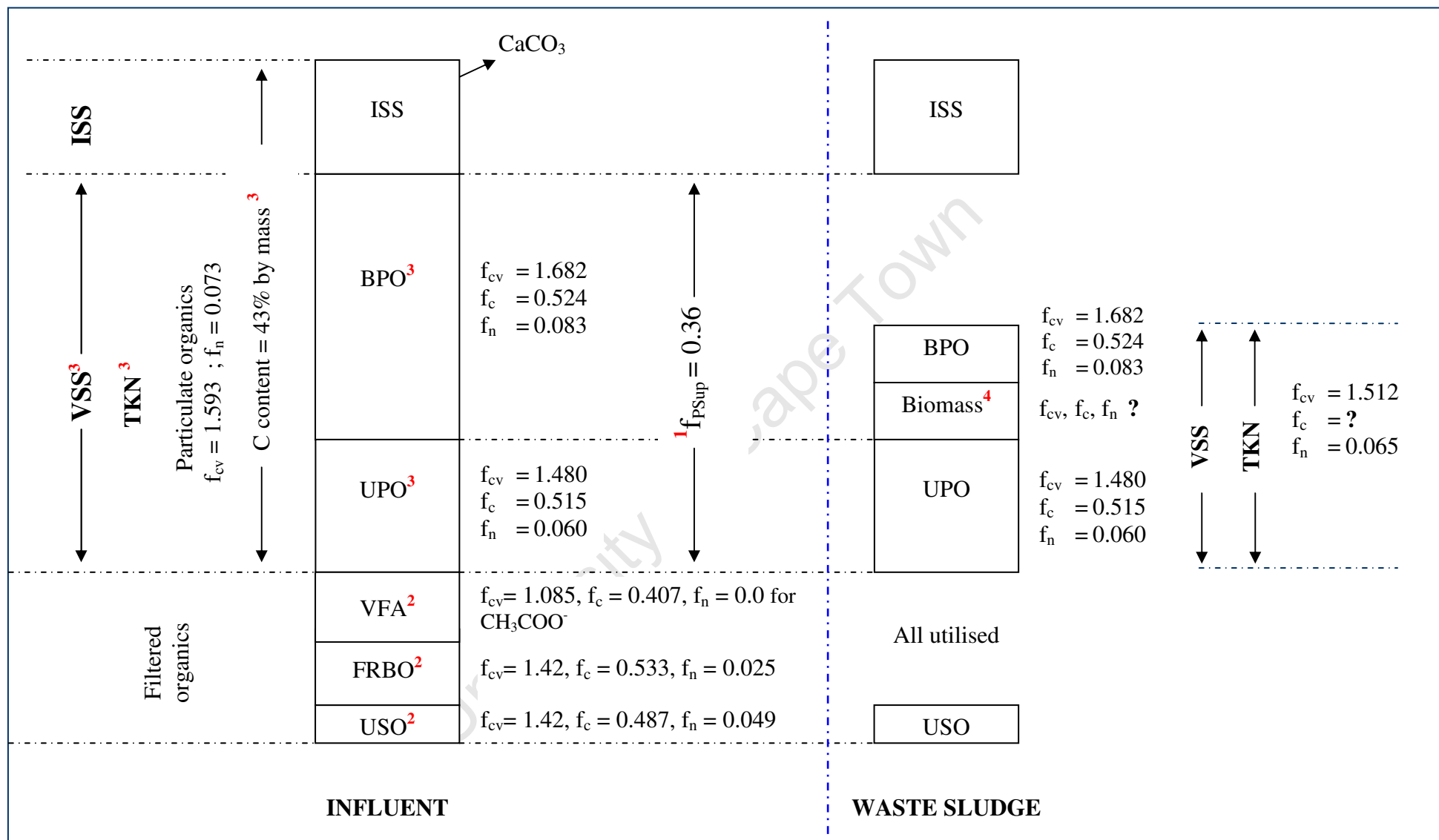
7.2.5.1 Characterisation of primary sewage sludge (PSS)

(i) Unbiodegradable particulate COD fraction (Figure 7.4; Note 1):

In this study, the unbiodegradable particulate fraction (f_{PSup}) of the PSS was set at 0.36. Ristow *et al.* (2005) and Sötemann *et al.* (2005b) conducted studies on the anaerobic digestion of PSS at different retention times (sludge ages) between 5 and 60 days and so were able to determine the f_{PSup} value of the PSS. They found that the f_{PSup} varied from 0.335 to 0.36. However, the f_{PSup} is a function of the characteristics of the PSS and varies depending on the type and nature of the wastewater. The PSS used in this study contained a significant proportion of industrial wastewater (~ 30%) of unknown unbiodegradable particulate organics concentration. Because running UASB systems at different sludge ages was beyond the scope of this investigation, the f_{PSup} value from previous studies was accepted. Accordingly, an f_{PSup} value of 0.36 was used in both the steady state (SS) BSR and kinetic simulation (UCTADM1-BSR) models developed in this study.

(ii) Dissolved organic compounds (Figure 7.4; Note 2):

The concentration of the unbiodegradable soluble organics (USO) of the PSS was assumed to be 75 mgCOD/L which is very low with respect to the total PSS COD (~ 50,000 mgCOD/L). The volatile fatty acids (VFA) concentration was measured using the 5-pH point titration method and the unit mgHAc/L converted to mgCOD/L. The concentration of the total soluble organic comprising the USO, VFA and fermentable readily biodegradable organics (FRBO) was measured in the COD test. Thus, by difference the FRBO concentration was calculated. The compositions of the USO and FRBO were determined using f_{cv} , f_{c} and f_{n} values of 1.42, 0.487, 0.049 and 1.42, 0.470, 0.022 respectively, taken from Brink *et al.* (2007), while the actual composition ($\text{C}_2\text{H}_4\text{O}_2$ for HAc and $\text{C}_2\text{H}_3\text{O}_2$ for Ac^-) for the VFA was used.



Superscripts 1 to 4 are described in the text.

Figure 7.4: Characterisation of primary sewage sludge (influent) and waste sludge in the development of the steady state model.

(iii) Biodegradable particulate organics composition (Figure 7.4; Note 3):

To determine the composition of the biodegradable particulate organics $C_xH_yO_zN_a$ of the PSS, 4 measurements are required, COD, TKN, VSS and total organic carbon (TOC) because there are 4 unknowns, namely x, y, z and a. The COD, TKN and VSS of the PSS particulate organics (comprising the unbiodegradable particulate organics (UPO) and biodegradable particulate organics (BPO)) were determined in the COD test, whereas the TOC was obtained from elemental analysis of dried PSS. The TOC of the influent PSS was found to be ~ 43% of the total suspended solids (TSS). From this, the TOC/VSS ratio (f_c) was calculated (see Appendix 7A).

With the accepted $f_{PSup} = 0.36$, the UPO concentration was calculated and its composition, i.e. x, y, z and a in $C_xH_yO_zN_a$ was determined from f_{cv} , f_c and f_n values of 1.480, 0.515 and 0.0597 respectively, taken from Wentzel *et al.* (2006). A composition of $C_{4.26}H_7O_{2.2}N_{0.42}$ was obtained for UPO. By fractionating the particulate COD concentrations of the PSS using the UPO f_{cv} , f_c and f_n values of 1.480, 0.515 and 0.0597 respectively, the biodegradable particulate organics (BPO) of the PSS was found by mass balance (and by difference) between the total (UPO + BPO) and unbiodegradable (UPO); f_{cv} , f_c and f_n values of 1.682, 0.524, 0.083 respectively were obtained. Accordingly, from these values, the composition of the biodegradable particulate organics of the PSS calculated from Eq(7.4) was found to be $C_{3.35}H_7O_{1.45}N_{0.45}$.

7.2.5.2 Characterisation of waste sludge (WS)

(i) WS concentration and composition (Figure 7.4; Note 4)

To characterise the waste sludge (WS), the same principle as above was applied except that the WS comprised (i) S_{upi} (or UPO) with known concentration (Eq.7.4) and the same composition as the influent UPO, (ii) residual biodegradable organics (BPO or S_{bpi}) with concentration calculated from the hydrolysis kinetic model (Eq.7.2) and the same composition as the influent S_{bpi} , and (iii) biomass with concentration also calculated from the hydrolysis kinetic model (Eq.7.3) but with an unknown composition (endogenous residue concentration is zero, $f_{AD} = 0$). The kinetic model saturation rate values were taken from Sötemann *et al.* (2005a) with K_M (the maximum specific hydrolysis rate constant) = 5.27 gCOD organics/(gCOD biomass.d) and K_S (the half saturation coefficient) = 7.98

gCOD organics/gCOD biomass, both at $T = 35\text{ }^{\circ}\text{C}$. The FRBO and VFA concentrations combined were very low ($< 0.8\%$) with respect to that of the total WS and were thus considered all utilised and therefore zero in the waste sludge.

To determine the biomass composition, 4 measurements are again required (COD, TKN, VSS and TOC). However, in using the TOC value determined from elemental analysis of the WS, it was found that the biomass composition was far out of the normal range obtained from previous studies, in that the oxygen composition (m) in the biomass generic formulation of $\text{C}_k\text{H}_l\text{O}_m\text{N}_n$ was < 1.2 (see Appendix 7A). This value was considered too low (possibly because some of the C (2-3%) was part of the inorganic suspended solids (ISS) as carbonates, see Appendix 7A) and so it was decided not to use the results from the elemental analysis of the waste sludge for determining the biomass composition. Accordingly, the composition of the biomass was obtained from the measured WS COD/VSS and TKN/VSS ratios and an assumed value for $m = 2$ on the biomass composition. This assumption makes a small difference to the overall WS composition because the biomass is only a small proportion ($< 8\%$, Table 7.1).

Adding the concentrations of all the 3 above waste organic constituents (residual S_{bp} , S_{upi} and biomass) gives the total particulate COD concentration of the waste sludge (and reactor sludge bed). The calculated waste total particulate COD concentration was found to be very close to the measured value (Table 7.1) which is significant because the biomass concentration is a very small part ($< 10\%$) and indicates the hydrolysis kinetic constants and unbiodegradable particulate COD fraction selected apply to the UASB systems.

Table 7.1: Comparisons between calculated waste particulate COD constituents against measured values.

	Waste sludge constituents	UASB R1 (1500 $\text{mgSO}_4^{2-}/\text{L}$) at $35\text{ }^{\circ}\text{C}$	UASB R1 (1800 $\text{mgSO}_4^{2-}/\text{L}$) at $35\text{ }^{\circ}\text{C}$	UASB R2 (1500 $\text{mgSO}_4^{2-}/\text{L}$) at $20\text{ }^{\circ}\text{C}$
Calculated from kinetics and stoichiometry	Sup (gCOD/L)	20.7	24.1	20.8
	Sbp residual (gCOD/L)	3.3	3.0	16.0
	Biomass (gCOD/L)	2.2	2.1	1.6
	Total (gCOD/L)	26.2	29.2	38.3
Measured	Total (gCOD/L)	26.1	30.3	37.9

Knowing the COD concentrations of the S_{upi} and residual S_{bp} in the WS, their VSS concentrations were calculated from their f_{cv} values of 1.48 and 1.682 respectively (as determined for the influent). The only f_{cv} ratio missing to obtain the overall (combined) f_{cv} of the total particulate organics in the WS is that of the biomass. For instance, in the case of R1 at $1500 \text{ mgSO}_4^{2-}/\text{L}$, the measured waste total particulate COD/VSS (f_{cv}) and TKN/VSS (f_{n}) ratios were 1.512 and 0.065 respectively. To match these measured values, the f_{cv} of the biomass was found by iteration so that the combined f_{cv} and f_{n} equalled to 1.52 and 0.065. This yielded a biomass f_{cv} of 1.599. Now, from this f_{cv} of 1.599, the k and n values for $l=7$ and $m=2$ on the $\text{C}_k\text{H}_l\text{O}_m\text{N}_n$ biomass composition were also determined by iteration and were found to be 5 and 0.55 giving a biomass composition of $\text{C}_5\text{H}_7\text{O}_2\text{N}_{0.55}$, identical to the $\text{C}_5\text{H}_7\text{O}_2\text{N}_1$ accepted by Sötemann *et al.* (2005a) in the UCTADM1 model except for the N content. This biomass composition gives TKN/VSS (f_{n}) ratio of 0.072 mgN/mgVSS compared with 0.124 mgN/mgVSS for $\text{C}_5\text{H}_7\text{O}_2\text{N}_1$. A different biomass N content is expected because Sötemann *et al.* assumed the $\text{C}_5\text{H}_7\text{O}_2\text{N}_1$ composition from the commonly accepted value for activated sludge. From the residual S_{bp} , S_{upi} and biomass individual COD concentrations in the WS and their respective f_{n} ratios, the combined f_{n} ratio of the WS was calculated and found to be 0.063 mgN/mgVSS, very close to the measured value of 0.065 mgN/mgVSS as expected and therefore the $\text{C}_5\text{H}_7\text{O}_2\text{N}_{0.55}$ was accepted here. The same principle was applied for UASB R1 fed $1800 \text{ mgSO}_4^{2-}/\text{L}$ and UASB R2 (20 °C) fed $1500 \text{ mgSO}_4^{2-}/\text{L}$. It was found that using the biomass composition of $\text{C}_5\text{H}_7\text{O}_2\text{N}_{0.55}$ and biomass f_{cv} ratio of 1.599, the calculated waste sludge f_{cv} and f_{n} matched closely the measured waste sludge f_{cv} and f_{n} values of both systems.

As stated above, the saturation (Contois) hydrolysis rate equation and its associated kinetic constants were used in the steady state model (and in the dynamic simulation model, UCTADM1-BSR, see later). At 35 °C, the saturation maximum specific hydrolysis rate $K_{\text{M}} = 5.27 \text{ gCOD organics}/(\text{gCOD biomass.d})$ and the half saturation coefficient $K_{\text{S}} = 7.98 \text{ gCOD organics/gCOD biomass}$. For UASB reactor R2 operated at 20 °C, both K_{M} and K_{S} were adjusted for temperature dependency in the steady state model application. The temperature function $\frac{K_2}{K_1} = \theta^{(T_2 - T_1)}$ was used where here K_1 and K_2 are the maximum specific hydrolysis rate constants at $T_1 = 35 \text{ °C}$ and $T_2 = 20 \text{ °C}$ respectively and $\Theta=1.133$. $K_{\text{M}20}$ was found to be $0.808 \text{ gCOD organics}/(\text{gCOD biomass.d})$ and $K_{\text{S}} = 1.223 \text{ gCOD organics/gCOD biomass}$.

7.2.5.3 SS BSR model application

Once developed and calibrated, the SS BSR model was validated by applying it to the UASB systems operated in this study. Table 7.2 compares the SS BSR predicted results with the experimental data from the 2 lab-scale UASB reactors.

Table 7.2: Comparison of experimentally measured (M) values with SS BSR model predictions (P).

Parameter	R1 (35 °C) (1500mgSO ₄ ²⁻ /L)		R1 (35 °C) (1800mgSO ₄ ²⁻ /L)		R2 (20 °C) ⁴ (1500mgSO ₄ ²⁻ /L)	
Influent total COD (mgCOD/L)	1880		2584		2596	
Influent unbiodegradable particulate COD ¹ (f _{up} = 0.36) (mgCOD/L)	677		930		935	
Influent SCFA (mgCOD/L)	126		164		169	
Influent fermentable readily biodegradable COD (mgCOD/L)	104		108		155	
Influent slowly biodegradable COD (mgCOD/L)	967		1375		1330	
Influent unbiodegradable soluble (mgCOD/L)	6		7		8	
Influent TKN/FSA (mgN/L)	79/10		82/11		92/11	
Reactor bed/liquid volume ratio	6.7/7.8		7.1/7.8		7.4/7.8	
Influent flow rate, Q _i (L/d)	13.8		10.1		9.2	
Sludge age, R _s (d), HRT (d)	18, 0.57		21, 0.77		24, 0.85	
E (sludge COD produced/COD utilised)	0.0680		0.0641		0.0602	
	M	P	M	P	M	P
COD removal (mgCOD/L)	1691	1632	2153	2242	2309	2444
Sulphate removal (mg SO ₄ ²⁻ /L)	1351	1351	1654	1655	1399	1396
Effluent alkalinity (H ₂ CO ₃ * alk + Alk H ₂ S) (mg/L as CaCO ₃)	1938	2063	1855	1974	1558	1672
Effluent H ₂ CO ₃ * alk (mg/L as CaCO ₃)	1611	1627	1358	1441	1144	1234
Effluent H ₂ S (mgS/L) ²	101 ³	173	184	213	166	185
Effluent HS ⁻ (mgS/L) ²	209 ³	277	318	339	261	280
Effluent TKN (mgN/L)	52	55	58	65	63	74
FSA	32	50	46	60	38	48
Mass balances (%) - COD	88.7 ³	100	96.5	100	96.1	100
- S	68.7 ³	100	95.8	100	95.9	100
- N	97.1	100	97.3	100	104.5	100
- C	98.4	100	94.0	100	90.3	100
Effluent pH	7.15	7.05	7.08	7.04	7.21	7.20

- 1: f_{cv} , f_c , f_n of unbiodegradable PSS and waste sludge particulate organics=1.480, 0.515, 0.0597 respectively.
- 2: Effluent H₂S/HS⁻ determined via filtered COD test before and after ZnS precipitation.
- 3: Loss of H₂S in analytical procedures particularly during vacuum filtration. Speciation of HS⁻/H₂S is based on pH 7.6 and total sulphide 310mgS/L after vacuum filtration. Procedure was corrected by vacuum filtering at pH≥10 which fixed the S-balance to approximately 100% (Refer to Chapter 5).
- 4: K_M and K_S were adjusted for temperature. K_{M20} =0.808 and K_{S20} =1.223 with Θ =1.133.

