THE DEVELOPMENT OF A KINETIC MODEL FOR BIOLOGICAL SULPHATE REDUCTION WITH PRIMARY SEWAGE SLUDGE AS SUBSTRATE

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ABSTRACT

Acid Mine Drainage (AMD) waters typically are characterized by high concentrations of heavy metals (Al = 50 – 2 000mg/ℓ; Fe = 10 – 6 700mg/ℓ; Zn = 10 – 100mg/ℓ), sulphate (3 000 – 30 000mg/ℓ) and total dissolved solids (1 800 – 45 000mg/ℓ), coupled with a low pH (2 – 3) (Christensen *et al.*, 1996). The Rhodes BioSURE® Process has been developed as a low cost active treatment system for AMD waters (Rose *et al.*, 2002). Central to this process is biological sulphate reduction (BSR) using primary sewage sludge (PSS) as the electron donor and organic carbon source, with the concomitant reduction of sulphate to sulphide and production of carbonate alkalinity.

To optimise the design, operation and control of BSR with PSS, a mathematical kinetic model of this system would be an invaluable aid. This study describes the development of such a kinetic model, and its application to a series of experimental lab-scale BSR systems fed PSS and sulphate.

The biological processes of importance require inclusion in a kinetic model for BSR. 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, in common with sewage sludge methanogenic anaerobic digestion systems. The products of these processes, the Volatile Fatty Acids (VFA) then enter into the methanogenic or sulphate reduction processes, which operate in competition. The end product of sulphate reduction is sulphide, which is inhibitory to the methanogens, and this inhibition would have to be included in the model. Further, the background weak acid base chemistry would have to be included, since the biological processes consume and produce significant weak acid/base species, e.g. VFA, sulphide, dissolved CO_2. Consumption and production of weak acid / base species will influence the pH established in the reactor, which in turn can influence the rates of the biologically mediated processes. Hence, pH will need to be incorporated directly into the model, as a model predictive parameter, and its interaction with the biological processes modelled. Some of the end products have gaseous equilibria (sulphide, carbon dioxide and methane), so that these also will require inclusion. Thus, identified for inclusion are the following processes, and any interactions between these :

Biological :

- PSS hydrolysis and acidogenesis; acetogenesis; acetoclastic and hydrogenotrophic methanogenesis

- BSR with propionate, acetate and hydrogen

Weak acid/base chemistry

- water, acetate, propionate, carbonate, ammonium, phosphate, sulphate, sulphide
- Gas exchange
- carbon dioxide, ammonia, hydrogen sulphide

Sötemann *et al.* (2005a) have proposed a two phase (aqeous / gas) physical, biological and chemical processes kinetic model for the methanogenic anaerobic digestion of sewage sludges. Using this model as a basis, it is extended to incorporate BSR, with associated additional gas exchange and weak acid/base chemistry processes.

In calibration of the BSR kinetic model, the hydrolysis rate constants and the PSS stoichiometric composition were obtained from analysis of experimental data. These data were measured by Ristow *et al.* (2005) on sulphidogenic reactors fed PSS from the Athlone Wastewater Treatment Works.

The developed model has been evaluated by comparison of predictions with experimental measurements, by simulating the performance of the laboratory scale sulphidogenic digesters operated by Ristow *et al.* (2005). From the comparison it is evident that the simulated results compare favourably with the experimental measurements. This provides support validating the model.

The system simulations described in this thesis have been restricted to steady state, since comprehensive data sets for BSR with PSS are limited, and available for steady state only. A summary of the conclusions that were reached are as follows :

- The PSS is Carbon (C) limited.
- The HS^-/H_2S system defines the pH.
- No gas production is evident as the CO_2 remains dissolved to supply alkalinity.

LIST OF SYMBOLS AND ABBREVIATIONS

Abbreviation	Description
Ac	Acetate
AD	Anaerobic Digestion
ADM1	Anaerobic Digester Model No. 1
ALD	Anoxic Limestone Drains
Alk	Alkalinity
AMD	Acid Mine Drainage
B	Biological
B	Biomass Decay Coefficient
BSR	Biological Sulphate Reduction
CIP	Chemical Ion Pairing
COD	Chemical Oxygen Demand
CP	Chemical / Physical
CPB	Chemical / Physical / Biological
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 Rate Constant for Surface Reaction

LIST OF SYMBOLS AND ABBREVIATIONS (CONTINUED)

Abbreviation	Description
K_S	Half Saturation Constant
μ_{max}	Monod Maximum Specific Rate
MS	Metal Sulphate
MW	Molecular Weight
OLC	Open Limestone Channels
Pr	Propionate
PSS	Primary Sewage Sludge
Q	Flow
Q_i	Influent Flow Rate (ℓ/d)
r^*_{AD}	Volumetric Acidogenic Rate
r^*_{AS}	Volumetric Sulphidogenic Rate
r^*_{HYD}	Volumetric Hydrolysis Rate
R_h	Hydraulic Retention time (d)
RSBR	Recycling Sludge Bed Reactor
SAPS	Successive Alkalinity Producing Systems
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 Acid
SOB	Sulphide Oxidizing Bacteria
SRR	Solids Retention Time
S_{te}	Total Effluent COD

LIST OF SYMBOLS AND ABBREVIATIONS (CONTINUED)

Abbreviation	Description
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
T	Temperature
TDS	Total Dissolved 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
V	Volume
V_d	Volume of Digesters (ℓ)
VFA	Volatile Fatty Acid
VFR	Vertical Flow Reactors
VSS	Volatile Suspended Solids
Y	Biomass Yield Constant
Y^*_{AD}	Acidogen Yield in COD Units
Y^*_{AS}	Acetotrophic Sulphidogen Yield in COD units
Z_{AD}	Acidogen Biomass
Z_{AS}	Acetotrophic Sulphidogen Biomass
Z_{HM}	Hydrogenotrophic Methanogenic Biomass

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CHAPTER 1

INTRODUCTION

1.1 ACID MINE DRAINAGE

Pollution of surface and groundwater resources as a result of mining activities is not unique to South Africa, but occurs in most countries where mining plays a crucial role in the economy. This pollution emanates mainly through the discharge, intentionally (e.g. pumping) or unintentionally (e.g. seepage), of acid mine drainage (AMD) waters to the environment. AMD waters are characterised by low pH (2 - 3), high iron (10 - 6 700 mg/ℓ) and sulphate (3 000 - 30 000 mg/ℓ) (salinity) concentrations, and varying non-ferrous (usually heavy, e.g. Aℓ 50 – 2 000 mg/ℓ) metal and TDS (1 800 – 45 000 mg/ℓ) concentrations (Christensen *et al.*, 1996). These characteristics arise when mining activities expose iron pyrite (FeS_2) in rock to oxygen and water, causing the biologically mediated oxidation of iron pyrite to iron and sulphuric acid, which are released to the water. The resultant low pH causes leaching of non-ferrous metals to the water. Discharge of this AMD water to the environment severely impacts receiving water quality and the environment. The problem of AMD pollution is exacerbated by the fact that AMD may only surface when the last operator in an area shuts down operation (Holtzhausen, 2005).

Accordingly, treatment of AMD prior to discharge, to lessen the environmental impact, has received increasing attention (Holtzhausen, 2005), particularly in South Africa. This treatment requires neutralisation of the pH and removal of the metals (ferrous and non-ferrous) and sulphate. To affect these, various treatment methods have been proposed.

Most conventional methods of treatment of AMD involve chemical and / or physical processes, such as precipitation (e.g. as barium sulphate, gypsum; Hammack *et al.*, 1994) and / or membrane filtration, which tend to be expensive and require skilled operators for the installation and maintenance of the various unit processes and their elements (Furter, 2005). Biological sulphate reduction (BSR) is an attractive alternative or supplement to these processes. In BSR, sulphate is reduced biologically to produce sulphide, consuming protons which neutralises the pH. The produced sulphide forms insoluble precipitates with the metals ions, removing these from solution (Ristow *et al.*, 2001). BSR requires an organic substrate to act as election and carbon source; with acetic acid, the reaction is :

$$CH_3COOH + 2H^+ + SO_4^{2-} \rightarrow 2CO_2 + H_2S + 2H_2O \qquad (1.1)$$

Various organic substrates for BSR have been evaluated, such as producer gas, ethanol, methanol and lactate (Dill *et al.*, 2001; Greben and Maree, 2000; Ristow *et al.*, 2001). The pure substrates have proven effective, but are costly.

As a lower cost alternative, in the Rhodes BioSURE ® process (Rose *et al.*, 2002) for the active treatment for AMD waters, primary sewage sludge has been proposed as organic substrate (electron donor and carbon source) for BSR. The process flow consists of a series of interconnected biological and chemical unit operations that allows the removal of heavy metals and salinity from AMD, see Figure 1.1, (Rose *et al.*, 2002; Ristow *et al.*, 2005). The central unit process in this treatment scheme is the BSR. For this, the primary sewage sludge (PSS) provides the electron donor and carbon source, producing hydrogen sulphide and carbonate alkalinity (Furter, 2005).

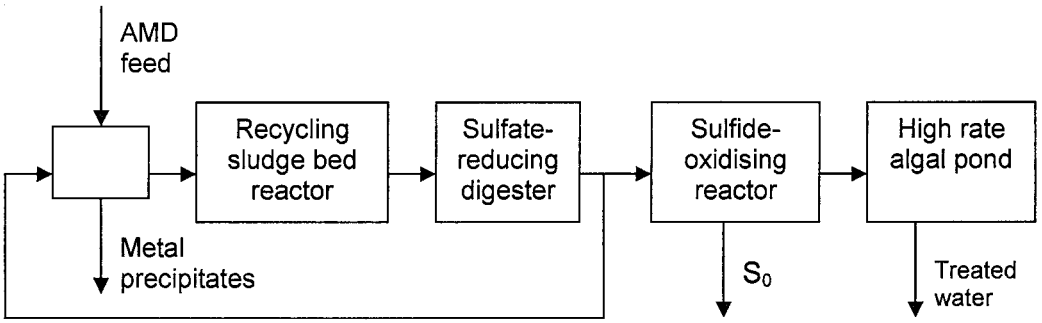


Figure 1.1 : Process flow diagram of the Rhodes Biosure ® system applied to the treatment of acid mine drainage (AMD) wastewater (Rose *et al.*, 2002; Ristow *et al.*, 2005).

The PSS is a by-product in municipal wastewater treatment and is thus a low cost organic substrate source. This co-disposal / treatment scheme provides an elegant solution to BSR. A pilot-scale study on the system has been implemented at the Grootvlei Gold Mine (Springs, South Africa) (Rose *et al.*, 2002). Initially, the BSR bioreactor was implemented in the Recycling Sludge Bed Reactor (RSBR) configuration (Rose *et al.*, 2002), but this has been changed to the Upflow Anaerobic Sludge Bed (UASB) configuration (Ristow *et al.*, 2005).

For this and similar treatment schemes, a kinetic model describing BSR with PSS would be an invaluable aid for design, operation and control. Further, the model would be a valuable research tool, to improve the understanding of the underlying fundamental processes and their interactions.

The primary objective in this research is to develop such a kinetic model for BSR with primary sewage sludge as substrate.

Recognising the potential benefits of such a kinetic model, Ristow *et al.* (2001) developed a kinetic model for BSR in a RSBR reactor with PSS as substrate. In this model, the focus was on the biological processes, and the chemical and physical processes considered to be important in BSR were not explicitly included. For the biological processes, Ristow *et al.* extracted the relevant process rate equations and associated stoichiometric and kinetic constants from the literature. However, they recognised that this model was subject to a number of deficiencies and limitations. In particular, they noted that under steady state the process of hydrolysis of PSS was the rate limiting step, and that it was the most critical factor in modelling this system. In the literature considerable uncertainty existed as to the kinetics for this process. A variety of kinetic rate formulations had been used to model the process, and incompatibilities in the available experimental data were evident. Accordingly, they recommended that future studies should focus on this process and its kinetics. Further, in the kinetic model of Ristow *et al.* the bioprocesses of growth and substrate transfer are uncoupled. Ristow *et al.* also concluded that vapour-liquid and acid-base equilibria would require inclusion in a kinetic model for BSR with PSS. Clearly, these aspects would need to be addressed in the kinetic model to be developed here.

Recognising the importance of the PSS hydrolysis step, and the lack of information on this process in the presence of BSR, Ristow *et al.* (2005) undertook an extensive experimental investigation into this aspect. This investigation quantified and modelled the rate of PSS hydrolysis under methanogenic, acidogenic and sulphidogenic conditions. A simple unified first order kinetics based model was developed to describe PSS hydrolysis under all three conditions, which takes into account the effects of retention time, feed COD concentration and pH. The model was extensively validated against the experimental data collected. From these modelling exercises, Ristow *et al.* concluded *inter alia* that BSR does not appear to influence the rate of PSS hydrolysis (implying that rate formulations and rate constants for methanic digestion can be applied under BSR conditions also) and that for simple steady state models first order kinetics (which analytically are simpler to apply) for PSS hydrolysis are adequate, but for more extensive kinetic models surface saturation (Contois) kinetics would be more suitable (and are followed by Sötemann, 2005, see below). In the model of Ristow *et al.,* pH was not incorporated directly in the model as a predictive parameter, only as an input parameter : The input pH value was used to adjust the value for the first order rate constant in the formulation for the PSS hydrolysis kinetics according to an empirically

developed relationship between these two parameters. Further, the kinetics for processes subsequent to the PSS hydrolysis step were not included, and hence dynamic conditions could not be simulated.

From the above, a dynamic simulation model for BSR with PSS as substrate should incorporate pH as a predictive parameter, which requires incorporating the weak acid / base chemistry as well as the gas exchange. The IWA task group for mathematical modelling of methanogenic anaerobic digestion processes developed Anaerobic Digestion Model No. 1 (ADM1, Batstone *et al.*, 2002), which includes biological, chemical and physical processes, but uses the charge balance to calculate pH. In this model the substrate, in this case PSS, is characterised into (and hydrolysed to) carbohydrates, lipids and proteins. For PSS, such measurements are not routinely available. In contrast, in the model developed by Van Rensburg *et al.* (2001), and extended and modified by Sötemann (2005) for methanogenic anaerobic digestion of sewage sludges, the sludge is characterised with the usual COD, TKN and VSS measurements and the carbon, hydrogen, oxygen and nitrogen (CHON) composition which can be readily derived from the listed measurements and model application or direct elemental analysis. Van Rensburg *et al.* (2001) and Sötemann (2005) 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). This integrated model includes the biological processes for hydrolysis, acidogenesis, acetogenesis, acetoclastic and hydrogenotrophic methanogenesis and endogenous respiration for the organism groups mediating these processes, the chemical processes for the weak acid / base systems commonly present in anaerobic digestors (eg. NH_4 / NH_3) with pH (via H^+) included directly as a compound and hence as a predictive parameter, and the physical processes for gas exchange of CO_2 and NH_3.

The model was calibrated and validated with data from the laboratory mesophilic anaerobic digesters of Izzett *et al.* (1992). For these digesters, 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. 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 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 (Sötemann, 2005). 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 composition based on influent COD, TKN and VSS measurement and on mass balances in model application was within 5 % of the average measured composition, providing persuasive validation of the model. Accordingly, the model of Sötemann (2005) (UCTADM1 Sötemann *et al.*, 2005c) was selected for further development; this model and the approach followed forms a convenient well validated basis for development of a kinetic model for BSR with PSS as substrate, the main objective in this research.

1.2 OBJECTIVES

The main objective in this research was to develop a kinetic model for biological sulphate reduction (BSR) with primary sewage sludge (PSS) as substrate. The aim of developing this kinetic model is to assist in optimising design, operation and control of BSR with PSS, and to improve understanding of the underlying active processes and their interactions. As described above, the two phase physical, biological and chemical processes kinetic model of Sötemann *et al.* (2005c) for the methanogenic anaerobic digestion of sewage sludges (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. The developed BSR model, will be validated by applying the model to simulate a series of experimental lab-scale systems which were fed a mixture of PSS and sulphate, operated over a range of retention times and pH values (Ristow *et al.*, 2005). Model implementation would be in AQUASIM (Reichert, 1998).

1.3 RESEARCH TASKS

The research tasks were identified :

- Familiarization with the simulation package AQUASIM.
- Review of acid mine drainage (AMD) and its treatment.
- Review of the literature on the mechanisms and kinetics of the weak acid / base chemistry, anaerobic digestion and biological sulphate reduction.

- Develop a thorough understanding of the existing kinetic models. To facilitate this, the following models will be implemented in AQUASIM :
  - Mixed weak acid base kinetic model of Musvoto *et al.* (1997).
  - Integrated chemical / physical and biological model – methanogenic anaerobic digestion of sewage sludges (UCTADM1) of Sötemann *et al.* (2005c).

At each stage the models will be validated against experimental data from the literature, and against predictions from the existing AQUASIM models.

- Extend the existing models to include BSR. This requires identification of appropriate :
  - Biological processes for BSR
  - Additional weak acid / bases and chemical processes
  - Additional physical processes for gas exchanges.
- With the processes identified, interactions between the processes need to be delineated. Thereafter, appropriate kinetic rate equations and associated stoichiometric and other parameters for the processes need to be selected.
- Validate the developed model by simulating experimental data obtained from the literature.
- Make recommendations for future studies to improve model predictions.

This thesis reports on these research endeavours.

CHAPTER 2

BACKGROUND

2.1 INTRODUCTION

From Chapter 1, the principal objective of this research is to develop a kinetic model for biological sulphate reduction (BSR) with primary sewage sludge (PSS) as substrate. This model is principally for application to systems incorporating BSR for the treatment of acid mine drainage (AMD) water, but can find wider application to BSR systems in general. In this chapter, AMD and its treatment will be reviewed briefly first. Thereafter the available kinetic models containing processes of relevance will be reviewed, to select the more promising and most suitable models, or parts of models, for development.

2.2 ACID MINE DRAINAGE (AMD)

Acid Mine Drainage (AMD) is drainage flowing from or caused by mining activities. It is typically highly acidic with elevated metal and sulphate concentrations (such drainage produced naturally is called Acid Rock Drainage). AMD can result from active mining, but also can continue long after mine closure. As described in Chapter 1, AMD waters pose a significant threat to the environment (Akcil and Koldas, 2006). In this section formation of AMD will be described, and the environmental impacts set out. AMD treatment alternatives will be reviewed briefly, to highlight the importance of BSR in the various treatment schemes.

2.2.1 Formation of Acid Mine Drainage

There appears to be common consensus on the origin of AMD, e.g. Kuenen and Robertson (1992); Pronk and Johnson (1992); Robb (1994); Johnson (1995); Ristow (1999); Johnson and Hallberg (2005); Akcil and Koldas (2006), which can be summarised as follows :

Mining operations expose large surface areas of rock to air and water. These rocks frequently contain sulphide minerals, predominantly iron disulphide (FeS_2) commonly known as iron pyrite (fool's gold), and in a variation in crystalline structure as marcasite, but also other metal sulphides such as pyrrhotite (FeS), chalcopyrite ($CuFeS_2$), covellite (CuS), etc., may be present. Using pyrite for illustrative purposes, in the presence of air and water the pyrite is chemically oxidized with oxygen (O_2) as electron acceptor releasing ferrous iron (Fe^{2+}), sulphate (SO_4^{2-}) and protons (H^+) :

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (2.1)$$

The release of H^+ in the reaction causes the pH to decrease. At a low pH this reaction is relatively slow (at pH ~ 2.0, the timescale of reaction is in terms of years).

The ferrous iron (Fe^{2+}) produced in Reaction (2.1) is released into the water, where it is oxidized with oxygen as electron aceptor to the ferric iron (Fe^{3+}), consuming H^+ :

$$Fe^{2+} + ¼\ O_2 + H^+ \rightarrow Fe^{3+} + ½\ H_2O \quad (2.2)$$

Under most abiotic conditions Reaction (2.2) is the rate limiting step in the oxidation of pyrite, since the chemical oxidation of Fe^{2+} to Fe^{3+} is a slow reaction at pH < 5 (Skousen *et al.*, 1998). However, the reaction is mediated by bacteria, of which the most important is *Acidithiobacillio ferro-oxidants* (formerly *Thiobacillus ferro oxidans*), which greatly accelerates the reaction rates. This bacteria is an acidophyllic, aerobic chemo autotroph (lithotroph) and its activity is central to the generation of most AMDs. If *A. ferro-oxidants* is present, then oxygen may become rate limiting. Availability of oxygen will depend on the specific conditions present (Skousen *et al.*, 1998). Where soils and rocks are relatively impermeable and have low porosity (eg. soft shales), limited oxygen penetration occurs and the pyrite oxidation is limited to the upper surface. In contrast, in porous and permeable soils, the oxygen penetration will ensure deeper pyrite oxidation. Further, in this latter case the heat generated by pyrite oxidation can cause air convection carrying oxygen deep into the soils, facilitating deep pyrite oxidation.

Due to the nett 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, SO_4^{2-} and H^+ :

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (2.3)$$

The H^+ generated in Reaction (2.3) causes the pH to decrease further, slowing the rate of Reaction (2.1). However, the ferrous iron generated enters Reaction (2.2) creating a cyclical propogation of rapid pyrite oxidation and sulphate and acid generation. Hence, the overall effect is an increase in the sulphate concentration and in the dissolved metals concentrations (particularly iron), and a decrease in pH. The resultant low pH can cause leaching of heavy metals into the water.

Accordingly, AMD waters are typically characterized by high concentrations of heavy metals (e.g. Al = 50 – 2 000 mg/ℓ; Fe = 10 – 67 000 mg/ℓ; Zn = 10 – 100 mg/ℓ), sulphate (3 000 – 30 000 mg/ℓ)

and total dissolved solids (1 800 – 45 000 mg/ℓ), coupled with a low pH (2 - 3) (Christensen *et al.*, 1996).

If the water pH remains sufficiently high (due to dissolution of alkalinity) or increases following discharge of the water, then provided pH > 3.5 ferric hydroxide will form and precipitate :

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (2.4)$$

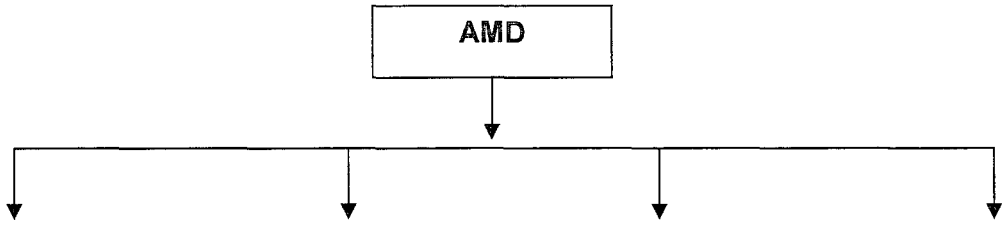
The $Fe(OH)_3$ is known as "yellow boy" and gives rise to the yellow or reddish colours frequently seen in AMD. At pH < 3.5 the precipitant does not form and the ferric iron remains dissolved in solution.

Akcil and Koldas (2006) group AMD sources into two categories, primary and secondary : Primary sources are mine rock dumps, tailings impoundments, underground and open pit mine workings, pumped or naturally discharged underground water, diffuse seeps from replaced overburden in rehabilitated areas and construction rock used in roads, dams, etc. Secondary sources are treatment sludge ponds, rock cuts, stockpiles, concentrated spills along roads and emergency ponds. The extent and particular characteristics from these various sources are unique to the specific site.

2.2.2 Effects of Acid Mine Drainage

AMD discharge can be intentional (e.g. pumping) or unintentional (e.g. seepages) (see above), and have significant short and long term impact, both for water re-use and environmentally. Environmental impacts arise principally through acidification of receiving water bodies and the toxic metal contents. Even where the receiving water body has sufficient capacity to buffer pH changes, the increase in pH causes precipitation of ferric hydroxide ($Fe(OH)_3$) which can blanket water bodies blocking sunlight, etc. Further, the high total dissolved solids (TDS) content of AMD (principally sulphate and metals) can significantly impact the salinity of the receiving waters.

The effects of AMD can be characterized as chemical, physical, biological and ecological. These are summarized in Figure 2.1.



Chemical	Physical	Biological	Ecological
Increased acidity	Substrate Modification	Behavioural	Habitat Modification
Reduction of pH	Increase in stream velocity	Respiratory	Niche loss
Deconstruction of bicarbonate buffering system	Turbidity	Reproduction	Bioaccumulation within food chain
Increase in soluble metals concentration	Sedimentation	Osmoregulation	Loss of food source or prey
Increase in particulate metals	Absorption of metals onto sediment	Acute and chronic toxicity	Elimination of sensitive species
	Reduction in turbulence due to sedimentation increasing laminar flow	Death of sensitive species	Reduction in primary production
	Decrease in light penetration	Acid-based balance failure in organisms	Food chain modification
		Migration or avoidance	

Figure 2.1 : The negative effects of acid mine drainage on an ecosystem (Ristow, 1999 and Gray, 1997).

Johnson and Hallberg (2005) state that in 1989 approximately 19 300 km of streams and rivers and 72 000 ha of lakes and reservoirs worldwide had been seriously damaged by AMD, but the true scale of the problem is difficult to assess accurately.

It is clear that the prevention or treatment of AMD represents a crucial issue (Furter, 2005).

2.2.3 Acid Mine Drainage Prevention

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 (e.g. Skousen *et al.*, 1998; Johnson and Hallberg, 2005; Chen *et al.*, 2006; Hilson and Murck, 2001).

2.2.3.1 Water Diversion / Management

Water can be diverted from pyrite containing surface spoils and surface and underground mines through the use of drainage ditches, channels, pipes, planned pumping, barriers, etc. The main objective is for the water to bypass the acid producing materials. Regulated pumping to discharge AMD at times and places to minimise impacts also may be possible.

2.2.3.2 Air / Oxygen Control

Another method to minimise AMD aims at preventing air contact with pyrite containing materials. A number of possibilities exist to achieve this : Tailings from mining can be completely submerged (e.g. in lakes or reservoirs such as in Norway), covered with impermeable layers (e.g. impermeable soils, PVC covers, fly ash, biosolids; Hallberg *et al.* (2005); encapsulated with alkaline materials such as kiln dust, power generation ashes (Skousen *et al.*, 1998), polyethylene polyamine coatings (Chen *et al.*, 2006) on lipids (Ristow *et al.*, 2005), backfills can be encased with grouting materials (Jones *et al.*, 1989), etc. In underground mines, mine submergence by high water tables, wet mine seals to allow water drainage but prevent air entering the mine, sealing of artesian wells, and inert gas blankets such as carbon dioxide, nitrogen, are some methods to minimize AMD (Skousen *et al.*, 1998).

2.2.3.3 Bacterial Inhibition

Inhibiting ferrous oxidizing bacteria through the application of anionic surfactants (e.g. Hedin *et al.*, 1994b), antibiotics, heavy metals, etc. have been found to reduce AMD production. However, surfactants leach from the surface or decompose requiring repeated applications, antibiotics and heavy metals are expensive and pose environmental threats themselves.

2.2.4 Acid Mine Drainage Treatment

Due to the practical and economic difficulties in preventing AMD generation, most often the only viable alternative (or supplement to prevention) is treatment (Johnson and Hallberg, 2005). Systems for AMD treatment incorporate variously 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 filtrations. The biological processes are dominated by biological sulphate reduction (BSR) to remove sulphate and generate alkalinity.

In the literature, AMD treatments are 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.

2.2.4.1 Passive Treatment

Active treatment systems often carry considerable financial cost due to continual chemical or substrate addition requirements. Accordingly, a number of different passive treatment systems have been developed, including aerobic and anaerobic wetlands, anoxic limestone drains, 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).

Selection of the appropriate passive treatment system has been summarised by Skousen *et al.* (1998), and is shown in Figure 2.2.

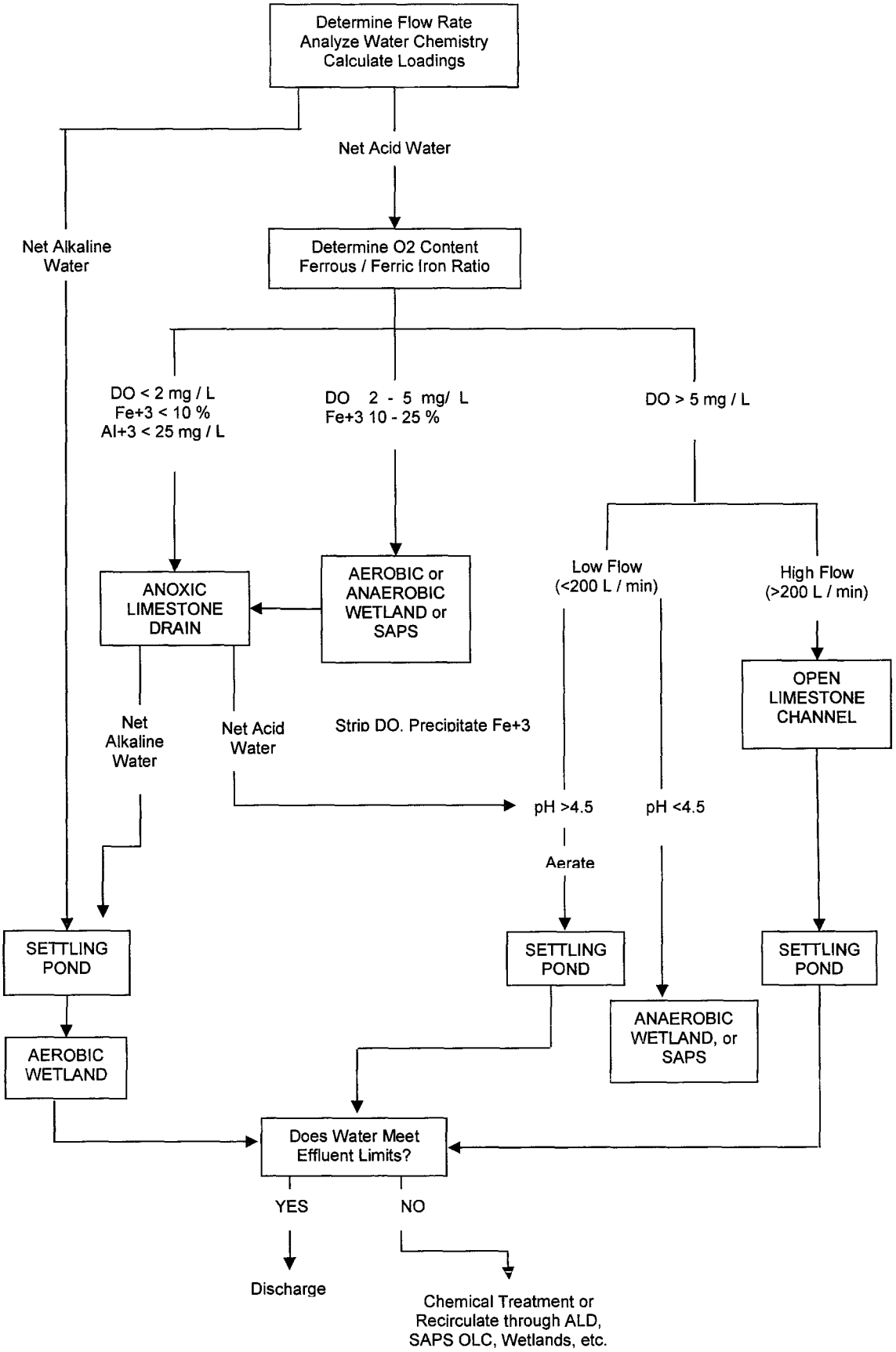


Figure 2.2 : Flowchart for selecting a passive AMD treatment system based on water chemistry and flow (Skousen *et al.*, 1998)

Wetlands

Amelioration of AMD on passing through natural wetlands apparently was first noted by Hutsman *et al.* (1978). However, AMD invariably degrades the quality of the natural wetlands, which is undesirable. Accordingly, numerous artificial wetlands have been constructed specifically to treat AMDs. These wetlands can be aerobic or anaerobic. The aerobic wetlands have large surface areas with horizontal surface flow. This promotes metal oxidation and hydrolysis which lead to precipitation, with the precipitants retained in the wetland. However, these chemical processes require higher pHs (>~6) and hence only are suitable for alkaline waters.

In anaerobic wetlands, the alkalinity and pH of the water are increased. This is achieved by passing a shallow stream of water over organic / compost and limestone layers. The dissolution of limestone generates alkalinity and increases the pH :

$$CaCO_3 + H^+ \leftrightarrows Ca^{2+} + HCO_3^- \qquad (2.5)$$

As the water passes through the organic / compost layer, biological sulphate reduction (BSR) mediated by bacteria such as *Desulphovibrio* occurs, reducing sulphate to sulphide with the organic as substrate, and generating alkalinity (see later) :

$$SO_4^{2-} + 2CH_2O \leftrightarrows H_2S + 2HCO_3^- \qquad (2.6)$$

The anaerobic conditions are necessary otherwise the ferrous (Fe^{2+}) is oxidized to ferric (Fe^{3+}) which will precipitate at the raised pH, coating (armouring) the limestone thereby retarding further dissolution.

The sulphides produced in the BSR will precipitate the metals, and additionally metal exchange and adsorption in the organic / compost layer can occur. The alkalinity generated (HCO_3^-) further raises the pH promoting conditions condusive to metal sulphide precipitation.

The upper surface water in the wetland is aerobic, promoting Fe and Mn oxidation and precipitation. Thus, anaerobic wetlands induce the same processes as their aerobic counterparts, but additionally promote several processes such as BSR with associated sulphate removal and alkalinity and sulphide production, the last of which induces metal sulphide precipitation.