From Table 7.2 above, overall the SS model predictions correspond well with the measured data for all three systems. The COD removal is lower for the measured data because the UASB effluent contains some particulate COD (since the effluent is not 100% soluble COD) while in the steady state model this is assumed zero. The predicted digester pH values for R1 (1800 mgSO₄²⁻/L) and R2 correspond very well to the measured values, while for R1 (at 1500 mgSO₄²⁻/L) it is 0.1 pH unit lower. Though not significant, this pH difference may be ascribed to either minor experimental error in pH measurements or to the composition of the primary sludge. The composition of the biodegradable influent organics C_xH_yO_zN_a is calculated from the influent PSS characterisation using the stoichiometric equations and is found to be C_{3.35}H₇O_{1.45}N_{0.45} which differs slightly from that found in previous studies on PSS (C_{3.5}H₇O₂N_{0.196} from Izzet *et al.*, 1992 and C_{3.65}H₇O_{1.97}N_{0.190} from Sötemann *et al.*, 2005b). In fact, with C deficient substrates as the BSR UASB systems were, it is possible to calculate the C released from the utilised biodegradable substrate from the C content of the HCO₃⁻ concentration, which is known from the H₂CO₃* alkalinity, because no CO₂ gas is generated by the system (Eq7.11) and the C in the biomass generated is small. For R1 (1500 mgSO₄²⁻/L), R1 (1800 mgSO₄²⁻/L) and R2, the C released in the utilisation of BPO, VFA and FRBO was 283, 347 and 296 mgC/L respectively and the C in the H₂CO₃ alk. measured was 279, 326 and 267 mgC/L respectively. This validates the C content of the biodegradable organics and the C balance over the systems.

In addition, the good correlation between the measured and steady state results suggests that the assumption of completely mixed digester for the UASB reactor bed is valid and reasonable. This was made possible because of the introduction of the sludge recycle line from the top to the bottom of the reactor.

7.3 KINETIC MODEL FOR BSR WITH PSS AS SUBSTRATE (UCTADM1-BSR)

7.3.1 INTRODUCTION

In parallel to this present research work, van Wageningen (2007) undertook as the main aim of her Masters research, the task of developing a kinetic model for BSR (UCTADM1-BSR) using PSS as energy source. In reviewing UCTADM1-BSR model, a few errors have been encountered in the development of the stoichiometric equations. In this section of this Chapter, the UCTADM1-BSR kinetic model will be reviewed in detail and the necessary corrections and adjustments made. Some of the adjustments will involve: - (i) changing the unstable linear hydrogen sulphide inhibition function to a more stable one, and (ii) the inclusion of a temperature function to simulate the effect of temperature on PSS hydrolysis/acidification and BSR processes. Thereafter, the model will be verified, calibrated and validated by modelling the UASB BSR systems operated in this investigation and the simulated results compared with the measured and steady state results.

As stated in Chapter 2, the kinetic model of Sötemann *et al.* (2005a) (UCTADM1) appeared most suitable amongst the existing kinetic models for anaerobic digestion (AD) with PSS and was therefore selected as a basis for the development of the kinetic model for BSR with PSS as substrate. In extending UCTADM1 to incorporate BSR processes, the kinetics and stoichiometry for the biological, chemical and physical processes of BSR in two phases (aqueous-gas) need to be developed. These will then be integrated with UCTADM1 taking due cognisance of any interactions brought up with the integration.

The development of the kinetic model for BSR and its integration into UCTADM1 was conducted in three parts as follows:

Part 1: Development of the biological mediated processes

In these processes, hydrolysis/solubilisation (usually the rate limiting step) of the PSS occurs first followed by acidification, mediated by the acidogenic organisms group, in common with sewage sludge methanogenic AD systems. The products of these processes, the Short Chain Fatty Acids (SCFA), hydrogen (H₂) and CO₂, then enter into either the

methanogenic or sulphidogenic (sulphate reduction) processes, which operate in competition (Fig. 7.5). One end product of BSR is sulphide, which is inhibitory to the methanogens, requiring that this inhibition be included in the model development.

Therefore, for the biological part of the model, these processes were identified for inclusion:

- (a) PSS hydrolysis, acidogenesis, acetogenesis and acetoclastic and hydrogenotrophic methanogenesis (UCTADM1)
- (b) BSR with substrates available from the above processes.

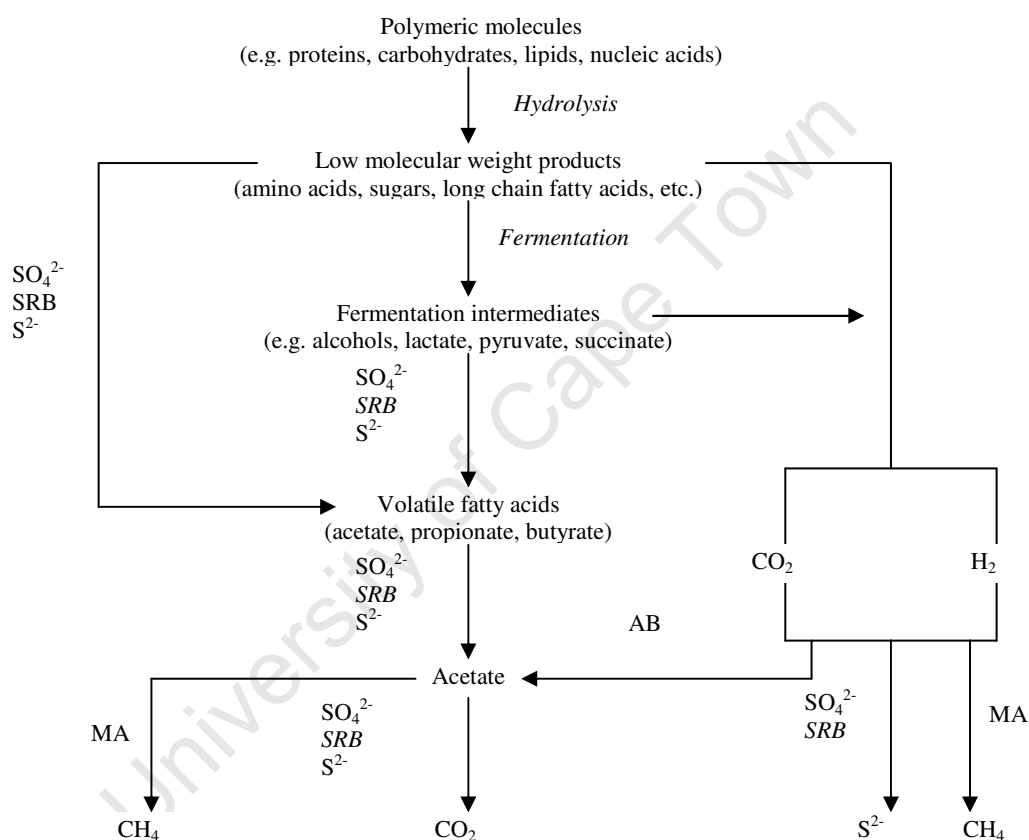


Figure 7.5: Pathways for the anaerobic degradation of organic matter (Gibson, 1990), showing potential interactions between methanogenic and sulphidogenic microorganisms (SRB = sulphate reducing bacteria; MB = methanogenic archaea; AB = acetogenic bacteria)

Part 2: Development and inclusion of the aqueous chemistry and physical processes

- a) *Weak acid/base chemistry:* The biological processes consume and produce significant acid/base species, e.g. SCFA, sulphide and sulphate. The weak acid/base chemistry of these species (subsystems) needed to be incorporated. In addition, the consumption and production of acid/base species will influence the pH established in

the reactor, which in turn can influence the biologically mediated processes. Hence, pH needed to be incorporated directly into the model as a model predicted parameter, and its interaction with the biological processes modelled.

The weak acid/base systems to be included are:

- i) water, acetate, propionate, carbonate, ammonium, phosphate (already included in UCTADM1).
 - ii) weak acid/base systems associated with BSR, i.e. sulphate and sulphide.
- b) *Gas exchange*: Some of the end products have gaseous equilibria (sulphide, carbon dioxide, ammonia and methane), so these physical processes also required inclusion (the third (solid) phase was not included at this stage).

The following gas exchange processes were included:

- i) carbon dioxide, ammonia, (UCTADM1): methane produced directly to the gas phase, and hydrogen remains dissolved in solution (UCTADM1). As shown from the BSR stoichiometry in Section 7.2 (Eq7.6), the PSS and the SCFA acids for carbon (x) >2 , are carbon deficient for BSR in that these organics do not contain sufficient C to supply all the required alkalinity as HCO_3^- . This results in zero CO_2 gas production and affects the relative $\text{HS}^-/\text{H}_2\text{S}$ concentrations (Eq7.12), which establishes a higher digester pH than without C deficiency.
- ii) hydrogen sulphide (H_2S) gas produced in BSR.

Part 3: Integration of the aqueous chemistry and physical processes with the biological processes for BSR with UCTADM1

For integration with UCTADM1, the BSR related processes needed to be formulated in the appropriate mole units.

The development of these 3 parts is described in more detail in the following sections. The end result will essentially be a two phase biological, chemical and physical processes model for the AD of PSS, with competitive methanogenesis and sulphidogenesis.

7.3.2 BIOLOGICAL PROCESSES FOR BSR

The approach of Kalyuzhnyi *et al.* (1998) reviewed in Chapter 2 constituted the basis for the biological processes part of the kinetic model for BSR. These researchers identified 9 trophic groups of microorganisms that convert substrates into products in an anaerobic reaction sequence. These bacterial groups are:

1. Fermentative bacteria	(Sugars $\rightarrow$ Acetate)
2. Butyrate degrading acetogenic bacteria	(Butyrate $\rightarrow$ Acetate)
3. Butyrate degrading SRB	(Butyrate $\rightarrow$ Acetate & H_2S)
4. Propionate degrading acetogenic bacteria	(Propionate $\rightarrow$ Acetate)
5. Propionate degrading SRB	(Propionate $\rightarrow$ Acetate & H_2S)
6. Acetotrophic methanogenic archae	(Acetate $\rightarrow$ Methane & CO_2)
7. Acetotrophic SRB	(Acetate $\rightarrow$ H_2S & CO_2)
8. Hydrogenotrophic methanogenic archae	(H_2 & CO_2 $\rightarrow$ Methane)
9. Hydrogenotrophic SRB	(H_2 $\rightarrow$ H_2S)

Amongst these 9 microorganism groups, only 3 SRB (5, 7 and 9) groups are of particular interest here when integrating BSR with the methanogenic and acetogenic UCTADM1 model which already explicitly incorporates microorganism groups (1), (4), (6) and (7). The butyrate degrading acetogenic (2) and SRB (3) bacterial groups were not included in the model, as butyrate is not usually present in significant concentrations in sewage sludge digestion systems. However, if required these trophic groups and their respective processes can be incorporated. Thus, the process stoichiometry and kinetics for only the 3 SRB groups (5, 7 and 9) were considered for both the organism growth and endogenous decay.

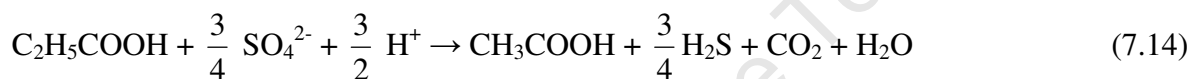
7.3.2.1 Stoichiometry of the growth process

The procedure of Sötemann *et al.* (2005a) in UCTADM1 was followed where the stoichiometry for the growth bioprocesses were determined by adding the catabolic and anabolic stoichiometry, linked via the yield coefficient of each SRB group. The development of this growth process stoichiometry for each of these 3 SRB bacterial groups is described below. UCTADM1 has embedded in it a biomass composition of $C_5H_7O_2N_1$ and the whole development of the stoichiometry of both the growth and endogenous respiration processes of the organisms will be based and programmed on this biomass

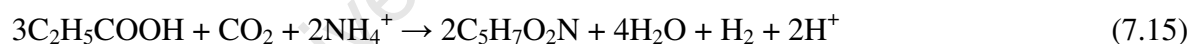
composition. Because this biomass composition is so close to the one calculated from the experimental data for the steady state model, ($C_5H_7O_2N_{0.55}$), it was decided not to change the stoichiometry equations in the dynamic model as this would have been a very extensive exercise. More importantly, small differences in biomass composition have negligible influence on the predicted results because the sulphidogenic (and methanogenic) biomass yields are so low and therefore the dynamic model is expected to give closely similar results as the steady state model.

Acetogenic sulphidogenesis (by propionate SRB)

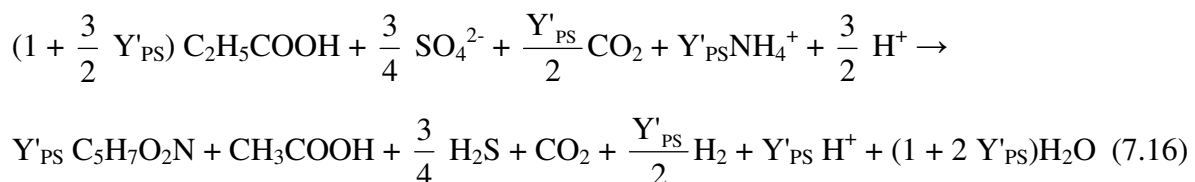
The reaction sequence for the substrate utilisation of propionate by the propionate degrading SRB (Z_{PS}) as reported by Kalyuzhnyi *et al.* (1998) is as follows:



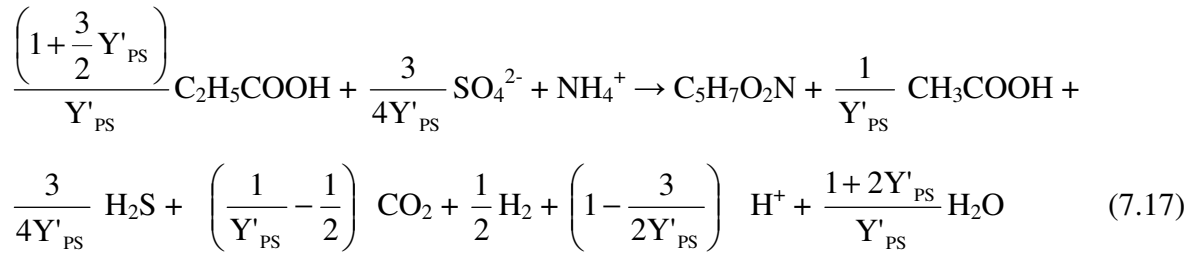
The anabolic growth process of Z_{PS} was accepted to be identical to that of the Acetogenic biomass group in the UCTADM1 model (since both use propionate as substrate). The organism stoichiometric composition of $C_5H_7O_2N$ for the Acetogenic (and hence propionate degrading bacteria group) follows the anabolic growth process below (Söttemann *et al.*, 2005a).



Multiplying Eq(7.15) by the anabolic organism yield (Y'_{PS}), dividing it by 2 to form 1 mole of biomass, and adding the associated Eq(7.14) gives:



Dividing Eq(7.16) by Y'_{PS} and simplifying yields for 1 mole of acetogens biomass formation:



The stoichiometry in terms of the anabolic organism yield Y'_{PS} for the growth process of the propionate degrading SRB is taken directly from Eq(7.17) and is listed in Table 7.3.

Table 7.3: Stoichiometry for propionate degrading SRB in terms of the anabolic organism yield (Y'_{PS}).

HPr mol	SO_4^{2-} mol	CO_2 mol	NH_4^+ mol	Z_{PS} mol	HAc mol	H_2S mol	H_2 mol	H^+ mol	H_2O mol
$-\left(\frac{1+\frac{3}{2}Y'_{PS}}{Y'_{PS}}\right)$	$-\left(\frac{3}{4Y'_{PS}}\right)$	$\left(\frac{1}{Y'_{PS}} - \frac{1}{2}\right)$	-1	1	$\frac{1}{Y'_{PS}}$	$\frac{3}{4Y'_{PS}}$	$\frac{1}{2}$	$\left(1 - \frac{3}{2Y'_{PS}}\right)$	$\frac{1+2Y'_{PS}}{Y'_{PS}}$

To represent the ratio of biomass formed per unit total substrate (in this case propionate) consumed, the anabolic yield (Y'_{PS}) is changed to the metabolic (anabolic + catabolic) yield (Y_{PS}) which is the usual way of expressing yield. The metabolic yield (Y_{PS}) is obtained from Eq(7.17).

From the stoichiometry (Table 7.3):

1 mole biomass (160 gCOD) is grown from $\frac{1+\frac{3}{2}Y'_{PS}}{Y'_{PS}}$ moles propionate. Expressing the metabolic (or true) yield Y_{PS} (mol/mol) in terms of Y'_{PS} gives:

$$Y_{PS} = \frac{Y'_{PS}}{\left(1 + \frac{3}{2} Y'_{PS}\right)} \quad (7.18)$$

Formulating Y'_{PS} the subject of Eq(7.18):

$$Y'_{PS} = \frac{Y_{PS}}{\left(1 - \frac{3}{2} Y_{PS}\right)} \quad (7.19)$$

Re-writing the stoichiometric terms in Table 7.3 by substituting Eq(7.19) for Y'_{PS} and accepting that $CO_2 + H_2O \rightarrow H_2CO_3^*$ gives the stoichiometry for propionate utilising SRB in terms of the true (metabolic) organism yield as shown in Table 7.4.

Table 7.4: Stoichiometry for propionate degrading SRB in terms of the true organism yield, Y_{PS} .

HPr mol	SO_4^{2-} mol	$H_2CO_3^*$ mol	NH_4^+ mol	Z_{PS} mol	HAc mol	H_2S mol	H_2 mol	H^+ mol	H_2O mol
$-\left(\frac{1}{Y_{PS}}\right)$	$-\left(\frac{3}{4Y_{PS}} - \frac{9}{8}\right)$	$\frac{1}{Y_{PS}} - 2$	-1	1	$\frac{1}{Y_{PS}} - \frac{3}{2}$	$\frac{3}{4Y_{PS}} - \frac{9}{8}$	$\frac{1}{2}$	$\frac{13}{4} - \frac{3}{2Y_{PS}}$	$\frac{5}{2}$

(2) Acetoclastic sulphidogenesis (by acetotrophic SRB)

The same method described above for the propionate degrading SRB is used for developing the stoichiometry for the growth acetotrophic SRB (Z_{AS}) based on the reaction sequence for the catabolic substrate (acetate) utilisation is taken from Kalyuzhnyi *et al.* (1998), i.e.



The stoichiometry for acetotrophic SRB in terms of the true (metabolic) organism yield as given in Table 7.5.

Table 7.5: Stoichiometry for acetotrophic SRB in terms of the true organism yield, Y_{AS} .

HAc mol	SO_4^{2-} mol	NH_4^+ mol	Z_{AS} mol	H_2S mol	$H_2CO_3^*$ mol	H^+ mol	H_2O mol
$-\left(\frac{1}{Y_{AS}}\right)$	$-\left(\frac{1 - \frac{5}{2}Y_{AS}}{Y_{AS}}\right)$	-1	+1	$\frac{\left(1 - \frac{5}{2}Y_{AS}\right)}{Y_{AS}}$	$\frac{(2 - 5Y_{AS})}{Y_{AS}}$	$1 - \frac{(2 - 5Y_{AS})}{Y_{AS}}$	+3

(3) Hydrogenotrophic sulphidogenesis (by hydrogenotrophic SRB)

Again the same approach was followed for the growth of the hydrogenotrophic SRB (Z_{HS}) based on their catabolic substrate utilisation taken from Kalyuzhnyi *et al.* (1998), i.e.



The stoichiometry for hydrogenotrophic SRB in terms of the true (metabolic) organism yield as listed in Table 7.6.

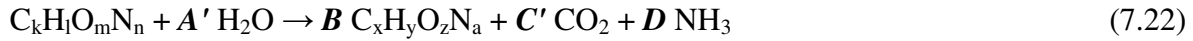
Table 7.6: Stoichiometry for hydrogenotrophic SRB in terms of the true organism yield, Y_{HS} .

H_2CO_3^* mol	H_2 mol	SO_4^{2-} mol	NH_4^+ mol	Z_{HS} mol	H_2S mol	H^+ mol	H_2O mol
-5	$-\left(\frac{1}{Y_{\text{HS}}}\right)$	$-\left(\frac{1}{4Y_{\text{HS}}} - \frac{5}{2}\right)$	-1	1	$\frac{1}{4Y_{\text{HS}}} - \frac{5}{2}$	$6 - \frac{1}{2Y_{\text{HS}}}$	$\frac{1}{Y_{\text{HS}}} + 3$

7.3.2.2 Endogenous decay for all bacterial groups

The organism death / decay for the SRB groups was assumed to be the same as that for the methanogenic microorganism groups in the UCTADM1 model, and therefore the same approach was followed here.

In this study, it was found from the measurements and assumptions (See Section 7.2.5), that the formulation of the organism mass is $\text{C}_5\text{H}_7\text{O}_2\text{N}_{0.55}$. However, a biomass composition of $\text{C}_5\text{H}_7\text{O}_2\text{N}_1$ is used in the UCTADM1-BSR model and likewise the stoichiometry of the growth and decay processes are based on this biomass composition. In endogenous decay, this organism mass transforms to biodegradable particulate COD (S_{bp}). Due to the low SRB organism yield and endogenous decay rates, it was accepted that generation of endogenous residue was small and was therefore neglected. It was also recognised that the endogenous biodegradable particulate COD (S_{bp}) composition is the same as the calculated PSS biodegradable particulate COD composition of $\text{C}_{3.35}\text{H}_7\text{O}_{1.45}\text{N}_{0.45}$ found in this investigation because the biodegradable organics from the dead biomass adds to the pool of biodegradable organics from the PSS. Because this transformation may need to be done with different biomass and PSS compositions, the transformation stoichiometry is developed in general for biomass of composition $\text{C}_k\text{H}_l\text{O}_m\text{N}_n$ and biodegradable substrate composition $\text{C}_x\text{H}_y\text{O}_z\text{N}_a$. The endogenous organics are transformed to become the influent biodegradable organics ($\text{C}_x\text{H}_y\text{O}_z\text{N}_a$) and added to the pool of these organics, i.e.



Re-writing the equation by recognising that $CO_2 + H_2O \rightarrow H_2CO_3^*$ gives:



where:

$$A = \frac{[k(3y-2z-9a)+l(z-3x)+m(2x+3a-y)+n(9x-3z)]}{[4x+y-2z-3a]} = \frac{[k(3y-2z-9a)+l(z-3x)+m(2x+3a-y)+n(9x-3z)]}{D_S}$$

$$B = \frac{[4k + l - 2m - 3n]}{[4x + y - 2z - 3a]} = D_B/D_S$$

$$C = \frac{[k(y-2z-3a)+x(2m+3n-l)]}{[4x+y-2z-3a]} = \frac{[k(y-2z-3a)+x(2m+3n-l)]}{D_S}$$

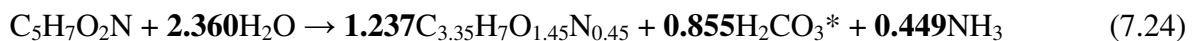
$$D = \frac{[n(4x+y-2z)+a(2m-4k-l)]}{[4x+y-2z-3a]} = \frac{[n(4x+y-2z)+a(2m-4k-l)]}{D_S}$$

The generalised stoichiometry equation for endogenous decay of all organism groups expressed in Eq(7.23) is listed in Table 7.7.

Table 7.7: Stoichiometry for the endogenous respiration of all SRB organism groups (Z_j) with biodegradable particulate COD composition of $C_k H_l O_m N_n$ generating a biodegradable particulate COD (S_{bp}) formulation as $C_x H_y O_z N_a$.

NH_3 mol	$H_2CO_3^*$ mol	S_{bp} mol	H_2O mol	Z_j mol
$\frac{n(4x+y-2z)+a(2m-4k-l)}{(4x+y-2z-3a)}$	$\frac{k(y-2z-3a)+x(2m+3n-l)}{(4x+y-2z-3a)}$	$\frac{(4k+l-2m-3n)}{(4x+y-2z-3a)}$	$\frac{k(3y-2z-9a)+l(z-3x)+m(2x+3a-y)+n(9x-3z)}{(4x+y-2z-3a)}$	-1

From the calculated compositions of the biodegradable components of the biomass and organics, the endogenous decay of the organisms was expressed by the following equation:



The stoichiometry for the organisms endogenous decay is taken from Eq(7.24) and is presented in Table 7.8.

Table 7.8: Stoichiometry for the endogenous respiration of all SRB organism groups (Z_j of composition $C_5H_7O_2N$), with biodegradable particulate COD (S_{bp}) formulation as $C_{3.35}H_7O_{1.45}N_{0.45}$.

Z_j mol	$H_2CO_3^*$ mol	H_2O mol	NH_3 mol	S_{bp}	
				g COD	mol
-1	0.855	2.360	0.449	129.2	1.237

Accepting the biomass composition of $C_5H_7O_2N_1$, the biomass COD/VSS ratio = **1.414** mgCOD/mgVSS and 1 mole biomass has a COD of ~ **160 gCOD**. Therefore, 160 g organism COD has an equivalent of ~**113.1** gVSS, which based on COD conservation produces **1.237 mol** substrate with a COD/VSS ratio of **1.682** mgCOD/mgVSS.

The complete biological kinetic model for SRB represented in the Petersen matrix format is shown in Table 7.9. The matrix includes both the growth and endogenous decay processes for all three SRB groups, namely the propionate degrading SRB (Z_{PS} , growth Process S1 and endogenous decay Process S2), acetotrophic SRB (Z_{AS} , growth Process S3 and endogenous decay Process S4) and hydrogenotrophic SRB (Z_{HS} , growth Process S5 and endogenous decay Process S6).

7.3.3 KINETIC PROCESS RATES

7.3.3.1 Growth kinetic rates

The approach adopted for the kinetic rate descriptions for the growth of SRB taken from Kalyuzhnyi *et al.* (1998) is as follows:

1. The bacterial growth of each SRB group was modelled using the Monod kinetics equation in terms of the relevant substrates, with concomitant inhibition by pH and undissociated H_2S .
2. The undissociated H_2S inhibition was formulated as first order for all SRB bacterial groups.

Accordingly, the generalised specific growth rate (μ_j) equation for SRB was as described by Kalyuzhnyi *et al.* (1998):

$$\mu_j = \mu_{\max, j} \frac{[S_i]F(pH)}{K_{Sj} + [S_i]} \left[1 - \left(\frac{[H_2S]_f}{K_{I,j}} \right) \right] \left(\frac{[SO_4^{2-}]}{K_n + [SO_4^{2-}]} \right) \quad (7.25)$$

where S_i is the substrate concentration for SRB organism i , the middle term is the undissociated H_2S inhibition equation with $K_{I,j}$ being the inhibition constant by undissociated H_2S for the bacterial group j and the last term is the sulphate switching function when $[SO_4^{2-}]$ is low.

The H_2S inhibition term $\left[1 - \left(\frac{[H_2S]_f}{K_{I,j}} \right) \right]$ in Eq(7.25) represents a 100% inhibition in SRB growth should $[H_2S]_f = K_I$. However, this equation is found to be unstable, namely when $[H_2S]$ is greater than the $K_{I,j}$ value. Should $[H_2S] > K_{I,j}$, the inhibition term becomes negative and the model simulation results become unstable with a see-saw effect. This inhibition term therefore was replaced by a more stable one which approaches zero more gradually, i.e.

$$\exp \left[- \left(\frac{[H_2S]_f}{0.60056K_{I,j}} \right)^2 \right] \quad (7.26)$$

This term has an exponential behaviour and can never become negative. The factor 0.60056 was found by matching the linear (or first order) inhibition term of Kalyuzhnyi *et al.* (1998) at the 50% inhibition point using the same value of K_I . For example, if $K_I = 206$ mgS/L, and $[H_2S]_f = 103$ mgS/L, then the $\left[1 - \left(\frac{[H_2S]_f}{K_{I,j}} \right) \right]$ term and Eq(7.26) must give the same 50% inhibition. If instead of Eq(7.26), a monod type inhibition term is used, i.e.

$\left[\left(\frac{K_{I,j}}{K_{I,j} + [H_2S]_f} \right) \right]$ the K_I value will be $206/2 = 103$ mgS/L to give 50% inhibition at $[H_2S]_f = 103$ mgS/L. Figure 7.6 illustrates the fraction uninhibited with $[H_2S]$ for the 3 inhibition terms. Also plotted is the fraction inhibition versus $[H_2S]$ concentration for the exponential inhibition term (Eq7.26).

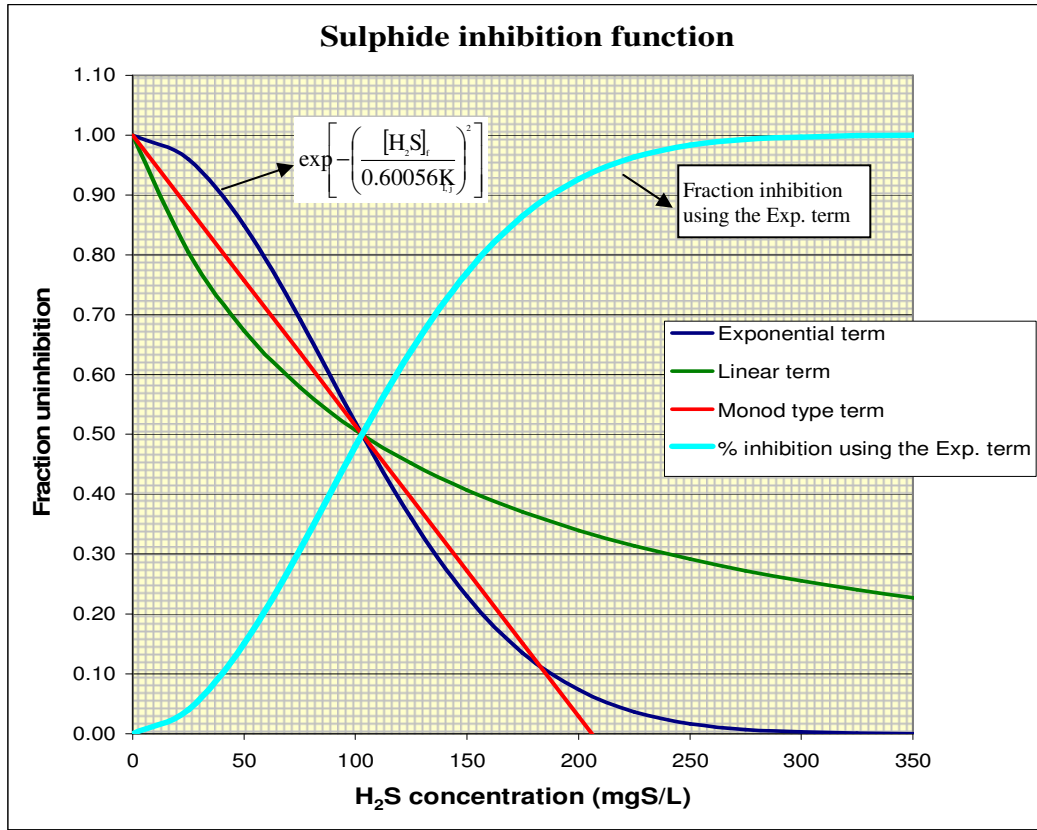


Figure 7.6: Fraction uninhibited with H_2S concentration using 3 inhibition terms.

Should pH inhibition be required, it can be added to the UCTADM1-BSR model. In integrating BSR with ADM1, Fedorovich *et al.* (2003) used the following pH inhibition function in ADM1:

$$I_{pH} = \frac{1 + 2 \times 10^{0.5(pK_1 - pK_2)}}{1 + 10^{(pH - pK_2)} + 10^{(pH - pK_1)}} \quad (7.27)$$

As far as the pH inhibition function is concerned, this was omitted in the model application because of its uncertainty.

Following the above and omitting pH inhibition, the final SRB growth rate used in the UCTADM1-BSR model was changed to:

$$\mu_j = \mu_{\max, j} \frac{[S_i]}{K_{Sj} + [S_i]} \exp \left[- \left(\frac{[H_2S]_f}{0.60056K_{I,j}} \right)^2 \right] \left(\frac{[SO_4^{2-}]}{K_n + [SO_4^{2-}]} \right) \quad (7.28)$$

When incorporating BSR into the UCTADM1 model, the H₂S inhibition term was also added to the existing kinetic rate equations for acidogenic, acetogenic and methanogenic bacterial groups. This was done by following the approach of Kalyuzhnyi *et al.* (1998) where:

$$\mu_j = \mu_{\max, j} \frac{[S_i]}{K_{Sj} + [S_i]} \exp \left[- \left(\frac{[H_2S]_f}{0.60056 K_{I, j}} \right)^2 \right] \quad (7.29)$$

In the literature, it is reported that the sensitivity of SRB to hydrogen sulphide toxicity depends on bacterial species (Maillacheruvu and Parkin, 1996; O'Flaherty *et al.*, 1998). Maillacheruvu and Parkin, 1996 investigated the effect of H₂S on propionate oxidising, acetate oxidising and hydrogenotrophic SRB and reported that particularly acetotrophic SRB were highly sensitive to H₂S. Likewise, Yamaguchi *et al.* (1999) reported that acetate utilisers were more susceptible to H₂S inhibition than the hydrogen utilisers. In the UCTADM1-BSR model, the K_I values of 185 mgS/L and 550 mgS/L for the propionate degrading and the hydrogenotrophic SRB respectively were taken directly from Kalyuzhnyi *et al.* (1998) while that of acetotrophic SRB was refined during model calibration.

7.3.3.2 Endogenous decay

Kalyuzhnyi *et al.* (1998) and Sötemann *et al.* (2005a) described bacterial decay by first order kinetics. This approach is also used for the three SRB considered. Accordingly, the general equation for the specific rate for the decay of a bacterial population X_j is given by:

$r_{xj} = b_j[X_j]$ where b_j is the specific decay constant for the bacterial population concerned X_j.

The specific rate equations for each SRB is listed in Table 7.9, see Processes S2, S4 and S5.

7.3.3.3 Matrix representation of the biological kinetic model for BSR

Table 7.9 below shows the biological processes for BSR represented in the Petersen matrix format.

Table 7.9: Petersen matrix representation of the biological kinetic model for sulphate reducing bacteria (SRB).