From the brief description above, central to anaerobic wetlands is BSR. This process requires a continual source of organic substrate and conditions favourable to the group of micro organisms

mediating the reaction, including *inter alia* absence of oxygen and pH in the ranges 5 to 9. The pH requirement limits the AMD loading rates; Hedin *et al.* (1994a) suggest a loading rate of 3,5 g acidity/m^2/d. This limits anaerobic wetlands to the treatment of "smaller AMD flows of moderate water quality" (Skousen *et al.*, 1998).

Pilot-scale applications of horizontal flow compost wetlands, to AMDs in South Africa were particularly unsuccessful (Pulles and Rose, 2002).

The requirement for organic substrate implies a requirement for continual replenishment, either naturally or artificially. If naturally, this will limit the sulphate loading rate; if artificially, this must be taken into account in design. If the organic substrate is not replenished, the anaerobic wetland will have a limited lifespan due to substrate depletion (Kalin *et al.*, 2005).

Anoxic Limestone Drains (ALD)

ALD's are buried cells or trenches of limestone, which are impervious to both air and water, into which oxygen free AMD is introduced (Skousen *et al.*, 1998). The objective is to dissolve limestone into the AMD thereby to add alkalinity and neutralize the pH to typically 6-7.5 (Equation (2.5)), while maintaining the iron in the reduced ferrous (Fe^{2+}) form to avoid precipitation of the oxidized ferric (Fe^{3+}) form as $Fe(OH)_3$ which armours the limestone significantly, reducing the rate of its dissolution (aluminium behaves similarly to the iron) (Johnson and Hallberg, 2005) : Fe^{2+} does not precipitate as $Fe(OH)_2$ at pH <8 (Skousen *et al.*, 1998).

ALDs produce alkalinity at a lower cost than constructed compost wetlands (Johnson and Hallberg, 2005). However, for AMDs containing significant ferric (and oxidized aluminium), longevity is a concern due to hydroxide precipitation and limestone armouring. Further, ferrous or mangenous carbonate gels also can retard limestone dissolution (Johnson and Hallberg, 2005). ALDs usually are introduced as a pre-treatment step for constructed wetlands.

Successive Alkalinity Producing System (SAPS)

SAPS, also called vertical flow reactors (VFR), combine ALDs and organic substrate in one system (Kepler and McCleary, 1994; Zipper and Jage, 2001; Skousen, 2006); the AMD flows vertically through an organic substrate layer, then through a limestone layer and then drains from the system. As described above, ALDs require oxygen free AMD. As the AMD flows through the organic layer, oxygen is consumed and ferric reduced to ferrous. BSR also can occur, with

resultant alkalinity production and metal sulphide precipitation, as described above. The AMD then flows through limestone which adds further alkalinity. The reduced state of the AMD ensures limestone armouring is minimised.

Various organic subtrates may be possible, e.g. mushroom compost, but clogging is a concern (Skousen, 2006). SAPS or VFRs require far less area than equivalent wetlands (Zipper and Jage, 2001).

Limestone Ponds

Limestone ponds are a relatively new passive treatment concept to treat AMD seep upwelling or an underground AMD water discharge (Skousen *et al.*, 1998). A limestone filled pond, with 1 – 2d retention is constructed on the discharge point, and the water flows upwards through the limestone for alkalinity generation. As for ALDs, the requirement is for low dissolved oxygen (DO) and ferric and oxidized $A\ell^{3+}$ free AMD water. However, since the system is open, limestone disturbance to minimise armouring and replenishment is readily possible (Skousen, 2006).

Open Limestone Channels (OLC)

OLCs are amongst the simplest passive treatment systems, and are open channels or ditches lined with limestone through which the AMD or AMD contaminated stream passes. To minimise limestone armouring, flow velocities are designed to keep the precipitants in suspension and to scour the limestone (Skousen *et al.*, 1998). OLCs are envisaged for long term treatment.

Passive Treatment Summary

As summarised above, a variety of passive treatment systems have been developed, and implemented with varying degrees of success. The passive treatment systems can be considerably cheaper than active treatment systems. However, relative to active treatment "passive systems require longer retention times and greater spaces, provide less certain treatment efficiency and are subject to failure in the long term" (Skousen, 2006). Also, the management of possible toxic sludges in passive treatment systems requires consideration for long term sustainability (Johnson and Hallberg, 2005).

Among the passive treatment systems, the anaerobic wetlands incorporate BSR with "compost" organics as substrate (electron donor). Although not the direct focus in this research, the BSR kinetic model with PSS as substrate (Chapter 1) to be developed can form a useful basis or

starting point for modelling the anaerobic wetlands BSR; both BSRs are with particulate organics. Further, the BSR processes are intimately connected to the chemical processes that take place in the wetlands, such as weak acid / base chemistry, chemical precipitation, etc. Since some of these interrelationships are common to the system being modelled, these are to be incorporated and explored in the kinetic model to be developed here, which will make the model more readily convertible to the wetland-type systems.

2.2.4.2 Active Treatment

As the name implies, active treatment requires continual management of the treatment and input of chemicals and / or substrates. Active treatments employ chemical / physical processes, principally for neutralisation and metals removal, and / or biological processes, for sulphate removal, alkalinity generation and metal sulphide precipitation. Active treatments holds the prospect of water reclamation from AMD (Gunther *et al.*, 2006) and allow control of the system efficiency and effluent quality.

Chemical / Physical Processes

In the treatment of AMD, the most widespread method is the addition of chemical neutralising agents (Johnson and Hallberg, 2005). This adds alkalinity to raise pH, which causes the precipitation of a number of metals as hydroxides and carbonates (Aubé, 2006). The resultant sludge containing precipitants is physically separated from the AMD, usually through gravity (Johnson and Hallberg, 2005; Aubé, 2006), but also through the use of membranes (e.g. 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), as mined materials such as limestone ($CaCO_3$) (Maree and Hill, 1989) or dolomite ($CaMg(CO_3)_2$) (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). The choice of the chemical neutralising agent depends on economic and technical considerations (Skousen *et al.*, 1998).

General consensus is that usually 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 ($CaSO_4 \cdot 2H_2O$) and / or as ettringite ($Ca_6A\ell_2(SO_4)_3 \cdot 3H_2O$) 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 (~2 000mg SO_4/ℓ; Potgieter-Vermaak *et al.*, 2006), and hence for sulphate removal alternative or supplementary unit processes are required.

For the removal of Fe, since the ferrous hydroxide ($Fe(OH)_2$) forms precipitants that are more difficult to remove than the ferric hydroxide ($Fe(OH)_3$), pre-, simultaneous or post-aeration is often implemented (e.g. Maree and Hill, 1989).

Separation of the metal rich sludge has been achieved principally by gravity in ponds, pits or clarifiers (Aubé, 2006), but limestone columns or fluidised beds also have been utilized (Maree *et al.,* 1996), as well as membranes (e.g. Juby and Schutte, 2000).

A number of system refinements have been developed to aid gravity sludge separation, 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). Additionally, these systems promote more efficient lime utilisation. Differences between the systems essentially are in the contacting of the recycled sludge with the AMD + lime (sludge recycling), sludge + lime (HDS) and sludge + AMD (Geco) (Aubé, 2006). Addition of coagulants and flocculants has also been used to aid sludge separation (Skousen *et al.*, 1998).

Alternative chemical / physical processes such as ion exchanges with resins or natural zeolites, bio-adsorption with low cost adsorbents (Santos *et al.*, 2004), etc. also have been implemented (Skousen *et al.*, 1998). A new novel chemical / physical processes based system for removal of metal ions has been developed recently, the ambient temperature ferrite system (Morgan *et al.*, 2004). 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 (Fe_3O_4), 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 to aid settlement. Non-iron metals are removed as hydroxides or are incorporated in the green rust matrix to give ferrite.

Active chemical treatment can provide effective neutralisation of AMD, but has high operating costs and produces large sludge volumes that contain a cocktail of metals (Johnson and Hallberg, 2005) that presents problems in disposal.

Biological Processes

As supplement or alternative to the chemical / physical processes for AMD remediation, biological treatment would seem an attractive option. This biological treatment usually will form one unit process in a treatment train encompassing additional chemical and / or physical treatment (e.g. Rose *et al.*, 2002; Maree, 2002) or may be stand alone (e.g. Luptakova and Kusnierova, 2005).

The biological processes make use primarily of sulphate reducing bacteria (SRB) (e.g. Christensen *et al.*, 1996; Elliott *et al.*, 1998; Maree, 2002; Rose *et al.*, 2002; Gilbert *et al.*, 2004; Boshoff *et al.*, 2004), but iron oxidising bioreactors also have been implemented for iron removal (Unita, 1996; Johnson and Hallberg, 2005).

BSR processes have been implemented in passive and active systems (see Sections 2.2.4.1 and 2.2.4.2 above) also termed off-line (Johnson and Hallberg, 2005). The engineered active systems have potential advantages over the passive systems (Johnson and Hallberg, 2005) : (i) performance is more readily controlled and optimised, (ii) have the potential to allow metal recovery and re-use, and (iii) significant sulphate removal can be achieved. However, these advantages can 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.

SRB are heterotrophic and accordingly require an organic electron donor with sulphate as electron acceptor : If CH_2O represents a generic organic substrate, the catabolic reaction for BSR is given by (Christensen *et al.*, 1996) :

$$2CH_2O + SO_4^{2-} + 2H^+ \rightarrow 2CO_2 + 2H_2O + H_2S \quad (2.7)$$

Hydrogen (H_2) may substitute as electron donor (Du Preez *et al.*, 1992) :

$$4H_2 + SO_4^{2-} + 2H^+ \rightarrow H_2S + 4H_2O \quad (2.8)$$

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

$$M^{2+} + H_2S \rightarrow MS + 2H^+ \quad (2.9)$$

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 H_2S; this H_2S – rich recycle passes to 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 substrate used. In this system, since only the recycle passes to the BSR, sulphate removal is partial only.

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 also is 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^O) by the action of sulphide oxidizing bacteria (SOB), controlled by oxygen entering this single reactor :

$$H_2S + 1/2\ O_2 \rightarrow S^O + H_2O \qquad (2.10)$$

Sulphide not converted to S^O is stripped and converted to S^O 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 (Johnson, 2003; Rein, 2005; Paques, 2002) 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. Carbon sources which have been evaluated for active BSR include sewage sludge, animal waste slurries, lactate and cheese whey, molasses, ethanol and methanol and producer gas (Ristow *et al.*, 2002).

In general, electron donors 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 supplement 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 (producer) gas ($C0+H_2$). Ethanol is a cheaper substrate for small-scale plants, but synthesis gas becomes cheaper at larger scales. These pure substrates have proven effective for BSR in AMD treatment but are costly. As a lower cost alternative, the Biosure ® process has been proposed for the active treatment of AMD in which primary sewage sludge (PSS) has been proposed as the substrate (electron donor and carbon source) for the central BSR unit process (Rose *et al.*, 2002).

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 allows for the removal of heavy metals and salinity (particularly sulphate) from AMD, see Figure 2.3. The core unit process in the overall system is BSR. In the Rhodes Biosure ® system BSR is achieved using PSS as the electron donor and organic carbon source, with the concomitant production of sulphide and carbonate alkalinity (Equation 2.7). PSS

is available as a by-product at municipal wastewater treatment plants, and this co-disposal proposal provides 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 2.3). The main aim of the RSBR is to solubilise the PSS to soluble organic matter such as short-chain fatly 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 alkalinity produced in this process are recycled and contacted 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). A high rate algal pond polishes this effluent. A technical pilot-plant has been successfully implemented at the Ancor Works (ERWAT, South Africa) to treat 10 Mℓ/d of HDS pre-treated AMD (Neba and Rose, 2006). In this implementation the RSBR and sulphate-reducing digesters have been replaced with an upflow anaerobic sludge bed (UASB) reactor to improve solids retention, sulphate contact with the PSS and solid liquid separation (Poinapen *et al.*, 2006).

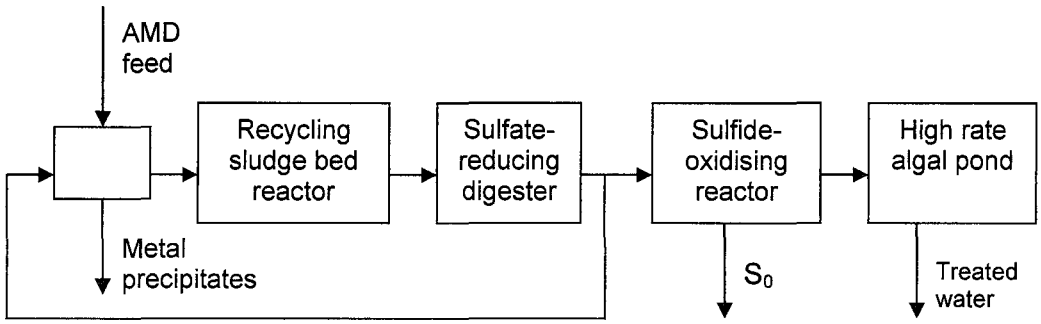


Figure 2.3 : Process flow diagram of the Rhodes Biosure ® system applied to the treatment of acid mine drainage (AMD) wastewater (from Rose *et al.*, 2002).

As noted above, the core unit process in the Rhodes 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. Also, 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.

As described in Chapter 1, the development of a kinetic model describing the BSR unit process in the Biosure ® and similar systems is the main objective in this research. This required an evaluation of existing kinetic models for anaerobic digestion with PSS.

2.3 EXISTING KINETIC MODELS

In the following sections the existing kinetic models for anaerobic digestion will be described briefly.

2.3.1 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; solid to 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, available kinetic models for methanogenic systems would seem a logical basis for frame work BSR model development. The products of the hydrolysis and acidification processes, the VFA, then can enter into the methanogenic or sulphate reduction 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 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. Some of the end products have gaseous equilibria (sulphide, carbon dioxide and methane), thus these also need to be modelled.

2.3.2 Available Models

Ristow *et al.* (2001) and Hansford (2004) developed a kinetic model for BSR in the RSBR reactor with PSS as substrate by extensively reviewing the literature and extracting relevant information. In this model, the focus was on the biological processes, and the chemical and physical processes considered to be important in BSR were not explicitly included. In development of their model, Ristow *et al.* (2002) recognised that under steady state conditions the hydrolysis of PSS is the rate limiting step. However, they noted that for this process a variety of kinetic rate formulations and data incompatibilities were evident in the literature. From the available information they were not able to determine the most appropriate kinetic rate formulation for this crucial process. Due to these deficiencies and 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 *inter alia* that, BSR does not appear to influence the rate of PSS hydrolysis (implying that rate formulations and rate constants for methanogenic conditions can be applied under BSR conditions also) and that for simple steady state models first order kinetics (which analytically are simpler to apply) for PSS hydrolysis are adequate, but for more extensive kinetic models surface saturation (Contois) kinetics would be more suitable, in agreement with Vavilin *et al.* (2001) (and are followed by Sötemann *et al.*, 2005c, see below). Ristow *et al.* included pH empirically, by adjusting the value for the first order rate constant according to pH and did not consider the kinetics for the reactions subsequent to the hydrolysis (since this was the rate limiting step).

The IWA task group for mathematical modelling of anaerobic digestion processes developed 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 (in the model based on the complex organic, i.e. PSS, characterisation, the three organic types are generated in a disintegration step, together with inert particulate and soluble compounds; the resultant carbohydrates, proteins and lipids are hydrolyzed separately to intermediate products). For PSS, measurements of carbohydrates, lipids and proteins and their COD equivalents are not routinely available. In contrast, in the model developed by Van Rensburg *et al.* (2001), and extended and modified by Sötemann *et al.* (2005c) for methanogenic anaerobic digestion of sewage sludges, the sludge is characterised with the usual COD, TKN, TSS and VSS measurements and the carbon, hydrogen, oxygen and nitrogen (CHON) composition which can be readily derived from the measurements listed above and model application. Van Rensburg *et al.* (2001) and Söteman *et al.*

(2005) 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 calibrated and validated with data from the laboratory mesophilic anaerobic digesters of Izzett *et al.* (1992) and O'Rourke. (1968) (Sötemann *et al.*, 2005a). 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. 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 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. 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.* (2005c) (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 cognizance 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.

2.3.3 Integrated Chemical, Physical and Biological Processes Modelling : Methanogenic Anaerobic Digestion of Sewage Sludges

Since the kinetic model UCTADM1 was selected for development, this model is reviewed in detail in this section.

Influent PSS Organics Characterisation

Sötemann *et al.* (2005c) followed the approach used for activated sludge simulation models (e.g. Wentzel *et al.*, 1990, 1992; Henze *et al.*, 1987) since the same PSS serves as substrate, and characterized the influent PSS organics as illustrated in Figure 2.4. This structure is based on COD units. Since the kinetic model by necessity was based on mole units (due to the requirement

to include CO_2), conversion between the influent COD characterisation and the mole units used in the model was required to generate the input for the model.

For this conversion, Sötemann *et al.* (2005c) accepted that (i) the SCFA would be available from direct measurement and hence could be readily converted between mg, COD and mole units, (ii) the dissolved fermentable readily biodegradable COD would require quantification, but that its concentration relevant to the particulate biodegradable organics is very small and hence with little error can be converted to mole units by accepting glucose as representative of this fraction, (iii) the unbiodegradable soluble COD concentration also is very low, and since it simply passes through the reactor, convertion to mole units is not required. Thus, remaining are the unbiodegradable and biodegradable particulate organic fractions, which are dominant in PSS. For these two fractions, Sötemann *et al.* accepted a generic composition $C_XH_YO_ZN_A$, with the stoichiometry determined from COD, TKN, FSA, TSS and VSS measurements on the PSS and product generation in experimental systems. More recently the PSS CHN content has been measured directly through elemental analysis (see later). The division of the PSS particulates between the unbiodegradable and biodegradable fractions needed to be determined from analysis of experimental data from operation ADS treating PSS.

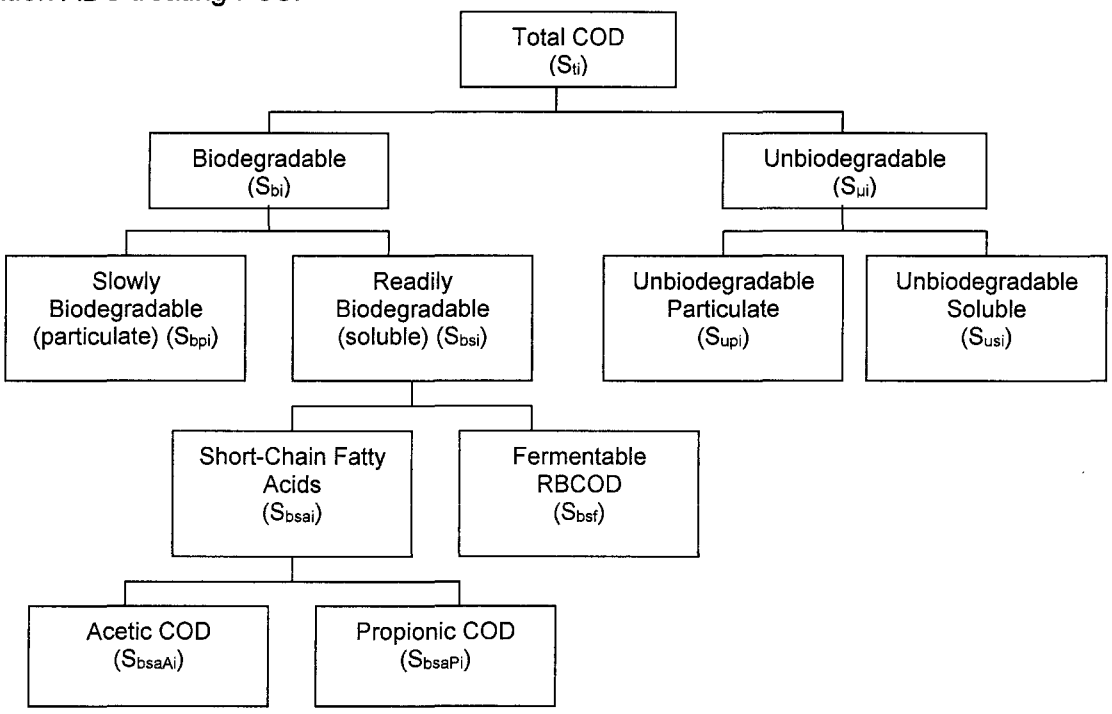


Figure 2.4 : Schematic layout showing the characterization of the influent sewage sludge organics, required as input to the model; the acetic and propionic acids require speciation from the influent pH.

Biological Processes

Sötemann *et al.* (2005a, b, c) revised the reaction scheme of Gujer and Zehnder (1983) as the basis for the methanogenic anaerobic digestion (AD) model developed as part of their study, see Figure 2.5.

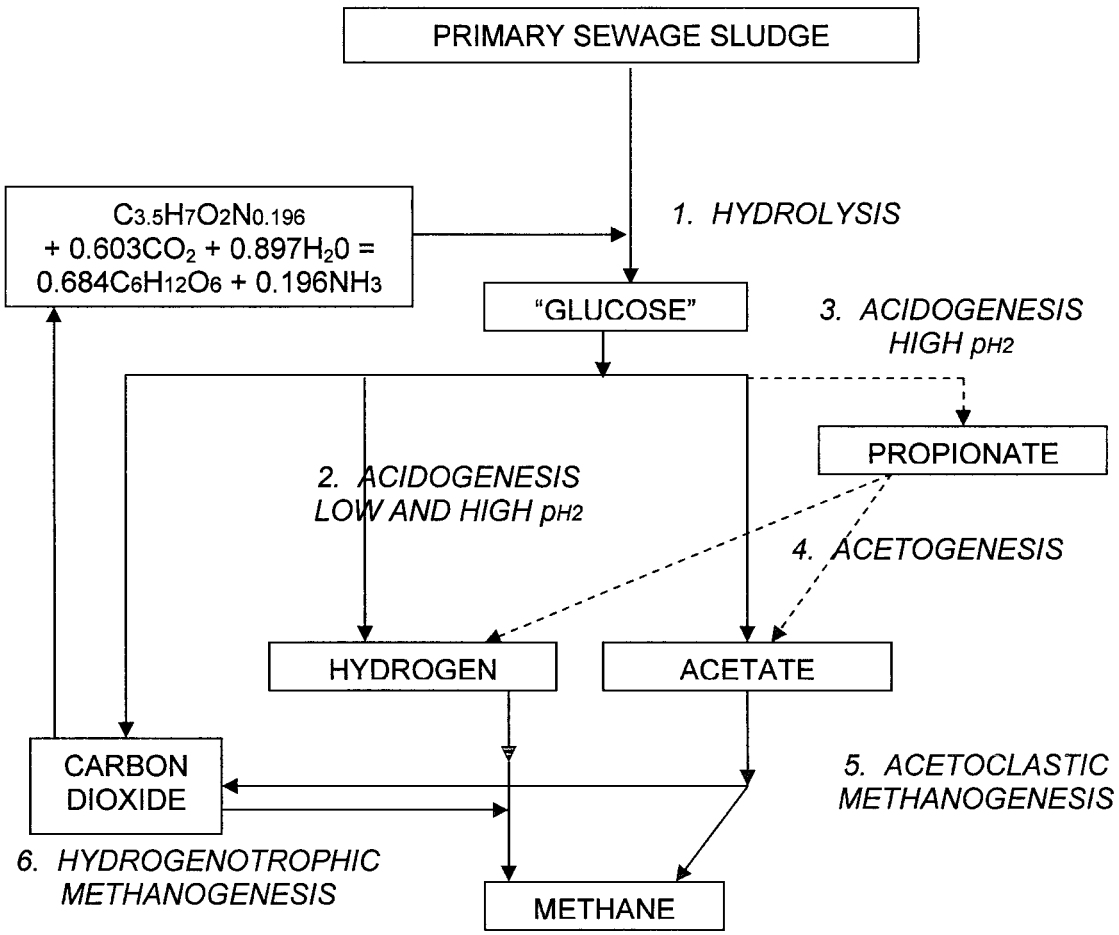


Figure 2.5 : Anaerobic digestion processes scheme of University of Cape Town as described by Sötemann *et al.* (2005a, c). Anaerobic Digestion Model No1 (UCTADM1) including (i) the effect of high hydrogen partial pressure on acidogenesis and (ii) COD, carbon and nitrogen mass balances with a generic CHON sludge composition. The "Primary Sewage Sludge" is the biodegradable particulate fraction.

Sötemann *et al.* (2005c) included the biological processes mediated by the four recognized AD organism groups (Table 2.1) in a two phase (aqueous-gas) chemical (C), physical (P) and biological (B) processes anaerobic digestion kinetic model (UCTADM1), see Table 2.2. Following the approach in Activated Sludge Models No's. 1, 2 and 2d (Henze *et al.*, 1987, 1995, 1999), the substrate consumption processes were formulated in terms of growth of the relevant organism group, and death / endogenous decay processes for each organism group. Sötemann *et al.* (2005b, c) formulated all the biological processes that act on the weak acid/base species in terms of the relevant dissociated or undissociated species, since the weak acid / base chemistry was included directly in UCTADM1. This included both the stoichiometric consumption or production of the weak acid / base species by the processes, and the formulation of the kinetic rate expressions. Because of the direct inclusion of the weak acid / base chemistry, the model automatically redistributes these species, including the hydrogen ion (H^+) to establish a new pH.

Table 2.1 : Biological processes in the two phase anaerobic digestion model, Table 1 in Sötemann *et al.* (2005b).

PROCESS	SPECIFIC BIOLOGICAL PROCESS	ORGANISM GROUP
Hydrolysis	D1. Hydrolysis of $C_XH_YO_ZN_A$ to "glucose"	Acidogens, Z_{AD}
Growth	D2. Acidogens on "glucose" under low p_{H2}	Acidogens, Z_{AD}
	D3. Acidogens on "glucose" under high p_{H2}	Acidogens, Z_{AD}
	D5. Acetogens on propionic acid	Acetogens, Z_{AC}
	D7. Acetoclastic methanogens on acetic acid	Acetoclastic methanogens, Z_{AM}
	D9. Hydrogenotrophic methanogens on H_2	Hydrogenotrophic methanogens, Z_{HM}
Death / Endogenous decay	D4. Acidogens	Acidogens, Z_{AD}
	D6. Acetogens	Acetogens, Z_{AC}
	D8. Acetoclastic methanogens	Acetoclastic methanogens, Z_{AM}
	D10. Hydrogenotrophic methanogens	Hydrogenotrophic methanogens, Z_{HM}

The 10 biological processes listed in Table 2.1, act on 14 compounds and cause changes in their concentrations, see Tables 2.2 and 2.3

Table 2.2 : Petersen matrix representation of the biological processes and associated compounds of the University 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 in Sötemann *et al.* (2005c).

	Number	C1	C2	C3	C7	C13	C28	C29	P1†	P4	D1	D2	D3	D4	D5	D6	D7	
	Compounds	NH_4^+	NH_3	$H_2CO_3^*$	H^+	HAc	HPr	Pr^-	CO_2	CH_4	$C_XH_YO_ZN_A$	$C_6H_{12}O_6$	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										$K_{fPr}[HPr]$
C47	Reverse dissociation of HPr				-1		1	-1										$K_{rPr}[Pr^-][H^+]$
P6†	Dissolution of CO_2 gas			1					-1									$K_{rCO2}(pCO_2)(K_{HCO2})$
P7†	Expulsion of CO_2 gas			-1					1									$K_{rCO2}[H_2CO_3^*]$
P8†	Expulsion of NH_3 gas		-1															$K_{rNH3}[NH_3]$
D1	Hydrolysis		S1	S2							-1	S3						Eq 4.16d in Sötemann *et al.* (2005c)
D2	Acidogenesis (low pH_2)	-1		S4	1	S5						$-1/Y_{AD}$	S6	1				Eq 4.17 in Sötemann *et al.* (2005c)
D3	Acidogenesis (high pH_2)	-1		S7	1	S8	S9					$-1/Y_{AD}$	S10	1				Eq 4.18 in Sötemann *et al.* (2005c)
D4	Acidogen endogenous decay		S11	S12							S13			-1				$b_{AD}[Z_{AD}]$
D5	Acetogenesis	-1		S14	1	S15	$-1/Y_{AC}$						S16		1			Eq 4.19 in Sötemann *et al.* (2005c)
D6	Acetogen endogenous decay		S11	S12							S13				-1			$b_{AC}[Z_{AC}]$
D7	Acetoclastic methanogenisis	-1		S17	1	$-1/Y_{AM}$				S18						1		Eq 4.20 in Sötemann *et al.*, (2005c)
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 4.21 in Sötemann *et al.* (2005c)
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	
	G COD/mol	-	-	-	-	64	112	112	0	64	131.3‡	192	16	160	160	160	160	
	G N/mol	14	14	-	-	-	-	-	-	-	2.744	-	-	-	-	-	-	
	G H_2CO_3* as $CaCO_3$/mol	-	-	0	-50	-	-	-	-	-	-	-	-	-	-	-	-	

† These processes and compound were included in the models of Musvoto *et al.* (1977, 2000a) 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.
‡ This is the g COD/mol for the primary sludge CHON content measured and predicted in this investigation, i.e. $C_{3.5}H_7O_2N_{0.196}$

Sötemann *et al.* (2005c) deduced the stoichiometry of the biological processes in the model directly from established biochemical stoichiometric equations for the processes, see Table 2.3. The biodegradable particulate COD entering the system was directly hydrolysed to the intermediate organic 'glucose', from which the remainder of the products were formed via known bio chemical pathways.

Table 2.3 : Stoichiometry of the AD processes. The S1 to S13 numbers cross reference to the stoichiometry in the Petersen matrix (Table 2.2), Table 3 and 4 in Sötemann *et al.* (2005c).

ACETOGENESIS (PROCESS D5)						
C1/B10 NH_4^+	C3(S14) H_2CO^{3*}	C7 H^+	C13(S15) HAc	C28 HPr	D3 (S16) H_2	D5 Z_{AC}
moles	moles	moles	moles	moles	moles	moles
-1	$\frac{1-2Y_{AC}}{Y_{AC}}$	1	$\frac{1-\frac{3}{2}Y_{AC}}{Y_{AC}}$	$-\frac{1}{Y_{AC}}$	$\frac{3-4Y_{AC}}{Y_{AC}}$	1

HYDROLYSIS (PROCESS D1)			
C2 – NH_3 (S1)	C3 – $H_2CO_3^*$(S2)	D1 – S_{bp}	D2/B2 – S_{bs} (S3)
moles	moles	moles	moles
$+A$	$\frac{2Z+3A-Y}{4}$	-1	$\frac{Y+4X-2Z-3A}{24}$

ACIDOGENESIS FOR LOW pH2 (PROCESS D2)						
C1/B10 NH_4^+	C3 (S4) $H_2CO_3^*$	C7 H^+	C13 (S5) HAc	D2/B2 S_{bsf}	D3 (S6) H_2	D4 Z_{AD}
moles	moles	moles	moles	moles	moles	moles
-1	$\frac{2(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	1	$\frac{2(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	$-\frac{1}{Y_{AD}}$	$\frac{4(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	1

ACIDOGENESIS FOR HIGH pH2 ONLY (PROCESS D3)							
C1/B10 NH_4^+	C3 (S7) $H_2CO_3^*$	C7 H^+	C13 (S8) HAc	C28 (S9) HPr	D2/B2 S_{bsf}	D3 (S10) H_2	D4 Z_{AD}
moles	moles	moles	moles	Moles	moles	moles	moles
-1	$\frac{(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	1	$\frac{(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	$\frac{(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	$-\frac{1}{Y_{AD}}$	$\frac{(1-\frac{5}{6}Y_{AD})}{Y_{AD}}$	1

ACETOCLASTIC METHANOGENESIS (PROCESS D7)					
C1/B10 NH_4^+	**C3 – $H_2CO_3^*$ (S17)**	**C7 – H^+**	**C13 – HAc**	**P4 – CH_4 (S18)**	**D6 – Z_{AM}**
moles	**moles**	**moles**	**Moles**	**moles**	**moles**
-1	$\frac{(1-\frac{5}{2}Y_{AM})}{Y_{AM}}$	1	$-\frac{1}{Y_{AM}}$	$\frac{(1-\frac{5}{2}Y_{AM})}{Y_{AM}}$	1
HYDROGENOTROPHIC METHANOGENESIS (PROCESS D9)					
C1/B10 NH_4^+	**C3 – $H_2CO_3^*$ (S19)**	**C7 – H^+**	**P4 – CH_4 (S20)**	**D3 – H_2**	**D7 – Z_{HM}**
moles	**moles**	**moles**	**Moles**	**moles**	**moles**
-1	$\frac{(1+10Y_{HM})}{4Y_{HM}}$	1	$\frac{(1-10Y_{HM})}{4Y_{HM}}$	$-\frac{1}{Y_{HM}}$	1

DEATH / ENDOGENOUS RESPIRATION (PROCESSES D4, D6, D8, D10)			
C2/B10 NH_3 (S11)	**C3 $H_2CO_3^*$ (S12)**	**D1 S_{bp} (S13)**	**D4, D6, D8, D10 Z_{AC}, Z_{AD}, Z_{AM}, Z_{HM}**
moles	**moles**	**moles**	**moles**
$\frac{Y+4X-2Z-23A}{Y+4X-2Z-3A}$	$\frac{5(Y-2Z-3A)}{Y+4X-2Z-3A}$	$\frac{20}{Y+4X-Z-3A}$	-1

Table 2.4 : Kinetic and stoichiometric constants at 37°C for the four anaerobic digestion organism groups. Sötemann *et al.* (2005c), (Table 5) obtained the Y, μ_{max}, K_S and b values from Sam-Soon *et al.* (1991); and the $k_{max,HYD}$ and $K_{s,HYD}$ by calibration.