	Number→	C1/B10	C2	C3	C7	C13	D4	D3	C31	C32	D1	S1	S2	S3		↓Process Rate
No.	Process↓ Compound→	NH ₄ ⁺	NH ₃ dis.	H ₂ CO ₃ *	H ⁺	HAc	HPr	H ₂ dissolved	SO ₄ ²⁻	H ₂ S	S _{bp}	Z _{PS}	Z _{AS}	Z _{HS}	H ₂ O ^c	
S1	Growth of propionate degrading SRB	-1		$\left(\frac{1}{Y_{PS}} - 2\right)$	$\left(\frac{13}{4} - \frac{3}{2Y_{PS}}\right)$	$\left(\frac{1}{Y_{PS}} - \frac{3}{2}\right)$	$-\left(\frac{1}{Y_{PS}}\right)$	$\frac{1}{2}$	$-\left(\frac{3}{4Y_{PS}} - \frac{9}{8}\right)$	$\left(\frac{3}{4Y_{PS}} - \frac{9}{8}\right)$		1			$\frac{5}{2}$	$\frac{\mu_{\max} [HPr]}{K_S + [HPr]} \left[\exp \left\{ - \left(\frac{[H_2S]_f}{0.60056K_{l,j}} \right)^2 \right\} \right] \left[\frac{[SO_4^{2-}]}{K_N + [SO_4^{2-}]} \right] Z_{PS}$
S2	Endogenous decay of propionate degrading SRB		0.449 ^b	0.855 ^b							129.27 ^b	-1			2.360	b _{PS} [Z _{PS}]
S3	Growth of acetotrophic SRB	-1		$\frac{(2 - 5Y_{AS})}{Y_{AS}}$	$1 - \frac{(2 - 5Y_{AS})}{Y_{AS}}$	$-\left(\frac{1}{Y_{AS}}\right)$			$-\left(\frac{1 - \frac{5}{2}}{Y_{AS}}\right)$	$\left(\frac{1 - \frac{5}{2}}{Y_{AS}}\right)$			1		3	$\frac{\mu_{\max} [HAc]}{K_S + [HAc]} \left[\exp \left\{ - \left(\frac{[H_2S]_f}{0.60056K_{l,j}} \right)^2 \right\} \right] \left[\frac{[SO_4^{2-}]}{K_N + [SO_4^{2-}]} \right] Z_{AS}$
S4	Endogenous decay of acetotrophic SRB		0.449 ^b	0.855 ^b							129.2 ^b		-1		2.360	b _{AS} [Z _{AS}]
S5	Growth of hydrogenotrophic SRB	-1		-5	$\left(6 - \frac{1}{2Y_{HS}}\right)$			$-\left(\frac{1}{Y_{HS}}\right)$	$-\left(\frac{1}{4Y_{HS}} - \frac{5}{2}\right)$	$\left(\frac{1}{4Y_{HS}} - \frac{5}{2}\right)$				1	$\frac{1}{Y_{HS}} + 3$	$\frac{\mu_{\max} [H_2]}{K_S + [H_2]} \left[\exp \left\{ - \left(\frac{[H_2S]_f}{0.60056K_{l,j}} \right)^2 \right\} \right] \left[\frac{[SO_4^{2-}]}{K_N + [SO_4^{2-}]} \right] Z_{HS}$
S6	Endogenous decay of hydrogenotrophic SRB		0.449 ^b	0.855 ^b							129.2 ^b			-1	2.360	b _{HS} [Z _{HS}]
		mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	mol/L	gCOD/L ^a	mol/L			mol/L	

^aSee Table 7.8 for units in mol/L^bThis is the COD for the biodegradable particulate (S_{bp}) substrate with formulation C_{3.35}H₇O_{1.45}N_{0.45}; see Table 7.7 for the generalised formulation for S_{bp} = C_xH_yO_zN_a. Z_j = SRB j concentration; Y = true organism yield; b = specific decay rate; rate symbols defined in Eq(7.25).

Subscripts PS, AS and HS = propionate degrading, acetotrophic and hydrogenotrophic SRB respectively.

Compound and process numbering system follows Sötemann *et al.* (2005a).^cH₂O is generally not included in the Petersen matrix but is shown here for consistency and to check the H & O mass balances.

7.3.3.4 Values for the stoichiometric and kinetic constants

Van Wageningen (2007) used values for the stoichiometric and kinetic constants for the SRB from Kalyuzhnyi *et al.* (1998), who obtained these values from model fitting to the data of Omil *et al.* (1996). These values are also employed here, see Table 7.10.

Table 7.10: Values for SRB stoichiometric and kinetic constants used in the BSR kinetic model (from Kalyuzhnyi *et al.*, 1998).

	$\mu_{\max}$	K_S^1	K_N^1	K_I^1	Y^1	b
	/d	gCOD/L	gSO ₄ ²⁻ /L	gS/L	gVSS/gCOD	/d
Propionate degrading SRB	0.583	0.295	0.0074	0.185	0.027	0.0185
Acetotrophic SRB	0.612	0.024	0.0192	0.164	0.033	0.0275
Hydrogenotrophic SRB	2.8	7E-05	0.0192	0.550	0.050	0.0600

¹Constants to be converted to mole units upon integration with the UCTADM1 model, to ensure consistency in units, see Table 7.11.

The concentration based constants shown in Table 7.10 are expressed in terms of g units. Since UCTADM1 and so also the kinetic model for BSR (Table 7.9) express concentrations as mole units, the constants were converted to the appropriate mole units. This was done by accepting a biomass composition of C₅H₇O₂N and substrates (acetic acid, propionic acid and hydrogen) as per the known chemical compositions, see Table 7.11. In addition, because the kinetic rates are expressed in terms of undissociated weak acid/base species instead of total species concentrations (in the original literature source), the appropriate half saturation constants needed to be adjusted to take this into consideration. This was done in model application by multiplying the appropriate half saturation constant in the rate formulation by the undissociated species to total species concentration ratio (van Wageningen, 2007). With this approach, the relative concentrations may change as the pH changes and was therefore considered more appropriate.

Table 7.11: Corrected values used in UCTADM1-BSR for the appropriate half saturation constants.

Organism Group	μ		K_s		K_n		Y		b	
	Kalyuzhnyi <i>et al.</i> (1998)	UCTADM1 (Sötemann <i>et al.</i> 2005a)	Kalyuzhnyi <i>et al.</i> (1998)	UCTADM1 (Sötemann <i>et al.</i> 2005a)	Kalyuzhnyi <i>et al.</i> (1998)	UCTADM1 (Sötemann <i>et al.</i> 2005a)	Kalyuzhnyi <i>et al.</i> (1998)	UCTADM1 (Sötemann <i>et al.</i> 2005a)	Kalyuzhnyi <i>et al.</i> (1998)	UCTADM1 (Sötemann <i>et al.</i> 2005a)
Comparison	mol(org)/mol(subs)/d	mol(org)/mol(subs)/d	mol(subs)/L	mol(subs)/L	molSO ₄ /L	molSO ₄ /L	mol(org)/mol(subs)	mol(org)/mol(subs)	mol(org)/mol(org)/d	mol(org)/mol(org)/d
Acidogens	4.000	0.80	7.676E-05	7.810E-04	N/A	N/A	0.10964	0.1074	0.0900	0.041
Acetogens	0.160	1.15	2.203E-03	8.900E-05	N/A	N/A	0.01586	0.0278	0.0140	0.015
Propionate degrading SRB	0.583	*	2.631E-03	*	7.703E-05	*	0.02676	*	0.0185	*
Acetoclastic methanogens	0.264	4.39	1.873E-03	1.300E-05	N/A	N/A	0.01218	0.0157	0.0200	0.037
Acetotrophic SRB	0.612	*	3.747E-04	*	1.999E-04	*	0.01869	*	0.0275	*
Hydrogenotrophic methanogens	1.000	1.20	7.500E-06	1.560E-04	N/A	N/A	0.00212	0.0040	0.0400	0.010
Hydrogenotrophic SRB	2.800	*	4.375E-06	*	1.999E-04	*	0.00707	*	0.0600	*

*Organism not included in UCTADM1. Constants for SRB used in UCTADM1-BSR are taken from Kalyuzhnyi *et al.* (1998).

Org = Organism; Subs = Substrate

7.3.4 INCLUSION OF THE AQUEOUS CHEMISTRY AND PHYSICAL PROCESSES

In the BSR processes described above, weak acid/base species are both produced and consumed. These species together with their associated weak acid/base chemistry need to be included in developing the kinetic model for BSR. In addition, the compound H_2CO_3^* which is both produced and consumed and the compound H_2S produced have physical gas exchange processes with the atmosphere and hence require inclusion in the model.

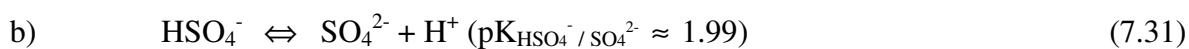
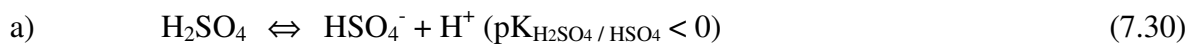
7.3.4.1 Acid/base chemistry

The acid base/base subsystems relevant to BSR were identified for inclusion in the model. These are:

1. Water : H^+ / OH^-
2. Carbonate : $\text{H}_2\text{CO}_3^* / \text{HCO}_3^- / \text{CO}_3^{2-}$
3. Ammonia : $\text{NH}_3 / \text{NH}_4^+$
4. Acetate : HAc / Ac^-
5. Propionate : HPr / Pr^-
6. Sulphate : $\text{H}_2\text{SO}_4 / \text{HSO}_4^- / \text{SO}_4^{2-}$
7. Sulphide : $\text{H}_2\text{S} / \text{HS}^- / \text{S}^{2-}$

The acid/base subsystems 1 to 5 are already included in the methanogenic UCTADM1 model (Sötemann *et al.*, 2005a) whereas 6 and 7 are not.

For the Sulphate subsystem (6); the dissociation reactions are given by:



Since the AMD to be treated usually has pH values ranging from 2 to 5, the species distribution of the equilibrium Eq(7.31) will be influenced in the influent and therefore this equilibrium needed to be included. In contrast, the equilibrium Eq(7.30) can be omitted because it is very unlikely to have an AMD with $\text{pH} < 0$. Hence, the sulphate acid/base subsystem was treated as a monoprotic system with the single equilibrium reaction

Eq(7.31). The approach developed by Musvoto *et al.* (1997) was used to model this chemical dissociation equilibrium reaction and hence two new processes (C48 and C49) and two new compounds (C30 and C31) were included (Table 7.12).

Table 7.12: Petersen matrix representation of the HSO_4^- acid / base dissociation processes.

		Number→	C7	C30	C31	
		Compound→	H ⁺	HSO ₄ ⁻	SO ₄ ²⁻	
↓No	↓Process	↓Process rates				
C48	Forward dissociation	HSO ₄ ⁻	+1	-1	+1	K _{fHSO4} '[HSO ₄ ⁻]
C49	Reverse dissociation	HSO ₄ ⁻	-1	+1	-1	K _{rHSO4} '[SO ₄ ²⁻][H ⁺]
		mol/L	mol/L	mol/L		

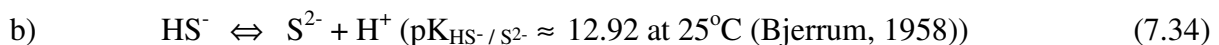
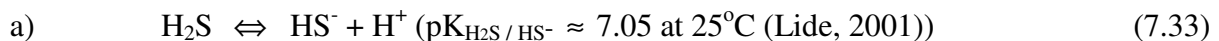
In the C49 process rate equation, K'_{rHSO_4} was given a very high value (from 10^7 to $10^{15}/\text{d}$) (Musvoto *et al.*, 1997). If required, this value can thereafter be refined in the solution procedure. The K'_{fHSO_4} value is fixed by the relationship with the equilibrium constant $\text{p}K_{\text{HSO}_4/\text{SO}_4}$ as follows:

$$K'_{\text{fHSO}_4} = K'_{\text{rHSO}_4} 10^{-\text{p}K_{\text{HSO}_4/\text{SO}_4}} f_m / f_d \quad (7.32)$$

where f_m and f_d are mono- and di-valent activity coefficients (Loewenthal *et al.*, 1988).

The above approach ensured immediate dissociation reactions and that the concentrations of the species established are the concentrations at equilibrium at each time step in the simulation.

For the Sulphide subsystem (7), the dissociation reactions are given by:



In Eq(7.34), S^{2-} acts as a strong base since the $\text{p}K_{\text{HS}^-/\text{S}^{2-}}$ is very high. Moreover, the pH range in BSR systems is very unlikely to >10 , therefore the sulphide subsystem was also considered a monoprotic weak acid/base subsystem with equilibrium Eq(7.33) only. It was

modelled the same way as the HSO_4^- subsystem, which introduced 2 new processes (C50 for forward dissociation and C51 for reverse dissociation) and 2 new compounds, H_2S (C32) and HS^- (C33) (Table 7.13).

Table 7.13: Petersen matrix representation of the H_2S weak acid / base dissociation processes.

		Number→	C7	C32	C33
		Compound→	H^+	H_2S	HS^-
↓No	↓Process	↓Process rates			
C50	Forward dissociation H_2S	+1	-1	+1	$K'_{\text{fH}_2\text{S}}[\text{H}_2\text{S}]$
C51	Reverse dissociation H_2S	-1	+1	-1	$K'_{\text{rH}_2\text{S}}[\text{HS}^-][\text{H}^+]$
		mol/L	mol/L	mol/L	

Here also, the reverse dissociation rate $K'_{\text{rH}_2\text{S}}$ was given a very high value (10^7 to $10^{15}/\text{d}$) with time units dependent on the integration period. The value for $K'_{\text{fH}_2\text{S}}$ determined $K'_{\text{rH}_2\text{S}}$ and the pK value for the $\text{HS}^-/\text{H}_2\text{S}$ equilibrium, i.e.

$$K'_{\text{fH}_2\text{S}} = K'_{\text{rH}_2\text{S}} 10^{-\text{pK}_{\text{H}_2\text{S}} / \text{HS}^-} / f_m \quad (7.35)$$

$$\text{where } \text{pK}_{\text{H}_2\text{S}} = 7.05^* + 1132.18/T_K - 3.7993 \text{ (Moosbrugger } et al., 1992)$$

$$T_K = \text{temperature in Kelvin}$$

$$* \text{ pK value of } \text{H}_2\text{S}/\text{HS}^- \text{ at } 25^\circ\text{C} \text{ obtained from Lide (2001).}$$

Phosphorous (P) was excluded in the stoichiometry for the SRB growth and decay processes (Table 7.9). However, the phosphate weak acid/base system is included in the BSR kinetic model and is taken directly from Musvoto *et al.* (1997). As stated earlier, P is not directly relevant to BSR as the biological uptake and release of phosphorous is small and can be neglected. Moreover, information on this aspect in the literature is very limited and hence requires further investigation. In addition, in the development of the BSR kinetic model, the solid phase (mineral precipitation reactions and the associated ion pairing reactions) were not included at this stage.

7.3.4.2 Physical processes

Those compounds which are associated with the biological processes for BSR, that have physical gas exchange processes with the atmosphere/head space in the reactor, were included, namely;



Gas exchange processes 1 and 2 were already in UCTADM1 (Sötemann *et al.* (2005a). For NH_3 exchange (2), only the gas expulsion was included because the atmosphere acts as an infinite sink for NH_3 gas (see Table 2.10 in Chapter 2).

As stated by van Wageningen (2007), H_2S gas exchange is not included in any of the models developed to date and was included in UCTADM1-BSR following the approach for CO_2 gas where both expulsion and dissolution reactions were incorporated. The CO_2 gas exchange approach was selected over the NH_3 gas exchange as the atmosphere in the sulphate reducing bioreactor can build up significant gas concentrations, i.e. it would be inappropriate to regard the atmosphere/head space as an infinite sink. Accordingly, 2 new processes (P12 for H_2S gas dissolution and P13 for H_2S gas expulsion and 2 new compounds, $\text{H}_2\text{S}(\text{aq})$ (C32) and $\text{H}_2\text{S}(\text{g})$ (P5) were included (Table 7.14), where $p_{\text{H}_2\text{S}}$ is the partial pressure of H_2S gas in the head space.

Table 7.14: Petersen matrix representation of the H_2S exchange physical processes.

		Number→	C32	C33	
		Compound→	H_2S	$\text{H}_2\text{S}(\text{g})$	
↓No	↓Process	Dslvd	Gas	↓Process rates	
P12	Dissolution of H_2S gas	+1	-1	$K'_{\text{rH}_2\text{Sg}}(\rho_{\text{H}_2\text{S}})(K_{\text{H}_2\text{S}})$	
P13	Expulsion of H_2S gas	-1	+1	$K'_{\text{rH}_2\text{Sg}}[\text{H}_2\text{S}]$	
		mol/L	mol/L		

The K'_{rH_2Sg} in Table 7.14 equals the $K_{La\_H_2S}$ for H_2S and this can be linked to the $K_{La\_O_2}$ for oxygen through the proportionality of the diffusivities for O_2 and H_2S (Sötemann *et al.*, 2005a); Musvoto *et al.*, 1997; Munz and Roberts, 1989). In anaerobic BSR systems, the actual $K_{La\_O_2}$ is zero since oxygen is absent. However, linking the $K_{La\_H_2S}$ to $K_{La\_O_2}$ is appropriate as it indirectly links the K_{La} values for CO_2 and H_2S . In order to link the K_{La} of a gas to that of O_2 as a reference gas, the dimensionless Henry's law constant (H_c) should be greater than 0.55. Hence,

$$H_c = 1/(K_H RT) > 0.55 \quad (7.39)$$

Ammonia is excluded here because $H_c < 0.55$ (Sötemann *et al.* 2005a).

For H_2S , Henry's law constant, K_H at 25 °C (298.15 K) is reported between 1×10^{-3} to 1×10^{-1} mol/(L.atm). Thus H_c is between 40.87 and 0.409.

Because H_c for H_2S is mostly > 0.55 , it is possible to link the K_{La} for H_2S to that of O_2 in a fixed relationship depending on the relative magnitudes of the diffusivities of H_2S to O_2 . In applying the model to BSR systems, $K_{La\_O_2}$ is calibrated which then sets the values for the $K_{La\_CO_2}$ and $K_{La\_H_2S}$ but in the absence of air (the aeration process is either switched off or excluded). In this research, only the steady state condition will be considered in the model application, hence, the K_{La} values for CO_2 and H_2S are of little significance on condition that they are high enough to ensure steady state between the gaseous and dissolved phases is reached (van Wageningen, 2007). However, in applying the model to a dynamic system, the relationship between the K_{La} 's for CO_2 and H_2S with oxygen is important and will require further investigation.