Organism Group	**Y**	**μ_{max}**	**K_S**	**b**
Acidogens (subscript AD)	0.1074	0.8	7.8×10^{-4}	0.041
Acetogens (subscript AC)	0.0278	1.15	8.9×10^{-5}	0.015
Acetoclastic methanogens (subscript AM)	0.0157	4.39	1.3×10^{-5}	0.037
Hydrogenotrophic methanogens (subscript HM)	0.0040	1.2	1.56×10^{-4}	0.01
Hydrogen inhibition coefficient for high p_{H2}	$K_{H2} = 6.25 \times 10^{-4}$ molH_2/ℓ			
Acidogenic hydrolysis of biodegradable particulate organics				
First order	$K_h = 0.381$			
First order specific	$K_H = 40$			
Monod	$\mu_{max,HYD} = 4.529$		$K_{SM,HYD} = 0.0486$	
Surface mediated reaction (Contois)	$k_{max,HYD} = 6.797$		$K_{SS,HYD} = 10.829$	

Y	=	yield coefficient (mol organism / mol substrate); μ_{max} = maximum specific growth rate (/d);
K_s	=	half saturation coefficient (mol/ℓ); b = endogenous respiration rate (/d);
K_h	=	first order hydrolysis rate constant (/d);
K_H	=	first order specific hydrolysis rate constant (ℓ/mol Z_{AD}.d);
$\mu_{max,HYD}$	=	Monod kinetics maximum specific hydrolysis rate (mol S_{bp}/mol Z_{AD}.d);
$K_{SM,HYD}$	=	Monod kinetics hydrolysis half saturation coefficient (mol S_{bp}/ℓ);
$k_{max,HYD}$	=	surface mediated reaction kinetics maximum specific hydrolysis rate (mol S_{bp}/mol Z_{AD}.d);
$K_{SS,HYD}$	=	surface mediated reaction kinetics half saturation coefficient (mol S_{bp}/mol Z_{AD})

For the kinetics, Sötemann *et al.* (2005c) obtained the rate equations for the 10 biological processes in Table 2.2 from various literature sources :

Hydrolysis process (D1) :

Sötemann *et al.* (2005a, b, c) and Ristow *et al.* (2005) evaluated various kinetic formulations for hydrolysis, namely first order, first order specific, Monod and surface saturation (Contois), and concluded that for kinetic simulation models Contois kinetics were preferable, in agreement with Vavilin *et al.* (2001), as it includes both the substrate and biomass, and has been extensively applied for utilisation of the same particulate substrates in activated sludge systems (e.g. Dold *et al.*, 1980, Henze *et al.*, 1987)

$$r_{HYD} = \left(\frac{k_{max,\,HYD} \dfrac{[S_{bp}]}{[Z_{AD}]}}{K_{SS,\,HYD} + \dfrac{[S_{bp}]}{[Z_{AD}]}} \right) [Z_{AD}]$$

(Equation (8d) in Sötemann *et al.*, 2005c)

where :

$k_{max,HYD}$	=	Maximum specific hydrolysis rate constant (mol S_{bp}/(mol Z_{AD}.d)
$K_{SS,HYD}$	=	Half saturation constant for hydrolysis (mol S_{bp}/mol Z_{AD})

For this formulation, two kinetic constants needed to be calibrated for constant pH and temperature.

Acidogenesis process (D2 and D3) :

The Acidogen growth rate was formulated according to Monod kinetics as commonly accepted, but included the hydrogen partial pressure effect of Sam-Soon *et al.* (1991).

Acidogen growth under low hydrogen partial pressure (p_{H2}) :

$$r_{Z_{AD}} = \frac{\mu_{max,\,AD}\,[S_{bsf}]}{K_{S,\,AD} + [S_{bsf}]}\left\{1 - \frac{[H_2]}{k_{H2} + [H_2]}\right\}[Z_{AD}]$$

(Equation (9) in Sötemann *et al.*, 2005c)

where :

$\mu_{max,AD}$ = Maximum specific growth rate constant for the acidogens (/d)
$K_{S,AD}$ = Half saturation concentration for acidogens (mol/ℓ)
$[S_{bsf}]$ = Biodegradable soluble (glucose) substrate concentration (mol/ℓ)
$[H_2]$ = Hydrogen concentration (mol/ℓ)
k_{H2} = Hydrogen inhibition constant for high p_{H2} (mol/ℓ)

Acidogen growth under high hydrogen partial pressure (p_{H2})

$$r_{Z_{AD}} = \frac{\mu_{max,\,AD}\,[S_{bsf}]}{K_{S,\,AD} + [S_{bsf}]}\left\{\frac{[H_2]}{k_{H2} + [H_2]}\right\}[Z_{AD}]$$

(Equation (10) in Sötemann *et al.*, 2005c)

Thus, from the above two equations and from Table 2.3 (Processes D2 and D3), the hydrogen concentration (via the hydrogen inhibition term in the kinetic formulations) determines which SCFA species (propionic and / or acetic acids) are produced in acidogenesis.

Acetogenesis process (D5) :

The rate for acetogenesis with propionic acid as substrate was modelled with Monod kinetics, and a non-competitive inhibition term ensuring the process operates under high hydrogen partial pressure. Due to the inclusion of weak acid / base chemical processes, the rate formulation is in terms of the undissociated propionic acid.

$$r_{Z_{AC}} = \frac{\mu_{max,\,AC}\,[HPr]}{K_{S,\,AC} + [HPr]}\left\{1 - \frac{[H_2]}{k_{H2} + [H_2]}\right\}[Z_{AC}]$$

(Equation (11) in Sötemann *et al.*, 2005c)

where :

$\mu_{max,AC}$ = Maximum specific growth rate constant for the acidogens (/d)
$K_{S,AC}$ = Half saturation concentration for acidogens (mol/ℓ)
$[HPr]$ = Undissociated propionic acid concentration (mol/ℓ)
$[Z_{AC}]$ = Acetogenic organism concentration (mol/ℓ)

Acetogenesis on butyrate was not modelled, as this SCFA is not commonly observed in sewage sludge digestion, but this can be readily added if required, by following the approach for HPr.

Acetoclastic methanogenesis process (D7) :

The acetoclastic methanogenesis growth rate also was modelled with Monod kinetics in terms of the undissociated acetic acid species.

$$r_{Z_{AM}} = \frac{\mu_{max,\ AM}\ [HAc]}{K_{S,\ AM} + [HAc]}\ [Z_{AM}]$$

(Equation (12) in Sötemann *et al.*, 2005c)

where :

$\mu_{max,AM}$	=	Acetoclastic methanogens maximum specific growth rate constant (/d)
$K_{S,AM}$	=	Half saturation concentration of acetoclastic methanogen growth on acetic acid (mol/ℓ)
[HAc]	=	Undissociated acetic acid concentration (mol/ℓ)
$[Z_{AM}]$	=	Acetoclastic methanogen organism concentration (mol/ℓ)

Hydrogenotrophic methanogenesis process (D9) :

The rate for hydrogenotrophic methanogen growth was modelled with Monod kinetics in terms of hydrogen.

$$r_{Z_{HM}} = \frac{\mu_{max,\ HM}\ [H_2]}{K_{S,\ HM} + [H_2]}\ [Z_{HM}]$$

(Equation (13) in Sötemann *et al.*, 2005c)

where :

$\mu_{max,HM}$	=	Maximum specific growth rate of hydrogenotrophic methanogens (/d)
$K_{S,HM}$	=	Half saturation concentration of hydrogenotrophic methanogen growth on hydrogen (mol/ℓ)
$[H_2]$	=	Molecular hydrogen concentration (mol/ℓ)
$[Z_{HM}]$	=	Hydrogenotrophic methanogen organism concentration (mol/ℓ)

Death / endogenous respiration of the four organism groups (processes D4, D6, D8 and D10) :

The death / endogenous respiration rates for the four organism groups were modelled as first order with respect to the relevant organism concentration, in common with the approach followed in activated sludge system modelling (Dold *et al.*, 1980; Henze *et al.*, 1987).

$$-r_Z = b_Z[Z]$$

where :

b_Z = the death / endogenous mass loss rate unique for a specific organism group (/d)
[Z] = specific organism group concentration (mol/ℓ)

Aqueous Chemistry Chemistry Processes

Sötemann *et al.* (2005c) retained the weak acid / base chemistry kinetic model of Musvoto *et al.* (1997, 2000 a, b, c) unchanged for inclusion in their two phase AD model. This encompassed the weak acid / base systems of water, ammonia, carbonate, phosphate and the SCFA represented by acetate, see Table 2.5. However, they added two additional chemical equilibrium processes, for the reverse (C46) and forward (C47) dissociation kinetic reactions for propionic acid with its two relevant compounds (C28 and C29), see Table 2.2.

TABLE 2.5 :

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 $CO_2(g)$**	**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									$K'_{fn}[NH^{4+}]$
Reverse dissociation of NH_4^+	1	-1					-1									$K'_{rn}[NH_3][H^+]$
Forward dissociation of $H_2CO_3^*$			-1	1			1									$K'_{fc1}[H_2CO_3^*]$
Reverse dissociation of $H_2CO_3^*$			1	-1			-1									$K'_{rc1}[HCO_3^-][H^+]$
Forward dissociation of HCO_3^-				-1	1		1									$K'_{fc2}[HCO_3^-]$
Reverse dissociation of HCO_3^-				1	-1		-1									$K'_{rc2}[CO_3^{2-}][H^+]$
Dissolution of CO_2			1			-1										$K'_{fco2}[CO_2(g)]$
Expulsion of CO_2 from solution			-1			1										$K'_{rco2}[H_2CO_3^*]$
Forward dissociation of H_3PO_4							1		-1	1						$K'_{fp1}[H_3PO_4]$
Reverse dissociation of H_3PO_4							-1		1	-1						$K'_{rp1}[H_2PO_4^-][H^+]$
Forward dissociation of $H_2PO_4^-$							1			-1	1					$K'_{fp2}[H_2PO_4^-]$
Reverse dissociation of $H_2PO_4^-$							-1			1	-1					$K'_{rp2}[HPO_4^{2-}][H^+]$
Forward dissociation of HPO_4^{2-}							1				-1	1				$K'_{fp3}[HPO_4^{2-}]$
Reverse dissociation of HPO_4^{2-}							-1				1	-1				$K'_{rp3}[PO_4^{3-}][H^+]$
Forward dissociation of HA							1						-1	1		$K'_{fa}[HA]$
Reverse dissociation of HA							-1						1	-1		$K'_{ra}[A^-][H^+]$
Forward dissociation of water							1	1								K'_{fw}
Reverse dissociation of water							-1	-1								$K'_{rw}[H^+][OH^-]$
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	

Ion Pairing

The 22 chemical ion pairing processes (CIP, C20-C40) with their associated chemical compounds (C15-C27) from Musvoto *et al.* (1997) were not included in the model of Sötemann *et al.* (2005c), because mineral precipitation was not considered in the two phase (aqueous gas) implementation.

Gas Exchange

The models of Musvoto *et al.* (2000 a) and Sötemann *et al.* (2005c) considered the following four gases, CO_2, CH_4, H_2 and NH_3. Of these four, only CO_2 was modelled with both expulsion and dissolution processes, because this gas is significantly soluble. Hence, Sötemann *et al.* (2005c) included both the dissolved and gaseous CO_2 compounds (Compound C3 and P1, Table 2.2). CH_4 is (i) very insoluble at near atmospheric pressures and (ii) not utilised in the biological or chemical processes, so Sötemann *et al.* (2005c) bypassed its dissolved (aqueous) phase and only a gas phase CH_4 compound was included. (Compound P4, Table 2.2). Sötemann *et al.* (2005c) therefore accepted that the acetoclastic and hydrogenotrophic methanogenesis processes (D7 and D9) produce CH_4 gas directly and no CH_4 expulsion or dissolution processes were included in the model (Table 2.2).

Although H_2 also is very insoluble, it is utilised at an interspecies level in the hydrogenotrophic methanogenesis process (D9) and so it cannot be transferred instantaneously to the gas phase. Sötemann *et al.* (2005c) therefore modelled H_2 as a dissolved compound (D3, Table 2.2).

Sötemann *et al.* (2005c) noted that NH_3 is readily soluble and its production from organically bound N in the sewage sludge is one of the processes governing the pH in the digester. It can therefore diffuse from the dissolved (aqueous) to the gas phases and so a process for expulsion of NH_3 was considered for inclusion in their model. However, because the rate and quantity of NH_3 expulsion into the gas phase are so slow and low respectively with respect to the total gas production of the digester, in particular in the usual digester pH range 6.8 to 8, the gas phase was assumed to maintain a negligible NH_3 partial pressure. An NH_3 dissolution process was thus not included in their model, but only an expulsion process (Process P8, Table 2.2) in agreement with Musvoto *et al.* (2000) and Van Rensburg *et al.* (2003).

The expulsion and dissolution processes for CO_2 and the expulsion process for NH_3 are shown in the Petersen matrix of the AD model (processes P6 – P8, Table 2.2). For CO_2, the dissolution rate is linked to the expulsion rate via Henry's Law and the digester CO_2 partial pressure. Thus, in

model calibration only the expulsion rate constants, $K_r'(=K_{La})$, for the two gases CO_2 and NH_3 needed to be considered. However, because transient conditions were not being modelled in this particular application, but only the final steady state, the expulsion rates of the gases were not important provided the simulation run times were long enough to reach steady state. From the above, the gas phase partial pressure required in the rate formulations for CO_2 gas exchange was calculated only from the CO_2 and CH_4 gas concentrations.

Model Calibration and Application

Sötemann *et al.* (2005c) 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 CO_2 ($K'_{H,CO2}$), 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 CO_2 ($K'_{H,CO2}$), 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. Following Musvoto *et al.* (1997), the weak acid / base apparent reverse dissociation rate constants (K'_r) were set at very high values to ensure that aqueous chemical equilibrium conditions are established very rapidly at every time step (<2 sec), e.g. ammonia $K'_{rN} = 10^{12}$/d, and the values were obtained from Table 2a in Musvoto *et al.* (1997). They noted that the weak acid / base apparent forward (K'_f) dissociation rate constants are linked to the apparent reverse rate constants (K'_r) and the equilibrium constants (pK) appropriately adjusted for ionic strength effects, e.g. for $H_2CO_3^* \leftrightarrow H^+ + HCO_3^-$, $K'_{fC1} = K'_{rC1}\ 10^{-pKC1}/f_m^2$, where f_m is the monovalent ion activity coefficient (Loewenthal *et al.*, 1989) see Table 2a, Musvoto *et al.* (1997). For the expulsion rate constants of the CO_2 and NH_3 gases modelled ($K'_r = K_{La}$), for CO_2 Sötemann assumed that the K_{LaCO2} to have a high value (1 000/d) since only steady state was initially simulated, while for NH_3 the K'_{rNH3} was accepted to have a low value (1/d). They noted that the value for K'_{rNH3} does not influence the simulations provided it is not too high, since little NH_3 is lost at pH<7.5.

In the biological processes part of the model, required were the kinetic and stoichiometric constants (Y, μ_{max}, K_S and b) for the four AD organism groups (Table 2.1). In the literature Sötemann *et al.* found that there is considerable variation and hence uncertainty in these values. Recognizing this uncertainty, they accepted values for these constants (Table 2.4) 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 (12) (in Sötemann *et al.*, 2005c)) 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, to reproduce the observation of low HAc/Ac^- residual concentrations under stable steady state; they found that due to the low HAc/Ac^- concentrations, since the rates are formulated in terms of HAc, decreasing the intuitively more satisfying half saturation constant ($K_{S,AM}$ in Equation (12) (in Sötemann *et al.*, 2005c)) as 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 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.

From theoretical evaluation for the experimental data of Izzett *et al.* (1992) Contois (saturation) kinetics were identified as most appropriate for hydrolysis. For Contois kinetics, through linearization techniques the unbiodegradable particulate fraction of the sewage sludge was estimated at 0.36 (the value varied from 0.32 to 0.36 depending on the kinetic formulation selected for hydrolysis). From influent sludge COD, TKN and VSS measurements of Izzett *et al.*, and AD system product generation (Alk, FSA, CH_4, $C0_2$) the stoichiometric composition of the influent sewage sludge was estimated to be $C_{3.4}H_7O_2N_{0.192}$.

Sötemann *et al.* (2005c) implemented the model in the computer programme AQUASIM (Reichert, 1998) and simulated the experimental systems of Izzet *et al.* (1992), see Figure 2.6. From the simulations and carbon recovery, the influent sewage sludge composition was refined to $C_{3.5}H_7O_2N_{0.196}$. Subsequent elemental analysis on PSS from two wastewater treatment plants in Cape Town (South Africa) gave an average measured composition of $C_{3.65}H_7O_{1.97}N_{0.19}$. The model determined C,H,O,N content and molar mass were 96 %, 100 %, 99 %, 95 % and 99 % of the measured values, providing persuasive validation of the kinetic model. Further, from Figure 2.6

reasonably close correlation was obtained between predicted and measured parameter values, providing further support for the model.

Similarly, Sötemann *et al.* (2005d) applied the kinetic model to the methanogenic experimental systems of Ristow *et al.* (2005), for example see Figure 2.7. 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.* 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, this was accepted as 0.335 from Ristow *et al.,* who determined the value from a 60 d retention time digester. Following the procedure described above for the Izzett *et al.* PSS characterization, the average stoichiometric formula for the Ristow *et al.* (2005) PSS was determined as $C_{4.17}H_7O_{2.63}N_{0.21}$ which is reasonably close to the value determined for the Izzett *et al.* data. Although for the Ristow *et al.* systems reasonably close correspondence between predicted and measured parameters was obtained, Sötemann *et al.* noted that there was scatter in the experimental data causing deviations between predicted and measured data for some of the systems. From the above model applications, Sötemann *et al.* (2005d) concluded that the COD, C and N mass balance and continuity basis of the model fixes quantitatively, via the interrelated chemical, physical and biological processes, the relationship between all the compounds of the system so that for a given sewage sludge biodegradation, the digester outputs (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.

UCTADM1 Closure

Sötemann *et al.* (2005c) successfully integrated in a kinetic simulation model, the two phase mixed weak acid / base chemistry and biological processes for 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.

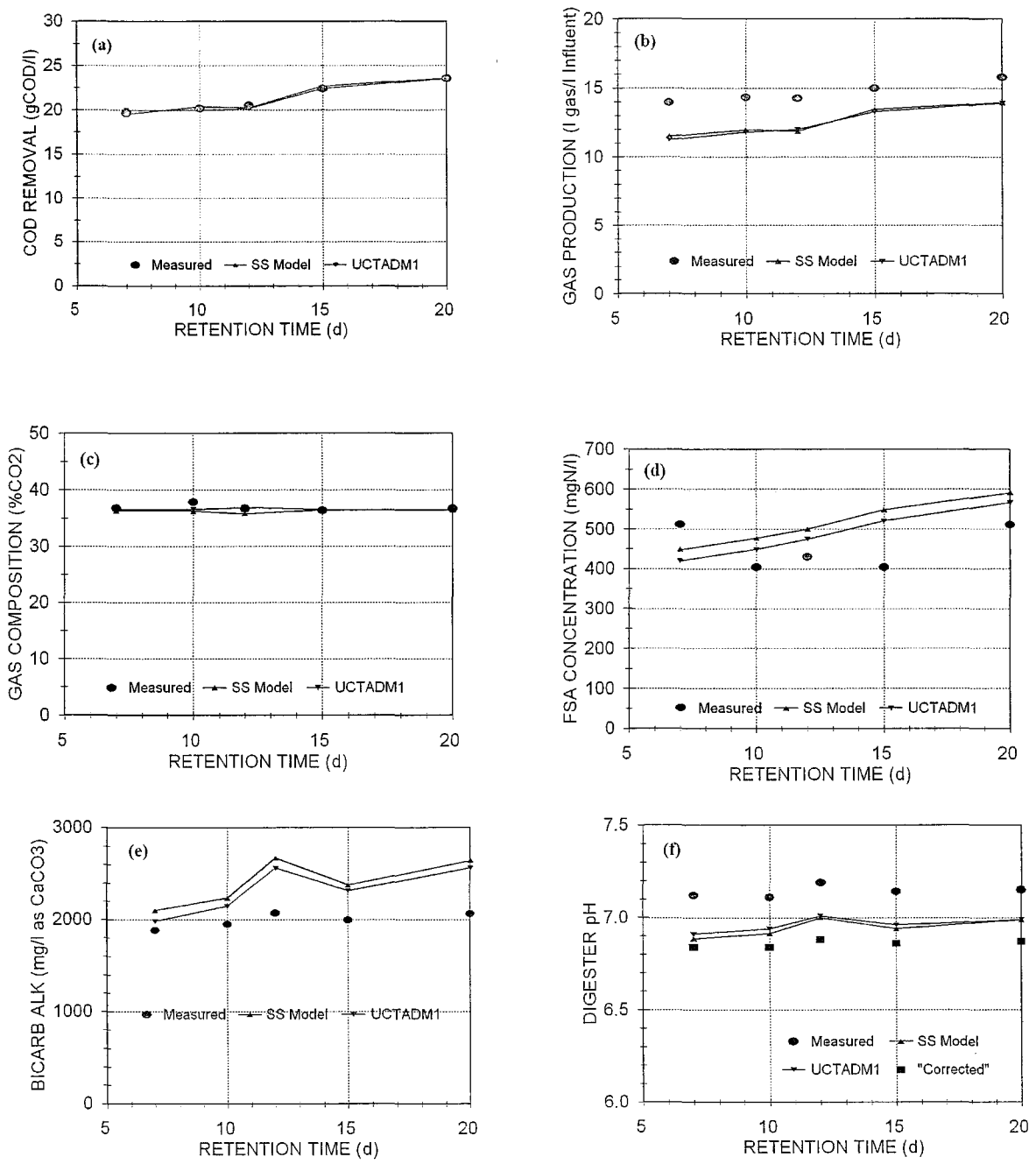
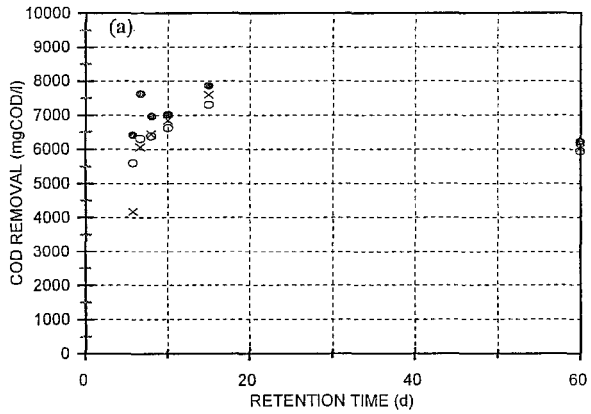
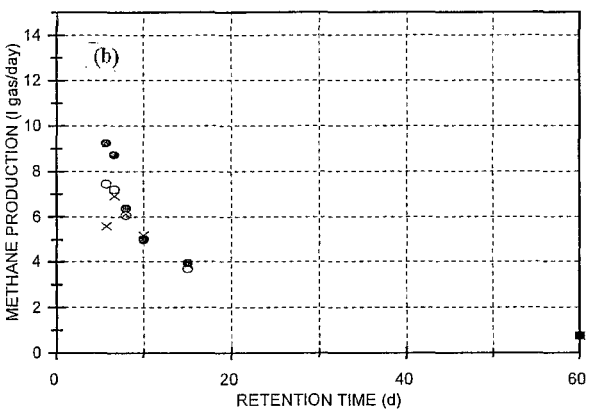
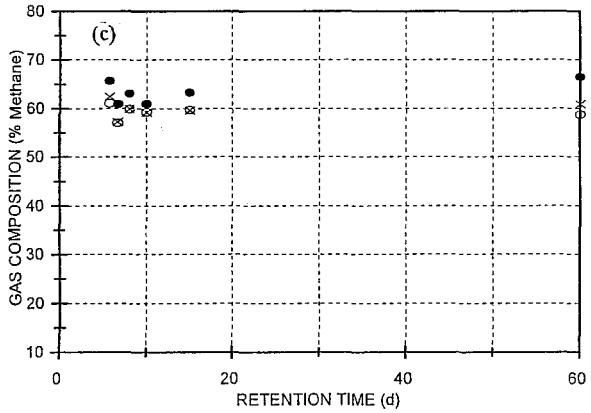
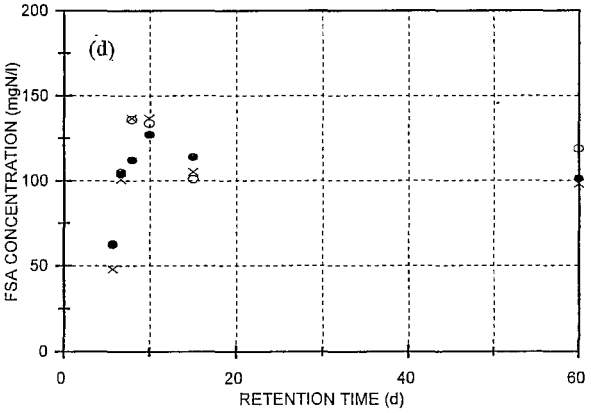


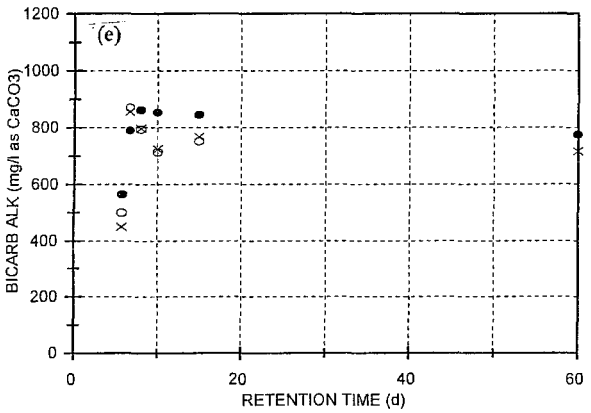
Figure 2.6 : Comparison between kinetic simulation model (UCTADM1) predicted (lines) and measured (points) (a) COD removal, (b) gas production, (c) gas composition, (d) free and saline ammonia, (e) $H_2CO_3^*$ alkalinity and (f) digester pH versus retention time for the Izzett *et al.* (1992) data set; also shown are the predictions of the steady state AD model.


(a)
COD REMOVAL (mgCOD/l)
RETENTION TIME (d)


(b)
METHANE PRODUCTION (l gas/day)
RETENTION TIME (d)


(c)
GAS COMPOSITION (% Methane)
RETENTION TIME (d)


(d)
FSA CONCENTRATION (mgN/l)
RETENTION TIME (d)


(e)
BICARB ALK (mg/l as CaCO3)
RETENTION TIME (d)

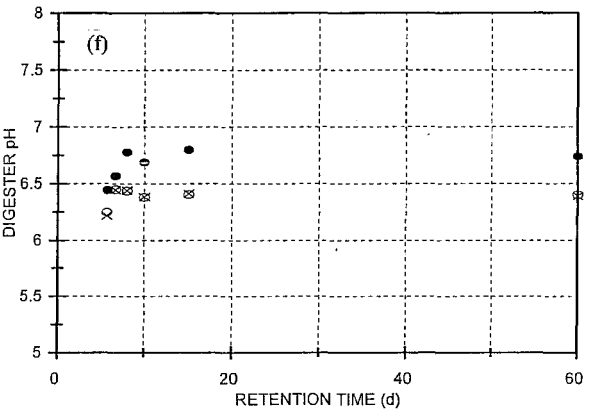

(f)
DIGESTER pH
RETENTION TIME (d)

Figure 2.7 : 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.

As stated in Chapter 1, the main objective of this research is to develop a kinetic model for BSR with PSS as substrate. To gain familiarity with UCTADM1 and the computer programme AQUASIM, it was decided to implement the existing UCTADM1 kinetic model in stages in AQUASIM; first weak acid / base chemistry, then methanogenic AD. At each stage the models were validated against data from the literature and the existing AQUASIM implementations of Sötemann *et al.* (2005c). Having successfully implemented UCTADM1, this model was extended to include the processes associated with biological sulphate reduction.

2.4 SULPHATE REDUCTION

The UCTADM1 described above was to be used as a basis for development of the kinetic model for BSR with PSS, since this model 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. Further, the included biological methanogenesis processes would allow modelling of competitive methanogenesis and sulphidogenesis. To extend the model for BSR, required that the BSR processes for inclusion in the model be identified, so also the interactions of BSR with the weak acid / base chemistry and physical gas exchange processes, and with the methanogenic anaerobic digestion processes already included in UCTADM1. To identify the appropriate BSR processes, available models for BSR in the literature were evaluated. Of these models, the model set developed by Kalyuzhnyi, Fedorovich and co-workers (Kalyuzhnyi and Fedorovich, 1997; Kalyuzhnyi *et al.*, 1998) and that of Ristow and co-workers (Ristow, 1999; Ristow *et al.*, 2001; Hansford, 2004) appear relevant. Both groups of researchers extensively reviewed and summarised preceding models of BSR processes, adopting generally accepted principles from these previous models and modifying and extending the processes, kinetics and stoichiometry where appropriate. Therefore, the BSR models preceding these will not be reviewed, only the models from the two research groups.

Kalyuzhnyi, Fedorovich and co-workers developed a model for BSR in reactors receiving sucrose, butyrate, propionate and acetate as influent substrates, with a focus on modelling sulphide inhibition of the biological processes, and competition between methanogens and sulphidogens. In reviewing the preceding models, they noted that only a few models for sulphate fed 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 fermantative, 2 acetogenic, 4 SRB, 2 methanogenic bacteria, see Chapter 3). The main features of the kinetic description for the processes mediated by these groups are (Kalyuzhnyi *et al.*, 1998) :

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 acid / bases of importance and the charge balance used to determine H^+ and associated pH. Weak acid / bases 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 anaerobic systems (see Section 2.4 above) 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 preceeding 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 will be used extensively for the BSR part of the model to be developed here, see Chapter 3. 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.* (2005c) would appear preferable.

Recognising the strengths of the Kalyuzhnyi, Fedorovich and co-workers models for BSR, Ristow *et al.* (2001) drew substantially from these models 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. This reactor configuration was selected as 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 was principally to hydrolyze the PSS to generate substrates for the subsequent treatment in a downstream reactor of the sulphate component of AMD by means of BSR; 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. Accordingly, 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, Ristow and co-workers used separate first order formulations with respect to the concentration of the specific organic group, in accordance with O'Rourke (1968). However, they did note that a variety of kinetic rate formulations for hydrolysis are available in the literature, and that from the available information they were not able to determine the most appropriate kinetic rate formulation for this crucial process. For the biological processes subsequent to hydrolysis, they followed the model proposed by Kalyuzhnyi and Fedorovich (1997) including the sulphide inhibitions and sulphate limitation formulations. Since the Kalyuzhnyi and Fedorovich model did not include anaerobic oxidation of the long chain fatty acids produced from lipid hydrolysis, Ristow *et al.* (2001) incorporated a

modified Monod formulation for this with a sulphide inhibition term. Further, from Costello *et al.* (1991) a competitive undissociated acetic acid inhibition term was included in the formulation for the lipid anaerobic oxididation process and a non-competitive term for the acetogenic process. To determine the undissociated acetic acid and hydrogen sulphide concentrations for the inhibition terms, Ristow *et al.* (2001) followed the approach of Musvoto *et al.* (1997) and modelled these weak acid / base equilibria via the kinetics of the forward and reverse dissociation reactions, with the relative rates linked through the equilibrium constant. They did not model pH, and this was set at a constant value of 7.0. Also, the physical gas exchange processes were not explicitly included.

Ristow *et al.* (2001) obtained values for kinetic and stoichiometric parameters from the literature, and implemented the model in the wastewater treatment simulation package AQUASIM (Reichert, 1998). They used the model predictions to suggest changes to the operational conditions of the RSBR that would achieve greater solubility of the particulate feed with minimum methane production, and to identify experimental work needed to improve the predictability of the model. This study concluded that, to improve the RSBR performance, an increase in the hydraulic retention time (HRT) would increase the amount of particulates that are hydrolysed. In contrast, a decrease in the solids retention time (SRT) would have little effect on the fraction of the particulates that are hydrolysed. Finally, they concluded that a higher COD: $SO4^{2-}$ ratio would result in more soluble COD being produced, but that the limit for the organic loading rate had not been determined.

As described earlier, 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.

2.5 CLOSURE

In this Chapter generation and treatment of AMD have been described briefly, to place the system of particular interest in this research, namely the Biosure ® system, in context. This highlighted the significant potential for BSR in AMD remediation. In such applications of BSR, the most significant factor economically and technically is the source and nature of the organic substrate to drive the BSR process. 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, potentially making AMD remediation via BSR costly. To reduce overall cost, one approach has been to use the biogenerated sulphide for metal recovery via selective metal sulphide precipitation. In the Biosure ® process this option is possible, but additionally BSR is achieved using PSS as the organic substrate. 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. 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 aid. Development of such a model is the primary objective of this research.

To gather information for developing such a model, relevant available models have been reviewed. From this review, the models of Sötemann *et al.* (2005c), 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 development is described in Chapter 3, and its validation against the Ristow *et al.* (2005) BSR ADs in Chapter 4.

CHAPTER 3

THE DEVELOPMENT OF A KINETIC MODEL FOR SULPHATE REDUCTION WITH PRIMARY SEWAGE SLUDGE AS SUBSTRATE

3.1 INTRODUCTION

To optimize the design, operation and control of, and aid research into, BSR with PSS, a mathematical kinetic model of this system would be an invaluable aid, and hence development of such a model forms the focus of this research, see Chapter 1. Chapter 3 describes the development of such a kinetic model. In Chapter 4 application of the kinetic model to a series of experimental lab-scale BSR systems fed PSS and sulphate is described.

From the review of kinetic models for anaerobic digestion with PSS (Chapter 2), the kinetic model of Sötemann *et al.* (2005c) (UCTADM1) was selected as a basis for the development of the kinetic model for BSR with PSS as substrate. This required development of the kinetics and stoichiometry for the biological, chemical and physical processes of 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 anaerobic digestion of PSS, with competitive methanogenesis and sulphidogenesis. The kinetic model for BSR was developed and integrated into the UCTADM1 model in three parts. Part 1 developed the biological processes: 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, in common with sewage sludge methanogenic AD systems. The products of these processes, the Short Chain Fatty Acids (SCFA), then can enter into the methanogenic or sulphate reduction processes, which operate in competition. One end product of BSR is sulphide, which is inhibitory to the methanogens, requiring that this inhibition be included.

Part 2 considered the aqueous chemistry and physical processes. The weak acid / base chemistry was included because the biological processes consume and produce significant acid / base species, e.g. SCFA, sulphide and sulphate. 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. Some of the end products have gaseous equilibria (sulphide, carbon dioxide, ammonia and methane), so that these physical processes also required inclusion (the third solid phase was not included at this stage).

Finally, Part 3 considered the integration of the aqueous chemistry and physical processes with the biological processes and the BSR with UCTADM1.

Identified for inclusion were the following processes and any interactions between these :

Biological *:*

-PSS hydrolysis, acidogenesis, acetogenesis and acetoclastic and hydrogenotrophic methanogenesis (UCTADM1)

-BSR with substrates available from the above processes

Figure 3.1 illustrates the pathways for the biological anaerobic degradation of organic matter, showing potential interactions between methanogenic and sulphate reducing bacteria.

Weak acid / base chemistry *:*

-water, acetate, propionate, carbonate, ammonium, phosphate (UCTADM1)

-weak acid / bases associated with BSR, sulphate and sulphide

Gas exchange *:*

-carbon dioxide, ammonia, (UCTADM1): methane produced directly to the gas phase, and hydrogen remains dissolved in solution (UCTADM1)

It can be shown from BSR stoichiometry that PSS and the SCFA acids for carbon >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 produced and affects the relative HS^- / H_2S concentrations, which establishes a higher digester pH than without C difficiency.

-gases produced in BSR, hydrogen sulphide

For integration with UCTADM1, the BSR related processes needed to be formulated in the appropriate mole units.

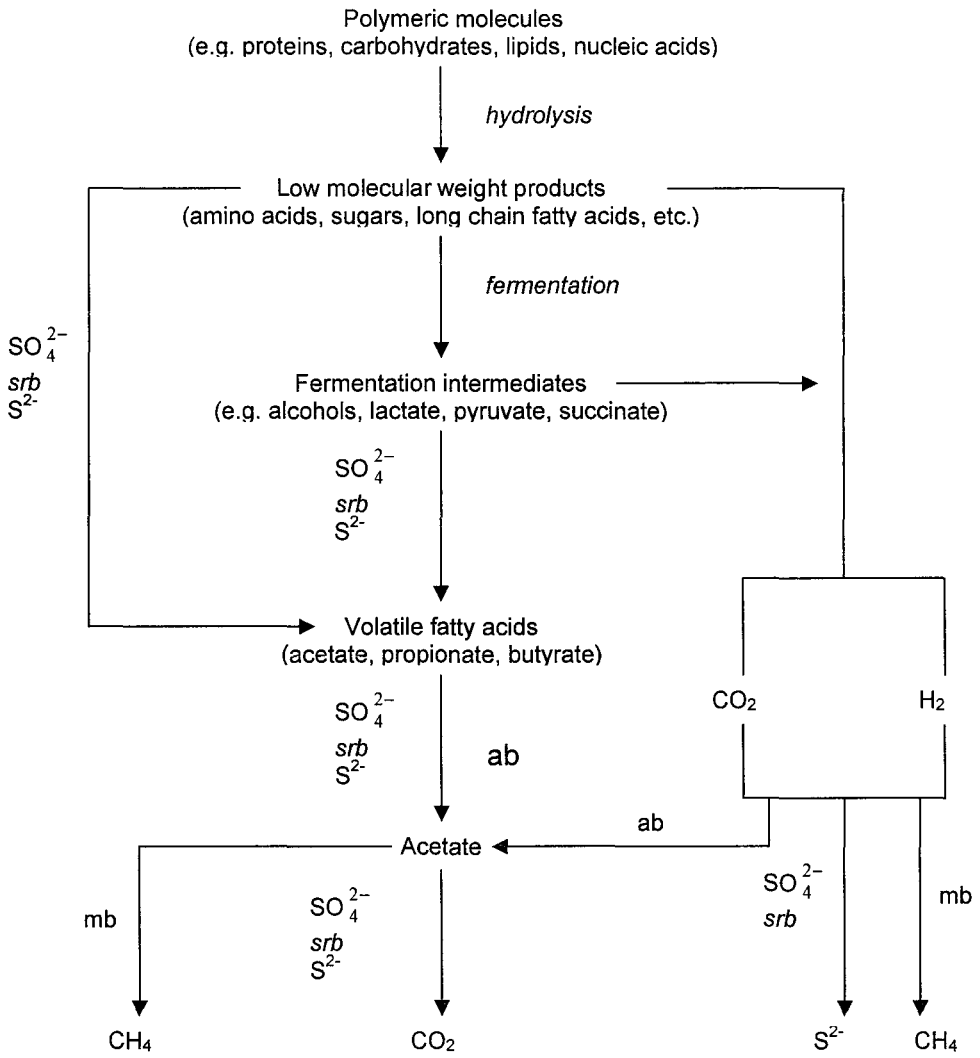


Figure 3.1 : Pathways for the anaerobic degradation of organic matter (Gibson, 1990), showing potential interactions between methanogenic and sulphate reducing bacteria (srb = sulphate-reducing bacteria; mb = methanogenic bacteria; ab = acetogenic bacteria).

3.2 BIOMASS POPULATION BIOLOGY

From the review of BSR kinetic models in Chapter 3, the approach of Kalyuzhnyi *et al.* (1998) formed the basis for the kinetic model for the biology of sulphate reducing bacteria (SRB). Kalyuzhnyi *et al.* (1998) described an anaerobic reaction sequence by which substrates are transformed by the following 9 trophic groups of bacteria :

(i)	Fermentative bacteria	(Sugars → Acetate)
(ii)	Butyrate degrading acetogenic bacteria	(Butyrate → Acetate)
(iii)	Butyrate degrading SRB	(Buryrate → Acetate & H_2S)
(iv)	Propionate degrading acetogenic bacteria	(Propionate → Acetate)
(v)	Propionate degrading SRB	(Propionate → Acetate & H_2S)
(vi)	Acetotrophic methanogenic bacteria	(Acetate → Methane & CO_2)
(vii)	Acetotrophic SRB	(Acetate → H_2S & CO_2)
(viii)	Hydrogenotrophic methanogenic bacteria	(H_2 & CO_2 → Methane)
(ix)	Hydrogenotrophic SRB	(H_2 → H_2S)

Of the 9 bacterial groups, of interest there are the four SRB groups only (i.e. iii, v, vii and ix), since BSR was to be integrated with the existing methanogenic and acetogenic UCTADM1 model of Sötemann *et al.* (2005c), which already explicitly includes (i), (iv) and (viii). Butyrate degrading acetogenic (ii) and SRB (iii) groups were not incorporated into the model, as butyrate is not commonly encountered in significant concentrations in sewage sludge digestion systems (but these processes can be readily incorporated if required). Accordingly, the process stoichiometry and kinetics for the four SRB groups were considered, for both organism growth and decay.

3.2.1 Growth Stoichiometry

For each SRB group, by following the procedure of Sötemann *et al.* (2005c) and adding the catabolic and anabolic stoichiometry, the stoichiometry for the SRB growth bioprocesses could be determined (Table 3.9). These processes are each described below.

(a) **Propionate degrading SRB**

For the propionate degrading SRB (Z_{PS}), the catabolic substrate utilisation is (Kalyuzhnyi *et al.*, 1998) :

$$C_2H_5COOH + \frac{3}{4} SO_4^{2-} + \frac{3}{2} H^+ \rightarrow CH_3COOH + \frac{3}{4} H_2S + CO_2 + H_2O \quad (3.1)$$

It is accepted that the anabolic growth process of the propionate degrading SRBs is identical to that of the acetogenic biomass group in the UCTADM1 model (both use propionate as substrate). With the stoichiometric composition for biomass of $C_5H_7O_2N$ for the acetogenic and hence propionate degrading SRB bacteria group, the anabolic growth process is as follows (Sötemann *et al.*, 2005c) :

$$3C_2H_5COOH + CO_2 + 2NH_4^+ \rightarrow 2C_5H_7O_2N + 4H_2O + H_2 + 2H^+ \quad (3.2)$$

Dividing Equation (3.2) by 2 and multiplying by the catabolic organism yield (Y'_{PS}), and adding Equations (3.1) and (3.2) :

$$(1 + \frac{3}{2} Y'_{PS})\, C_2H_5COOH + \frac{3}{4} SO_4^{2-} + \frac{Y'_{PS}}{2} CO_2 + Y'_{PS} NH_4^+ + \frac{3}{2} H^+ \rightarrow$$
$$Y'_{PS}\, C_5H_7O_2N + CH_3COOH + \frac{3}{4} H_2S + CO_2 + \frac{Y'_{PS}}{2} H_2 + Y'_{PS} H^+ + (1 + 2Y'_{PS}) H_2O \quad (3.3)$$

Dividing Equation (3.3) by Y'_{PS} and simplifying gives :

$$\frac{\left(1+\frac{3}{2}Y'_{PS}\right)}{Y'_{PS}} C_2H_5COOH + \frac{3}{4Y'_{PS}} SO_4^{2-} + NH_4^+ \rightarrow C_5H_7O_2N + \frac{1}{Y'_{PS}} CH_3COOH +$$
$$\frac{3}{4Y'_{PS}} H_2S + \left(\frac{1}{Y'_{PS}} - \frac{1}{2}\right) CO_2 + \frac{1}{2} H_2 + \left(1 - \frac{3}{2Y'_{PS}}\right) H^+ + \frac{1+2Y'_{PS}}{Y'_{PS}} H_2O \quad (3.4)$$

The stoichiometry, in terms of **the catabolic organism yield Y'_{PS}** for the growth process of propionate degrading SRBs is taken directly from Equation (3.4) and is listed in Table 3.1.

Table 3.1 : Stoichiometry for propionate degrading SRB in terms of the catabolic 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	$\frac{1}{Y'_{PS}}$	$\frac{3}{4Y'_{PS}}$	$\frac{1}{2}$	$\left(1-\frac{3}{2Y'_{PS}}\right)$	$\frac{1+2Y'_{PS}}{Y'_{PS}}$

It should be noted that the catabolic organism yield Y'_{PS} is not the true yield, because it is the organism yield per unit of propionate substrate consumed in catabolism and hence does not directly include the anabolic propionate requirement of the organisms; thus it does not represent the ratio of biomass formed per unit total substrate consumed. The metabolic (anabolic + catabolic) yield is a true yield in terms of total propionate utilisation and since it is more conventional to express yields as true yields, this approach is taken here also. The metabolic yield is found from Equation (3.4).

Let Y_{PS} = metabolic yield.

From Table 3.1, 1 mole biomass (160 g COD) grows from $\frac{1+\frac{3}{2}Y'_{PS}}{Y'_{PS}}$ moles propionate. Hence, the true yield Y_{PS} (in mol/mol units) is expressed as :

$$Y_{PS} = \frac{Y'_{PS}}{\left(1+\frac{3}{2}Y'_{PS}\right)} \tag{3.5}$$

Making Y'_{PS} the subject of Equation (3.5) :

$$Y'_{PS} = \frac{Y_{PS}}{-\frac{3}{2}Y_{PS}} \tag{3.6}$$

Substituting Equation (3.6) into the stoichiometric terms shown in Table 3.1 and recognising that $CO_2 + H_2O \rightarrow H_2CO_3^*$ results in the stoichiometry for propionate degrading SRBs in terms of the true (metabolic) organism yield, shown in Table 3.2.

Table 3.2 : 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	$\frac{1}{Y_{PS}}-\frac{3}{2}$	$\frac{3}{4Y_{PS}}-\frac{9}{8}$	$\frac{1}{2}$	$\frac{13}{4}-\frac{3}{2Y_{PS}}$	$\frac{5}{2}$

(b) **Acetotrophic SRB**

Using the same approach described above for the propionate utilising SRBs, the stoichiometry for the growth of acetotrophic SRBs (Z_{AS}) was determined. From Kalyuzhnyi *et al.* (1998), the catabolic substrate utilisation for acetotrophic SRB is :

$$CH_3COOH + SO_4^{2-} + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O \quad (3.7)$$

For anabolic growth of acetotrophic SRB, from acetoclastic methanogen growth in the UCTADM1 model :

$$5CH_3COOH + 2NH_4^+ \rightarrow 2C_5H_7O_2N + 6H_2O + 2H^+ \quad (3.8)$$

Dividing Equation (3.8) by 2 and multiplying by the catabolic organism yield (Y'_{AS}), and adding Equation (3.7) to Equation (3.8) :

$$(1 + \frac{5}{2}Y'_{AS})CH_3COOH + SO_4^{2-} + Y'_{AS}NH_4^+ + 2H^+ \rightarrow Y_{AS}C_5H_7O_2N +$$
$$H_2S + 2CO_2 + Y'_{AS}H^+ + (2 + 3Y'_{AS})H_2O \quad (3.9)$$

Dividing Equation (3.9) by Y'_{AS} and simplifying :

$$\frac{1+\frac{5}{2}Y'_{AS}}{Y'_{AS}}CH_3COOH + \frac{1}{Y'_{AS}}SO_4^{2-} + NH_4^+ + \frac{2}{Y}H^+ \rightarrow C_5H_7O_2N + \frac{1}{Y'_{AS}}H_2S$$
$$+ \frac{2}{Y'_{AS}}CO_2 + H^+ + \frac{(2+3Y'_{AS})}{Y'_{AS}}H_2O \quad (3.10)$$

The stoichiometry in terms of the catabolic yield for the growth process of acetotrophic SRBs is taken directly from Equation (3.10) and is listed in Table 3.3.

Table 3.3 : Stoichiometry for acetotrophic SRB in terms of catabolic organism yield, Y'_{AS}.

HAc mol	SO_4^{2-} mol	NH_4^+ mol	Z_{AS} mol	H_2S mol	CO_2 mol	H^+ mol	H_2O mol
$-\left(\frac{1+\frac{5}{2}Y'_{AS}}{Y'_{AS}}\right)$	$-\left(\frac{1}{Y'_{AS}}\right)$	+1	1	$\frac{1}{Y'_{AS}}$	$\frac{2}{Y'_{AS}}$	+1	$\frac{2+3Y'_{AS}}{Y'_{AS}}$

Let Y_{AS} = metabolic yield. Therefore :

$$Y_{AS} = \frac{Y'_{AS}}{1+\frac{5}{2}Y'_{AS}} \tag{3.11}$$

and

$$Y'_{AS} = \frac{Y_{AS}}{1+\frac{5}{2}Y_{AS}} \tag{3.12}$$

Substituting Equation (3.12) into the stoichiometry shown in Table 3.3 and using $H_2CO_3^*$ gives the stoichiometry for acetotrophic SRBs in terms of the true (metabolic) yield, shown in Table 3.4 :

Table 3.4 : 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	CO_2 mol	H^+ mol	H_2O mol
$\frac{1}{Y_{AS}}$	$\frac{\left(1-\frac{5}{2}\right)Y_{AS}}{Y_{AS}}$	+1	+1	$\frac{\left(1-\frac{5}{2}\right)Y_{AS}}{Y_{AS}}$	$\frac{(2-5)Y_{AS}}{Y_{AS}}$	$1-\frac{(2-5)Y_{AS}}{Y_{AS}}$	$\frac{(2-5)Y_{AS}}{Y_{AS}}+3$

(c) **Hydrogenotrophic SRB**

For the hydrogenotrophic SRB (Z_{HS}), from Kalyuzhnyi *et al.* (1998), the catabolic substrate utilisation is :

$$4H_2 + SO_4^{2-} + 2H^+ \rightarrow H_2S + 4H_2O \tag{3.13}$$

For hydrogenotrophic SRB organism growth :

$$5CO_2 + 10H_2 + NH_4^+ \rightarrow C_5H_7O_2N + 8H_2O + H^+ \quad (3.14)$$

Multiplying Equation (3.14) by the catabolic organism yield (Y'_{HS}) and adding Equation (3.13) to Equation (3.14) :

$$5Y'_{HS}CO_2 + (4 + 10Y'_{HS})H_2 + SO_4^{2-} + Y'_{HS}NH_4^+ + 2H^+ \rightarrow Y'_{HS}C_5H_7O_2N + H_2S + Y'_{HS}H^+ + (4 + 8Y'_{HS})H_2O \quad (3.15)$$

Dividing Equation (3.15) by Y'_{HS} and simplifying :

$$5CO_2 + \left(\frac{4+10Y'_{HS}}{Y'_{HS}}\right)H_2 + \frac{1}{Y'_{HS}}SO_4^{2-} + NH_4^+ \rightarrow C_5H_7O_2N + \frac{1}{Y'_{HS}}H_2S + \left(1-\frac{2}{Y'_{HS}}\right)H^+ + \left(\frac{4+8Y'_{HS}}{Y'_{HS}}\right)H_2O \quad (3.16)$$

The stoichiometry in terms of catabolic organism yield for the growth process of acetotrophic SRBs is taken directly from Equation (3.16) and is listed in Table 3.5 :

Table 3.5 : Stoichiometry for hydrogenotrophic SRB in terms of catabolic organism yield, Y'_{HS}

CO_2 mol	H_2 mol	SO_4^{2-} mol	NH_4^+ mol	Z_{hs} mol	H_2S mol	H^+ mol	H_2O mol
-5	$-\left(\frac{4+10Y'_{HS}}{Y'_{HS}}\right)$	$-\frac{1}{Y'_{HS}}$	-1	1	$\frac{1}{Y'_{HS}}$	$1-\frac{2}{Y'_{HS}}$	$\frac{4+8Y'_{HS}}{Y'_{HS}}$

Let Y_{HS} = metabolic yield. Therefore :

$$Y_{HS} = \frac{Y'_{HS}}{4+10Y'_{HS}} \quad (3.17)$$

and

$$Y'_{HS} = \frac{4Y_{HS}}{1-10Y_{HS}} \quad (3.18)$$

Substituting Equation (3.18) into the stoichiometry shown in Table 3.5 and using $H_2CO_3^*$ gives the stoichiometry for hydrogenotrophic SRBs in terms of the true (metabolic) yield, shown in Table 3.6.

Table 3.6 : 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	$-\left(\frac{1}{Y_{HS}}\right)$	$-\left(\frac{1}{4Y_{HS}}-\frac{5}{2}\right)$	-1	1	$\frac{1}{4Y_{HS}}-\frac{5}{2}$	$6-\frac{1}{2Y_{HS}}$	$\frac{1}{Y_{HS}}+3$

The matrix presenting the full biological kinetic model for SRB is shown in Table 3.9, and includes the above growth processes for propionate SRB (Z_{PS}, Process S1), acetotrophic SRB (Z_{AS}, Process S3) and hydrogenotrophic SRB (Z_{HS}, Process S5.)

3.2.2 Endogenous Decay for all Bacterial Groups

It was assumed that organism death / decay for the SRB groups is the same as for the methanogenic bacterial groups in the UCTADM1 model, and therefore the same approach was followed here.

In the UCTADM1 model and in this SRB model, it was accepted that the organism mass is represented by the $C_5H_7O_2N$ formulation. 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 so was neglected. It was accepted that the endogenous biodegradable particulate COD (S_{bp}) composition is $C_{3.5}H_7O_2N_{0.196}$, the same as PSS biodegradable particulate COD as accepted by Sötemann *et al.* (2005c). These endogenous organics are transformed to become the variable ($C_xH_yO_zN_A$) influent biodegradable organics and added to the pool of these organics.

The COD/VSS ratio for $C_5H_7O_2N$ = 1.413 mgCOD/mgVSS and 1 mol $C_5H_7O_2N$ ~ 160 mgCOD. Therefore, 160 g organism COD is 113 gVSS organisms which based on COD conservation equates to 1.219 mol $C_{3.5}H_7O_2N_{0.196}$ (COD/VSS ratio of $C_{3.5}H_7O_2N_{0.196}$ = 1.566 mgCOD/mgVSS). Accordingly, endogenous decay of the organisms was represented by the following equation :

$$C_5H_7O_2N + 1.905H_2O \rightarrow 1.219C_{3.5}H_7O_2N_{0.196} + 0.7335CO_2 + 0.761NH_3 \qquad (3.19)$$

The stoichiometry for endogenous decay was taken directly from Equation (3.19) and is shown in Table 3.7.

Table 3.7 : Stoichiometry for the endogenous respiration of all SRB organism groups (Z_j), with biodegradable particulate COD (S_{bp}) formulation as $C_{3.5}H_7O_2N_{0.196}$

Z_j mol	$H_2CO_3^*$ mol	NH_3 mol	S_{bp}	
			g COD	mol
-1	0.7335	0.761	160	1.219

If the generalised formulation for S_{bp} of $C_XH_YO_ZN_A$ is accepted, then the stoichiometry for endogenous decay can be extracted directly from Sötemann *et al.* (2005c), and is shown in Table 3.8 for the generalised SRB (Z_j) and in Table 3.9 for the three SRB groups.

Table 3.8 : Stoichiometry for the endogenous respiration of all SRB organism groups (Z_j), with biodegradable particulate COD (S_{bp}) formulation as $C_XH_YO_ZN_A$.

NH_3 mol	$H_2CO_3^*$ mol	S_{bp} mol	Z_j mol
$\frac{Y+4X-2Z-23A}{Y+4X-2Z-3A}$	$\frac{5(Y-2Z-3A)}{Y+4X-2Z-3A}$	$\frac{20}{Y+4X-2Z-3A}$	-1

3.2.3 Growth Kinetic Rates

For the growth of SRB the principles for the kinetic rate descriptions were taken from Kalyuzhnyi *et al.* (1998) :

i. Bacterial growth of each SRB group was modelled using Monod kinetics in terms of the relevant substrate, with simultaneous inhibition by pH and undissociated H_2S.

ii. The undissociated H_2S inhibition was formulated as first order for all SRB bacterial groups.

Thus, the generalized specific growth rate (μ_j) equation for SRB was taken from Kalyuzhnyi *et al.* (1998) who described this as :

$$\mu_j = \mu_{max,\,j}\frac{[S_i]F(pH)}{K_{Sj}+[S_i]}\left[1-\left(\frac{[H_2S]_f}{K_{I,j}}\right)\right]\left(\frac{[SO_4^{2-}]}{K_n+[SO_4^{2-}]}\right) \qquad (3.20)$$

where :

F(pH)	=	pH inhibition function
$\mu_{max,j}$	=	Maximum specific growth rate for SRB group j
$[S_i]$	=	Organic substrate i concentration
K_{Sj}	=	Monod saturation constant for organic substrate
$K_{I,j}$	=	Inhibition constant for undissociated hydrogen sulphide $[H_2S]$
K_n	=	Monod saturation constant for sulphate $[SO_4^{2-}]$

In the H_2S inhibition term in Equation (3.20) $[H_2S]$ must be less than $K_{I,j}$, otherwise the inhibition term becomes negative; if this is encountered in model application the alternative non-competitive inhibition kinetics (Sötemann *et al.*, 2005c) will be considered.

With regard to pH inhibition formulation, initially Kalyuzhnyi and Fedorovich (1997) excluded this "to avoid an excessive complexity of the model". Kalyuzhnyi *et al.* (1998) followed Kalyuzhnyi and Fedorovich (1997) and described the effect of pH on the SRB growth rates with a bell-shaped pH function normalised to give a value of 1,0 as the centre value. However, this pH effect was not extensively evaluated and validated. Fedorovich *et al.* (2003) in integrating BSR with ADM1 (Batstone *et al.*, 2002) used a pH inhibition function analogous to the approach followed in ADM1 :

$$IpH = \frac{1+2x10^{0.5(pK_1-pK_2)}}{1+10^{(pH-pK_2)}+10^{(pH-pK_1)}} \qquad (3.21)$$

However, again this inhibition function was not extensively evaluated and validated. Due to the uncertainty in pH inhibition, pH inhibition initially will be neglected. If required, the formulation used for the pH inhibition of methanogens in the UCTADM1 model ($1 + I/K_I$) can be used for pH inhibition of the SRBs also, once the SRBs are integrated in the UCTADM1 model. Hence, the SRB growth rate used here is :

$$\mu_j = \mu_{max,\,j}\frac{[S_i]}{K_{sj}+[S_i]}\quad\left(1-\frac{[H_2S]_f}{K_{I,\,j}}\right)\left(\frac{[SO_4^{2-}]}{K_n+[SO_4^{2-}]}\right) \tag{3.22}$$

For acidogenic, acetogenic and methanogenic bacterial groups the approach to formulating the kinetic rates of Kalyuzhnyi *et al.* (1998) is the same as that used in the UCTADM1, but Kalyuzhnyi *et al.* do include an inhibition term for H_2S. Hence, only the H_2S inhibition term has to be added to the existing kinetic rate equations for the acidogenic, acetogenic and methanogenic bacterial groups in the UCTADM1 model, once SRBs are integrated into the UCTADM1 model. For this, the approach of Kalyuzhnyi *et al.* can be followed; for the acidogenic, acetogenic and methanogenic bacteria :

$$\mu_j = \mu_{max,\,j}\frac{[S_i]}{K_{sj}+[S_i]}\left(1-\frac{H_2S_f}{K_{I,j}}\right) \tag{3.23}$$

3.2.4 Endogenous Decay Kinetic Rates

Bacterial decay both in Kalyuzhnyi *et al.* (1998) and UCTADM1 Sötemann *et al.* (2005c) is described by first order kinetics, and hence this approach was followed here also for the SRBs. The specific rate for bacterial decay is thus = $b_j[X_j]$ where b_j is the specific decay constant for the bacterial population concerned, X_j, Table 3.9.

3.2.5 Matrix Representation of Biological Processes

The Petersen matrix of the biological processes for BSR is presented in Table 3.9.

Table 3.9 : Petersen matrix of the biological kinetic model for SRBs.

	Number→	C1/B10	C2	C3	C7	C13	D4	D3	C31	C32	D1	S1	S2	S3	
No	**Process↓ Compound→**	**NH_4^+**	**NH3 dis.**	**$H_2CO_3^*$**	**H^+**	**HAc**	**HPr**	**H_2 dslvd**	**SO_4^{2-}**	**H_2S**	**S_{bp}**	**Z_{PS}**	**Z_{AS}**	**Z_{HS}**	**↓Process Rate**
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			$\frac{\mu_{max}[HPr]}{K_S+[HPr]}\left[1-\frac{[H_2S]}{K_I}\right]\left[\frac{[SO_4^{2-}]}{K_N+[SO_4^{2-}]}\right]Z_{PS}$
S2	Endogenous decay of propionate degrading SRB		0.761[2]	0.7335[2]							160[2]	-1			$b_{PS}[Z_{PS}]$
S3	Growth of acetotrophic SRB	+1		$\frac{(2-5)Y_{AS}}{Y_{AS}}$	$1-\frac{(2-5)Y_{AS}}{Y_{AS}}$	$\left(\frac{1}{Y_{AS}}\right)$			$\frac{\left(1-\frac{5}{2}\right)Y_{AS}}{Y_{AS}}$	$\frac{\left(1-\frac{5}{2}\right)Y_{AS}}{Y_{AS}}$			1		$\frac{\mu_{max}[HAc]}{K_S+[HAc]}\left[1-\frac{[H_2S]}{K_I}\right]\left[\frac{[SO_4^{2-}]}{K_N+[SO_4^{2-}]}\right]Z_{SA}$
S4	Endogenous decay of acetotrophic SRB		0.761[2]	0.7335[2]							160[2]		-1		$b_{AS}[Z_{AS}]$
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	$\frac{\mu_{max}[H_2]}{K_S+[H_2]}\left[1-\frac{[H_2S]}{K_I}\right]\left[\frac{[SO_4^{2-}]}{K_N+[SO_4^{2-}]}\right]Z_{HS}$
S6	Endogenous decay of hydrogenotrophic SRB		0.761[2]	0.7335[2]							160[2]			-1	$b_{HS}[Z_{HS}]$
		mol/l	**mol/l**	**mol/l**	**mol/l**	**mol/l**	**mol/l**	**mol/l**	**mol/l**	**mol/l**	**gCOD/l[1]**	**mol/l**			

[1]See Table 3.8 for units in mol/l

[2]This is for the formulation for biodegradable particulate substrate $S_{bp} = C_{3.5}H_7O_2N_{0.196}$; see Table 3.8 for the generalised formulation for $S_{bp} = C_XH_YO_ZN_A$

Zj = SRB j concentration; Y = true organism yield; b = specific decay rate; rate symbols defined in Eq [3.22].

Subscripts PS, AS and HS = propionate degrading, acetotrophic and hydrogenotrophic SRB respectively.

Compound and process numbering system follows Sötemann *et al.* (2005c).

3.2.6 Values for Constants

Values for the stoichiometric and kinetic constants for the SRBs were taken from Kalyuzhnyi *et al.* (1998), who obtained values for these parameters from model fitting to the data of Omil *et al.* (1996), and are listed in Table 3.10.

Table 3.10 : Values for SRB stoichiometric and kinetic constants used in the BSR kinetic model (from Kalyuzhnyi *et al.*, 1998).

	μ_{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

[1] Constants to be converted to mole units upon integration with the UCTADM1 model, to ensure consistency in units, see Table 3.11.

The values for these constants were evaluated through model application to experimental data (see Chapter 4). If required, the values can be refined using the values extracted from the literature by Ristow *et al.* (2005) and Hansford (2004), who also accepted the Kalyuzhnyi *et al.* (1998) constants for application in their models. The concentration based constants listed in Table 3.10 are expressed in terms of g units. Since the kinetic model for BSR (Table 3.9) and UCTADM1 are in terms of mole units, the constants were converted to the appropriate mole units by accepting the formulation for biomass as $C_5H_7O_2N$ and that for the substrates (propionic acid, acetic acid and hydrogen) as per the known chemical formulations, see Table 3.11. Further, since the kinetic rates are expressed in terms of undissociated weak acid / base species (due to the direct inclusion of weak acid / base chemistry) instead of total species concentrations in the original literature source, the appropriate half saturation constants had to be adjusted to take this into account. 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. This was considered more appropriate as the relative concentrations may change as the pH changes. Thus, the half saturation constants listed in Table 3.10 are not corrected for the use of undissociated weak acid / base species. The values for the constants are listed in Table 3.11.

Table 3.11 : Values for the appropriate half saturation constants.

Organism Group	μ		Ks		Kn		Y		b	
	Kaly.	UCTADM	Kaly.	UCTADM	Kaly.	UCTADM	Kaly.	UCTADM	Kaly.	UCTADM
Comparisson	/d	/d	mol(subs)/ℓ	mol(subs)/ℓ	molSO_4/ℓ	molSO_4/ℓ	mol(org)/ mol(subs)	mol(org)/ mol(subs)	/d	/d
Acidogens	4.000	0.80	7.675903E-05	0.000781	N/A	N/A	0.109644	0.1074	0.0900	0.041
Acetogens	0.160	1.15	0.0022030428	8.90E-05	N/A	N/A	0.015859	0.0278	0.0140	0.015
Proprionate Degrading SRB	0.583	-	0.0026311645	-	7.703358E-05	-	0.026762	-	0.0185	-
Acetoclastic Methanogens	0.264	4.39	0.0018733303	1.30E-05	N/A	N/A	0.012175	0.0157	0.0200	0.037
Acetotrophic SRB	0.612	-	0.0003746661	-	0.0001998709	-	0.018688	-	0.0275	-
Hydrogenotrophic Methanogens	1.000	1.20	7.500468E-06	0.000156	N/A	N/A	0.002122	0.0040	0.0400	0.010
Hydrogenotrophic SRB	2.800	-	4.375273E-06	-	0.0001998709	-	0.007072	-	0.0600	-

3.3 AQUEOUS CHEMISTRY AND PHYSICAL PROCESSES

The BSR processes described above both produce and consume weak acid / base species, and hence these and the associated weak acid / base chemistry required inclusion in developing a kinetic model for BSR. Further, the compound H_2S is produced and the compound H_2CO_3* is both produced and consumed. Both these compounds have physical gas exchange processes with the atmosphere, and therefore these processes were also included in the model.