7.3.5 INTEGRATING THE AQUEOUS CHEMISTRY, PHYSICAL PROCESSES AND THE BIOLOGICAL PROCESSES WITH UCTADM1

The biological processes (stoichiometric and kinetics), aqueous chemistry and physical processes relevant to BSR, were integrated with the existing methanogenic UCTADM1 model in Aquasim (Reichert, 1998). This resulted in an integrated kinetic model for both BSR and methanogenesis in competition for the short chain fatty acids (SCFA) and H_2 substrates. A summary of the compounds and processes is given in Table 7.15. Should BSR

be required as the only biological processes consuming the SCFA and H_2 substrates, the methanogenic processes can be switched off in the model application. This will result in a “stand alone” integrated two phase chemical, physical and biological processes model for BSR with PSS as energy source. In a real BSR system, methanogenesis would be outcompeted by sulphidogenesis resulting in an exclusively BSR system as was the case in this investigation. Hence, integrating the biological, chemical and physical processes for BSR with UCTADM1 gave a complete two phase chemical, physical and biological methanogenic and sulphidogenic anaerobic digestion with PSS as substrate (see Table 7.15). In this research, the latter model type (i.e. UCTADM1-BSR) was applied to simulate the R1 and R2 UASB BSR systems.

Table 7.15: Processes and compounds for biologically mediated processes for inclusion in kinetic model for combined biological sulphate reduction and methanogenesis with PSS

Organism group	Compounds	Processes		Source
Acidogens	D1 : C _X H _Y O _Z N _A (S _{bp})	D1	Hydrolysis	Sötemann <i>et al.</i> (2005a), Table 2
	D2 : C ₆ H ₁₂ O ₆ (S _{bsf})	D2	Acidogenesis (low pH ₂)	
	C1 : NH ₄ ⁺			
	C3 : H ₂ CO ₃ *			
	C7 : H ⁺			
	C13 : HAc			
	D2 : C ₆ H ₁₂ O ₆ (S _{bsf})			
	D3 : H ₂			
	D4 : Z _{AD}			
	C1 : NH ₄ ⁺	D3	Acidogenesis (high pH ₂)	
	C3 : H ₂ CO ₃ *			
	C7 : H ⁺			
	C13 : HAc			
	C28 : HPr			
	D2 : C ₆ H ₁₂ O ₆ (S _{bsf})			
	D3 : H ₂			
	D4 : Z _{AD}			
	C2 : NH ₃	D4	Acidogen endogenous decay	
	C3 : H ₂ CO ₃ *			
	D1 : C _X H _Y O _Z N _A (S _{bp})			
	D4 : Z _{AD}			
Acetogens	C1 : NH ₄ ⁺	D5	Acetogenesis	Sötemann <i>et al.</i> (2005a), Table 2
	C3 : H ₂ CO ₃ *			
	C7 : H ⁺			
	C13 : HAc			
	C28 : HPr			
	D3 : H ₂			
	D5 : Z _{AC}			
	C2 : NH ₃	D6	Acetogen endogenous decay	
	C3 : H ₂ CO ₃ *			

	D1 : C _X H _Y O _Z N _A (S _{bp})			
	D4 : Z _{AC}			
Propionate SRB	C1 : NH ₄ ⁺	S1	Growth of propionate SRB	
	C3 : H ₂ CO ₃ *			
	C7 : H ⁺			
	C13 : HAc			
	C28 : HPr			
	D3 : H ₂			
	C31 : SO ₄ ²⁻			
	C32 : H ₂ S			
	S1 : Z _{PS}			
	C2 : NH ₃	S2	Propionate SRB endogenous decay	
	C3 : H ₂ CO ₃ *			
	D1 : C _X H _Y O _Z N _A (S _{bp})			
	S1 : Z _{PS}			
Acetotrophic SRB	C1 : NH ₄ ⁺	S3	Growth of acetotrophic SRB	
	C3 : H ₂ CO ₃ *			
	C7 : H ⁺			
	C13 : HAc			
	C32 : H ₂ S			
	S1 : Z _{AS}			
	C2 : NH ₃	S4	Acetotrophic SRB endogenous decay	
	C3 : H ₂ CO ₃ *			
	D1 : C _X H _Y O _Z N _A (S _{bp})			
D4 : Z _{AS}				
Hydrogenotrophic SRB	C1 : NH ₄ ⁺	S5	Growth of hydrogenotrophic SRB	
	C3 : H ₂ CO ₃ *			
	C7 : H ⁺			
	D3 : H ₂			
	C31 : SO ₄ ²⁻			
	C32 : H ₂ S			
	S1 : Z _{HS}			
	C2 : NH ₃	S6	Hydrogenotrophic SRB endogenous decay	
	C3 : H ₂ CO ₃ *			
	D1 : C _X H _Y O _Z N _A (S _{bp})			
	S1 : Z _{HS}			
Acetoclastic methanogens	C1 : NH ₄ ⁺	D7	Acetoclastic methanogenesis	Sötemann <i>et al.</i> (2005a), Table 2
	C3 : H ₂ CO ₃ *			
	C7 : H ⁺			
	C13 : HAc			
	P4 : CH ₄			
	D6 : Z _{AM}			
	C2 : NH ₃	D8	Acetoclastic methanogen endogenous decay	
	C3 : H ₂ CO ₃ *			
	D1 : C _X H _Y O _Z N _A (S _{bp})			
D4 : Z _{AM}				

Hydrogenotrophic methanogens	C1 : NH_4^+	D9	Hydrogenotrophic methanogenesis	Sötemann <i>et al.</i> (2005a), Table 2
	C3 : H_2CO_3^*			
	C7 : H^+			
	P4 : CH_4			
	D3 : H_2			
	D6 : Z_{HM}			
	C2 : NH_3	D10	Hydrogenotrophic methanogen endogenous decay	
	C3 : H_2CO_3^*			
	D1 : $\text{C}_X\text{H}_Y\text{O}_Z\text{N}_A (\text{S}_{\text{bp}})$			
	D4 : Z_{HM}			

The aqueous chemistry processes were extracted from Musvoto *et al.* (1997) for the ammonia, carbonate, phosphate, acetate and water subsystems (see Table 2.9); from Sötemann *et al.* (2005a) for the propionate subsystem (see Table 2.10); and from Tables 7.12 and 7.13 here for the sulphate and sulphide subsystems. In addition, the physical gas exchange processes for CO_2 and NH_3 were taken from Sötemann *et al.* (2005a) (see Table 2.10 whereas the H_2S gas exchange processes were taken from Table 7.14. Further, methane gas being very insoluble was modelled following the approach of Sötemann *et al.* (2005a). Methane is included as a gas phase compound, that is, it is generated directly as a gas and is not utilised in any of the processes.

In addition, in this model the gas compounds were accepted to remain part of the bulk liquid and exit the digester with the effluent flow. This is acceptable because at steady state the gas composition does not change. However, for dynamic simulations, the gas composition of the headspace may change with time and can influence the dissolved species bulk liquid concentrations through the gas exchange processes. In this case, a separate gas stream needs to be implemented following the processes set out in Batstone *et al.* (2002) and Sötemann *et al.* (2005a). All the compounds and processes relevant to BSR (Table 7.15) were integrated into the UCTADM1 model using the computer programme AQUASIM. The next step was to calibrate the model using relevant available kinetics and stoichiometric constants from the literature.

7.3.6 UCTADM1-BSR MODEL CALIBRATION AND VERIFICATION

The various kinetic and stoichiometric constants required as input to the UCTADM1-BSR kinetic model were obtained from the literature and from the experimental data set of this research. These are reported as follows:

- (i) The UCTADM1 constant values were mostly taken from the literature and were calibrated in UCTADM1 by Sötemann *et al.* (2005a). This is briefly described in Section 2.9 of Chapter 2.
- (ii) The kinetic constants required for the chemical and physical processes for ammonia, carbonate, acetate, phosphate and water were taken from Musvoto *et al.* (1997).
- (iii) The constants for propionate weak acid/base subsystem were taken from Sötemann *et al.* (2005a).
- (iv) The 2 new acid/base systems (sulphate and sulphide) were taken from Eqs(7.31) and (7.34) in this Chapter. The appropriate equilibrium constant (pK) was corrected for ionic strength effects. The Henry's law constant for H₂S (K_{H, H_2S}) was taken from Eq(7.39).
- (v) The kinetic and stoichiometric constants (Y , μ_{max} , K_s , K_N and b) for the BSR biological processes mediated by the 3 SRB organism groups were obtained from the literature (Table 7.10).
- (vi) The specific weak acid/base species were included in the growth rate equations instead of the total species concentrations. The adjusted values for the constants of the biological processes are listed in Table 7.11.
- (vii) The unbiodegradable particulate COD fraction of the primary sewage sludge (f_{PSup}) in this study was assumed to be 0.36 which is close enough to values used in previous studies.
- (viii) The saturation kinetic rate equation and its associated kinetic constants for the hydrolysis process were taken from Sötemann *et al.* (2005b). The maximum specific hydrolysis rate ($K_{max, HYD}$) and half saturation coefficient ($K_{ss, HYD}$) are 5.27 gCODS_{bp}/gCODZ_{AD.d} and 7.98 gCODS_{bp}/gCODZ_{AD} respectively. Converting these hydrolysis rate constants from the above COD units to mole units gave $K_{max, HYD} = 6.45 \text{ molS}_{bp}/\text{molZ}_{AD.d}$ and $K_{ss, HYD} = 9.77 \text{ molS}_{bp}/\text{molZ}_{AD}$. These values were therefore used in UCTADM1-BSR for simulating the R1 and R2 UASB systems.

- (ix) The sewage sludge stoichiometric composition, $C_xH_yO_zN_a$ was determined from experimental data as described in Section 7.2.5 above. The PSS composition was found to be $C_{3.35}H_7O_{1.45}N_{0.45}$.
- (x) The H_2S inhibition term integrated into the UCTADM1-BSR model was $\exp\left[-\left(\frac{[H_2S]_f}{0.60056K_{i,j}}\right)^2\right]$ as described in Section 7.3.3 of this Chapter.
- (xi) For the UASB system R2 (at 20 °C), a temperature correction factor was implemented for the hydrolysis process only because information on the effect of temperature on the other kinetic parameters is scarce and this requires further investigation. Therefore, only the maximum specific hydrolysis rate ($K_{max, HYD}$) and half saturation coefficient ($K_{ss, HYD}$) were adjusted for temperature effect when simulating UASB BSR system R2 (20 °C). The temperature correction equation for the hydrolysis process was taken from ADM1 (Batstone *et al.*, 2002) and was refined accordingly in the simulation procedure. The temperature function was found to be $K_2 = K_1(e^{\tau(T_2-T_1)})$ where $\tau = 0.108$, $T_1 = 35$ °C, $T_2 = 20$ °C, [equivalent to $K_2 = K_1 * 1.114^{(T_2-T_1)}$], K_1 and K_2 are the kinetic parameter values at these 2 respective temperatures.

7.4 UCTADM1-BSR MODEL APPLICATION AND VALIDATION

7.4.1 SYSTEMS SIMULATED AND INFLUENT CHARACTERISTICS

After the calibration exercise, the UCTADM1-BSR model was validated by applying it to simulate the 3 UASB BSR systems, namely:

1. R1 at 1500 mgSO₄²⁻/L at 35 °C with PSS COD/SO₄²⁻ ratio of 1.25.
2. R1 at 1800 mgSO₄²⁻/L at 35 °C with PSS COD/SO₄²⁻ ratio of 1.44 and no NaHCO₃ dosed to feed.
3. R2 at 1500 mgSO₄²⁻/L at 20 °C with PSS COD/SO₄²⁻ ratio of 1.75 and no NaHCO₃ dosed to feed.

Table 7.16 below lists the average measured/calculated influent characteristics of the 3 UASB BSR systems and these values were used as inputs to the UCTADM1-BSR model.

The COD units were converted to mole units with the relevant stoichiometric composition of the organic for the corresponding COD component, namely:

- (i) Biodegradable particulate (S_{bp}) – PSS stoichiometric composition of $C_xH_yO_zN_a$ where x , y , z and a are calculated from measured values (Section 7.2.5).
- (ii) Biodegradable soluble fermentable (S_{bsf}) – represented by glucose ($C_6H_{12}O_6$).
- (iii) Biodegradable soluble acetic and propionic acids (S_{bsa} , S_{bsp}) – known stoichiometric compositions ($C_2H_4O_2$ and $C_3H_6O_2$ for associated and $C_2H_3O_2^-$ and $C_3H_5O_2^-$ for dissociated respectively).
- (iv) Unbiodegradable soluble and particulate (S_{us} , S_{up}) – not converted since these are not degraded and utilised in the system and hence appear in the effluent (only S_{us}) and the waste (both S_{us} and S_{up}) flows respectively.

Table 7.16: Average measured/calculated influent characteristics of the 3 UASB BSR systems used as inputs to the UCTADM1-BSR model.

Input/influent parameters	Units	R1 at 35°C (1500 mgSO ₄ ²⁻ /L)	R1 at 35°C (1800 mgSO ₄ ²⁻ /L)	R2 at 20°C (1500 mgSO ₄ ²⁻ /L)
Total COD	mgCOD/L	1880	2584	2596
Unbiodegradable particulate COD ($f_{PS,up}=0.36$)	mgCOD/L	677	930	935
Total soluble COD	mgCOD/L	236	337	339
SCFA COD	mgCOD/L	126	164	169
Unbiodegradable soluble COD	mgCOD/L	6	7	8
Biodegradable particulate COD	mgCOD/L	967	1317	1322
Sulphate	mgSO ₄ ²⁻ /L	1500	1800	1500
Free and saline ammonia (FSA)	mgN/L	10.0	9.2	9.6
pH	-	7.20	5.99	5.94
H ₂ CO ₃ * alkalinity	mg/L as CaCO ₃	456	22	23
Volume of reactor bed/digester (V_r) ^a	L	7.2	7.4	7.6
Feed flow rate, Q_i	L/d	13.8	10.1	9.2
Hydraulic retention time (HRT)	h	13.7	18.5	20.4
Sludge age, R_s	d	18	21	24
Waste flow rate, Q_w	L/d	0.40	0.35	0.32

a: Reactor bed volume includes waste volume

As mentioned earlier, the UASB reactor is simulated as a completely mixed digester because of the effect of the sludge recycle line which continuously mixed the top sludge with the bottom one.

7.4.2 COMPARISONS OF MODELS (BOTH SS AND UCTADM1-BSR) PREDICTIONS WITH EXPERIMENTALLY MEASURED DATA

The simulated results were compared to the experimental measured values and the steady state results. These comparisons are listed in Table 7.17. A graphical representation of the comparisons of the 3 UASB BSR systems for the measured, steady state and kinetic simulated results is also illustrated in Figures 7.7 to 7.15.

Table 7.17: Comparison of experimentally Measured (M) effluent values with the Steady State (SS) BSR and the UCTADM1-BSR kinetic (Sim) model predictions.

Parameters	Units	UASB R1 at 35°C (fed 1500 mgSO ₄ ²⁻ /L)			UASB R1 at 35°C (fed 1800 mgSO ₄ ²⁻ /L)			UASB R2 at 20°C (fed 1500 mgSO ₄ ²⁻ /L)		
		M	SS	Sim	M	SS	Sim	M	SS	Sim
Effluent sulphate	mgSO ₄ ²⁻ /L	149	149	136	146	145	115	101	104	103
Sulphate removal	mgSO ₄ ²⁻ /L	1351	1351	1364	1654	1355	1685	1399	1396	1397
Organic COD removal	mgCOD/L	1624	1632	1757	2153	2242	2264	2309	2444	2410
Effluent total soluble COD	mgCOD/L	761 ^a	761 ^b	1031	1234	1234 ^b	1442	951	951 ^b	1116
Effluent organic soluble COD	mgCOD/L	141	141 ^b	123	229	229 ^b	320	96	96 ^b	186
Effluent HS/H ₂ S	(mgS/L)/(mgS/L)	209/101 ^a	277/173	336/120	318/184	339/213	409/153	261/166	280/185	321/145
Reactor pH	-	7.15	7.05	7.19	7.08	7.04	7.17	7.21	7.20	7.26
Effluent sum of H ₂ CO ₃ * alk and Alk H ₂ S	mg/L as CaCO ₃	1938 ^a	2063	2039	1855	1974	1982	1558	1672	1668
Effluent H ₂ CO ₃ * alkalinity	mg/L as CaCO ₃	1611 ^a	1627	1516	1358	1441	1343	1144	1234	1166
Effluent VFA	mgHAc/L	48	48 ^b	22	72	72 ^b	82	62	62 ^b	42
Effluent FSA	mgN/L	32	50	57	46	60	76	38	48	57
H ₂ S effluent gas stream	mgS/L influent	0	0	0	0	0	0	0	0	0
CO ₂ effluent gas stream	mol/L	0	0	0	0	0	0	0	0	0

a: H₂S measurement problem during the first 280 days of UASB R1 operation period, system total alkalinity unaffected by loss of H₂S while H₂CO₃* alk. and Alk H₂S are affected.

b: The Steady State (SS) model for BSR is based on substrate utilisation, hence the concentration of the effluent solubles is given the experimental values.

(i) Comparison of the effluent sulphate and sulphate removal

Figure 7.7 compares the average effluent sulphate concentration measured with the predictions by both the SS and UCTADM1-BSR models. Though the data points appear relatively far from the diagonal line, the magnitude of the difference in the effluent sulphate concentration values compared with the sulphate removal is very small. Figure 7.8 illustrates the sulphate removal comparisons and shows that good correlation between the measured and simulated values.