3.3.1 Aqueous Chemistry

The following acid / base systems were identified having direct relevance to BSR :

1.	Water	:	H^+ / OH^-
2.	Ammonia	:	NH_3 / NH_4^+
3.	Carbonate	:	$H_2CO_3^*$ / HCO^{3-} / CO_3^{2-}
4.	Acetate	:	HAc / Ac^-
5.	Propionate	:	HPr / Pr^-
6.	Sulphate	:	H_2SO_4 / HSO_4^- / SO_4^{2-}
7.	Sulphide	:	H_2S / HS^- / S^{2-}

Of these the acid / base systems, 1 to 5 already have been included in the methanogenic UCTADM1 model, whereas 6 and 7 have not (Sötemann *et al.*, 2005c). Accordingly, for 1 to 4, the compounds and processes were taken unmodified from Table 1 in Musvoto *et al.* (1997) and for 5 (propionate) this was taken unmodified from Table 2 in Sötemann *et al.* (2005c) (Table 2.2).

For 6 (sulphate), the dissociation reactions are as follows :

1) $H_2SO_4 \Leftrightarrow HSO_4^- + H^+ \ (pK_{H2SO4\,/\,HSO4} < 0)$ (3.24)

2) $HSO_4^- \Leftrightarrow SO_4^{2-} + H^+ \ (pK_{HSO4\,/\,SO4} \approx 1.99)$ (3.25)

Sulphuric acid acts as a strong acid, and since the pK values for both the equilibria are so low (< 0, 1.99) and the pH range of the systems to be modelled is unlikely to be < ≈ 4, it could be accepted in the kinetic model that the only sulphate system species of any consequence is SO_4^{2-}. However, in the AMD to be treated, the pH values may be very low (pH ≈ 2-5). This will influence the species distribution of the equilibrium Equation (3.24) in the influent, and hence this equilibrium needed to be included in the kinetic model. Thus, the sulphate acid / base system was treated as

a monoprotic acid / base, with the single equilibrium reaction, Equation (3.24). To model this chemical dissociation equilibrium reaction, the approach developed by Musvoto *et al.* (1997) for acid / base equilibria modelling was followed, namely that the kinetics of the forward and reverse dissociation processes are modelled. This required the inclusion of 2 new processes (C48 for forward dissociation, C49 for reverse dissociation), and two new compounds, HSO_4^- (C30) and SO_4^{2-} (C31), see Table 3.12.

Table 3.12 : 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	

From Musvoto *et al.* (1997), K'_{rHSO4} was given a very high value (of the order of 10^7 to 10^{15} with time units dependent on the integration period), the exact value depending on the stability of the solution procedure. The value for K'_{fHSO4} was then determined from the relationship with the equilibrium constant $pK_{HSO4/SO4}$:

$$K'_{fHSO4} = K'_{rHSO4}\ 10^{-pkHSO4\,/\,SO4}\ f_m / f_d \qquad (3.26)$$

where f_m, f_d are mono- and di-valent activity coefficients (Loewenthal *et al.*, 1988).

This ensured that the dissociation reactions are effectively instantaneous and that the concentrations of the species established are the equilibrium concentrations.

For 7 (sulphide), the dissociation reactions are as follows :

1) $H_2S \Leftrightarrow HS^- + H^+ \ (pK_{H2S\,/\,HS} \approx 7.1)$ (3.27)

2) $HS^- \Leftrightarrow S^{2-} + H^+ \ (pK_{HS\,/\,S} \approx 17.4)$ (3.28)

Since the $pK_{HS/S}$ is so high (i.e. S^{2-} acts as a strong base) and the pH range of the systems to be modelled is unlikely to be > ≈ 10, in the kinetic model the sulphide acid / base system could be accepted to act as a monoprotic weak acid / base with equilibrium Equation (3.26) only. To model this equilibrium reaction, again the approach developed by Musvoto *et al.* (1997) for acid / base equilibrium modelling was accepted, namely that the kinetics of the forward and reverse dissociation processes are modelled. This required the inclusion of 2 new processes (C50 for forward dissociation, C51 for reverse dissociation), and two new compounds, H_2S (C32) and HS^- (C33), see Table 3.13.

Table 3.13 : 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	$K'_{fH2S}[H_2S]$
C51	Reverse dissociation H_2S	-1	+1	-1	$K'_{rH2S}[HS^-][H^+]$
		mol/ℓ	mol/ℓ	mol/ℓ	

Similarly to the sulphate system above, in Table 3.13 K'_{rH2S} was given a very high value (of the order of 10^7 to 10^{15} with time units dependent on the integration period), the exact value depending on the stability of the solution procedure. The value for K'_{fH2S} was then determined from the relationship with the equilibrium constant $pK_{H2S/HS}$:

$$K'_{fH2S} = K'_{rH2S}\ 10^{-pkH2S\,/\,H2S} / f_m \qquad (3.29a)$$

For initial simulations pK_{H2S} was accepted to be (Moosbrugger *et al.*, 1992) :

$$pK_{H2S} = 7.00 + 1132.18/T_K - 3.7993 \qquad (3.29b)$$

where

T_K = temperature in Kelvin.

The phosphate weak acid / base system was not included in the stoichiometry for the SRB growth and decay processes (Table 3.9), but it is included in the weak acid / base chemistry model of Musvoto *et al.* (1997). This weak acid / base system also required inclusion in the BSR model, since this system may impact on the pH through buffering type effects depending on its' total species concentration. The kinetics and stoichiometry for this system were taken directly from Musvoto *et al.* For exactness, including the phosphate weak acid / base system would require that the biological processes kinetic model (Table 3.9) be revised to include uptake of phosphorus for growth of SRB, and release in death of these organisms. However, in sulphate reduction systems the biological uptake and release of phosporus is extremely small and accordingly was neglected. This requires further investigation.

In the kinetic model developed for BSR, mineral precipitation reactions (i.e. the third solid phase) have not been included at this stage. Hence, ion paring reactions which directly impact on the precipitation (Musvoto *et al.*, 1997) also have not been included.

3.3.2 Physical Processes

In BSR the compound H_2S is produced and the compound $H_2CO_3^*$ are both produced and consumed. The weak acid/base species NH_3 is present and involved in the biological processes. All these compounds have physical gas exchange processes with the atmosphere in the reactor, and therefore these processes were included :

1. $H_2CO_3^* \Leftrightarrow CO_2(g)$ exchange, where $H_2CO_3^* = CO_2(aq) + H_2CO_3$ (3.30)

2. $NH_3(aq) \Leftrightarrow NH_3(g)$ exchange (3.31)

3. $H_2S(aq) \Leftrightarrow H_2S(g)$ exchange (3.32)

For gas exchange 1. (CO_2), this has been included in the methanogenic UCTADM1 of Sötemann *et al.* (2005c), see Table 2.2 and could be taken unmodified from this model, i.e. physical processes for dissolution (P6) and expulsion (P7), and associated compounds $CO_2(g)$ (P1) and $H_2CO_3^*$ (C3).

For gas exchange 2. (NH_3), in the UCTADM1 model it was accepted that the atmosphere acts as an infinite sink for NH_3, and hence only gas expulsion required inclusion (Table 2.2). This was accepted for the BSR model also, and hence the single expulsion process (P8) was included, with associated compound NH_3(aq) C2 from weak acid / base chemistry, and could be taken unmodified from Sötemann *et al.* (2005c), see Table 2.2.

For gas exchange 3. (H_2S), this is not included in any of the models developed to date and hence required inclusion. Either of the approaches for CO_2 or NH_3 could have been followed. However, it was considered prudent to follow the approach for CO_2 and include both expulsion and dissolution reactions, as the head space in the sulphate reducing bioreactor may develop significant sulphide gas concentrations, i.e. the gas phase cannot be considered as an infinite sink. This required the inclusion of 2 new processes (P12 for H_2S dissolution and P13 for H_2S expulsion), and two new compounds, H_2S(aq) (C32) and H_2S(g) (P5), refer Table 3.14.

Table 3.14 : Petersen Matrix representation of the H_2S exchange physical processes.

	Number→	**C32**	**C33**	
	Compound→	**H_2S**	**H_2S(g)**	
↓No	**↓Process**	**Dslvd**	**Gas**	**↓Process rates**
P12	Dissolution of H_2S gas	+1	-1	$K'_{rH2Sg}(\rho_{H2S})(K_{H2S})$
P13	Expulsion of H_2S gas	-1	+1	$K'_{rH2Sg}[H_2S]$
		mol/ℓ	mol/ℓ	

In Table 3.14, K'_{rH2Sg} equals the K'_{La_H2S} for H_2S, which possibly could be linked to the K_{La_O2} for oxygen, through the proportionality of the diffusivities for O_2 and H_2S (Sötemann *et al.*, 2005 b; Musvoto *et al.*, 1997; Munz and Roberts, 1989). Even though BSR systems are not aerated and significant O_2 is not present or introduced (and hence the actual K_{La_O2} is zero), linking the K_{La_H2S} to K_{La_O2} would be an advantage because this indirectly links the K_{La} values for CO_2 and H_2S via the K_{La_O2} The requirement to link the K_{La} of a gas to that of O_2 as a reference gas is that the dimensionless Henry's law constant of the gas, H_c [=1/(K_HRT)]>0.55 (this excludes ammonia as H_c<0.55, Sötemann *et al.*, 2005 b). For H_2S, Henry's law constant at 298.15 K is $1x10^{-3}$ to $1x10^{-1}$ M/atm. This gives :

$H_c = 1/(K^{\theta}_H RT) = 1/(1x10^{-3} \cdot 8.20575x10^{-2} \cdot 298.15)$ to $1/(1x10^{-1} \cdot 8.20575x10^{-2} \cdot 298.15)$
$= 40.87$ to 0.4087 (3.33)

Thus, a strong possibility exists that the K_{La} for H_2S can be linked in a fixed relationship to the K_{La} for O_2 dependent on the relative magnitudes of the diffusivities of H_2S to O_2. In model application to BSR systems, the K_{La_O2} is calibrated which sets also the values for K_{La_CO2} and K_{La_H2S}, but the system is not aerated with air (aeration process excluded, or switched off). However, in the intended applications of the model in this initial research, only steady state application is considered. Hence, the magnitude of the K_{La} values for CO_2 and H_2S are not of significance provided the values are sufficiently high to ensure steady state between the gaseous and dissolved phases is reached. In future research the option of linking the K_{LA}'s for CO_2 and H_2S via oxygen, will need to be explored in model application to dynamic systems.

3.4 INTEGRATING THE AQUEOUS CHEMISTRY AND PHYSICAL PROCESSES WITH THE BIOLOGICAL PROCESSES

In the descriptions above, (i) a mathematical model has been developed describing the stoichiometry and kinetics of the biological processes directly involved with BSR (Table 3.9); (ii) the compounds associated with the aqueous chemical and the physical processes have been identified; and (iii) the kinetics and stoichiometry for the new aqueous chemistry and physical processes introduced by BSR have been developed. It remains for these various processes to be combined and integrated with the UCTADM1 model (Table 2.2), to give an integrated kinetic model for BSR systems. This integration was done to give two model types :

1. BSR as the "sole" biological processes consuming the short-chain fatty acids (SCFA) and H_2 substrates (i.e. methanogenesis excluded), and

2. both BSR and methanogenesis are present in competition for the SCFA and H_2 substrates.

In both models the chemical and physical processes are common. For the aqueous chemistry, the relevant processes were extracted from the various sources as described above (ammonia, carbonate, phosphate, acetate, water from Table 1 in Musvoto *et al.* (1997); propionate from Table 2 in Sötemann *et al.* (2005c) (Table 2.2 here); sulphate and sulphide from Tables 3.12 and 3.13 respectively here). Similarly for the physical gas exchange processes (carbon dioxide and ammonia from Table 2 in Sötemann *et al.* (2005c) (Table 2.2 here); sulphide from Table 3.14 here). When methanogenesis was included (model Type 2), the approach of Sötemann *et al.* (2005c) to modelling methane was followed, in which methane was considered as very insoluble

and, since it is not utilised in any of the processes, needed only to be included as a gas phase compound (i.e. methane is generated directly as a gas).

For the Type 1 model, since the substrate being considered is PSS, the bioprocesses generating the substrates for BSR need to be included. These were taken from UCTADM1 (acidogens – Processes D1 to D4; acetogens – processes D5 and D6; Tables 1, 3 and 4 and Equations [8] to [11] and [14] in Sötemann *et al.*, 2005c) (Table 2.2 here). These were combined with the SRB bioprocesses developed above and listed in Table 3.9 (propionate consuming SRB, processes S1 and S2; acetotrophic SRB, processes S3 and S4 and hydrogenotrophic SRB, processes S5 and S6). Integrating these bioprocesses with the chemical and physical processes gave a "stand alone" integrated two phase chemical, physical and biological processes model for BSR with PSS as substrate, see Table 3.15.

For the Type 2 model, additionally to the above the acetotrophic (clastic) and hydrogenotrophic methanogen associated processes required inclusion. These were extracted from UCTADM1 (acetotrophic (clastic) methanogens – Processes D7 to D8; hydrogenotrophic methanogens – processes D9 and D10; Tables 1, 3 and 4 and Equations [12] to [13] in Sötemann *et al.*, 2005c) (Table 2.2 here). Integrating these bioprocesses with the Type 1 model above gave a complete two phase chemical, physical and biological processes kinetic model for competitive methanogenic and sulphidogenic anaerobic digestion with PSS as substrate, see Table 3.16.

Table 3.15 : Processes and compounds for biologically mediated processes for inclusion in kinetic model for biological sulphate reduction with PSS (Type 1).

Organism Group	**Compounds**	**Processes**		**Source**
Acidogens	D1 : $C_XH_YO_ZN_A$ (S_{bp})	D1	Hydrolysis	Sötemann *et al.* (2005c), Table 2
	D2 : $C_6H_{12}O_6$ (S_{bsf})			
	C1 : NH_4^+	D2	Acidogenesis (low pH_2)	
	C3 : $H_2CO_3^*$			
	C7 : H^+			
	C13 : HAc			
	D2 : $C_6H_{12}O_6$ (S_{bsf})			
	D3 : H_2			
	D4 : Z_{AD}			

	C1 : NH_4^+	D3	Acidogenesis (high pH_2)	
	C3 : $H_2CO_3^*$			
	C7 : H^+			
	C13 : HAc			
	C28 : HPr			
	D2 : $C_6H_{12}O_6$ (S_{bsf})			
	D3 : H_2			
	D4 : Z_{AD}			
	C2 : NH_3	D4	Acidogen endogenous decay	
	C3 : $H_2CO_3^*$			
	D1 : $C_XH_YO_ZN_A$ (S_{bp})			
	D4 : Z_{AD}			
Acetogens	C1 : NH_4^+	D5	Acetogenesis	Sötemann *et al.* (2005c), Table 2
	C3 : $H_2CO_3^*$			
	C7 : H^+			
	C13 : HAc			
	C28 : HPr			
	D3 : H_2			
	D5 : Z_{AC}			
	C2 : NH_3	D6	Acetogen endogenous decay	
	C3 : $H_2CO_3^*$			
	D1 : $C_XH_YO_ZN_A$ (S_{bp})			
	D4 : Z_{AC}			
Propionate SRB	C1 : NH_4^+	S1	Growth of propionate SRB	
	C3 : $H_2CO_3^*$			
	C7 : H^+			
	C13 : HAc			
	C28 : HPr			
	D3 : H_2			
	C31 : SO_4^{2-}			
	C32 : H_2S			
	S1 : Z_{PS}			

	C2 : NH_3	S2	Propionate SRB endogenous decay	
	C3 : $H_2CO_3^*$			
	D1 : $C_XH_YO_ZN_A$ (S_{bp})			
	S1 : Z_{PS}			
Acetotrophic SRB	C1 : NH_4^+	S3	Growth of acetotrophic SRB	
	C3 : $H_2CO_3^*$			
	C7 : H^+			
	C13 : HAc			
	C32 : H_2S			
	S1 : Z_{AS}			
	C2 : NH_3	S4	Acetotrophic SRB endogenous decay	
	C3 : $H_2CO_3^*$			
	D1 : $C_XH_YO_ZN_A$ (S_{bp})			
	D4 : Z_{AS}			
Hydrogeno-trophic SRB	C1 : NH_4^+	S5	Growth of hydrogenotrophic SRB	
	C3 : $H_2CO_3^*$			
	C7 : H^+			
	D3 : H_2			
	C31 : SO_4^{2-}			
	C32 : H_2S			
	S1 : Z_{HS}			
	C2 : NH_3	S6	Hydrogenotrophic SRB endogenous decay	
	C3 : $H_2CO_3^*$			
	D1 : $C_XH_YO_ZN_A$ (S_{bp})			
	S1 : Z_{HS}			

Table 3.16 : Processes and compounds for biologically mediated processes for inclusion in kinetic model for combined biological sulphate reduction and methanogenesis with PSS (Type 2); in addition to processes in Table 3.15.

Organism Group	Compounds	Processes		Source
Acetoclastic methanogens	C1 : NH_4^+	D7	Acetoclastic methanogenesis	Sötemann *et al.* (2005c), Table 2
	C3 : $H_2CO_3^*$			
	C7 : H^+			
	C13 : HAc			
	P4 : CH_4			
	D6 : Z_{AM}			
	C2 : NH_3	D8	Acetoclastic methanogen endogenous decay	
	C3 : $H_2CO_3^*$			
	D1 : $C_XH_YO_ZN_A$ (S_{bp})			
	D4 : Z_{AM}			
Hydrogeno-trophic methanogens	C1 : NH_4^+	D9	Hydrogenotrophic methanogenesis	Sötemann *et al.* (2005c), Table 2
	C3 : $H_2CO_3^*$			
	C7 : H^+			
	P4 : CH_4			
	D3 : H_2			
	D6 : Z_{HM}			
	C2 : NH_3	D8	Hydrogenotrophic methanogen endogenous decay	
	C3 : $H_2CO_3^*$			
	D1 : $C_XH_YO_ZN_A$ (S_{bp})			
	D4 : Z_{HM}			

All the above compounds and processes regarding BSR were integrated into the UCTADM1 model and encoded in the computer programme AQUASIM, and the complete code is presented in Annexure A.

3.5 CLOSURE

In this Chapter, by extracting, and where necessary modifying, relevant processes and kinetics from the literature, and developing and adding processes where required, two types of integrated kinetic models for the biological, chemical and physical processes active in BSR with PSS as substrate have been developed, namely :

1. BSR as the "sole" biological processes consuming the SCFA and H_2 substrates generated from PSS hydrolysis and acidification, i.e. methanogenesis excluded, and

2. Both BSR and methanogenesis are present in competition for the SCFA and H_2 substrates.

These models now require further calibration, see Chapter 4, and evaluation, see Chapter 5.

Although the BSR models have been developed specifically for situations where PSS serves as the feed substrate, the models have much wider potential application. For particulate substrates (e.g. compost), only the feed substrate composition and kinetic constants for hydrolysis would require modification, for soluble substrates (e.g. acetate) these would be used directly as input to the model since they serve as intermediates in the processes already included. In other words because the model is based on a generic organic compound as substrate for BSR (and / or methanogenesis), the model is not restricted to PSS only. It can be used for any slowly biodegradable organic provided its XYZ and A composition in $C_XH_YO_ZN_A$ is known. However, it does have the limitation that only one influent organic (excluding acetate and propionate) can be modelled.

CHAPTER 4

BSR MODEL CALIBRATION AND VERIFICATION

4.1 INTRODUCTION

In Chapter 3, the two phase (aqueous / gas) biological, chemical and physical processes kinetic model describing methanogenic anaerobic digestion UCTADM1 (Sötemann *et al.*, 2005c) was selected as a basis for development of a kinetic model for BSR with PSS as substrate. To extend UCTADM1 to include BSR, the appropriate biological processes were extracted from the literature, and the necessary chemical and physical processes associated with BSR identified and formulated. Through integrating the relevant processes, two types of BSR kinetic models with PSS were developed, namely :

1. BSR as the "sole" biological processes, i.e. methanogenesis excluded.

2. Both BSR and methanogenesis present in competition for the substrates.

Both model types were implemented in the computer programme AQUASIM (Reichert, 1998). The Type 1 model was applied to simulate hypothetical systems, as this enabled a cross-check to ensure that in the absence of methanogenesis model predictions conformed to expected behaviour, such as relevant substrate consumption with associated sulphate reduction and alkalinity production and biomass growth, etc. With this verified, attention was focused on model Type 2, as this includes the competition between methanogenesis and BSR to be expected in full-scale operating systems, and would provide a much more information-rich model.

Accordingly from the description of the model development in Chapter 3, BSR and associated processes were integrated into the UCTADM1 model (Tables 2.2 and 2.5) by adding he following : (1) the 6 biological processes for BSR (S1 to S6) and their associated compounds (C1/B10, C2, C3, C7, C13, D1, D3, D4, C31, C32 and S1 to S3); Table 3.9; (2) the associated weak acid / base chemistry processes for the dissociation of HSO_4^- and H_2S (C48 to C51) and their associated compounds (C7, C30 to C33); Tables 3.12 and 3.13; (3) the physical gas exchange processes of dissolution / expulsion of H_2S (P12 and P13) and its associated compounds (C32 and C33); Table 3.14. The integration of BSR into the UCTADM1 was as summarised in Tables 3.15 and 3.16 and was implemented in the computer program AQUASIM (Reichert, 1998).

The following were omitted from the model : The five mineral precipitation processes (P1/C19 – Musvoto *et al.*, 1997 and P2/C42 - P5/C45 – Musvoto *et al.*, 2000 a), because mineral precipitation was not included in the two phases BSR AD model. Also omitted were the 22 chemical iron pairing (CIP) processes (C20 - C41) and their associated compounds (C15 - C27), because these processes are important mainly for multiple mineral precipitation modelling, which was beyond the scope of this research study, but will be included in the next phase of the AD and wastewater treatment plant model development by UCT Research Group.

In implementation of the model in AQUASIM, since initial simulations were to be of steady state anaerobic digesters, the gas compounds were accepted to remain part of the bulk liquid, and to leave the digester with the effluent flow. This, was possible because at steady state the gas composition does not change. However, for dynamic simulations, the gas composition may change significantly with time and this may influence the dissolved species bulk liquid concentrations through the gas exchange processes, and hence a separate gas stream may need to be included. This can be readily implemented by following the producers set out in Batstone *et al.* (2002) and Sötemann *et al.* (2005c).

The resultant model was to be calibrated and validated against experimental data in the literature. This Chapter describes the calibration; the validation is described in Chapter 5.

4.2 AVAILABLE KINETICS AND STOICHIOMETRIC CONSTANTS

Calibration of the various constants in UCTADM1 by Sötemann *et al.* (2005c) has been described in Chapter 2. Sötemann *et al.* obtained the UCTADM1 constant values mostly from the literature, which reduced calibration of UCTADM1 to determine (i) the unbiodegradable particulate COD fraction of the 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 $C_XH_YO_ZN_A$.

Sötemann *et al.* determined these three components interactively and iteratively through calculation using measured influent data from experimental systems in the literature and by simulation of the response of these experimental systems.

For the BSR kinetic model, the values for the kinetic, stoichiometric and other constants from UCTADM1 were accepted, except for (i), (ii) and (iii) above, which would require calibration for the particular experimental data to be simulated, see below and Chapter 5. Additionally, values were required for the constants associated with the biological, chemical and physical processes introduced with the BSR.

The kinetic constants required for the chemical and physical processes associated with BSR are the equilibrium constants (pK) of the two new weak acid base systems (sulphate, sulphide), Henry's law constant for H_2S ($K'_{H,H2S}$), and the apparent reverse dissociation and expulsion rate constant (K'_r) respectively for these processes. Following Musvoto *et al.* (1997) and Sötemann *et al.* (2005c), as described in Chapter 3, the apparent reverse dissociation rate constants (K'_r) for the two weak acid / base systems were given very high values, to ensure that the dissociation reactions were effectively instantaneous. The values for the apparent forward dissociation rate constants (K'_f) were then determined from the relationship between the K'_r and the appropriate equilibrium constant (pK) corrected for ionic strength effects, see Equations (3.26) and (3.29) for sulphate and sulphide respectively. The equilibrium constants (pK) and Henry's law constant for H_2S ($K'_{H,H2S}$), and their temperature sensitivity equations were obtained from the literature as discussed in Chapter 3 :

(i) For the pK of HSO_4^-/SO_4^{2-}, this was accepted as constant at 1.99 since, due to its low magnitude, an exact value is not of importance.

(ii) For the pK of H_2S/HS^-, this was accepted as

$$pK_{H2S} = 7.0 + \frac{1132.18}{T_k} - 3.7993 \qquad (4.1)$$

(iii) For the Henry's low constant for H_2S;

$$K_H = 0.011e^{\left(-2300\left(\frac{1}{T_K}-\frac{1}{298.15}\right)\right)} \qquad (4.2)$$

For the BSR biological processes part of the model, values for kinetic and stoichiometric constants (Y, μ_{max}, K_s and b) are required for the three SRB organism groups. As described in Chapter 3, values for these constants were obtained from the literature (Table 3.10).

However, as described in Chapter 3 the values for the concentration related constants in the literature are in COD units, whereas the BSR kinetic model is formulated in mole units. This required conversion of these constants to the appropriate units, see Chapter 3.

Furthermore, where specific weak acid / base species are included in the rate formulation growth of (e.g. propionate degrading SRB, Table 3.9) instead of the total species concentration used in the original literature sources, the rate constants (i.e. Monod half saturation coefficients) had to be appropriately adjusted to take into account weak acid / base speciation. This was done by multiplying the half saturation constants in the rate formulation by the undissociated to total species concentration ratio, see Chapter 3. The appropriately converted and adjusted values for the biological processes constants are listed in Table 3.11.

For application of the BSR kinetic model to experimental data, this left two main parts of the model to be calibrated :

(i) the kinetic constants for the hydrolysis process, i.e. maximum specific hydrolysis rate ($k_{max,HYD}$) and half saturation coefficient ($K_{S,HYD}$) in the surface saturation (Contois) kinetic formulation in UCTADM1, and

(ii) the sewage sludge stoichiometric composition, i.e. X, Y, Z and A in $C_XH_YO_ZN_A$.

Additionally, in model application the sewage sludge constituent fractions and the input concentrates of the various compounds would need to be quantified. Values for these parameters were obtained from the experimental data set of Ristow *et al.* (2005), as described below.

4.3 EXPERIMENTAL SULPHIDOGENIC DIGESTERS (RISTOW *ET AL.*, 2005)

The experimental data set of Ristow *et al.* (2005) was used to calibrate (and validate, see Chapter 5) the BSR kinetic model.

Ristow *et al.* (2005) studied the rate of hydrolysis of primary sewage sludge under methanogenic, acidogenic and sulphate reducing conditions and the influence of system physical constraints on the hydrolysis rate. The aims of their research were to (i) determine the rate of hydrolysis of primary sludge under methanogenic conditions, (ii) determine the effects of feed COD concentration, hydraulic retention time and pH on the rate of hydrolysis under methanogenic conditions, (iii) develop a mathematical model for the biological processes mediating the hydrolysis of primary sludge in methanogenic systems, so that the hydrolysis rate can be predicted for various

feed COD concentrations, hydraulic retention times and operating pH, based only on the feed characterisation and system operation, (iv) evaluate the various rate formulations for the primary sludge hydrolysis, also at varying operating conditions, to identify the most appropriate rate formulation for hydrolysis of primary sludge under methanogenic conditions, (v) determine the rate of primary sludge hydrolysis under acidogenic conditions (i.e. to repeat (i) to (iii) above for acidogenic conditions), (vi) appropriately modify the mathematical model selected in (iv) above to predict the rate of hydrolysis under acidogenic conditions, (vii) determine the rate of primary sludge hydrolysis under sulphate reducing conditions, and (viii) determine the effect of sulphate reduction on the rate of hydrolysis of primary sludge.

The research approach adopted by Ristow *et al.* (2005) was to operate parallel laboratory scale, completely mixed anaerobic digesters with primary sewage sludge as influent, and to monitor the behaviour of these systems under a range of feed COD concentrations, retention times, pH and feed sulfate conditions under stable methanogenic, acidogenic and sulfate reducing conditions.

To calibrate the model developed in Chapter 3, the experimental data from the laboratory scale completely mixed sulphidogenic anaerobic digesters operated by Ristow *et al.* (2005) were analysed.

4.3.1 Reactor Set-up and Operation

During their research, Ristow *et al.* (2005) operated 6 parallel laboratory scale completely mixed anaerobic digesters at a controlled temperature of 35°C. The digesters were operated under 21 steady state conditions, at various feed concentrations and hydraulic retention times, under methanogenic and sulphidogenic conditions. Eight steady state digesters were fed sulphate at hydraulic retention times between 8 and 16 days. The sulphidogenic digesters were fed primary sewage sludge at influent concentrations from 0.989 gCOD/ℓ to 25.953 gCOD/ℓ. The feed primary sewage sludge originated from the primary settling tanks at the Athlone Wastewater Treatment Works (City of Cape Town, South Africa), which treats municipal wastewater of mainly domestic origin, but with a significant mixed industrial component. The primary sludge was collected in batches using a number of 25 ℓ plastic drums, and each batch of feed was given a feed batch number (for details see Ristow *et al.*, 2005). The feed batches were stored at 4°C and served as feed source for up to 7 months. Table 4.1 gives a summary of the operating conditions for the 8 digesters which were fed sulphate, operated by Ristow *et al.* (2005), where FB is the number of the feed batch fed to the digesters.

Table 4.1 : Laboratory scale, completely mixed anaerobic digesters, with Sulphate addition, operated by Ristow *et al.* (2005). Values in brackets refer to steady state period index in Ristow *et al.* (2005).

Feed COD Concentration g/COD/ℓ	Hydraulic Retention Time (days)			
	16	13.3	10	8
25.95			FB12 (6)	
13.27				FB13 (15)
1.950				FB14 (20,22)
1.950				FB15 (36)
2.013		FB15 (42)		
2.015	FB15 (41)			
0.989			FB15 (46)	

4.3.2 Experimental Data

For the experimental systems, Ristow *et al.* (2005) measured the total COD (S_{ti}), soluble (0.45 µm filtered) COD (S_{si}), free and saline ammonia and FSA (N_{ai}) on the undiluted primary sludge. Taking account of the dilution with tap water of the PSS to the required reactor feed concentrations, the corresponding diluted concentration could be determined, see Table 4.2. Influent sulphate concentrations were available from the known sulphate addition, see Table 4.2. To monitor the response of the systems, Ristow *et al.* measured effluent total COD, total soluble COD, VFA, $H_2CO_3^*$ alkalinity, free and saline ammonia (FSA) and sulphate concentrations; reactor pH; and gas and methane production (for those sulphidogenic systems where these were significant), see Table 4.3.

Additionally, Ristow *et al.* measured influent $H_2CO_3^*$ alkalinity and pH on the undiluted feedbatches FB9 to FB13. Since Ristow *et al.* (2005) did not measure the influent alkalinity and pH on the diluted feed, Sötemann *et al.* (2005d) calculated the alkalinity and pH values of the diluted feeds by entering the measured undiluted PSS concentrations and the corresponding dilution with tap water into the computer program STASOFT version 2.41 (Loewenthal *et al.*, 1988) to obtain an estimate for the primary sludge / tap water blend (i.e. reactor feed) alkalinity and pH, see Table 4.4. For feed batches FB14 and FB15, no measured alkalinity and pH values were available from Ristow *et al.* Accordingly, Sötemann *et al.* used the average $H_2CO_3^*$ alkalinity and pH values from FB9 to

FB13 and FB15, see Table 4.4. The Sötemann *et al.* determined feed alkalinity and pH values were accepted.

4.3.3 Feed Characterisation

For calibration of the hydrolysis rate constants in the BSR kinetic model with the experimental data of Ristow *et al.* (see below) the influent PSS that served as feed to the experimental digesters needed to be characterised into the COD fractions described in Figure 2.5, i.e.

$$S_{ti} = S_{bpi} + S_{bsfi} + S_{bsai} + S_{usi} + S_{upi} \quad \text{(mg COD/ℓ)} \quad (4.3)$$

where

S_{ti} = Total feed COD.

S_{bsfi} = Biodegradable soluble fermentable COD in feed.

S_{bpi} = Biodegradable particulate COD in the feed.

S_{bsai} = Influent VFA.

S_{upi} = Uniodegradable particulate COD om the feed.

S_{usi} = Uniodegradable soluble COD in the feed.

For the experimental data set of Ristow *et al.*, S_{ti} and total soluble COD ($S_{si} = S_{bsai} + S_{bfi} + S_{ufi}$) were available from measurement (Table 4.2). From the experimental measurements of Lilley *et al.* (1990) and Ristow *et al.*, S_{bsfi} could be accepted as equal to S_{bsai}, and it could be accepted that S_{usi} is small compared with S_{bsai} and S_{bsfi}. Accordingly, $S_{bsai} = S_{bsfi}$ = 0.45 µm filtered, COD devided by 2 and hence S_{bsai} and S_{bsfi} could be quantified. Furthermore, for the PSS used in their experiments Ristow *et al.* determined S_{upi} and S_{usi} as 0.3345 and 0.008 respectively. The S_{upi} value was determined from a 60d methanogenic anaerobic digester, in which it was accepted that the residual biodegradable COD would be negligible, while the S_{usi} value was determined from the average of the measured soluble effluent CODs of all the experimental systems operated (effluent VFAs were very low). These values for S_{upi} and S_{usi} were accepted here also. This characterised the influent PSS COD sufficiently for determination of the hydrolysis rate constants (see below). For model application to the system of Ristow *et al.*, additionally the PSS stoichiometric composition was required; determining this will be described in the relevant sections below.