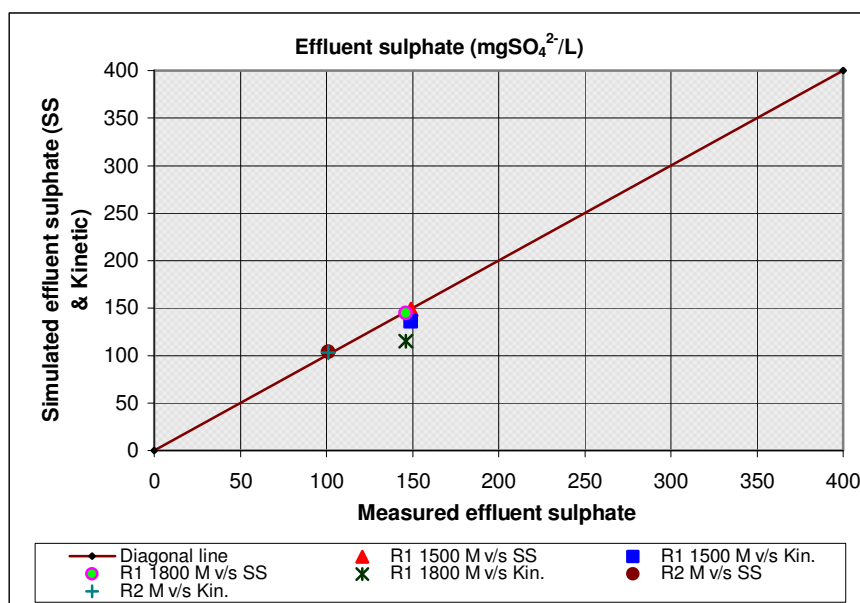


Figure 7.7: Comparison of models predicted effluent sulphate concentrations with measured values.

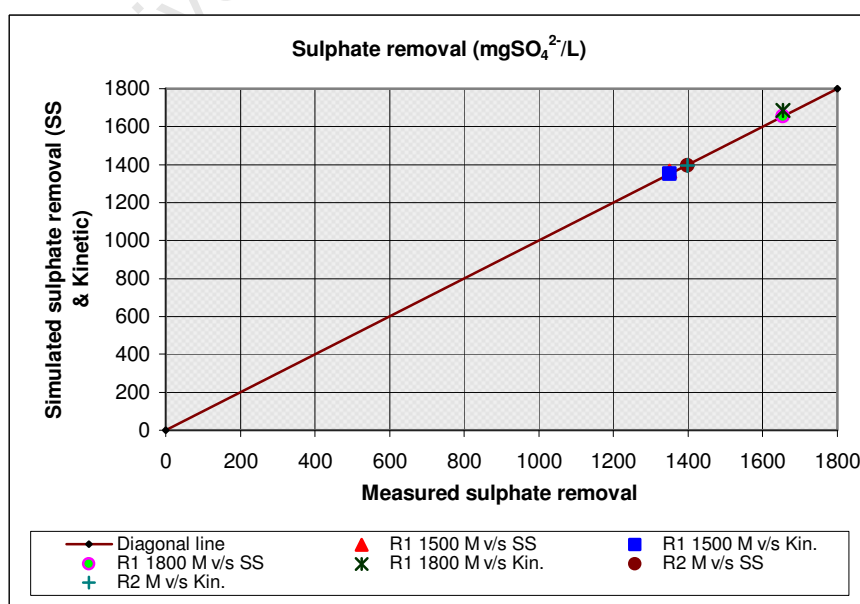


Figure 7.8: Comparison of models predicted sulphate removal with measured values.

(ii) Comparison of the organic COD removal (excludes H_2S)

The predicted system organic COD removal results compare well with the experimental measured one (Figure 7.9). In both models, it was assumed that the effluent consists of only soluble constituents (i.e. no solids flow with the effluent). This good correlation, therefore, further highlights the particularly good solids-liquid separation observed in the UASB systems.

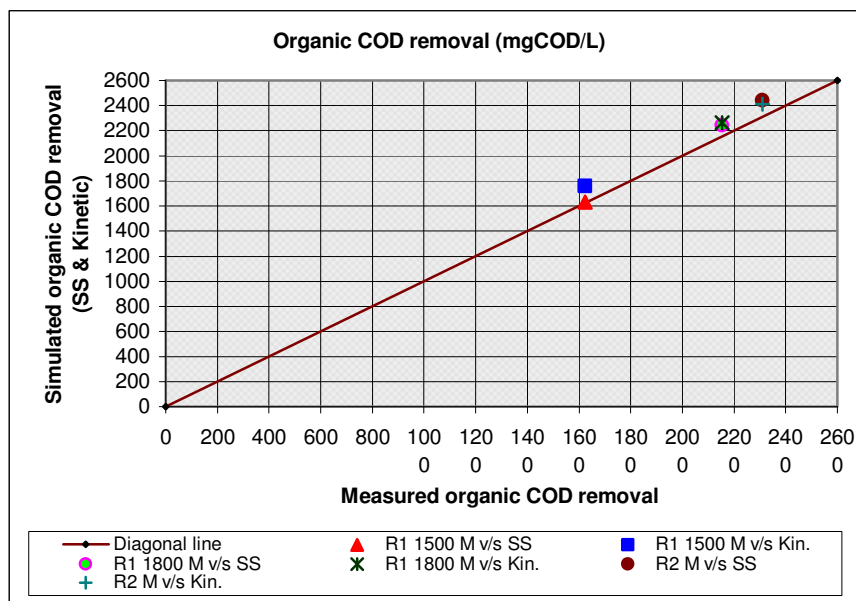


Figure 7.9: Comparison of models predicted organic COD removal concentrations with measured values.

(iii) Comparison of the effluent total soluble COD

For the effluent total soluble COD (organic + sulphide COD), again the simulated results are in good agreement with the experimental values (Figure 7.10). As discussed earlier, H_2S measurement was a problem during the first 280 days of UASB R1 operation period, indicated by the poor correlation. However, for the rest of the data points, good comparisons were predicted by the models.

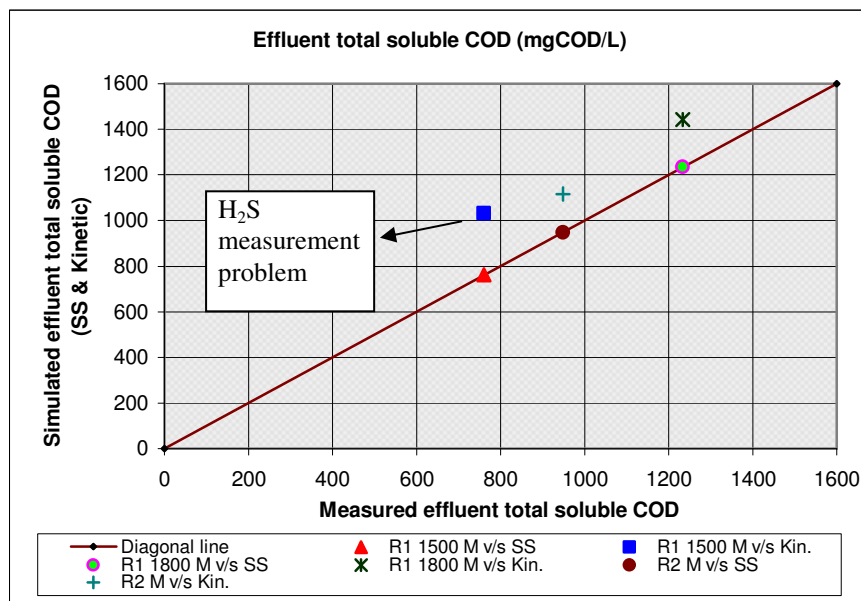


Figure 7.10: Comparison of models predicted effluent total soluble concentrations with measured values.

(iv) Effluent/Reactor pH

The effluent/reactor pH was particularly well predicted by both the steady state and UCTADM1-BSR models (Figure 7.11). Though not significant, the kinetic model pH prediction is slightly higher (~ 0.1 of a pH unit) than the SS model and measured values. This is because of the slightly better simulation model predicted sulphate removal which in turn increased the total alkalinity (contributed by the higher HS^- and HCO_3^- species concentrations).

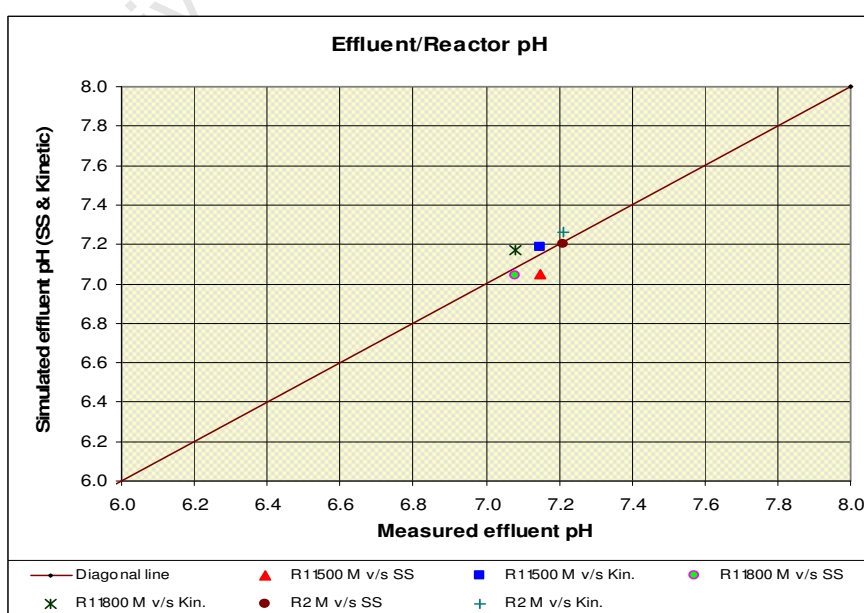


Figure 7.11: Comparison of models predicted effluent/reactor pH with measured values.

(v) Effluent VFA

The simulated behaviour of the effluent VFA conforms well to that experimentally measured except for one data point (Figure 7.12). The small differences in the plot are probably due to variations in the experimentally measured data which have a high standard deviation of the mean (e.g. 72 ± 67 mgHAc/L for R1 fed $1500 \text{ mgSO}_4^{2-}/\text{L}$). However, these differences are irrelevant when considering the organic removal concentrations of the UASB (see Figure 7.9).

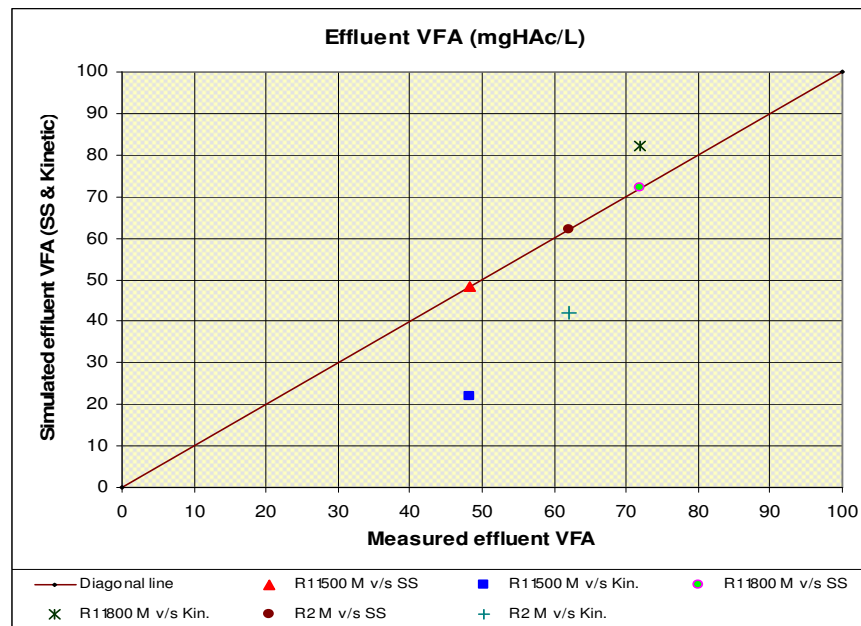


Figure 7.12: Comparison of models predicted effluent VFA concentrations with measured values.

(vi) Effluent FSA

The predicted FSA concentrations compare reasonably well with the measured effluent values, with the exception of the same data point R1 ($1800 \text{ mgSO}_4^{2-}/\text{L}$) (Figure 7.13). This data point mirrors the VFA concentration shown in the previous graph (Figure 7.12) suggesting that a slightly higher sulphate reduction is achieved, especially in UASB R1 ($1800 \text{ mgSO}_4^{2-}/\text{L}$) in the UCTADM1-BSR model. However, again, the deviation is not significant and overall the predictions are considered reasonably accurate.

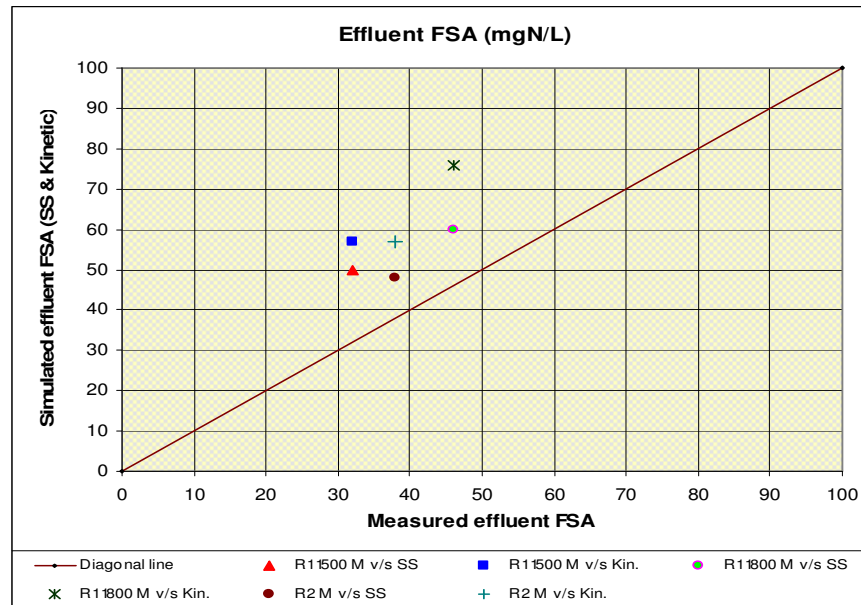


Figure 7.13: Comparison of models predicted with measured effluent FSA concentrations.

(vii) Effluent alkalinity

The measured and predicted alkalinities (both sum of H_2CO_3^* alk + Alk H_2S and H_2CO_3^* alk) correspond reasonably well (Figures 7.14 and 7.15). As discussed earlier, measurements of aqueous H_2S was problematic at the beginning of this investigation, namely during R1 (1500 $\text{mgSO}_4^{2-}/\text{L}$) operation period. However, the difference is not very significant considering the magnitude of the absolute difference and the complexity of the mixed acid/base systems involved in BSR.

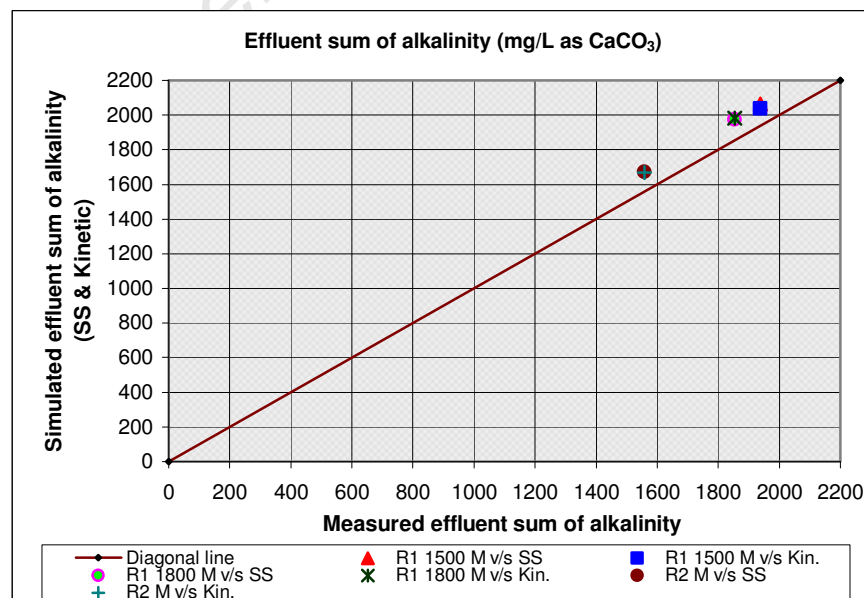


Figure 7.14: Comparison of models predicted effluent sum of H_2CO_3^* alk and Alk H_2S concentrations with measured values.

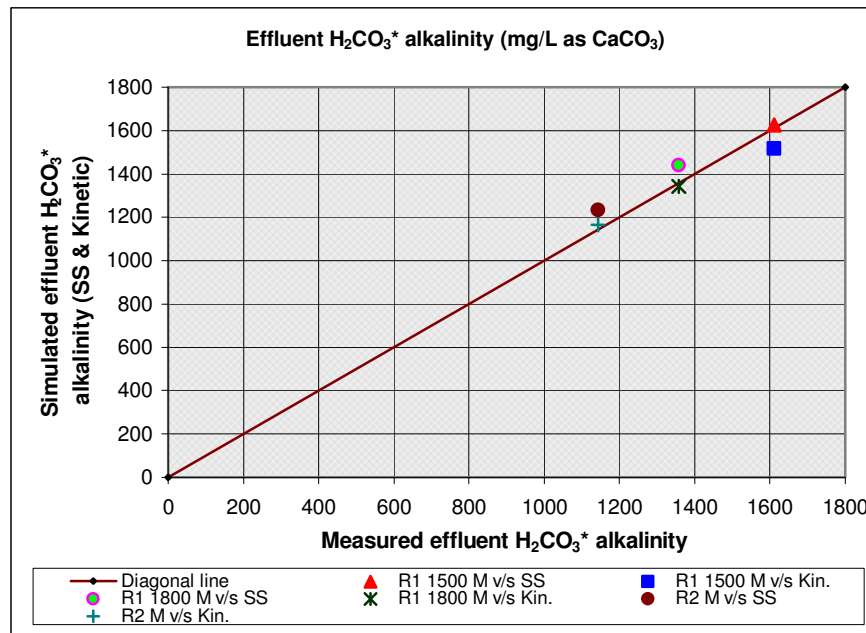


Figure 7.15: Comparison of models predicted effluent H_2CO_3^* alk concentrations with measured values.