4.4 DETERMINING HYDROLYSIS RATE CONSTANTS

For determining the hydrolysis rate constants, the analytic procedure of Sötemann *et al.* (2005c) was accepted and applied to the experimental data from Ristow *et al.* (2005) described above.

For the effluent COD concentration from a flow-through anaerobic digester, under stable operating conditions Sötemann *et al.* noted that :

$$S_{te} = S_{bpe} + S_{bsfe} + S_{bsae} + S_{use} + S_{upe} + \text{biomass} \qquad (4.4)$$

where

subscript e denotes effluent; definitions as in Equation (4.3).

In stable methanogenic anaerobic digesters, Sötemann *et al.* identified three main groups of organisms making up the biomass, acidogens (Z_{AD}), acetoclastic (Z_{AM}) and hydrogenotrophic (Z_{HM}) methanogens, but accepted that the mass of Z_{HM} is very much smaller than that of Z_{AD} and Z_{AM}. Accordingly, they substituted $Z_{AD} + Z_{AM}$ into Equation (4.4). From mass balances around the anaerobic digesters and recognising that death of biomass releases organics which add to S_{bp}, Sötemann *et al.* developed equations for the volumetric rates of hydrolysis (r^*_{HYD}) acidogenesis (r^*_{AD}) and acetoclastic methanogenesis (r^*_{AM}), and for the concentrations of Z_{AD} and Z_{AM} (see Sötemann *et al.*, 2005c).

Following the procedures set out by Sötemann *et al.*, but recognising that in substrate limited sulphidogenic reactors, methanogenesis is negligible (i.e. Z_{AM} can be accepted to be zero) and replaced by sulphidogenic processes, from mass balances similar equations can be developed for sulphidogenic digesters. In this development, it was recognised that with PSS as substrate, the dominant sulphidognic reaction would be acetotrophic sulphidogenesis, generating acetotrophic sulphidogens (Z_{AS}). Accordingly :

Effluent COD

$$S_{te} = S_{bpe} + S_{bsfe} + S_{bsae} + S_{use} + S_{upe} + Z_{AD} + Z_{AS} \qquad (\text{mg COD}/\ell) \qquad (4.5)$$

Noting that the biodegradable organics (assumed to be 100 % of the biomass) of the acidogens and acetogenotrophic sulphidogens are hydrolysable substrate, the volumetric hydrolysis rate (r^*_{HYD}) is :

$$r^*_{HYD} = \frac{1}{R_h}(S_{bpi} - S_{bpe}) + b_{AD}Z_{AD} + b_{AS}Z_{AS} \quad \text{(mg COD/ℓ/d)} \quad (4.6)$$

R_h = V_d/Q_i = hydraulic retention time (d)
V_d = volume of digesters (ℓ)
Q_i = influent flow rate (ℓ / d)
b_{AD} = Specific mass loss rate for acidogens (/d)
b_{AS} = Specific mass loss rate for acetotrophic sulphidogens (/d)

Volumetric acidogenic rate (r^*_{AD})

$$r^*_{AD} = \frac{1}{R_h}(S_{bsfi} - S_{bsfe}) + r^*_{HYD} \quad \text{(mg COD / ℓ / d)} \quad (4.7)$$

Volumetric sulphidogenic rate (r^*_{AS})

$$r^*_{AS} = \frac{1}{R_h}(S_{bsai} - S_{bsae}) + f_{Sbsa\,/\,Sbsf}\, r^*_{HYD} \quad \text{(mg COD / ℓ / d)} \quad (4.8)$$

where

$f_{sbsa\,/\,sbsf}$ = fraction of S_{bsf} appearing as S_{bsa} in acidogenesis.

= 0.607 (mg COD / mg COD), Sötemann *et al.* (2005c).

Acidogen biomass (Z_{AD}) :

$$Z_{AD} = \frac{r^*_{AD} Y^*_{AD} R_h}{(1 + b_{AD} R_h)} \quad \text{(mg COD/ℓ)} \quad (4.9)$$

where

Y^*_{AD} = acidogen yield in COD units (mg COD / mg COD).

Noting that the biodegradable organics (assumed to be 100 % of the biomass) of the acidogens and acetogenotrophic sulphidogens are hydrolysable substrate, the volumetric hydrolysis rate (r^*_{HYD}) is :

$$r^*_{HYD} = \frac{1}{R_h}(S_{bpi} - S_{bpe}) + b_{AD}Z_{AD} + b_{AS}Z_{AS} \quad \text{(mg COD/ℓ/d)} \quad (4.6)$$

R_h = V_d/Q_i = hydraulic retention time (d)
V_d = volume of digesters (ℓ)
Q_i = influent flow rate (ℓ / d)
b_{AD} = Specific mass loss rate for acidogens (/d)
b_{AS} = Specific mass loss rate for acetotrophic sulphidogens (/d)

Volumetric acidogenic rate (r^*_{AD})

$$r^*_{AD} = \frac{1}{R_h}(S_{bsfi} - S_{bsfe}) + r^*_{HYD} \quad \text{(mg COD / ℓ / d)} \quad (4.7)$$

Volumetric sulphidogenic rate (r^*_{AS})

$$r^*_{AS} = \frac{1}{R_h}(S_{bsai} - S_{bsae}) + f_{Sbsa\,/\,Sbsf}\, r^*_{HYD} \quad \text{(mg COD / ℓ / d)} \quad (4.8)$$

where

$f_{sbsa\,/\,sbsf}$ = fraction of S_{bsf} appearing as S_{bsa} in acidogenesis.

= 0.607 (mg COD / mg COD), Sötemann *et al.* (2005c).

Acidogen biomass (Z_{AD}) :

$$Z_{AD} = \frac{r^*_{AD} Y^*_{AD} R_h}{(1 + b_{AD} R_h)} \quad \text{(mg COD/ℓ)} \quad (4.9)$$

where

Y^*_{AD} = acidogen yield in COD units (mg COD / mg COD).

Acetotrophic sulphidogen biomass (Z_{AS}) :

$$Z_{AS} = \frac{r^*_{AS} \cdot Y^*_{AS} \cdot R_h}{(1 + b_{AS} R_h)} \qquad (4.10)$$

where

Y^*_{AS} = acetotrophic sulphidogen yield in COD units (mg COD / mg COD).

In the equation set above, a number of parameters need to be quantified before the equations can be solved. In the Ristow *et al.* systems, for the effluent, total COD (organics and sulphide), total soluble COD (organic and sulphide) and soluble organic COD were available from measurements (Table 4.3). Hence, effluent total organic COD could be calculated as effluent total COD – total soluble COD + soluble organic COD (i.e. by subtracting the sulphide contribution to the total COD), to give S_{te} in Equation (4.4). The effluent VFA (S_{bsae} in Equation (4.5)) were available from direct measurement for the Ristow *et al.* data (Table 4.3), and following Sötemann *et al.* it could be accepted that $S_{bsfe} = S_{bsae}$ (values low and do not influence analysis significantly). Further, in Equation (4.4) $S_{use} = S_{usi}$ and $S_{upe} = S_{upi}$, with both S_{usi} and S_{upi} known for the Ristow *et al.* PSS (see above). Thus, in the equation set this left S_{bpe}, Z_{AD} and Z_{AS} as the principle unknowns. Accordingly S_{bpe}, Z_{AD} and Z_{AS} could be calculated through iteration, as well as the volumetric hydrolysis rate (r^*_{HYD}), all in COD units.

For the surface saturation (Contois) kinetics for hydrolysis in the BSR kinetic model, equating r^*_{HYD} with the appropriate kinetic rate expression yields :

$$r^*_{HYD} = \left[\frac{k^*_{max,HYD} \frac{S_{bp}}{Z_{AD}}}{K^*_{SS,HYD} + \frac{S_{bp}}{Z_{AD}}} \right] Z_{AD} \qquad \text{(in COD units)} \qquad (4.11)$$

where * denotes COD units.

In Equation (4.11) above, the values for the two constants needed to be determined, namely $k^*_{max,HYD}$ and $K^*_{SS,HYD}$ respectively. To determine these two constants, following Sötemann *et al.* (2005c) the equations were linearised by three different methods, i.e. (i) Lineweaver-Burke, (ii) Inversion and (iii) Eadie-Hofstee, to give respectively :

i. $$\frac{Z_{AD}}{r^{*}_{HYD}} = \frac{K^{*}_{SS,HYD}}{k^{*}_{max,HYD}} \cdot \frac{Z_{AD}}{S_{bpe}} + \frac{1}{k^{*}_{max,HYD}} \quad (4.12)$$

ii. $$\frac{S_{bpe}}{r^{*}_{HYD}} = \frac{K^{*}_{SS,HYD}}{k^{*}_{max,HYD}} + \frac{S_{bpe}}{Z} \cdot \frac{1}{k^{*}_{max,HYD}} \quad (4.13)$$

iii. $$\frac{r^{*}_{HYD}}{Z_{AD}} = -K^{*}_{SS,HYD} \cdot \frac{r^{*}_{HYD}}{S_{bpe}} + k^{*}_{max,HYD} \quad (4.14)$$

For the three linearization methods, linear regression was fitted to the Ristow *et al.* (2005) experimental data see Figures 4.1 a, b and c respectively for the surface mediated reaction kinetics. From the slopes and y-intercepts of the fitted lines, the appropriate pair of kinetic constants was determined. The hydrolysis rate constants so determined from the Lineweaver-Burke, Inversion and Eadie-Hofstee methods were $k_{max,HYD}$ and $K_{SS,HYD}$ of 1.62 $S_{bp}/(Z_{AD}.d)$ and 0.048 S_{bp}/Z_{ac}, 1.54 $S_{bp}/(Z_{AD}.d)$ and 0.013 S_{bp}/Z_{ac}, 1.59 S_{bp} $(Z_{AD}.d)$ and 0.036 S_{bp}/Z_{AD} respectively, with average 1.58 and 0.032 respectively, all in COD units. To evaluate these constants, the specific hydrolysis rate was plotted against the S_{bpe}/Z_{AD} ratio, for both the experimental data and the theoretical lines with the derived constants, see Figure 4.2.

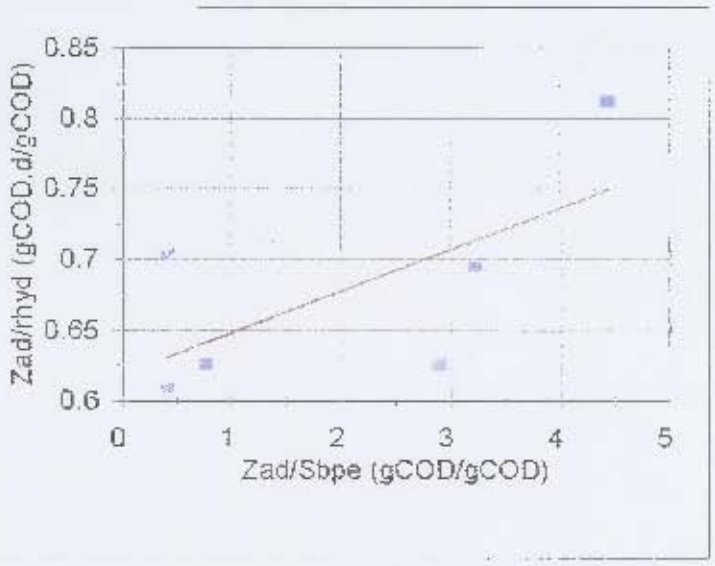


Figure 4.1 a : Linearisation by Lineweaver-Burke of surface mediated reaction kinetics for hydrolysis of sewage sludge for the data of Ristow *et al.* (2005) for retention times 8, 10, 13.3 and 16 d, with linear regression fit of straight line to data.

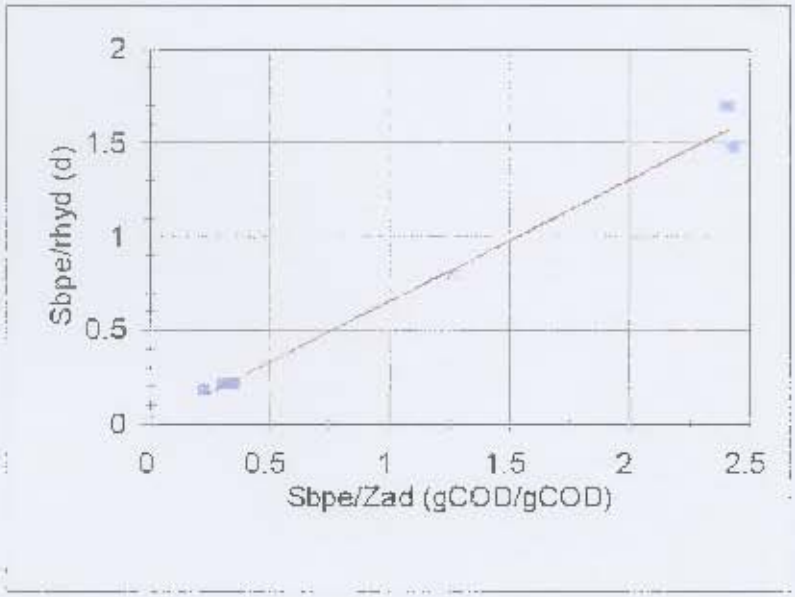


Figure 4.1 b : Linerasation by inversion of surface mediated reaction kinetics for hydrolysis of sewage sludge for the data of Ristow *et al.* (2005) for retention times 8, 10, 13.3 and 16 d, with linear regression fit of straight line to data.

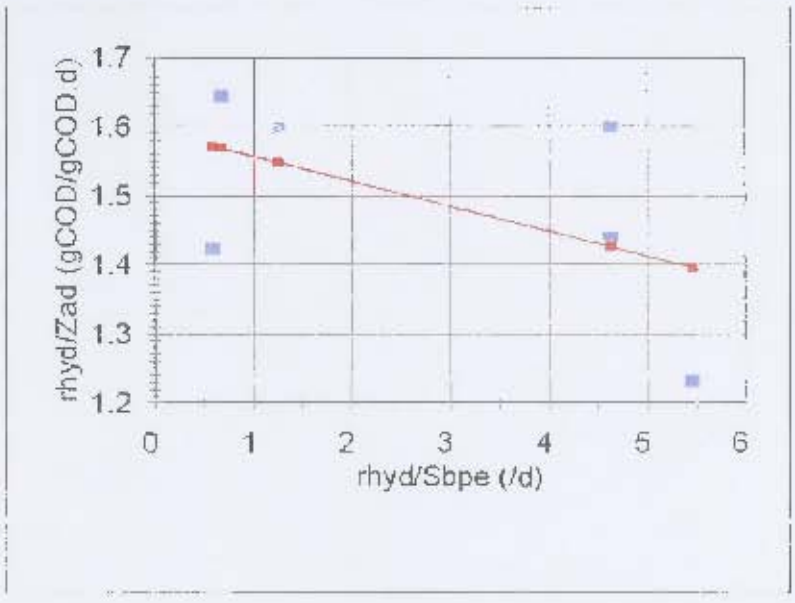


Figure 4.1 c : Linearisation by Eadie-Hofstee of surface mediated reactions kinetics for hydrolysis of sewage sludge for the data of Ristow *et al.* (2005) for retention times 8, 10, 13.3 and 16d. with linear regression fit of straight line to data.

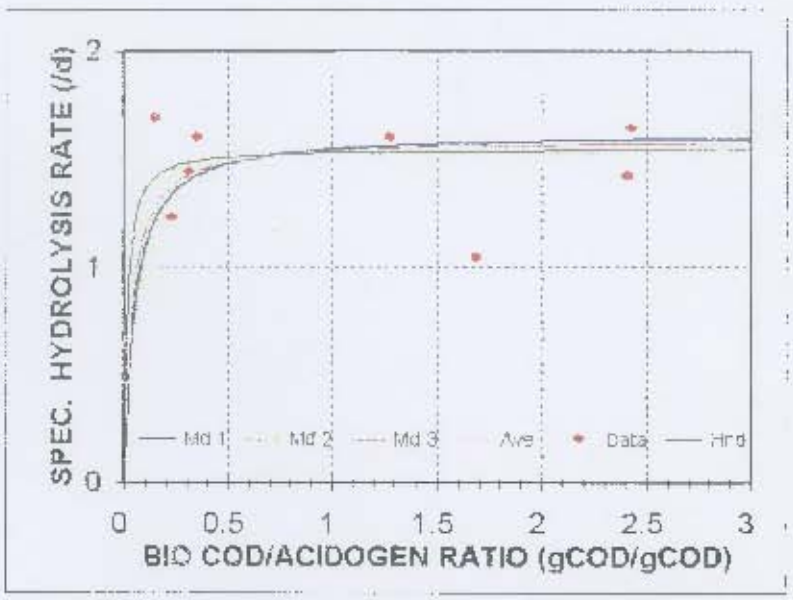


Figure 4.2 : Specific hydrolysis rate vs. the biodegradable COD / acidogen ratio for the anaerobic digesters fed sulphate of Ristow *et al.* (2005), for surface mediated reaction kinetics. The data (each laboratory scale system) is represented by a solid dot (•); lines represent Md1 Lineweaver Burke, Md2 Inversion, Md3 Eadie-Hofstee linearization and Ave the average of these; Hnd is the fit by "eye".

From the values for the linear regression fits to the data linearized with the three methods (R^2 = 0.437, 0.988 and 0.275 respectively) and the comparison of the experimental data with the theoretical lines in Figure 4.2, it is evident that there is considerable scatter in the experimental data. Furthermore, from Figure 4.2 the specific hydrolysis rate remained high at low residual S_{bpe} to Z_{AD} ratios. This makes definitive selection of particularly the $K_{SS,HYD}$ value difficult. Accordingly, a further set of hydrolysis rate constants were obtained by fitting a line through the data by "eye". This resulted in the hydrolysis rate constants of $k_{max,HYD}$ = 1.55 $S_{bp}/(Z_{AD}.d)$ and $K_{SS,HYD}$ = 0.0132 S_{bp}/Z_{AD} in COD units, which were accepted for simulation purposes.

As input to the BSR kinetic model, the hydrolysis rate constants are required in mol units. To convert the COD values to mol units

$$r_{HYD} = r'_{HYD} / \left(\frac{COD}{mol} \right)_{S_{bp}} \qquad (mol\ S_{bp}/\ell.d) \qquad (4.15)$$

$$[S_{bpe}] = S_{bpe} / \left(\frac{COD}{mol} \right)_{S_{bp}} \qquad (mol\ S_{bp}/\ell) \qquad (4.16)$$

$$[Z] = Z/\left(\frac{COD}{mol}\right)_Z \qquad \text{(mol Z/ℓ)} \qquad (4.17)$$

where :

$$\left(\frac{COD}{mol}\right)_{S_{bp}} = \text{COD/mol ratio for } S_{bp} = 131.3 \text{ gCOD/mol for } C_{3.5}H_7O_2N_{0.196} = 8(Y + 2(2X - 2) - 3A) \text{ for } C_XH_YO_ZN_A \qquad (4.18)$$

$$\left(\frac{COD}{mol}\right)_Z = \text{COD/mol ratio for biomass} = 160 \text{ gCOD/mol for } C_5H_7O_2N$$

$[\ ]$ = mole concentration

Accepting the average stoichiometry for the Athlone PSS used in the Ristow *et al.* (2005) experiments (see below) of X = 4.1725, Y = 7, Z = 2.6275 and A = 0.2175 in Equation (4.18) and applying Equation (4.15) to (4.17) gave "eye" fit $k_{max,HYD}$ and $K_{SS,HYD}$ values of 1.743 $S_{bp}/(Z_{AD}.d)$ and 0.0148 S_{bp}/Z_{AD} respectively, in mole units. These values were accepted for subsequent simulations of the Ristow *et al.* (2005) systems (see Chapter 5).

Table 4.2 : Feed data for the methanogenic laboratory scale, completely mixed anaerobic digesters, fed sulphate, operated by Ristow *et al.* (2005).

Stready* State no.	Retention Time (days)	React Volume (ℓ)	Feed Batch (No.)	S_{ti} (mgCOD/ℓ)	S_{si} (mgCOD/ℓ)	S_{bsai} (= S_{bsfi}) (mgCOD/ℓ as HAc)	N_{ai} (mgCOD/ℓ)	Sulphate ($mgSO_4$/ℓ)
41	16	20	15	2 015	207	110.30	6	2 000
42	13.3	20	15	2 013	221	117.75	10	2 000
6	10	16	12	25 953	2 647	1 410.42	39	1 000
46	10	20	15	989	102	54.35	7	1 000
15	8	16	13	13 270	1 503	800.85	72	9 600
20	8	16	14	1 950	293	155.59	8	2 000
22	8	16	14	1 950	298	158.78	10	2 000
36	8	16	15	1 950	278	148.13	13	2 000

* Refers to Ristow *et al.* (2005).

Table 4.3 : Effluent data for the methanogenic laboratory scale completely mixed anaerobic digesters, fed sulphate, operated by Ristow *et al.* (2005).

Steady State No. ***	Retention Time (days)	Effluent total COD (mgCOD /ℓ)	Effluent total Soluble COD (mg COD/ℓ)	Effluent Soluble Organic COD (mg COD/ℓ	Effluent Total Organic COD (mg COD/ ℓ	Effluent VFA (mgCOD/ℓ as HAc)	Effluent Alk (mg/ℓ as $CaCO_3$)	pH	Effluent Sulphate (mg SO_4/ℓ)	Methane production (ℓ/day)	Effluent FSA (mgN/ℓ)
41	16	1 697	897	85	885	0	1 633	7.64	No Data	-	11
42	13.3	1 749	964	129	914	57	1 573	7.75	147	-	19
6	10	10 684	157	157	10684	37	2 534	7.06	34	8,88	207
46	10	897	466	42	473	3	1 025	7.92	51	-	-
15	8	13 001	197	197	6362**	6	2 894	6.87	733	0,02	69
20	8	1 532	790	61	803	0	1 386	7.52	530	0	18
22	8	1 406	655	155	906	63	782	6.99	770*	-	11
36	8	1 304	521	80	863	0	354	6.47	436	-	16

* Storage of sample questioned – may have increased.

** Correct for FeS (Ristow *et al.*, 2005)

*** Refers to Ristow *et al.* (2005)

\- Not measured.

Table 4.4 : Sludge stoichiometric formula, alkalinity and pH data for feed batches 12 to 15 from Ristow *et al.* (2005), Table 4.8 in Sötemann *et al.* (2005d).

Feed Batch (No)	Sludge Stoichiometric Formula	Alkalinity (mg/ℓ as CaCO3)	pH
12	$C_{4.15}H_7O_{2.42}N_{0.22}$	47.3	4.91
13	$C_{4.17}H_7O_{2.63}N_{0.22}$	151.6	5.73
14	$C_{4.31}H_7O_{3.03}N_{0.24}$	90.28 *	5.38 *
15	$C_{4.06}H_7O_{2.43}N_{0.19}$	90.28 *	5.38 *

* Calculated averages from feed batches 9 to 13.

4.5 PRIMARY SEWAGE SLUDGE STOICHIOMETRIC COMPOSITION

In UCTADM1, and carried through to the BSR kinetic model, the units are in terms of moles to enable biological CO_2 production to be simulated and to be linked to the weak acid / base chemistry and physical processes. This requires that the CHON stoichiometric composition of S_{bpi} be known. In the implementation of the models, the stoichiometric composition was retained as a variable, and hence X, Y, Z and A in $C_XH_YO_ZN_A$ need to be quantified as input, for model simulations. For the PSS from the Athlone Treatment Works that served as influent feed to the Ristow *et al.* digesters, Sötemann *et al.* (2005c) measured TSS, VSS, COD, TKN, TP, soluble COD, FSA and ortho P. Additionally samples were analyzed for % composition as % C, % H and % N. From the TSS and particulate COD (total minus soluble) measurements and the % composition, Sötemann *et al.* (2005d) derived the PSS stoichiometric compositions for the feed batches that served as influent feed to the Ristow *et al.* sulphidogenic digesters, see Tables 4.1 and 4.4. These feed batch PSS stoichiometric compositions served as input for simulations of the corresponding system responses, see Chapter 5. Averaging the feed batch compositions gave $C_{4.1725}H_7O_{2.6275}N_{0.2175}$. This generic composition was used to convert the hydrolysis rate constants from the COD units in the calculations above to mole units required as input to the kinetic model.

4.6 MODEL VERIFICATION

Once calibrated the model was verified for consistency by checking the COD, N and S mass balances. It was found that the COD, N and S exiting a flow through AD reactor were within 0.1 % of the COD, N and S entering the reactor. This fixes quantitatively, via the interrelated chemical, physical and biological process, the relationship between all the compounds of the system so that for a given biodegradation the effluent results are completely goverened by the input sludge characteristics and sulphate feed.

4.7 CLOSURE

In this Chapter, the various kinetic and stoichiometric constants required as input to the BSR kinetic model have been quantified, thereby to calibrate the BSR kinetic model. Values for these constants were obtained from the literature, except for :

(i) The hydrolysis process kinetic constants, $k_{max,HYD}$ and $K_{ss,\ HYD}$, and

(ii) the sewage sludge stoichiometric composition, i.e. X, Y, Z and A in $C_XH_YO_ZN_A$.

To determine the hydrolysis process kinetic constants, the COD based analytical procedure of Sötemann *et al.* (2005c) developed for methanogenic digesters was adapted for sulphidogenic systems. This modified procedure was applied to the experimental data from the sulphidogenic systems of Ristow *et al.* (2005), thereby to derive estimates for the hydrolysis process kinetic constants. Values from the three linearization techniques used in the analysis gave $k_{max,HYD}$ = 1.62, 1.54 and 1.59 gCOD S_{bp}/gCODZ_{AD}.d and $K_{SS,HYD}$ = 0.048; 0.013 and 0.036 gCOD S_{bp}/gCOD Z_{AD}, with average values 1.58 and 0.032 respectively.

Although the $k_{max,HYD}$ values are reasonably consistent, the $K_{SS,HYD}$ values vary considerably, indicating difficulty in determining this constant with confidence. However, the low values for $K_{SS,HYD}$ indicate that the exact value probably will not have a significant influence in simulations.

A fit by "eye" to the experimental data gave values of 1.55 and 0.0132 respectively. Compared with the values for $k_{max,HYD}$ = 1.63 to 2.43 $K_{SS,HYD}$ = 0.055 to 0.736 obtained by Sötemann *et al.* (2005c), using the same analytical procedure, for the methanogenic anaerobic digesters also operated by Ristow *et al.* the values for $k_{max,HYD}$ and $K_{SS,HYD}$ obtained here for the equivalent sulphidogenic digesters are reasonably similar. This would indicate that sulphate reduction *per se* does not influence the PSS hydrolysis rate significantly, in agreement with the conclusion of Ristow *et al.* (2005). However, the scatter in the experimental data with surface saturation kinetics applied precludes a definitive judgement on this aspect.

Since the BSR kinetic model is formulated in mole units, the derived values for $k_{max,HYD}$ and $K_{SS,HYD}$ required conversion from the COD units to mole units. This necessitated that the stoichiometric composition of the PSS that served as feed to the Ristow *et al.* digesters be known. Furthermore, the PSS stoichoimetric composition also is included as a variable in the BSR kinetic model, and is required as input to the model.

For the PSS stoichiometric composition, from the sets of analytical measurements made on each batch of the Athlone Wastewater Treatment Works PSS that served as feed to the Ristow *et al.* digesters, Sötemann *et al.* (2005d) delineated the respective feed batch PSS stoichiometric compositions. The average composition of the four feed batches was $C_{4.1725}H_7O_{2.6275}N_{0.2175}$. This differs somewhat from the composition of $C_{3.5}H_7O_2N_{0.196}$ determined by Sötemann *et al.* (2005c) for the feed to the digesters operated by Izzett *et al.* (1992), which may be ascribed to difference in feed type – Izzett *et al.* used a mixture of PSS and humus sludge whereas Ristow *et al.* (2005) used pure PSS.

With the average PSS stoichiometric composition, the hydrolysis rate constants were converted from the COD units to mole units, to give $k_{max,HYD}$ = 1.82; 1.74 and 1.79 mol S_{bp}/mol Z_{AD}.d and $K_{SS,HYD}$ = 0.054; 0.015 and 0.04 mol S_{bp}/mol Z_{AD} respectively, with averages 1.782 and 0.0365 respectively. Converting these "eye" fit constants gave values of 1.743 and 0.0148 respectively, which were used for subsequent simulations.

In calibration of the BSR kinetic model, the hydrolysis rate constants and the PSS stoichiometric composition were obtained from analysis of experimental data measured by Ristow *et al.* on sulphidogenic reactors fed PSS from the Athlone Wastewater Treatment Works. It is not certain whether the values thus derived for these constants are specific to this particular PSS, or are generic to PSS in general. To clarify this requires a more detailed investigation.

Having completed calibration of the BSR kinetic model, the model required evalution and validation. This was done by simulation of the Ristow *et al.* (2005) sulphidogenic digesters, and comparison of predicted with measured data, see Chapter 5.

CHAPTER 5

BSR KINETIC MODEL APPLICATION AND VALIDATION

5.1 INTRODUCTION

In Chapter 4, the BSR kinetic model has been calibrated, primarily through obtaining values for the relevant stoichiometric and kinetic constants from the literature, but also from analyses of experimental data on (i) direct measurements (COD, TKN, VSS, TSS) on PSS (the PSS stoichiometric composition), and (ii) the influent and effluent COD components (the hydrolysis rate constants) from the Ristow *et al.* (2005) sulphidogenic digesters. The calibrated model now requires validation. In this Chapter, the model will be validated by application to simulate the response to the Ristow *et al.* (2005) sulphidogenic systems, and comparison of predictions with measured data.

5.2 SIMULATION REQUIREMENTS

Simulation of the response of the Ristow *et al.* (2005) experimental sulphidogenic systems requires the model constants, influent characteristics and system constraints to be defined.

5.2.1 Model Constants

Values for the model constants determined in Chapter 4 were accepted for simulation purposes, including the determined values for the hydrolysis rate constants and the influent PSS stoichiometric composition.

5.2.2 System Constraints

The sulphidogenic anaerobic digesters to be simulated are those operated by Ristow *et al.*, as detailed in Section 4.3, and listed in Table 4.2, steady states 6, 15, 22, 20, 36, 41, 42 and 46. Systems constraints required as input includes : (i) influent flow rate, reactor volume, and hence retention time which were all defined for each steady state (see Table 4.2); (ii) mixing regime which was completely mixed flow-through; and (iii) temperature which was controlled at 35°C.

During their experimental investigation, Ristow *et al.* controlled the reactor pH between 6.8 and 7.5 for steady state numbers 15, 20, 22, and 36; tests all operated at a retention time of 8 days. The kinetic model uses the steady state H^+ concentration to calculate the pH. Thus, during simulations

of these steady states the pH was controlled by keeping the H^+ concentration in the model constant, thus also keeping the pH constant at the specific controlled value. In practise, this was achieved by dosing a negligible flow of H^+ to the reactor at the concentration that gave the predicted pH equal to the controlled pH values. For steady state numbers 6, 41, 42 and 46, the pH was not controlled and established "naturally" both in operation and simulation.

In presenting the simulation results, the pH controlled and non-pH controlled steady states will be presented together.

5.2.3 Influent Characteristics

Influent characteristics required as input to the simulations are the (i) organic components, (ii) free and saline ammonia, (iii) alkalinity, (iv) pH, (v) sulphate and (vi) influent PSS stoichiometric composition (which serves both as a model constant and as an influent characteristic). For the influent organics, by following the logic and procedures set out in Chapter 4 the influent organic COD components could be quantified from the experimental measurements. The units of COD were converted to the mole units required as input to the model through the relevant stiochiometric composition of the organic that represents the corresponding COD fraction :

(i) Biodegradeable particulate (S_{bp}) – PSS stoichiometric composition of $C_XH_YO_ZN_A$ where X, Y, Z and A are known for each feed batch (Table 4.4).

(ii) Biodegradable soluble fermentable (S_{bsf}) – represented by glucose ($C_6H_{12}0_6$).

(iii) Biodegradeable soluble acetic and propionic acids (S_{bsa}, S_{bsp}) – known stoichiometric compositions ($C_2H_4O_2$ and $C_3H_6O_2$ respectively).

(iv) Unbiodegradable soluble and particulate (S_{us}, S_{up}) – not converted since these are not acted on in the system and hence appear in the effluent where comparisons between predicted and measured data will be in COD units.

With the known stoichiometric compositions above, the theoretical COD/mole ratios could be determined and hence COD converted to the corresponding mole units.

The influent total species concentrations for sulphate and free and saline ammonia (FSA) were available from measurement (Table 4.2). However, since acid / base chemistry is included directly in the model, the concentrations of the individual species making up the weak acid / base are

required as input. This includes also the acetic and propionic acids. The influent pH was available (Table 4.4) and was used to speciate the influent acid / bases into dissociated and undissociated species by using the relevant pK value adjusted for ionic strength effects. The influent pH also served directly as input (via H^+).

For the inorganic carbon (carbonate) weak acid / base, the total species concentration was not available. However, influent alkalinity was determined (Table 4.4), and hence, from the pH and relevant pK values adjusted for ionic strength, the influent inorganic carbon weak acid / base could be speciated as required for model input.

For all steady states, the influent sulphide concentrations were accepted to be negligible compared with the sulphide generated in the system, and hence the influent concentrations were accepted as zero.

5.3 SIMULATION RESULTS

5.3.1 Comparison of Predicted with Measured Data as per Table 5.1

Tables 5.1 compares the experimentally measured parameter values with the corresponding predicted values obtained from the model simulations for the non pH controlled and pH controlled systems respectively of Ristow *et al.* (2005). Unfortunately Ristow *et al.* (2005) did not measure all the constituents that the model can predict. Predicted and measured values are also compared in Figures 5.1 and 5.2.

Table 5.1 : Comparison of Measured (M) effluent values with the predicted (P) values obtained from simulations using the developed BSR model, for the experimental sulphidogenic systems of Ristow *et al.* (2005).

Parameter	Units		No pH Control				pH Control			
			Steady State No.				Steady State No.			
			6	41	42	46	15	20	22	36
Effluent Total COD	mg COD/ℓ	M	10 684	1 697	1 749	897	6 165	1 532	1 406	1 304
		P	10 910	1 815	1 695	1 003	6 009	1 803	1 770	1 474
Effluent Soluble Organic COD	mg COD/ℓ	M	157	85	129	42	-	61	155	80
		P	296	51.03	57.06	59.8	-	95	79.4	60.22
Effluent Total Soluble COD	mg COD/ℓ	M	-	897	964	466	197	790	655	521
		P	-	1 027	1 071	519.4	286.2	984	989	679.7
Effluent VFA	mg/ℓ as HAC	M	37	0	57	3	6	0	63	0
		P	153.1	8.63	9.25	14.78	138	10.8	9.5	10.99
Effluent Alfalinity	mg/ℓ as $CaCO_3$	M	2 534	1 633	1 573	1 025	2 894	1 386	***782	354
		P	2 298	1 738	1 738	678.2	2 854	1 682	1 682	1 099
Reactor pH	-	M	7.06	7.64	7.75	7.92	6.87	7.52	6.99	6.47
		P	6.88	6.74	6.74	6.29	6.86	6.72	6.7	6.45
Effluent Sulphate Concentration	mg SO_4/ℓ	M	34.0	-	147	51	733	530	770	436
		P	2.31	218	237	398	9.39	343	343	365
Effluent FSA	mg N/ℓ	M	207	11	19	-	69	18	11	16
		P	-	23.2	26.17	15.63	210	27.15	33.05	27.04
CO_2 Effluent Gas Stream	ℓ/ℓ Influent	P	4.232	0.8455	0.07792	0.00847	0.4636	0.097	0.0838	0.3004
H_2S Effluent Gas Stream	ℓ/ℓ Influent	P	0.2403	0.1202	0.09735	0.008381	2.193	0.097	0.103	0.2403
CH_4 Effluent Gas Stream	ℓ/ℓ Influent	P	5.541	0.00326	0.002488	0.00606	0.4807	0.0014	0.024	0.0094
Percentage Methone Gas	%	P	55.34	0.1087	0.09763	18.03	7.725	0.0086	0.00184	0.04237
Effluent HS^-	mg/ℓ	P	13.35	224.8	223.8	49.57	181.8	195.3	198.3	88.63
Effluent H_2S	mg/ℓ	P	11.33	271.2	271.9	165.2	169.7	256.9	258.4	214.8

*** Storage of samples questioned – may have increased.

Table 5.1 : Comparison of Measured (M) effluent values with the predicted (P) values obtained from simulations using the developed BSR model, for the experimental sulphidogenic systems of Ristow *et al.* (2005).

Parameter	Units		No pH Control				pH Control			
			Steady State No.				Steady State No.			
			6	41	42	46	15	20	22	36
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		P	10 910	1 815	1 695	1 003	6 009	1 803	1 770	1 474
Effluent Soluble Organic COD	mg COD/ℓ	M	157	85	129	42	-	61	155	80
		P	296	51.03	57.06	59.8	-	95	79.4	60.22
Effluent Total Soluble COD	mg COD/ℓ	M	-	897	964	466	197	790	655	521
		P	-	1 027	1 071	519.4	286.2	984	989	679.7
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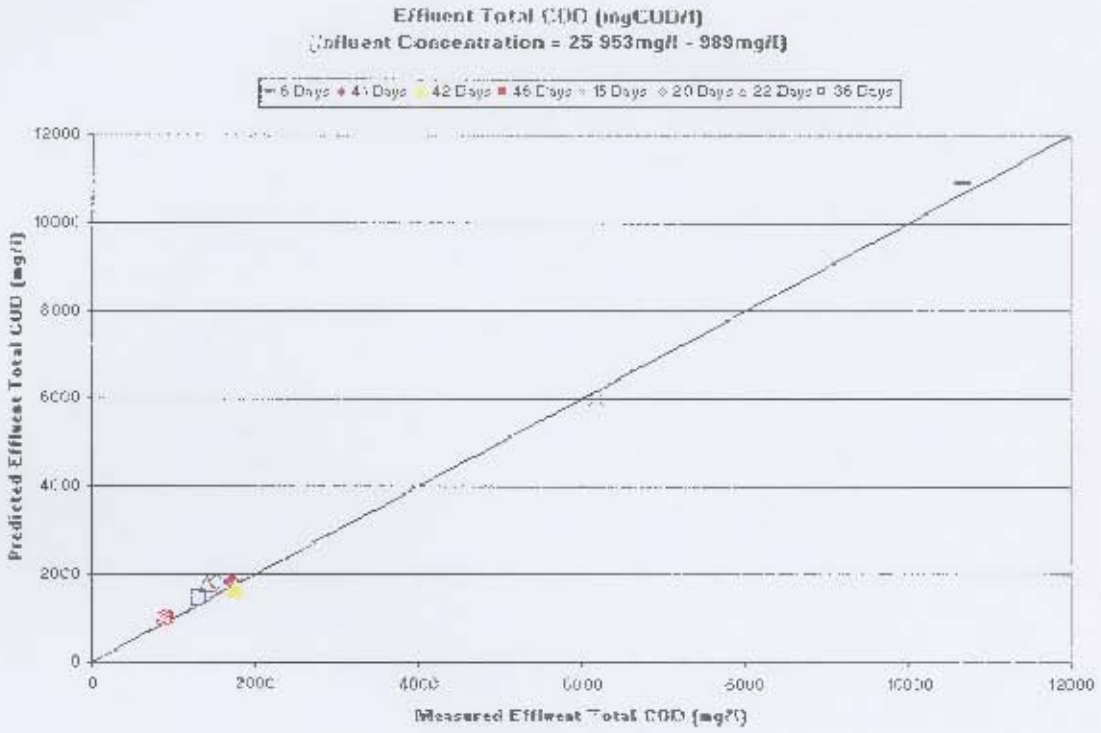
		P	153.1	8.63	9.25	14.78	138	10.8	9.5	10.99
Effluent Alfalinity	mg/ℓ as $CaCO_3$	M	2 534	1 633	1 573	1 025	2 894	1 386	***782	354
		P	2 298	1 738	1 738	678.2	2 854	1 682	1 682	1 099
Reactor pH	-	M	7.06	7.64	7.75	7.92	6.87	7.52	6.99	6.47
		P	6.88	6.74	6.74	6.29	6.86	6.72	6.7	6.45
Effluent Sulphate Concentration	mg SO_4/ℓ	M	34.0	-	147	51	733	530	770	436
		P	2.31	218	237	398	9.39	343	343	365
Effluent FSA	mg N/ℓ	M	207	11	19	-	69	18	11	16
		P	-	23.2	26.17	15.63	210	27.15	33.05	27.04
CO_2 Effluent Gas Stream	ℓ/ℓ Influent	P	4.232	0.8455	0.07792	0.00847	0.4636	0.097	0.0838	0.3004
H_2S Effluent Gas Stream	ℓ/ℓ Influent	P	0.2403	0.1202	0.09735	0.008381	2.193	0.097	0.103	0.2403
CH_4 Effluent Gas Stream	ℓ/ℓ Influent	P	5.541	0.00326	0.002488	0.00606	0.4807	0.0014	0.024	0.0094
Percentage Methone Gas	%	P	55.34	0.1087	0.09763	18.03	7.725	0.0086	0.00184	0.04237
Effluent HS^-	mg/ℓ	P	13.35	224.8	223.8	49.57	181.8	195.3	198.3	88.63
Effluent H_2S	mg/ℓ	P	11.33	271.2	271.9	165.2	169.7	256.9	258.4	214.8

*** Storage of samples questioned – may have increased.

5.3.2 Predicted effluent HS / H_2S and Gas Flow and Composition

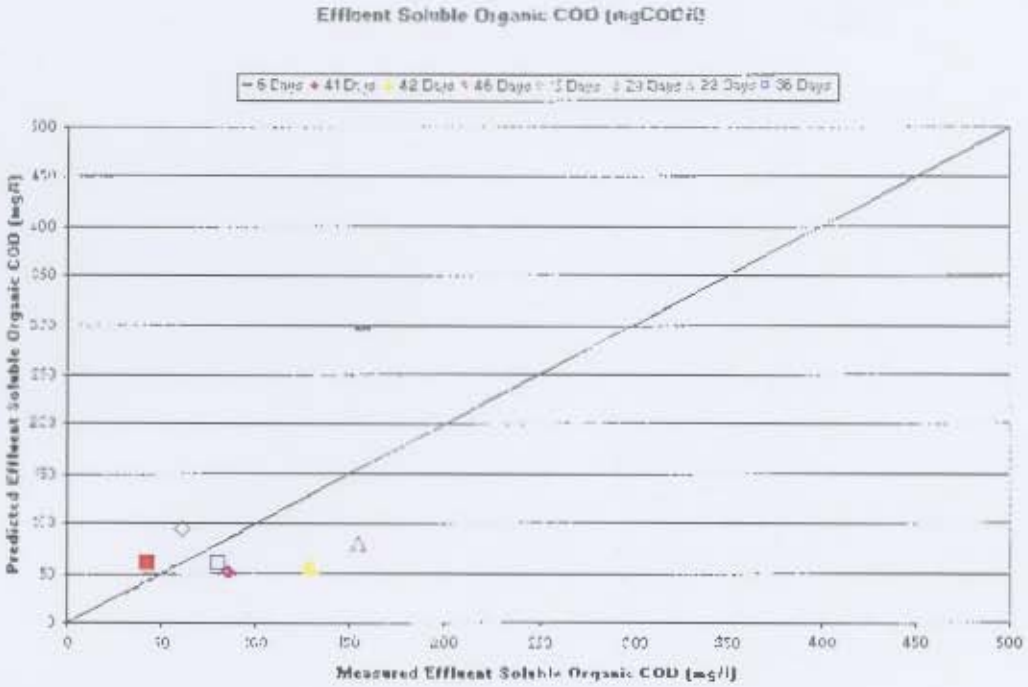
Under SO_4 limited conditions, significant methanogenics is evident i.e. competition is operative but while sifficent SO_4 is present, sulphidogens outcompete the methanogens. This is particularly evident from the simulation results of Steady State Nr. 6 (Table 5.1).

(i)



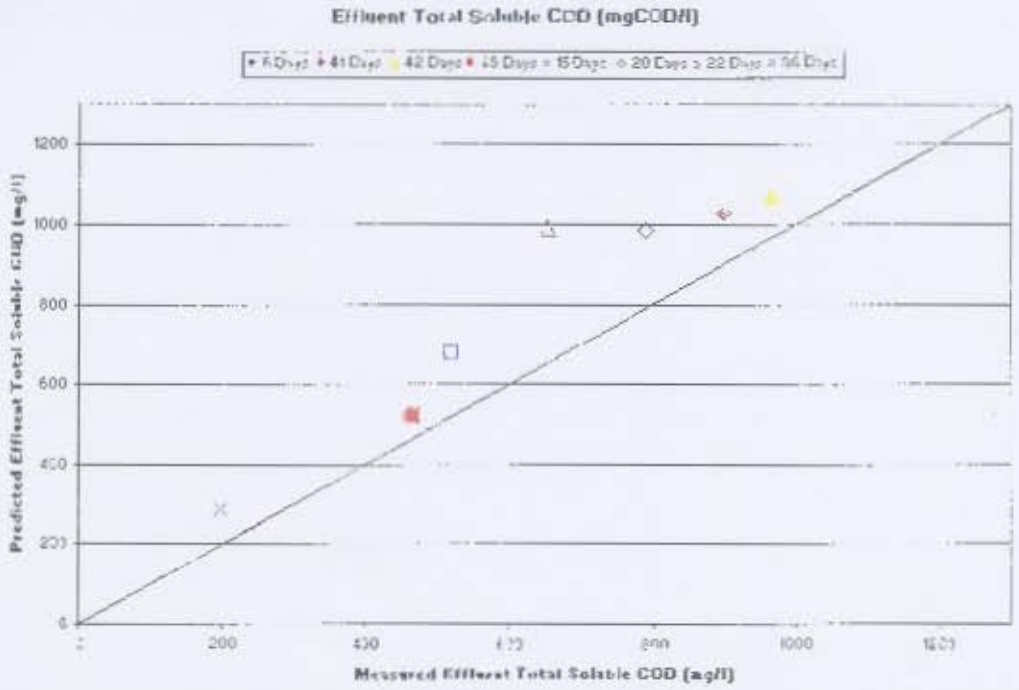
Comparing the COD removal measured by Ristow *et al.* (2005) with the predictions by the model using the hydrolysis rates as described in Chapter 4 (Section 4.4), it seems that all the steady state systems compare very well.

(ii)



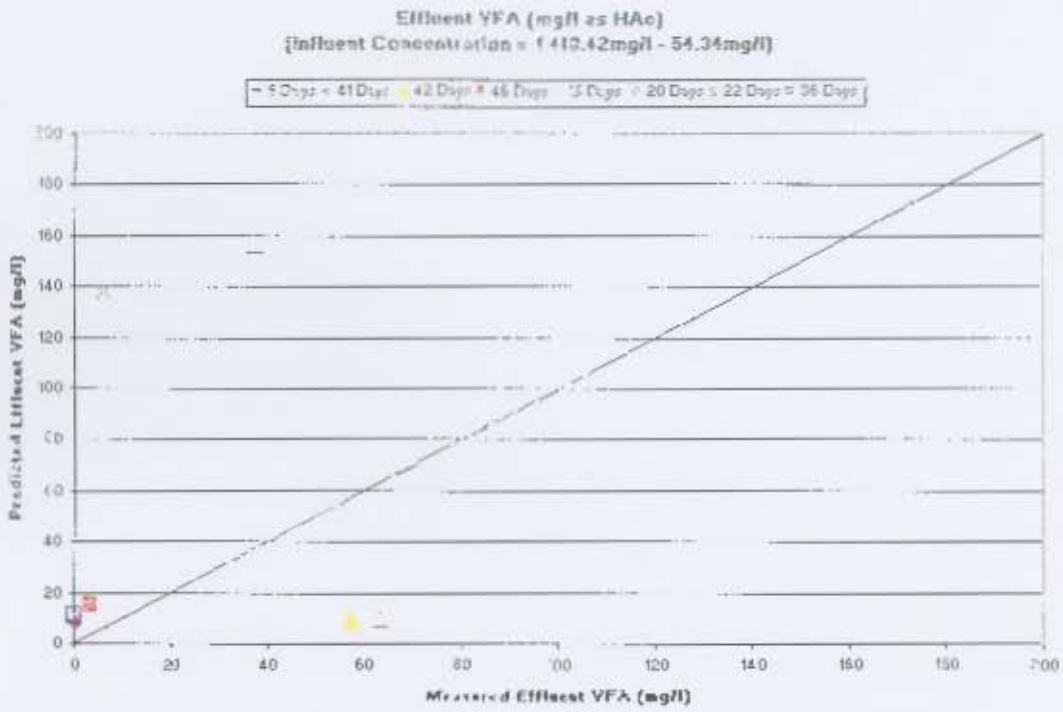
The predicted effluent total soluble organic COD concentrations (excludes H_2S) compare well with the experimental measured effluent results from Ristow *et al.* (2005).

(iii)



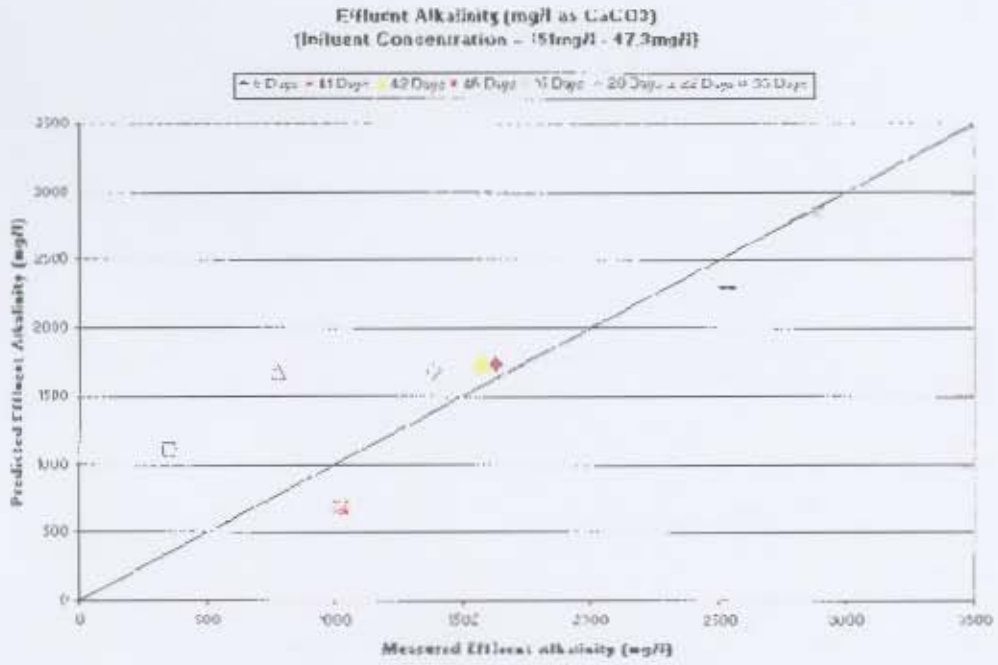
The predicted effluent total soluble COD concentrations (includes H_2S) compare well with the experimental measured efficient results from Ristow *et al.* (2005).

(iv)



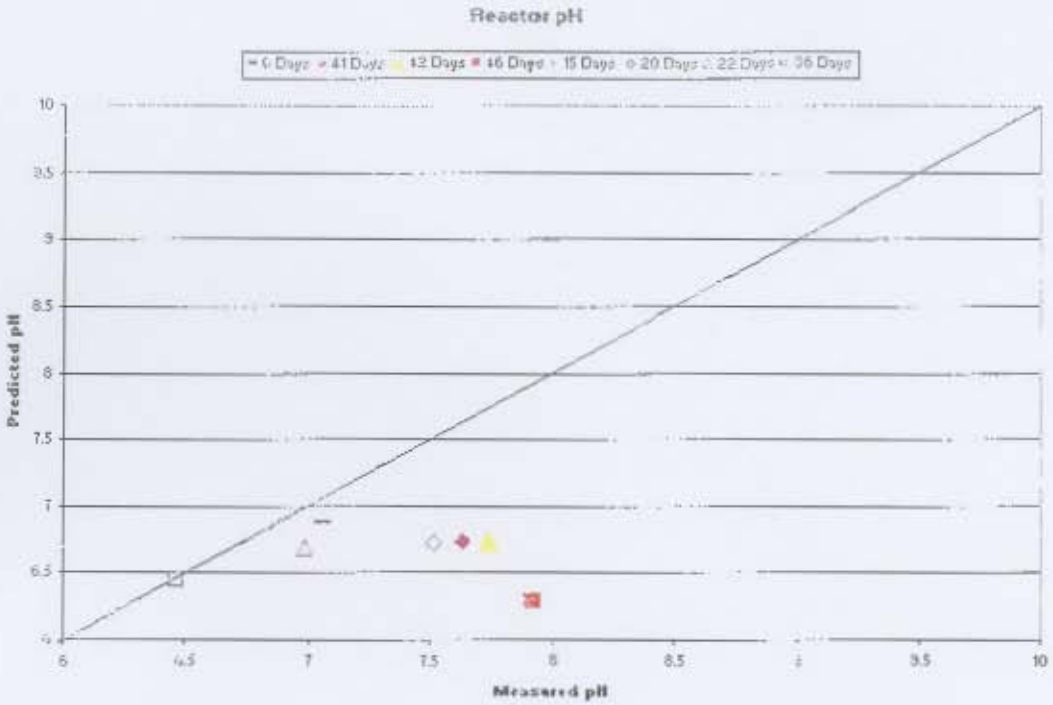
The simulated behaviour conforms well to that experimentally measured in that the effluent concentrations are very low compared to the influent VFA concentrations.

(v)



The measured and predicted alkalinities correspond reasonably well, considering that the influent alkalinity values were estimated because they were not directly measured by Ristow *et al.* (2005). Had more accurate influent alkalinity data been available, the simulated effluent alkalinity results would most likely have corresponded better to the measured values.

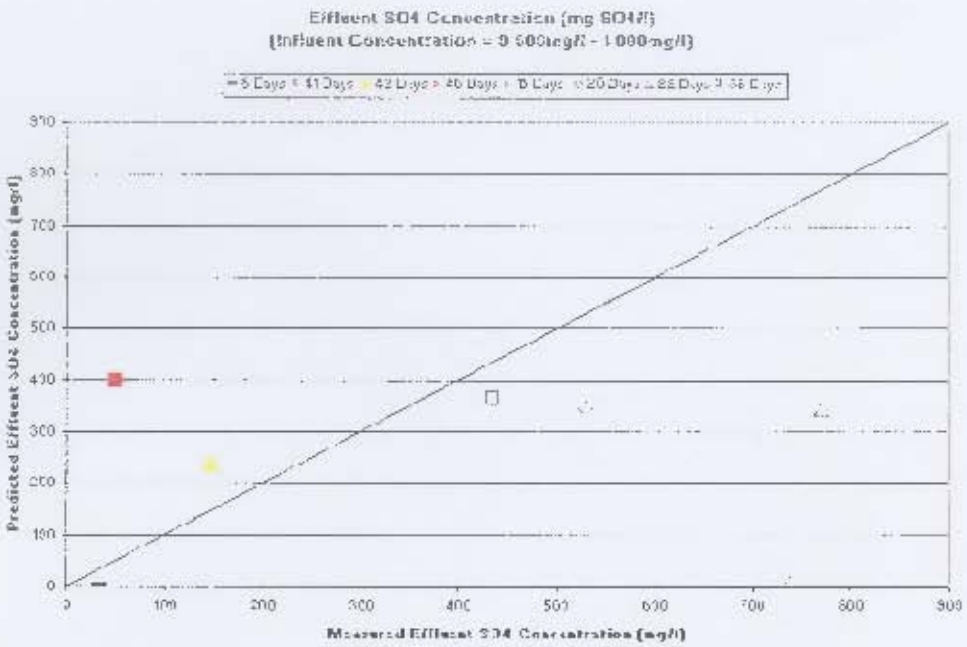
(vi)



The simulated pH's are all lower than the measured values. The influent pH values were estimated (not measured), which will have had an effect on the simulated values. A possible explanation could be the following :

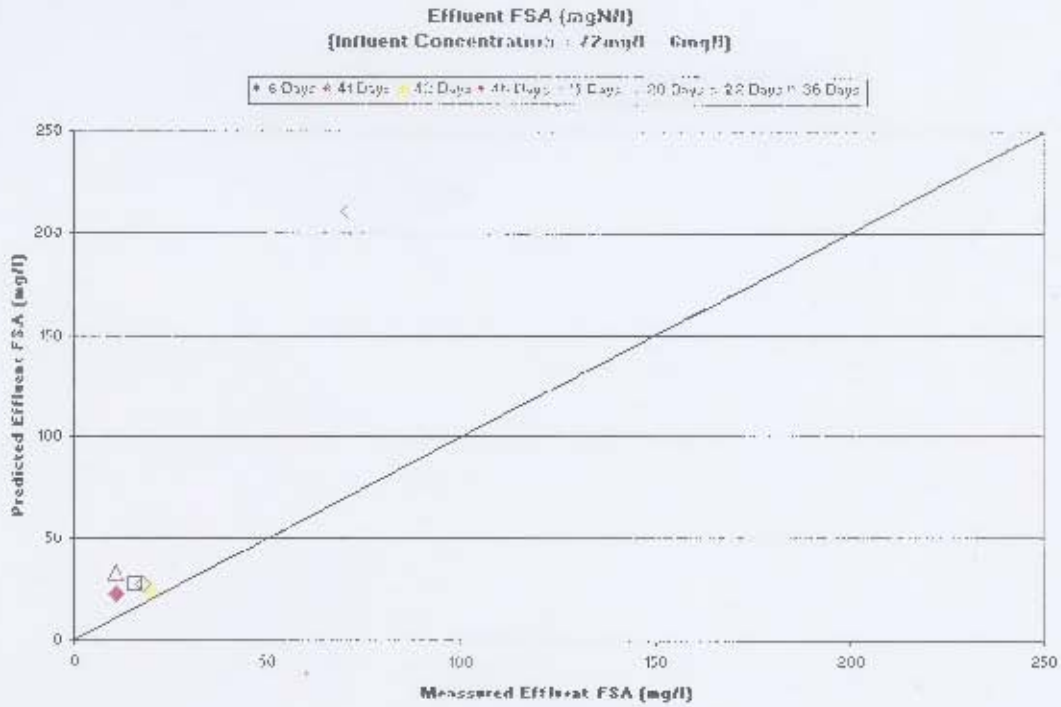
The system is not producing sufficient dissolved CO_2 (the balance of the alkalinity) required to reduce the SO_4, therefore HS^- is produced instead of H_2S. In this way the sulphide system determines the pH, not the carbonate system. This can be addressed by decreasing the carbon content of the sludge. This should result in less HCO_3^- alkalinity and more HS^- production. This should therefore increase the HS^- / H_2S ratio, which results in an increase in pH.

(vii)



The predicted effluent SO_4 concentrations compare favourably with the experimental measured effluent results from Ristow *et al.* (2005). Sulphate inhibition is not apparent from these results. The reason being that in all the steady state systems of Ristow *et al.*, sulphate was slightly in excess and the effluent VFA concentrations low, indicating the absence of such inhibitions.

(viii)



The measured and simulated FSA concentrations mirror the COD removal, with the exception of Steady State Nr. 15. The reason for this could be the lower COD removal. Lower COD removal equates to less biodegradable particulate organics hydrolysed and therefore less organic N is released as FSA.

Figure 5.1 : Comparison of values obtained from predictions using the kinetic simulation model (UCTADM1 with SR) with measured values for the Ristow *et al.* (2005) data sets fed sulphate, for the following : (i), (ii) and (iii) COD removal, (iv) VFA Concentration, (v) Bicarbonate alkalinity, (vi) Effluent pH, (vii) Sulphate Concentration and (viii) FSA Concentration.

5.3.3 Summary

In Figure 5.1 the solid markers represent the model predictions where the pH was not controlled and the open markers show the model prediction where the pH was controlled, using the hydrolysis rate constants calculated, as described earlier. The difference on some of the graphs might seem large but the absolute difference is very small if compared to the influent concentrations, as listed with each graph.

From these graphs, it is clear that most of the simulated results for the different constituents compare favourably with the experimental results with the exception of the pH values. The investigation into the possible reasons for this phenomena however falls outside the scope of this study and should be investigated by further study some of the differences arose because the model has 100 % COD, N and S mass balances but the experimental data not. The only test of which most of the simulated values does not compare well with the experimental data is steady state test No. 15. It is suspected that various factors influencing the outcome of the laboratory experiment could be the result of this, because all the other model predicted results compare reasonably well with the simulated data.

The simulated behaviour conforms well to that expected. The expected results include the following :

i) The VFA concentration in the effluent is very low.

ii) CH_4 gas production is very low. SRB's growth rate is faster should the influent contain sufficient sulphate concentrations. The acidogens consume the glucose, and the methanogens are inhibited, resulting in low methane gas production. Gaseous CO_2 production also is zero. It

can be shown from the stoichiometry of BSR, that for PSS ($C_{3.5}H_7O_2N$ and, as found in this investigation $C_{4.17}H_7O_{2.63}N_{0.218}$) there is insufficient C with respect to the electrons it can donate, to generate enough dissolved CO_2 to meet the alkalinity (HCO_3^-) requirements for the H^+ uptake in the BSR process.

iii) H^+ ions is consumed during the process of SR, resulting in an increase in alkalinity .

vi) With the consumption of slowly biodegradable COD and SO_4, an increase in dissolved H_2S, HS^- and pH is affected, and gas production is zero. This is because H_2S gas is very soluble and all the CO_2 generated stays in solution supplying some of the alkalinity required. In fact the carbon in PSS generates too little unorganic carbon causing the HS^- / H_2S system to respeciate to make up the alkalinity defect. It can be shown from stoichiometry that organics which have COD / C ratios of greater than that of CH_2O (i.e. >2.67) are carbon deficient for BSR. The simulation model correctly reflected this behaviour. Organics with COD / C < 2.67 will generate excess CO_2 for alkalinity required and hence some CO_2 (and H_2S) gas.

vii) Sulphide should inhibit SRB since the effluent SO_4 concentration decreases significantly and H_2S is very soluble. This however is not achieved with this model because the inhibition term has not been included yet.

5.4 CLOSURE

In this Chapter, the two phase integrated biological, chemical and physical processes BSR kinetic model developed in Chapter 3 and calibrated in Chapter 4 has been evaluated by comparison of predictions with experimental measurements, by simulating the performance of the laboratory-scale sulphidogenic digesters operated by Ristow *et al.* (2005). From the comparison, it is evident that the simulated results compare favourably with the experimental measurements. This provides support validating the BSR kinetic model. In this validation exercise it has been realised that data from the same experimental systems have been used to both calibrate and validate the BSR kinetic model. However, in the calibration (Chapter 4), only the experimental system COD parameters were used to calibrate one set of constants, those for the hydrolysis process; values for the other constants were derived almost exclusively from literature sources (see Chapter 4). In the model validation, close prediction of measured effluent total COD's confirm the selection of the hydrolysis rate constants and that the single pair of the hydrolysis rate constants are applicable over a wide range of hydraulic retention times. Furthermore, model validation is supported by the

reasonable correlation between predicted and measured values for the wide variety of parameters compared.

The system simulations described in this Chapter have been restricted to steady state, since comprehensive data sets for BSR with PSS are limited and available for steady state only. For more extensive model evaluation and validation, application to simulate dynamic states would be desirable, which requires comprehensive dynamic data sets. This aspect requires further investigation.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

As part of a larger objective to develop a mass balances based model for all the unit operations in WWTP's, this thesis project makes a significant contribution, specifically where BSR is required. The main objective in this research study was to develop an integrated two phase chemical, physical and biological processes kinetic model for competitive methanogenic and sulphidogenic anaerobic digestion with PSS as substrate.

This model can aid in the design of BSR systems in which PSS is used in the treatment of AMD, furthermore the model is general and include other substrate types such as VFA and therefore can be applied where these are used in BSR.

In gathering information for developing such a model, relevant available models have been reviewed. From the review, the models of Sötemann *et al.* (2005c), Kalyuzhnyi, Fedorovich and co-workers (Fedorovich *et al.,* 2003) and Ristow and co-workers (Ristow *et al.,* 2005) appear suitable. These models provided virtually all the necessary building blocks for development of an integrated two-phase, biological, chemical and physical processes kinetic model for competitive methanogenic and sulphidogenic anaerobic digestion with PSS as substrate.

6.1 THE DEVELOPMENT OF A KINETIC MODEL FOR SULPHATE REDUCTION WITH PRIMARY SEWAGE SLUDGE AS SUBSTRATE

By extracting, and where necessary modifying, relevant processes and kinetics from the literature, and developing and adding processes where required, two types of kinetic models for the biological, chemical and physical processes active in BSR with PSS as substrate have been developed namely :

1. BSR as the "sole" biological processes consuming the SCFA and H_2 substrates generated from PSS hydrolysis and acidification, i.e. methanogenesis excluded, and

2. Both BSR and methanogenesis are present in competition for the SCFA and H_2 substrates.

Although the BSR models have been developed specifically for situations where PSS serves as the feed substrate, the models have much wider potential application. For particulate substrates

(e.g. compost), only the feed substrate composition and kinetic constants for hydrolysis required modification; for soluble substrates (e.g. acetate) these were being used directly as input to the model since they serve as intermediates in the processes already included.

6.2 MODEL CALIBRATION AND VERIFICATION

The various kinetic and stoichiometric constants required as input to the BSR kinetic model have been quantified, thereby to calibrate the BSR kinetic model. Values for these constants were obtained from the literature, except for :

(i) The hydrolysis process kinetic constants, $k_{max,HYD}$ and $K_{ss,\ HYD}$, and

(ii) the sewage sludge stoichiometric composition, i.e. X, Y, Z and A in $C_XH_YO_ZN_A$.

To determine the hydrolysis process kinetic constants, the COD based analytical procedure of Sötemann *et al.* (2005c) developed for methanogenic digesters was adapted for sulphidogenic systems. This modified procedure was applied to the experimental data from the sulphidogenic systems of Ristow *et al.* (2005), thereby to derive estimates for the hydrolysis process kinetic constants. Values from the three linearization techniques used in the analysis gave $k_{max,HYD}$ = 1.62, 1.54 and 1.59 gCOD S_{bp}/gCODZ_{AD}.d and $K_{SS,HYD}$ = 0.048; 0.013 and 0.036 gCOD S_{bp}/gCOD Z_{AD}, with average values 1.58 and 0.032 respectively.

Although the $k_{max,HYD}$ values are reasonably consistent, the $K_{SS,HYD}$ values vary considerably, indicating difficulty in determining this constant with confidence. However, the low values for $K_{SS,HYD}$ indicate that the exact value probably will not have a significant influence in simulations.