7.4.3 GENERAL DISCUSSION

The above comparison graphs (Figures 7.7 to 7.15) depict a very good correlation between the experimental measured data and the simulated results from both the steady state (SS) and the UCTADM1-BSR (kinetic) models. The difference on one or two graphs for effluent concentrations may appear significant but the absolute difference is very small when compared with the removal concentrations (e.g. the effluent sulphate concentration as compared with the sulphate removal concentration). Moreover, some of the differences (though not significant) possibly come from imperfect mass balances - with the models, all the mass balances (COD, S and N) are 100% while with the experimental data they are between 95-105%.

As expected from the stoichiometry, the models predict almost zero (10^{-7} mol/L influent) CH_4 gas production. This shows that SRB growth is faster and completely outcompetes the methanogens in a sulphate rich environment. Further, the gaseous CO_2 production in the UCTADM1-BSR also is zero as anticipated from the steady state stoichiometry of BSR, where the PSS ($\text{C}_{3.35}\text{H}_7\text{O}_{1.45}\text{N}_{0.45}$) is carbon deficient.

Another interesting outcome from the good UCTADM1-BSR model predictions is the successful integration and calibration of the sulphide inhibition term and the temperature dependency equation (in the case of R2 at 20 °C). The K_{I-as} value for the acetotrophic SRB was found to be 206 mgS/L for a 94% growth inhibition by the undissociated H_2S using the exponential inhibition term $\exp[-([H_2S]_i/0.60056K_{I,j})^2]$. The θ value for the temperature dependency equation was 1.114 in the UCTADM1-BSR model, representing a 30% decrease in the PSS biodegradable organics hydrolysed when the temperature is decreased from 35 °C to 20 °C.

7.5 CLOSURE

In this Chapter, 2 models for BSR have been successfully developed and validated – the steady state (SS) and the UCTADM1-BSR kinetic model. The SS anaerobic digestion model for BSR using PSS as carbon source and electron donor comprises three sequential parts: a COD based hydrolysis kinetics part, a CHONS and COD mass balance based stoichiometry part and a mixed weak acid/base chemistry part. The hydrolysis kinetics of PSS have been taken from Ristow *et al.* (2005) and Sötemann *et al.* (2005a) since they concluded that this is the same for both sulphidogenic and methanogenic systems. The stoichiometry of BSR indicated that the PSS is C deficient in that its utilisation releases too little CO_2 to meet the alkalinity (HCO_3^-) demand for the sulphate reduction. This causes a respeciation of the H_2S/HS^- system and establishes the reactor pH. The model predicted results including pH, correlate very well with the experimental results from 3 lab-scale UASB BSR systems. This provides support for the developed BSR stoichiometry which gives considerable insight into the inter-relationship between the biological processes and weak acid/base chemistry systems. The SS BSR model also provides a basis for crosschecking the results from the UCTADM1-BSR model developed in this same Chapter.

With regard to the integrated 2 phase (aqueous-gas) mixed weak acid/base chemistry and biological processes simulation model for competitive methanogenic and sulphidogenic anaerobic digestion with PSS as energy source for BSR (UCTADM1-BSR), this model was reviewed and fine-tuned to simulate the lab-scale UASB BSR systems. The kinetic model predictions (restricted to steady state conditions) conform favourably well to the experimental measurements and the SS model results and therefore provides support for the

successful development, calibration and validation of the kinetic simulation model. For more extensive model evaluation and validation, application to simulate dynamic states would be desirable. This is beyond the scope of this project but can be considered for further investigation using the comprehensive dynamic experimental data sets gathered from this detailed study. The AQUASIM electronic file for UCTADM1-BSR model is available on request at the Water Research Group of the University of Cape Town.

University of Cape Town

APPENDIX 7A

Results from elemental analyses of dried primary sewage sludge (PSS) and waste sludge (WS).

	Waste sludge composition (% by mass on TSS)				
Parameters	R1 A	R1 B	R2 A	R2 B	PSS
Moisture	3.1	3.2	3.1	2.8	
Ash	33.9	33.1	29	28.9	
Volatile	55.4	55.4	59	59.2	
Fixed Carbon	7.6	8.3	8.9	9.1	
Carbon	34.65	35.28	38.58	38.5	43.01
Hydrogen	4.87	4.9	5.45	5.52	7.31
Nitrogen	3.35	3.36	3.91	3.91	6.61
Carbonates	3.21	3.22	1.93	1.93	
Total Sulphur	3.49	3.32	2.95	2.62	
Oxygen	13.43	13.62	15.08	15.82	
Phosphorus (P ₂ O ₅)	8.19	16.21	11.92	10.99	
Moles Carbon	0.958	0.976	1.067	1.065	1.182
Moles Hydrogen	1.617	1.626	1.809	1.832	2.426
Moles Oxygen	0.279	0.283	0.313	0.328	
Moles Nitrogen	0.079	0.080	0.093	0.093	0.157
Factor w.r.t. y=l=7	4.330	4.304	3.869	3.820	2.885
x (k)	4.150	4.200	4.129	4.069	3.411
y (l)	7.000	7.000	7.000	7.000	7.000
z (m)	1.206	1.216	1.211	1.254	
a (n)	0.344	0.343	0.359	0.354	0.452

Table A7.1: Elemental analysis of dried PSS and waste sludge.

The value of m in the CHON composition of the biomass is too low and was therefore not utilised. Instead, m was assigned a value of 2 and y=7. The biomass composition was thereafter calculated by iteration to match the measured f_{cv} and f_n ratios.

Chapter 8

Conclusions

Since the economics of biological sulphate reduction (BSR) are governed by the economics of the organic source, the BioSURE[®] process has been developed as a low-cost effective system where BSR is achieved using primary sewage sludge (PSS) as energy source. In this research the use of PSS for BSR in an upflow anaerobic sludge bed (UASB) reactor was investigated in detail to exploit and further develop this novel technology. As a result, a number of significant outcomes of this thesis project are brought about and these are enumerated below.

1. The capabilities and limitations of BSR with PSS in a UASB reactor configuration at 2 operating temperatures, 35 and 20 °C and at different organic and sulphate loading rates have been comprehensively understood. The design and operating parameters of the UASB systems have been determined from the analysis of the extensive experimental data gathered from the lab work.
2. One very important design parameter is the upflow velocity (V_{up}) which is directly related to the hydraulic retention time (HRT). HRT and V_{up} directly impact the sludge bed stability in the UASB system. By means of a settleometer the settling rate of the various solids fractions in the sludge bed was measured. From the settleability test it was found that bed expansion rather than sludge settleability was the capacity limiting process beyond the lowest optimal HRT. This finding helped to establish the optimum balance between the HRT (and V_{up}) and the bed expansion (which governs the sludge age).
3. New simple wet chemistry analytical procedures for the accurate determination and measurement of aqueous hydrogen sulphide to balance the mass of COD and sulphur around the UASB BSR system have been successfully developed. These methods resulted in COD and S mass balances close to 100%.

4. Both a steady state (SS) and a dynamic (UCTADM1-BSR) anaerobic digestion models for BSR were successfully developed. The model predicted results correlate very well to the experimental values. The stoichiometry part of the steady state model showed that the PSS (and other organic compounds with COD/C ratios > 2.67) is carbon deficient in that it can donate more electron than the C (CO_2) required for the alkalinity increase. As a consequence, the sulphate system supplies the missing alkalinity as Alk H_2S , and the $\text{H}_2\text{S}/\text{HS}^-$ ratio governs the pH of the reactor.

The salient features of each of the above outcomes are elaborated below and the appropriate conclusions and recommendations made.

8.1 OPERATION AND PERFORMANCE OF UASB REACTORS R1 (35 °C) AND R2 (20 °C)

The first part of the investigation focused mainly on the potential of PSS to serve as an energy source for BSR using the UASB reactor (R1 fed $1500 \text{ mgSO}_4^{2-}/\text{L}$ at 35 °C). The UASB reactor R1 was operated for 280 days with an influent sulphate concentration of $1500 \text{ mgSO}_4^{2-}/\text{L}$ and COD $1875 \text{ mgCOD}/\text{L}$ ($\text{COD}/\text{SO}_4^{2-} = 1.25$) and it was concluded from the results obtained that this sulphate concentration level was successfully reduced under sulphidogenic conditions with an average effluent sulphate concentration of $149 \text{ mgSO}_4^{2-}/\text{L}$ at a HRT of 13.5h and a bed volume of 86% of the reactor liquid volume. Excellent solid-liquid separation in the system was obtained with unfiltered organic COD $<200 \text{ mgCOD}/\text{L}$, achieved even at a HRT of 13.5h, with very low solids content in the effluent. From bed solids concentration-height profiles, the bed sludge age (R_s), i.e. the mass of sludge in the bed in relation to the mass of sludge wasted per day (to maintain the bed volume) and mass of sludge in the effluent was determined to be 18d. The PSS and likewise the reactor sludge, which had a good settleability, appeared to enmesh and entrap fine solids arising from biodegradable particulate organic breakdown. Sludge bed granulation in the system was observed, which further enhanced solid-liquid separation.

When the reactor was operated at a HRT lower than 13.5h while maintaining the sludge bed height constant, effluent quality from the UASB reactor deteriorated. This deterioration was ascribed to the reduced sludge bed biomass caused by sludge bed expansion and sludge loss with the effluent as a result of the increased upflow velocity (see later).

Particular attention was focussed on the effect of a sludge mass recycle line (at half the influent flow rate) from the top to the bottom of the reactor bed, by conducting profile tests along the axis of flow through the UASB reactor. The sludge recycle allowed greater SRB biomass distribution throughout the bed, facilitating sulphate reduction as soon as the feed entered the reactor. This recycling of the sludge bed therefore adds considerable advantages to the UASB BSR configuration. Based on the results of this preliminary investigation, the pilot plant of the Grootvlei Mines Ltd (Springs, South Africa) was scaled up from 2 ML/d to 10 ML/d.

During this part of the investigation the COD, S and N mass balances over the UASB R1 system averaged 88.7%, 68.7% and 97.1% respectively. The relatively low COD and S mass balances were attributed to the loss of H_2S during sample handling and vacuum filtration. The measured total effluent sulphide concentration was too low when compared with the sulphate reduced. This prompted an investigation to develop simple wet chemistry analytical procedures to address the problem of sulphide measurement to fix the COD and S mass balances close to 100% (see Section 8.2 below). After modifying the analytical procedures to minimise H_2S gas loss, very good COD, N and S mass balances were obtained on all the systems operated ((Table 8.1).

Table 8.1: COD, Sulphur and Nitrogen mass balances of UASB reactors R1 and R2 under steady state conditions at their respective lowest optimal hydraulic retention times.

UASB reactor	Mass Balances (%)		
	COD	Sulphur	Nitrogen
R1 (1500 mgSO ₄ ²⁻ /L) at 35 °C	88.7 ± 0.8*	68.7 ± 3.4*	97.1
R1 (1800 mgSO ₄ ²⁻ /L) at 35 °C	96.5 ± 0.8	95.8 ± 2.9	102.5 ± 8.1
R2 (1500 mgSO ₄ ²⁻ /L) at 20 °C	98.8 ± 2.9	95.9 ± 0.1	104.5 ± 4.9

* Prior to the development of the new analytical methods for accurate H_2S measurement.

Following the successful operation of the UASB reactor R1 at 35 °C (fed 1500 mgSO₄²⁻/L for a period of 280 days), the performance of BSR using PSS at ambient temperature, namely 20 °C was studied in a second identical UASB reactor (R2). Initially, reactor R2 (T=20 °C) was run with a feed sulphate and PSS concentrations of 1500 mgSO₄²⁻/L and 1995 mgCOD/L representing a feed PSS COD to sulphate ratio of 1.33 mgCOD/mgSO₄²⁻,

but this ratio was later increased to 1.75 to improve the system efficiency and achieve low effluent sulphate concentration ($< 250 \text{ mgSO}_4^{2-}/\text{L}$). The minimum HRT was 20.5h, the bed volume was 95% of the reactor liquid volume, and the sludge age 24d. A disadvantage of the 20°C system as operated in this investigation is the significantly lower % of PSS biodegradable organics utilised (~60%) than at 35°C (~90%). This can be overcome by increasing the sludge age (i.e. bed volume and HRT) allowing more time for hydrolysis, higher % PSS biodegradable organics utilisation and lower influent $\text{COD}/\text{SO}_4^{2-}$ ratio.

The successful operation of UASB reactor R2 at 20°C is important because it demonstrates the viability of treating sulphate-rich water without heating. In fact, the 10 ML/d Ancor mine AMD treatment plant operates at ambient temperature. This investigation shows that the two critical design parameters are sludge age and HRT but that length of sludge age can be traded off by increasing the feed $\text{COD}/\text{SO}_4^{2-}$ ratio.

The UASB R1 (at 35°C) was operated at a higher influent sulphate concentration ($1800 \text{ mgSO}_4^{2-}/\text{L}$) to study possible inhibition by higher undissociated hydrogen sulphide concentration. A high sulphate reduction (~92%) was achieved even at the relative low HRT of 18.5h. These R1 results were useful for calibrating the value of the acetotrophic SRB inhibition constant (K_I) used in the kinetic simulation model (UCTADM1-BSR).

Initially the influent to the UASB reactors was dosed with alkalinity to assist in establishing a reactor pH of 7-8. For the last 2 to 3 sludge ages of both R1 (35°C) and R2 (20°C), alkalinity dosing was stopped. The systems maintained a $\text{pH} > 7.0$ indicating that the bioprocesses are pH self-regulatory, which is important for the economics of the system.

For R1 (35°C), batch tests were conducted on top, bottom and mixed bed sludges to qualitatively and quantitatively assess the process rates taking place in the UASB reactor. The batch results confirmed the need to recycle sludge from the top to the bottom of the bed because without recycle sulphidogenesis (and not acidogenesis) is the rate limiting step at the bottom part of the sludge bed. The sulphate reduction rates with the top, bottom and mixed sludges were 1184, 595 and 929 $\text{mgSO}_4^{2-}/\text{L}/\text{d}$ respectively. These batch sulphate reduction rates were used to calculate the process kinetic rates. The value of the saturation maximum hydrolysis rate constant (K_M) was found to be 6.68, 5.01 and 3.67 $\text{gCOD}_{\text{substrate}}/(\text{gCOD}_{\text{biomass}}\cdot\text{d})$ from batch tests conducted on the reactor top, mixed and

bottom sludge respectively. The first 2 rates are close enough to the value of 5.27 gCODsubstrate/(gCODbiomass.d) reported by Sötemann *et al.* (2005a) for methanogenic systems. Batch tests results using acetic acid as substrate gave sulphate reduction rates of 649.4-851.2 mgSO₄²⁻/L/d and yielded values of 0.502-0.658 (mgCOD/mgCODbiomass)/d for the maximum specific acetic acid utilisation rate ($\mu_{\max}$), closely similar to the $\mu_{\max}$ value of 0.612 (mgCOD/mgCODbiomass)/d from Kalyuzhnyi *et al.* (1998).

From the experimental data of this detailed investigation, a summary of the design and operating parameters established for the 3 UASB BSR systems is listed in Table 8.2.

Table 8.2: Design and operating parameters for BSR UASB system using PSS as carbon and energy source.

Design and operating parameters	Unit	Average values		
		R1 (35 °C)	R1 (35 °C)	R2 (20 °C)
Feed PSS COD based on f_{PSup} of 0.36	mgCOD/L	1880	2584	2596
Feed sulphate	mgSO ₄ ²⁻ /L	1500	1800	1500
Influent pH	-	7.20 ^a	5.99	5.94
Influent flow rate, Q_i	L/d	13.6	10.4	9.2
Organic loading rate, OLR	g/m ³ /d	3886	3788	3224
Sulphate loading rate, SLR	g/m ³ /d	3100	2637	1863
Reactor liquid volume	L	7.8	7.8	7.8
Reactor bed volume	L	6.7	7.1	7.4
Sludge recycle ratio (w.r.t. Q_i)	-	0.5	0.5	0.5
Upflow velocity, V_{up}	m/h	0.127	0.096	0.085
Hydraulic retention time, HRT	h	13.8	18.0	20.4
Sludge aspect ratio (bed height/diameter)	-	10.5	11.2	11.6
Bed hydraulic retention time, BRT	h	11.8	16.4	19.3
Sludge retention time (Sludge age), R_s	d	18	21	24
Waste flow rate, Q_w	L/d	0.37	0.34	0.31
Expected sulphate removal rate	g/m ³ /d	2792	2423	1737
Expected sulphate reduction	%	90.1	91.9	93.3

a: Alkalinity dosage to feed but concluded not necessary since the system is pH self-regulatory

8.2 DEVELOPMENT OF SIMPLE WET CHEMISTRY ANALYTICAL PROCEDURES

Initially the measurements of the total aqueous hydrogen sulphide, S_T ($= H_2S$ and HS^-) were inaccurate. For calibration of models based on mass balances, and operation of full-scale systems, it was imperative to develop simple wet chemistry analytical procedures for the accurate measurement of parameters like sulphide, COD, alkalinities and VFA in order to monitor BSR systems and achieve 100% COD and S mass balances.

To address the issue of poor S balances, three different analytical methods were investigated to minimise the loss of undissociated H_2S . Method 1 which is the recommended Standard Methods (1985) COD test method resulted in poor S mass balance (64-75%) due to loss of H_2S during sample handling, mainly vacuum filtration. Method 2, in which 3 drops of 10 M NaOH are added immediately upon effluent sample collection to raise the pH to > 10 and converting undissociated H_2S species into the HS^- species resulted in minimal sulphide is lost during sample vacuum filtration, dilution, mixing and standing. Method 3, in which a polyelectrolyte is added to the effluent sample to coagulate the organic particles and uses centrifugation for solid-liquid separation instead of vacuum filtration. Results from Method 3 showed an improvement in the S mass balance with respect to Method 1 - 91% against 75% without a long sample standing period and 88% against 65% with a long sample standing period). However, S mass balance with Method 3 was still relatively low when compared with Method 2 (86-91% against 92-95%). Therefore, Method 2 was the best simple wet chemistry analytical procedure to accurately measure S_T ($= H_2S + HS^-$) and achieve close to 100% COD and S mass balances. Accurate S_T measurement is essential to correctly speciate the total alkalinity into $H_2CO_3^*$ alk. and Alk H_2S .

With the measurement problem of S_T resolved, the effects of S_T loss were investigated on the total and subsystem alkalinities as determined with the 5-pH point titration method of Moosbrugger *et al.* (1992). This method for measuring the $H_2CO_3^*$ alk. and volatile fatty acid (VFA) concentrations requires the sulphide concentration to be known when above negligible concentration. By testing standard solutions with known carbonate, acetate and sulphide species and UASB effluent samples, it was found that (1) the total alkalinity concentration is not affected by H_2S (and CO_2) loss as the subsystem alkalinities re-speciate due to a change in pH and (2) to obtain accurate $H_2CO_3^*$ alk. and volatile fatty acid (VFA)

concentrations, accurate sulphide concentrations are required, i.e. those obtained from Method 2.

Because one of the objectives of this research was to develop simple (but accurate) wet chemistry methods for operation and control of full-scale BSR systems, the prospect of developing a 7-pH point titration method was explored with standard solutions but found not feasible. To characterise a system with e.g. the phosphate, ammonium, sulphide, acetate, carbonate and water weak acid/base subsystems, 6 measurements are required, one for each subsystem. For the first four, these are the total species concentrations (P_T , N_T , S_T and A_T), for the carbonate subsystem the $H_2CO_3^*$ alk. and for the water subsystem the pH. The $H_2CO_3^*$ alk. allows loss of CO_2 without affecting the accuracy of the results. Because significant S_T (H_2S) loss was observed during the titration S_T measurement falls away requiring a substitute to be found. The Alk H_2S cannot be substituted because the titration approach allows only one subsystem to change – with two the change in each is not known. It is possible to change the 5-pH point titration programme to assume H_2S loss but no CO_2 and obtain C_T from an inorganic carbon analyser. Because this defeated the objective of developing simple and inexpensive analytical procedures to monitor BSR systems, this approach was abandoned – the method of determining S_T separately with the COD test (Method 2) is better. With S_T accurately known before the 5-pt titration, H_2S loss during the titration does not affect the accuracy of the $H_2CO_3^*$ alk. and VFA concentrations obtained.

8.3 MEASUREMENT OF SLUDGE SETTLEABILITY

From the operation of the R1 (35 °C) and R2 (20 °C) UASB reactors, it was found that decreasing the HRT below the optimal (13.5h for R1 at 1500 mgSO₄²⁻/L, 18h for R1 at 1800 mgSO₄²⁻/L and 20h for R2 at 1500 mgSO₄²⁻/L) resulted in unstable bed conditions and progressive system failure, indicated by poor effluent quality - high effluent VFA, SO₄²⁻ and particulate COD. To examine bed dynamics, a sludge settleability device (called a settleometer) was designed following the principle outlined by Moosbrugger (1994). From the results obtained, it is concluded that both R1 and R2 sludges settled well as 99% of the total sludge settled faster than 1.16 m/h. This upflow velocity was 9.1 and 13.7 times higher than the maximum operating upflow velocity (V_{up}) of R1 (0.127 m/h) and R2 (0.085 m/h). Tests were also done to observe the effect of upflow velocity on sludge bed expansion. Based on V_{up} at minimum HRT, it was found that R1 sludge had a bed expansion ratio of

1.8 at V_{up} of 0.127 m/h while R2 sludge had a bed expansion ratio of 2.0 at V_{up} 0.085 m/h. Since the bed was maintained at constant volume, the mass of sludge removed from the system increased with increasing upflow velocity, causing reduction in the sludge bed mass, the sludge age and concomitantly a reduction in the biomass available to mediate the BSR reactions. It was concluded that bed expansion rather than the sludge settleability causes system failure at upflow velocities higher than the optimum. The R1 sludge (35 °C) had a better settleability and expanded less compared with R2 sludge (20 °C) at the same upflow velocity. Hence the shorter minimum HRT for R1 compared with R2 at the same influent sulphate concentration.

8.4 STEADY STATE AND KINETIC MODELS FOR BIOLOGICAL SULPHATE REDUCTION

Two models for BSR have been successfully developed and validated – the steady state (SS) and the UCTADM1-BSR kinetic models. The SS model for BSR using PSS as carbon source and electron donor comprises three sequential parts: (i) a COD based kinetic part for PSS hydrolysis from which the % PSS COD, sulphate removal and (acidogen) biomass concentration are calculated for a given sludge retention time (sludge age). This is the same as that developed by Sötemann *et al.* (2005a) for methanogenic AD systems; (ii) a C,H,O,N,S, COD and charge mass balance based stoichiometry part from which the alkalinity generated (from both the HCO_3^- and HS^-) are determined from the % COD and sulphate removal and (iii) a mixed weak acid/base chemistry part from which the digester pH is calculated from the HCO_3^- and $\text{H}_2\text{S}/\text{HS}^-$ species formed.

In the kinetic part it is accepted that the hydrolysis/acidogenesis process is the overall BSR rate limiting step and proceeds at the same rate as under methanogenic conditions (Ristow *et al.* 2005). Accordingly, the hydrolysis kinetics of PSS were taken from Ristow *et al.* (2005) and Sötemann *et al.* (2005b). From the stoichiometry, it was found that the PSS with composition $\text{C}_{3.35}\text{H}_{7.0}\text{O}_{1.45}\text{N}_{0.45}$ (determined from CHN elemental analysis) is C-deficient in that it does not generate sufficient HCO_3^- alkalinity for the sulphate reduction, i.e. its COD/C ratio is too high (>2.67) which accounts for the observed (and predicted) zero gas (CO_2) generation. This CO_2 deficiency causes respeciation of the $\text{H}_2\text{S}/\text{HS}^-$ system which provides the alkalinity shortfall and establishes the system pH. The absence of a gaseous CO_2 generation allowed the carbon released from the biodegraded organics to be measured

via the H_2CO_3^* alk.. From this and the CHN elemental analysis 98.4, 94.0 and 90.3 % carbon mass balances were achieved over the R1 (1500 $\text{mgSO}_4^{2-}/\text{L}$), R1 (1800 $\text{mgSO}_4^{2-}/\text{L}$) and R2 systems.

The SS model predicted results including pH, correlate very well with the experimental results from 3 lab-scale UASB BSR systems (Table 8.3). This provides support for the developed BSR stoichiometry which gives considerable insight into the inter-relationship between the biological processes and weak acid/base chemistry systems. The SS BSR model also provides a basis for crosschecking the results from the UCTADM1-BSR model developed.

Following the development of the SS BSR model, the integrated 2 phase (aqueous-gas) mixed weak acid/base chemistry and biological processes simulation model for BSR (UCTADM1-BSR) developed by van Wageningen *et al.* (2007) was revised and fine-tuned to simulate the lab-scale UASB BSR systems operated in this research investigation. In the development of this dynamic model, some of the relevant processes and kinetics for BSR were extracted from Kalyuzhnyi *et al.* (1998) and Fedorovich *et al.* (2003). Where required, other relevant processes and kinetics were modified or added to the existing ones and integrated into the PSS methanogenic anaerobic digestion model (UCTADM1) developed by Sötemann *et al.* (2005a) to yield the UCTADM1-BSR dynamic model for competitive methanogenic and sulphidogenic anaerobic digestion with PSS as energy source.

In modifying the BSR dynamic model, a sulphide inhibition term for the acetotrophic SRB growth rate equation and a temperature dependency term for the maximum specific hydrolysis rate and the half saturation coefficient in the saturation hydrolysis rate equation (in the case of UASB R2 at 20 °C) were incorporated. The K_{I-as} value for the acetotrophic SRB was found to be 206 mgS/L for a 94% growth inhibition by the undissociated H_2S using an exponential inhibition term $\exp[-([\text{H}_2\text{S}]_i/0.60056K_{I,i})^2]$. The θ temperature dependency value was 1.114, representing a 30% decrease in the PSS biodegradable organics hydrolysed when the temperature is decreased from 35 °C to 20 °C. The kinetic simulation model predictions (restricted to steady state conditions) conform favourably well to the experimental measurements and the SS model results (Table 8.3) and therefore provides support for the successful development, calibration and validation of the kinetic simulation model.

Table 8.3: Comparison of experimentally Measured (M) effluent values with the Steady State (SS) BSR and the UCTADM1-BSR kinetic (Sim) model predictions.

Parameters	Units	UASB R1 at 35°C (fed 1500 mgSO ₄ ²⁻ /L)			UASB R1 at 35°C (fed 1800 mgSO ₄ ²⁻ /L)			UASB R2 at 20°C (fed 1500 mgSO ₄ ²⁻ /L)		
		M	SS	Sim	M	SS	Sim	M	SS	Sim
Effluent sulphate	mgSO ₄ ²⁻ /L	149	149	136	146	145	115	101	104	103
Sulphate removal	mgSO ₄ ²⁻ /L	1351	1351	1364	1654	1355	1685	1399	1396	1397
Organic COD removal	mgCOD/L	1624	1632	1757	2153	2242	2264	2309	2444	2410
Effluent total soluble COD	mgCOD/L	761 ^a	761 ^b	1031	1234	1234 ^b	1442	951	951 ^b	1116
Effluent organic soluble COD	mgCOD/L	141	141 ^b	123	229	229 ^b	320	96	96 ^b	186
Effluent HS/H ₂ S	(mgS/L)/(mgS/L)	209/101 ^a	277/173	336/120	318/184	339/213	409/153	261/166	280/185	321/145
Reactor pH	-	7.15	7.05	7.19	7.08	7.04	7.17	7.21	7.20	7.26
Effluent sum of H ₂ CO ₃ * alk and Alk H ₂ S	mg/L as CaCO ₃	1938 ^a	2063	2039	1855	1974	1982	1558	1672	1668
Effluent H ₂ CO ₃ * alkalinity	mg/L as CaCO ₃	1611 ^a	1627	1516	1358	1441	1343	1144	1234	1166
Effluent VFA	mgHAc/L	48	48 ^b	22	72	72 ^b	82	62	62 ^b	42
Effluent FSA	mgN/L	32	50	57	46	60	76	38	48	57
H ₂ S effluent gas stream	mgS/L influent	0	0	0	0	0	0	0	0	0
CO ₂ effluent gas stream	mol/L	0	0	0	0	0	0	0	0	0

a: H₂S measurement problem during the first 280 days of UASB R1 operation period, system total alkalinity unaffected by loss of H₂S while H₂CO₃* alk. and Alk H₂S are affected.

b: The Steady State (SS) model for BSR is based on substrate utilisation, hence the concentration of the effluent solubles is given the experimental values.

Both the steady state and kinetic simulation models are very useful tools for the design of BSR systems in which PSS is used in the treatment of AMD. Furthermore, because they were developed for multi-organic general substrate formulation, they can accommodate other substrate types such as VFA (or a mixture of SCFA) and therefore can be applied where other organics are used for BSR.

8.5 FURTHER RESEARCH

Laboratory scale research on the UASB system for BSR using PSS has been completed in this research project and all aspects relevant for determining the important design and operating parameters have been investigated in detail. Further research should focus on

applying the test methods – sulphide via COD, 5-pH point titration and settleometer – to operation and control of full-scale systems in particular the BioSURE[®] system at Ancor WWTP. While additional data on UASB sludge settleability and bed expansion would be useful, these results are probably fairly site specific and would need to be measured *in situ* to optimise a particular UASB system.

With regard to modelling, both a steady state and a dynamic simulation kinetic model have been developed, calibrated and validated against the UASB system data. These models allow multi-organic variable composition feed specification. Should a BSR model with the sole biological processes consuming the SCFA and H₂ substrates generated from PSS hydrolysis and acidification be required, the methanogenic processes can be switched off in the UCTADM1-BSR model resulting in an exclusive sulphidogenic model. Moreover, although UCTADM1-BSR has been developed purposely for situation where PSS serves as the feed substrate, it offers nonetheless a much broader potential application. For instance, should the feed be a particulate substrate (e.g. a mixture of PSS and compost, compost alone or a mixture of PSS and waste activated sludge), only the feed substrate composition and kinetic constants for hydrolysis would require modification. For soluble organics (e.g. acetate or a mixture of SCFA), they would be used directly as input to the model as they serve as intermediates in the processes already included in the model. In fact, other organic sources have been explored for BSR in South Africa such as grass cuttings (work conducted by the CSIR) and high strength organic wastes such as Sasol's Coal to liquid Fischer Tropsch reaction (Rx) water (work commenced at the University of Cape Town). This water is produced in South Africa in such high concentration (18 gCOD/L) and volume (30 ML/d) that it may be worth transporting to other acid mine drainage sites and used for BSR. It would be interesting to apply and test the steady state and UCTADM1-BSR models against these organic sources.

Another aspect of BSR that requires research is the removal of hydrogen sulphide from the BSR effluent. Though this stream can be recycled to precipitate the metals in the raw mine water, a relative high H₂S concentration still remains in the residual stream which needs to be removed before discharge. The conversion of H₂S (stripped from the effluent) into elemental sulphur which has a market value seems to be a feasible option for investigation.

Chapter 9

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviation	Description
Ac	Acetate
AD	Anaerobic Digestion
ADM1	Anaerobic Digester Model No. 1
Alk	Alkalinity
AMD	Acid Mine Drainage
BSR	Biological Sulphate Reduction
BRT	Bed hydraulic Retention Time (d)
C	Carbon
°C	Degrees Centigrade
COD	Chemical Oxygen Demand
d	Day
Eq	Equation
DO	Dissolved Oxygen
f_d	Di-valent Activity Coefficient
f_m	Monovalent Activity Coefficient
FSA	Free and Saline Ammonia
FSBR	Falling Sludge Bed Reactor
H	Hydrogen
HAc	Acetic Acid
HDS	High Density Sludge
HPr	Propionic Acid
HRT	Hydraulic Retention Time
IWA	International Water Association
$k_{\max}$	Maximum specific hydrolysis rate constant for surface reaction
K_s	Half Saturation coefficient
$\mu_{\max}$	Monod Maximum Specific Rate
MS	Metal Sulphide
MW	Molecular Weight
N	Nitrogen
O	Oxygen
OLC	Open Limestone Channels

LIST OF ABBREVIATIONS AND SYMBOLS (CONTINUED)

Abbreviation	Description
Pr	Propionate
PSS	Primary Sewage Sludge
Q	Flow (L/d)
Q_w	Waste flow rate (L/d)
Q_i	Influent Flow Rate (L/d)
r_h	Hydrolysis Rate
R_h	Bed hydraulic retention time (d)
R	Universal gas constant
R_s	Sludge age (or solids retention time)
RSBR	Recycling Sludge Bed Reactor
S_{bpe}	Biodegradable Particulate COD in Effluent
S_{bpi}	Biodegradable Particulate COD in Feed
S_{bsai}	Influent VFA
S_{bsae}	Effluent VFA
S_{bsfe}	Biodegradable Soluble Fermentable COD in Effluent
S_{bsfi}	Biodegradable Soluble Fermentable COD in Feed
SCFA	Short Chain Fatty Acids
SOB	Sulphide Oxidising Bacteria
SRT	Solids Retention Time
SS	Steady State
S_T	Total aqueous sulphide concentration
S_{te}	Total Effluent COD
S_{ti}	Total Feed COD
S_{upe}	Unbiodegradable Particulate COD in Effluent
S_{upi}	Unbiodegradable Particulate COD in Feed
S_{use}	Unbiodegradable Soluble COD in Effluent
S_{usi}	Unbiodegradable Soluble COD in Feed

LIST OF ABBREVIATIONS AND SYMBOLS (CONTINUED)

Abbreviation	Description
T	Temperature in °C
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
Tk	Temperature in Kelvin
TKN	Total Kjeldahl Nitrogen
UASB	Upflow Anaerobic Sludge Bed
UCT	University of Cape Town
UCTADM1	University of Cape Town Anaerobic Digestion Model 1
UCTADM1-BSR	University of Cape Town Anaerobic Digestion Model 1-Biological Sulphate Reduction
V	Volume
V_d	Volume of Digester
VFA	Volatile Fatty Acids
VSS	Volatile Suspended Solids
Y	Biomass Yield Constant
Y_{AD}	Acidogenic biomass Yield constant
Y_{AS}	Acetotrophic Sulphidogenic biomass Yield constant
Z_{AD}	Acidogenic Biomass
Z_{AS}	Acetotrophic Sulphidogenic Biomass
Z_{HM}	Hydrogenotrophic Methanogenic Biomass

Note: Only abbreviations and symbols used in the text are included, those in equations are defined below the appropriate equations.

BIOLOGICAL SULPHATE REDUCTION USING PRIMARY SEWAGE SLUDGE AS ENERGY SOURCE IN AN UPFLOW ANAEROBIC SLUDGE BED REACTOR

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January 2008

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