A fit by "eye" to the experimental data gave values of 1.55 and 0.0132 respectively. Compared with the values for $k_{max,HYD}$ = 1.63 to 2.43 $K_{SS,HYD}$ = 0.055 to 0.736 obtained by Sötemann *et al.* (2005c), using the same analytical procedure, for the methanogenic anaerobic digesters also operated by Ristow *et al.* the values for $k_{max,HYD}$ and $K_{SS,HYD}$ obtained here for the equivalent sulphidogenic digesters are reasonably similar. This indicated that sulphate reduction *per se* does not influence the PSS hydrolysis rate significantly, in agreement with the conclusion of Ristow *et al.* However, the scatter in the experimental data with surface saturation kinetics applied, precludes a definitive judgement on this aspect.

Since the BSR kinetic model is formulated in mole units, the derived values for $k_{max,HYD}$ and $K_{SS,HYD}$ required conversion from the COD units to mole units. This necessitated that the stoichiometric

composition of the PSS that served as feed to the Ristow *et al.* digesters, be known. Furthermore, the PSS stoichiometric composition also is included as a variable in the BSR kinetic model, and is required as input to the model.

For the PSS stoichiometric composition, from the sets of analytical measurements made on each batch of the Athlone Wastewater Treatment Works PSS that served as feed to the Ristow *et al.* digesters, Sötemann *et al.* (2005c) delineated the respective feed batch PSS stoichiometric compositions. The average composition of the four feed batches was $C_{4.1725}H_7O_{2.6275}N_{0.2175}$. This differs somewhat from the composition of $C_{3.5}H_7O_2N_{0.196}$ determined by Sötemann *et al.* (2005c) for the feed to the digesters operated by Izzett *et al.* (1992), which may be ascribed to difference in feed type – Izzett *et al.* used a mixture of PSS and human sludge whereas Ristow *et al.* used pure PSS.

With the average PSS stoichiometric composition, the hydrolysis rate constants were converted from the COD units to mole units, to give $k_{max,HYD}$ = 1.82; 1.74 and 1.79 mol S_{bp}/mol Z_{AD}.d and $K_{SS,HYD}$ = 0.054; 0.015 and 0.04 mol S_{bp}/mol Z_{AD} respectively, with averages 1.782 and 0.0365 respectively. Converting this "eye" fit constants gave values of 1.743 and 0.0148 respectively, which were used for subsequent simulations.

In calibration of the BSR kinetic model, the hydrolysis rate constants and the PSS stoichiometric composition were obtained from analysis of experimental data measured by Ristow *et al.* on sulphidogenic reactors fed PSS from the Athlone Wastewater Treatment Works. It is not certain whether the values thus derived for these constants are specific to this particular PSS, or are generic to PSS in general. To clarify this requires a more detailed investigation.

Having completed calibration of the BSR kinetic model, the model required evalution and validation. This was done by simulation of the Ristow *et al.* sulphidogenic digesters, and comparison of predicted with measured data.

6.3 BSR KINETIC MODEL APPLICATION AND VALIDATION

The two phase integrated biological, chemical and physical processes BSR kinetic model that was developed and calibrated has been evaluated by comparison of predictions with experimental measurements, by simulating the performance of the laboratory-scale sulphidogenic digesters operated by Ristow *et al.* (2005). From the comparison it was evident that the simulated results compare favourably with the experimental measurements. This provided support validating the

BSR kinetic model. In this validation exercise it has been realised that data from the same experimental systems have been used to both calibrate and validate the BSR kinetic model. However, in the calibration only the experimental system COD parameters were used to calibrate one set of constants, those for the hydrolysis process; values for the other constants were derived almost exclusively from literature sources. In the model validation, close prediction of measured effluent total COD's confirm the selection of the hydrolysis rate constants and that the single pair of the hydrolysis rate constants are applicable over a wide range of hydraulic retention times. Furthermore, model validation is supported by the reasonable correlation between predicted and measured values for the wide variety of parameters compared.

The system simulations have been restricted to steady state, since comprehensive data sets for BSR with PSS are limited and available for steady state only. For more extensive model evaluation and validation, application to simulate dynamic states would be desirable, which requires comprehensive dynamic data sets. This aspect requires further investigation.

6.4 FURTHER RESEARCH

This thesis project made some significant advances towards developing a kinetic model for BSR where PSS is used as substrate.

The pH values obtained for the steady state simulations were however consistently lower than those values from the experimental systems. The reason for should be investigated by further research. As explained in Chapter 5 decreasing the carbon content of the sludge composition could possibly address this problem.

The extension of the existing UCTADM1 model to include BSR did however not make provision for hydrogen sulphate inhibition in anaerobic digestion. The reason being that, the only experimental data available, to validate the model developed, was that of Ristow et al. (2005). In all their systems, sulphate was slightly in excess and effluent VFA concentrations were low (< 50mgHAc/L), indicating absence of inhibitions. Thus, at lower aqueous sulphide concentrations, sulphate reduction is not inhibited. Soluble sulphides can however produce toxic or inhibitory effects in anaerobic treatment. This toxicity is initially evident by a decrease in gas production and severely retarded digestion by an increase in the volatile acid concentration (Alonzo et al., 1966).

In order to keep the sulphide concentration low, H_2S stripping with a carrier H_2, CO_2 gas should be considered. The CO_2 gas would supply the C defecit if the organic is C deficient. It would be interesting to see how the CO_2 content of the stripping gas will affect the digester pH established.

In future research, inclusion of hydrogen sulphate inhibition in anaerobic digestion needs to be considered further. As explained in Chapter 3, the approach to the kinetic rates in Kalyuzhnyi et al. (1998) is the same as that used in the UCTADM1 model, hence only the H_2S inhibition term has to be added to the existing kinetic rate equations for the fermentative, acetogenic and methanogenic bacterial groups in the UCTADM1 model once SRBs are integrated into the UCTADM1 model.

The successful integration in a kinetic way of the two phase mixed weak acid/base chemistry and biological processes of SR has provided a sound basis for further model development. Still to be included in the UCTADM1 model with SR, are mineral precipitation and the P content of sewage sludges. This will extend the model to digestion of biological excess P removal waste activated sludges and provide a direct and quantitive link between feed sludge composition and mineral precipitation problems in digesters as described by Sötemann *et al.* (2005c).

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ANNEXURE A :
AQUASIM CODE

****

AQUASIM Version 2.0 (win/mfc) - Listing of System Definition

****

Date and time of listing: 02/17/2007 14:55:44

****
Variables
****

AAA_README:	Description:	Nomenclature: Now conforms to paper . This revision: (i) Fixed pH = -log10(H+): activity, i.e. pH = -log10 [[H+]fm] and not pH = -log10[H+] (ii) Corrected Ka and Kp, which are actually K'a and K'p.
	Type:	Constant Variable
	Unit:	
	Value:	0.1
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
ALK:	Description:	H2CO3 alkalinity in digestor
	Type:	Formula Variable
	Unit:	mg/l asCaCO3
	Expression:	ALKmol*MW_CaCO3*1000
ALKmol:	Description:	H2CO3 alkalinity in digestor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	2*C5_CO3+C4_HCO3+C8_OH-C7_H
AW_C:	Description:	Atomic weight of carbon
	Type:	Constant Variable
	Unit:	amu
	Value:	12.011
	Standard Deviation:	1
	Minimum:	0
	Maximum:	20
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
AW_H:	Description:	Atomic weight of hydrogen
	Type:	Constant Variable
	Unit:	amu
	Value:	1.0079
	Standard Deviation:	1
	Minimum:	0
	Maximum:	20
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
AW_N:	Description:	Atomic weight of nitrogen
	Type:	Constant Variable
	Unit:	amu
	Value:	14.007
	Standard Deviation:	1
	Minimum:	0
	Maximum:	20
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
AW_O:	Description:	Atomic weight of oxygen

	Type:	Constant Variable
	Unit:	amu
	Value:	15.999
	Standard Deviation:	1
	Minimum:	0
	Maximum:	20
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
AW_P:	Description:	Atomic weight of phosphorus
	Type:	Constant Variable
	Unit:	amu
	Value:	15.999
	Standard Deviation:	1
	Minimum:	0
	Maximum:	20
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
AW_S:	Description:	Atomic weight of Sulfar
	Type:	Constant Variable
	Unit:	amu
	Value:	32.066
	Standard Deviation:	1
	Minimum:	0
	Maximum:	40
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
B1_CODus:	Description:	Unbiodegradable soluble COD conc.
	Type:	Dyn. Volume State Var.
	Unit:	gram COD/l - NNB!!
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
B3_CODup:	Description:	Unbiodegradable particulate COD con c.
	Type:	Dyn. Volume State Var.
	Unit:	gram COD/l - NNB!!
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
bas:	Description:	Acetotrophic SRB death rate
	Type:	Constant Variable
	Unit:	/d
	Value:	0.0275
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
bhs:	Description:	Hydrogenotrophic SRB death rate
	Type:	Constant Variable
	Unit:	/d
	Value:	0.06
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
bps:	Description:	Propionic degrading SRB death rate
	Type:	Constant Variable
	Unit:	/d
	Value:	0.0185
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive

b_AC:	Description:	Acetogen specific death rate
	Type:	Constant Variable
	Unit:	/d
	Value:	0.015
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
b_AD:	Description:	Acidogen specific death rate
	Type:	Constant Variable
	Unit:	/d
	Value:	0.041
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
b_AM:	Description:	Acetoclastic methanogen specific death rate
	Type:	Constant Variable
	Unit:	/d
	Value:	0.037
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
b_HM:	Description:	Hydrogenotrophic methanogen specific death rate
	Type:	Constant Variable
	Unit:	/d
	Value:	0.01
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
C10_H2PO4:	Description:	Molar concentration of dissolved H2PO4 ion
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C11_HPO4:	Description:	Molar concentration of dissolved HPO4 ion
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C12_PO4:	Description:	Molar concentration of dissolved PO4 ion
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C13_HAc:	Description:	Molar concentration of acetic acid
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C14_Ac:	Description:	Molar concentration of acetate ions

	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C1_B10_NH4:	Description:	Molar concentration of ammonium ions
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C28_HPr:	Description:	Molar concentration of propionic acid
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C29_Pr:	Description:	Molar concentration of propionate ions
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C2_NH3:	Description:	Molar concentration of ammonia in solution
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C30_HSO4:	Description:	Molar concentration of sulphate
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C31_SO4:	Description:	Molar concentration of SO4
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C32_H2S:	Description:	Undissociated Hydrogen sulfide concentration
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C33_H2Sgas:	Description:	Gaseous H2S Concentration
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C34_HS:	Description:	HS concentration
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C3_H2CO3:	Description:	Molar concentration of dissolved carbonic acid (H2CO3) plus dissolved CO2
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006

C4_HCO3:	Description:	Molar concentration of dissolved bi carbonate ions
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C5_CO3:	Description:	Molar concentration of dissolved ca rbonate ions
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C7_H:	Description:	Molar concentration of dissolved hy drogen ions (protons)
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C8_OH:	Description:	Molar concentration of OH- ion
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
C9_H3PO4:	Description:	Molar concentration of dissolved ph osphoric acid
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
CT:	Description:	Total dissolved carbon species conc entration in digester
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	C3_H2CO3+C4_HCO3+C5_CO3
D1_Sbp:	Description:	Biodegradable particulate COD conc.
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
D2_B2_Sbsf:	Description:	Biodegradable soluble COD conc. = G lucose
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
D3_H2:	Description:	Concentration of H2
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
D4_Z_AD:	Description:	Acidogenic biomass concentration
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
D5_Z_AC:	Description:	Acetogen biomass concentration
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006

D6_Z_AM:	Description:	Acetoclastic methanogen biomass concentration
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
D7_Z_HM:	Description:	Hydrogenotrophic methanogen biomass concentration
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
EndogenousProt:	Description:	Intermediate step to simplify calcs for endogenous respiration
	Type:	Formula Variable
	Unit:	
	Expression:	(160/(((HydrolysisProt/2)*AW_O)/(AW_C*in_PsChon+AW_H*in_PscHon+AW_O*in_PschOn+AW_N*in_PschoN)))/(AW_C*in_PsChon+AW_H*in_PscHon+AW_O*in_PschOn+AW_N*in_PschoN)
fd:	Description:	Divalent activity coefficient
	Type:	Formula Variable
	Unit:	
	Expression:	10^(-(1.825e+006*(78.3*Tk)^(-1.5))*((2)^(2))*((((0.000168*SC)^(0.5))/(1+((0.000168*SC)^(0.5))))-(0.3*0.000168*SC)))
fm:	Description:	Monovalent activity coefficient
	Type:	Formula Variable
	Unit:	
	Expression:	10^(-(1.825e+006*(78.3*Tk)^(-1.5))*((1)^(2))*((((0.000168*SC)^(0.5))/(1+((0.000168*SC)^(0.5))))-(0.3*0.000168*SC)))
ft:	Description:	Trivalent activity coefficient
	Type:	Formula Variable
	Unit:	
	Expression:	10^(-(1.825e+006*(78.3*Tk)^(-1.5))*((3)^(2))*((((0.000168*SC)^(0.5))/(1+((0.000168*SC)^(0.5))))-(0.3*0.000168*SC)))
f_C5H7O2NCOD:	Description:	COD/organism ration
	Type:	Constant Variable
	Unit:	mgCOD/mgorganisms
	Value:	1.4145559
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
H2CO3mol:	Description:	Stoichiometry for endogenous respiration for all organism groups
	Type:	Formula Variable
	Unit:	mol
	Expression:	(5*(in_PscHon-2*in_PschOn-3*in_PschoN))/(in_PscHon+4*in_PsChon-2*in_PschOn-3*in_PschoN)
H2S_in:	Description:	Influent H2S concentration
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(inH*HS_in)/KH2S

H2S_init:	Description:	Initial H2S concentration in the an aerobic reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(SulphideT_init*vinit_H)/(vinit_H+K H2S)
H2_in:	Description:	Influent H2 Species
	Type:	Constant Variable
	Unit:	mol/l
	Value:	0.00035
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Hin:	Description:	Constant variable
	Type:	Constant Variable
	Unit:	mol/l
	Value:	260
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1000
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
HPr_init:	Description:	Initial propionate concentration in the reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(PT_init*vinit_H)/(vinit_H+Kp)
HSO4_in:	Description:	Influent Sulphate
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(inH*SO4_in)/KHSO4
HSO4_init:	Description:	Initial sulphate concentration in t he reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(SulphateT_init*vinit_H)/(vinit_H+K HSO4)
HS_in:	Description:	Influent HS concentration
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(KH2S*(SulphideT_in/1000/MWS))/(inH +KH2S)
HS_init:	Description:	Initial HS concentration in the an aerobic reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(SulphideT_init*KH2S)/(vinit_H+KH2S)
HydrolysisProt:	Description:	Intermediate step to simplify calcs for hydrolysis
	Type:	Formula Variable
	Unit:	
	Expression:	in_PscHon+(4*in_PsChon)-(2*in_PschO n)-(3*in_PschoN)
inALK:	Description:	Influent Alkalinity
	Type:	Constant Variable
	Unit:	as mg/l CaCO3
	Value:	90.28
	Standard Deviation:	1

	Minimum:	0
	Maximum:	10000
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
inALKmol:	Description:	alkalinity converted to mol/l
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(inALK/1000)/MW_CaCO3*2
inCO3:	Description:	CO3 species in influent
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(inALKmol-inOH-inH)/(2+(inH/Kc2))
inCO3acidity:	Description:	CO3 2- acidity in the influent
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(((1+((2*inH)/Kc1))/(1+((2*Kc2)/inH)))*(inALKmol-(Kw/inH)+(inH/fm)))-(Kw/inH)+(inH/fm)
inCT:	Description:	Total dissolved C species in influe nt
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(inALKmol+inCO3acidity)/2
inH:	Description:	H+ species in the influent
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(10^(-inpH))/fm
inH2CO3:	Description:	H2CO3 species in influent
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(inHCO3*inH)/Kc1
inHCO3:	Description:	HCO3 species in influent
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(inCO3*inH)/Kc2
inNai:	Description:	Influent free and saline ammonia
	Type:	Constant Variable
	Unit:	mgN/l
	Value:	8
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10000
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
inNH3:	Description:	Influent NH3 species
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(Kn*((inNai/1000)/AW_N))/(inH+Kn)
inNH4:	Description:	Influent NH4 species
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(inNH3*inH)/Kn
inOH:	Description:	OH species in the influent
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(10^(-(14-inpH)))/fm
inpH:	Description:	pH of the influent
	Type:	Constant Variable
	Unit:	

	Value:	5.38
	Standard Deviation:	1
	Minimum:	0
	Maximum:	14
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
inSbpi:	Description:	Influent particulate COD that is biodegradable
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	inSpi-inSupi
inSbpi_mol:	Description:	Influent particulate COD that is biodegradable
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	((inSbpi/in_f_CODPS)/1000)/(AW_C*in_PsChon+AW_H*in_PscHon+AW_O*in_PschOn+AW_N*in_PschoN)
inSbsaAAc_mol:	Description:	Influent PC Ac species
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(inSbsaAi_mol*Ka)/(inH+Ka)
inSbsaAHAc_mol:	Description:	Influent HAc species
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	inSbsaAi_mol-inSbsaAAc_mol
inSbsaAi:	Description:	Influent soluble COD that is acetic acid
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	inSbsai*in_f_HAcCOD*in_f_HAc
inSbsaAi_mol:	Description:	Influent total HAc+Ac
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	inSbsaAi/(in_f_HAcCOD*1000*MW_HAc)
inSbsai:	Description:	SCFA in the soluble influent COD as mg/l acetic acid
	Type:	Constant Variable
	Unit:	mgHAC/l
	Value:	155.59
	Standard Deviation:	1
	Minimum:	0
	Maximum:	100000
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
inSbsaPHPr_mol:	Description:	Influent HPr species
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	inSbsaPi_mol-inSbsaPPr_mol
inSbsaPi:	Description:	Influent soluble COD that is propionic acid
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	inSbsai*in_f_HPrCOD*in_f_HPr
inSbsaPi_mol:	Description:	Influent total propionic HPr+Pr
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	inSbsaPi/(in_f_HPrCOD*1000*MW_HPr)
inSbsaPPr_mol:	Description:	Influent Pr- species
	Type:	Formula Variable

	Unit:	mol/l
	Expression:	(inSbsaPi_mol*Kp)/(inH+Kp)
inSbsfi:	Description:	Influent soluble COD that is not SCFA but biodegradable
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	inSsi-inSusi-inSbsaAi-inSbsaPi
inSC:	Description:	Conductivity of the influent
	Type:	Constant Variable
	Unit:	mS/m
	Value:	208
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10000
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
inSpi:	Description:	Influent particulate COD
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	inSti-inSsi
inSsi:	Description:	Influent soluble COD
	Type:	Constant Variable
	Unit:	mgCOD/l
	Value:	292
	Standard Deviation:	1
	Minimum:	0
	Maximum:	100000
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
inSti:	Description:	Influent COD - in g COD/l
	Type:	Constant Variable
	Unit:	mgCOD/l
	Value:	1950
	Standard Deviation:	1
	Minimum:	0
	Maximum:	100000
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
inSupi:	Description:	Influent particulate COD that is unbiodegradable
	Type:	Formula Variable
	Unit:	gCOD/l
	Expression:	inSti*in_f_Sup
inSusi:	Description:	Influent soluble COD that is unbiodegradable
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	inSti*in_f_Sus
in_f_CODPS:	Description:	COD / CxHyOzNa ratio
	Type:	Formula Variable
	Unit:	mgCOD/mgSludge
	Expression:	((HydrolysisProt/2)*AW_O)/(AW_C*in_PsChon+AW_H*in_PscHon+AW_O*in_PschOn+AW_N*in_PschoN)
in_f_GlucCOD:	Description:	COD/Glucose Ratio
	Type:	Constant Variable
	Unit:	mgCOD/mg glucose
	Value:	1.0656835
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive

	Parameter Estimation:	inactive
in_f_H2COD:	Description:	COD/H2 Ratio
	Type:	Constant Variable
	Unit:	mgCOD/mgH2
	Value:	7.9368
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
in_f_HAc:	Description:	Fraction of SCFA (IN COD UNITS) that is acetic acid
	Type:	Constant Variable
	Unit:	
	Value:	1
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
in_f_HAcCOD:	Description:	COD/HAc Ratio
	Type:	Constant Variable
	Unit:	mgCOD/mgHAc
	Value:	1.06568
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
in_f_HPr:	Description:	Fraction of SCFA (IN COD UNITS) that is propionic acid
	Type:	Constant Variable
	Unit:	
	Value:	0
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
in_f_HPrCOD:	Description:	COD/HPr Ratio
	Type:	Constant Variable
	Unit:	mgCOD/mgHPr
	Value:	1.5118172
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
in_f_Sup:	Description:	Fraction of the influent total COD that is unbiodegradable
	Type:	Constant Variable
	Unit:	
	Value:	0.3345
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
in_f_Sus:	Description:	Fraction of the total influent COD that is unbiodegradable
	Type:	Constant Variable
	Unit:	
	Value:	0.008
	Standard Deviation:	1

	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
in_PsChon:	Description:	Relative proportion of carbon in fed material (Chon)
	Type:	Constant Variable
	Unit:	
	Value:	4.31
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
in_PsCHon:	Description:	Relative proportion of hydrogen in feed material (cHon)
	Type:	Constant Variable
	Unit:	
	Value:	7
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
in_PschOn:	Description:	Relative proportion of oxygen in fed material (chOn)
	Type:	Constant Variable
	Unit:	
	Value:	3.03
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
in_PschoN:	Description:	Relative proportion of nitrogen in feed material (choN)
	Type:	Constant Variable
	Unit:	
	Value:	0.24
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Ka:	Description:	Equilibrium constant for HAc<=>Ac system
	Type:	Formula Variable
	Unit:	
	Expression:	(10^(-pKa))/(fm^2)
Kc1:	Description:	Equilibrium constant for H2CO3/HCO3 system
	Type:	Formula Variable
	Unit:	
	Expression:	(10^(-pKc1))/(fm^2)
Kc2:	Description:	Equilibrium constant for HCO3/CO3 system
	Type:	Formula Variable
	Unit:	
	Expression:	(10^(-pKc2))/(fd)
Kfa:	Description:	Forward dissociation constant for Hac <-> Ac + H
	Type:	Formula Variable
	Unit:	/s

	Expression:	Kra*((10^(-pKa))/(fm^2))
Kfc1:	Description:	Forward dissociation constant for H 2CO3 <-> HCO3 + H
	Type:	Formula Variable
	Unit:	/s
	Expression:	Krc1*((10^(-pKc1))/(fm^2))
Kfc2:	Description:	Forward dissociation constant for H CO3 <-> CO3 + H
	Type:	Formula Variable
	Unit:	/s
	Expression:	Krc2*((10^(-pKc2))/(fd))
KfH2S:	Description:	Forward dissociation constant for H 2S <-> HS + H
	Type:	Formula Variable
	Unit:	/s
	Expression:	KrH2S*((10^(-pKH2S))/(fm^2))
KfHSO4:	Description:	forward dissociation for HSO4 <-> H + SO4
	Type:	Formula Variable
	Unit:	
	Expression:	KrHSO4*((10^(-pKHSO4))/fd)
Kfn:	Description:	Forward dissociation constant for N H4 <-> NH3 + H
	Type:	Formula Variable
	Unit:	/s
	Expression:	Krn*(10^(-pKn))
Kfp1:	Description:	Forward dissociation constant for H 3PO4 <-> H2PO4 + H
	Type:	Formula Variable
	Unit:	/s
	Expression:	Krp1*((10^(-pKp1))/(fm^2))
Kfp2:	Description:	Forward dissociation constant for H 2PO4 <-> HPO4 + H
	Type:	Formula Variable
	Unit:	/s
	Expression:	Krp2*((10^(-pKp2))/(fd))
Kfp3:	Description:	Forward dissociation constant for H PO4 <-> PO4 + H
	Type:	Formula Variable
	Unit:	/s
	Expression:	Krp3*((10^(-pKp3))*(fd/(ft*fm)))
KfPr:	Description:	Forward dissociation constant for H Pr <-> Pr + H
	Type:	Formula Variable
	Unit:	/s
	Expression:	KrPr*((10^(-pKPr))/(fm^2))
KfW:	Description:	Forward dissociation constant for H 2O <-> OH(-) + H
	Type:	Formula Variable
	Unit:	/s
	Expression:	KrW*((10^(-pKW))/(fm^2))
KH2:	Description:	Hydrogen inhibition constant
	Type:	Constant Variable
	Unit:	mol H2 / l
	Value:	0.000625
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive

KH2S:	Description:	Equilibrium constant for H2S <-> HS +H
	Type:	Formula Variable
	Unit:	
	Expression:	(10^(-pKH2S))/(fm^2)
KH2Sgas:	Description:	Henry's law constant
	Type:	Formula Variable
	Unit:	
	Expression:	0.011*exp(-2300*(1/Tk-1/298.15))
KHCO2:	Description:	Henry's Law constant
	Type:	Formula Variable
	Unit:	mol/l.atm
	Expression:	10^(-pKHCO2)
KHSO4:	Description:	equilibrium constant for HSO4 <-> H + SO4
	Type:	Formula Variable
	Unit:	
	Expression:	(10^(-pKHSO4))/fd
KImol_as:	Description:	Acetotrophic SRB inhibition sonstan t
	Type:	Formula Variable
	Unit:	molS/l
	Expression:	KI_as/MWH2S
KImol_hs:	Description:	Hydrogenotrophic SRB inhibition con stant
	Type:	Formula Variable
	Unit:	molS/l
	Expression:	KI_hs/MWH2S
KImol_ps:	Description:	Propionate degrading SRB inhibition constant
	Type:	Formula Variable
	Unit:	molS/l
	Expression:	KI_ps/MWH2S
KI_as:	Description:	Acetogrophic SRB inhibition constan t
	Type:	Constant Variable
	Unit:	gS/l
	Value:	0.164
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
KI_hs:	Description:	Hydrogenotrophic SRB inhibition con stant
	Type:	Constant Variable
	Unit:	gS/l
	Value:	0.55
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
KI_ps:	Description:	Propionate degrading SRB inhibition constant
	Type:	Constant Variable
	Unit:	gS/l
	Value:	0.185
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10

	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive

Kmax_Hyd:	Description:	Maximum rate constant for hydrolysis
	Type:	Constant Variable
	Unit:	molSbp/molZAD
	Value:	1.743
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1000
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive

Kn:	Description:	Equilibrium constant for NH3/NH4 system
	Type:	Formula Variable
	Unit:	
	Expression:	10^(-pKn)

KNmol_as:	Description:	Acetotrophic SRB half saturation constant for Sulphate
	Type:	Formula Variable
	Unit:	mol substrate/l
	Expression:	KN_as/MWHSO4

KNmol_hs:	Description:	Hydrogenotrophic SRB half saturation constant for Sulphate
	Type:	Formula Variable
	Unit:	mol substrate/l
	Expression:	KN_hs/MWHSO4

KNmol_ps:	Description:	Propionate degrading SRB half saturation constant for Sulphate
	Type:	Formula Variable
	Unit:	mol substrate/l
	Expression:	KN_ps/MWHSO4

KN_as:	Description:	Acetogrophic SRB half saturation constant for sulphate
	Type:	Constant Variable
	Unit:	g/l
	Value:	0.0192
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive

KN_hs:	Description:	Hydrogenotrophic SRB half saturation constant for sulphate
	Type:	Constant Variable
	Unit:	g/l
	Value:	0.0192
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive

KN_ps:	Description:	Propionate degrading SRB half saturation constant for Sulphate
	Type:	Constant Variable
	Unit:	g/l
	Value:	0.0074
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive

Kp:	Description:	Equilibrium constant for HPr<=>Pr system
	Type:	Formula Variable
	Unit:	
	Expression:	(10^(-pKPr))/(fm^2)
Kra:	Description:	Reverse dissociation constant for Hac <-> Ac + H
	Type:	Constant Variable
	Unit:	/s
	Value:	10000000
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+015
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Krc1:	Description:	Reverse dissociation constant for H2CO3 <-> HCO3 + H
	Type:	Constant Variable
	Unit:	/s
	Value:	10000000
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+010
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Krc2:	Description:	Reverse dissociation constant for HCO3 <->CO3 + H
	Type:	Constant Variable
	Unit:	/s
	Value:	1e+010
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+010
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
KrCO2:	Description:	Dissociation constant for CO2 expulsion
	Type:	Constant Variable
	Unit:	/s
	Value:	1e+012
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+015
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
KrH2S:	Description:	Reverse dissociation constant for H2S <-> H + HS
	Type:	Constant Variable
	Unit:	/s
	Value:	1e+010
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+015
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
KrH2Sgas:	Description:	Dissociation constant for H2S expulsion
	Type:	Constant Variable
	Unit:	/s
	Value:	1e+012
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+015
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive

KrHSO4:	Description:	Reverse dissociation constant for HSO4 <-> H + SO4
	Type:	Constant Variable
	Unit:	/s
	Value:	1e+008
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+015
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Krn:	Description:	Reverse dissociation constant for NH4 <-> NH3 + H
	Type:	Constant Variable
	Unit:	/s
	Value:	1e+012
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+015
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Krp1:	Description:	Reverse dissociation constant for H3PO4 <-> H2PO4 + H
	Type:	Constant Variable
	Unit:	/s
	Value:	1e+008
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+010
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Krp2:	Description:	Reverse dissociation constant for H2PO4 <-> HPO4 + H
	Type:	Constant Variable
	Unit:	/s
	Value:	1e+012
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+020
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Krp3:	Description:	Reverse dissociation constant for HPO4 <-> PO4 + H
	Type:	Constant Variable
	Unit:	/s
	Value:	1e+015
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+020
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
KrPr:	Description:	Reverse dissociation constant for HPr <-> Pr + H
	Type:	Constant Variable
	Unit:	/s
	Value:	10000000
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+015
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
KrW:	Description:	Reverse dissociation constant for H2O <-> OH(-) + H
	Type:	Constant Variable
	Unit:	/s

	Value:	1e+010
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1e+015
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
KSmol_as:	Description:	Acetotrophic SRB half saturation constant for organic substrate
	Type:	Formula Variable
	Unit:	mol substrate/l
	Expression:	KS_as*((1/in_f_HAcCOD)/MW_HAc)
KSmol_hs:	Description:	Hydrogenotrophic SRB half saturation constant for organic substrate
	Type:	Formula Variable
	Unit:	mol substrate/l
	Expression:	KS_hs*((1/in_f_H2COD)/MWH2)
KSmol_ps:	Description:	Propionate degrading SRB half saturation constant for organic substrate
	Type:	Formula Variable
	Unit:	mol substrate/l
	Expression:	KS_ps*((1/in_f_HPrCOD)/MW_HPr)
Ks_AC:	Description:	Acetogen half saturation constant
	Type:	Constant Variable
	Unit:	mol substrate/l
	Value:	0.0026786
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Ks_AD:	Description:	Acidogen half saturation constant
	Type:	Constant Variable
	Unit:	mol substrate/l
	Value:	0.000781
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Ks_AM:	Description:	Acetoclastic methanogen half saturation constant
	Type:	Constant Variable
	Unit:	mol substrate/l
	Value:	1.3e-005
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
KS_as:	Description:	Acetotrophic SRB half saturation constant for organic substrate
	Type:	Constant Variable
	Unit:	gCOD/l
	Value:	0.024
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Ks_HM:	Description:	Hydrogenotrophic methanogen half saturation constant
	Type:	Constant Variable

	Unit:	mol substrate/l
	Value:	0.000156
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
KS_hs:	Description:	Hydroogenotrophic SRB half saturation constant for organic substrate
	Type:	Constant Variable
	Unit:	gCOD/l
	Value:	7e-005
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Ks_Hyd:	Description:	Half saturation constant for hydrolysis
	Type:	Constant Variable
	Unit:	molSbp/molZAD
	Value:	0.01485
	Standard Deviation:	1
	Minimum:	0
	Maximum:	1000
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
KS_ps:	Description:	Propionate degrading SRB half saturation constant for organic substrate
	Type:	Constant Variable
	Unit:	gCOD/l
	Value:	0.295
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Kw:	Description:	Equilibrium constant for water system
	Type:	Formula Variable
	Unit:	
	Expression:	(10^(-pKW))/(fm^2)
K_NH4:	Description:	Half saturation for ammonia for growth
	Type:	Formula Variable
	Unit:	molN/l
	Expression:	0.01/18
muMax_AC:	Description:	Maximum specific growth rate of the acetogens
	Type:	Constant Variable
	Unit:	/d
	Value:	1.15
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
muMax_AD:	Description:	Maximum specific acidogen growth rate constant
	Type:	Constant Variable
	Unit:	/d
	Value:	0.8
	Standard Deviation:	1

	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
muMax_AM:	Description:	Maximum specific acetoclastic methanogen growth rate const.
	Type:	Constant Variable
	Unit:	/d
	Value:	0.3
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
muMax_as:	Description:	Maximum specific acetoclastic Aceotrophic SRB growth rate constant
	Type:	Constant Variable
	Unit:	/d
	Value:	0.612
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
muMax_HM:	Description:	Maximum specific hydrogenotrophic methanogen growth rate const.
	Type:	Constant Variable
	Unit:	/d
	Value:	0.86
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
muMax_hs:	Description:	Maximum specific Hydrogenotrophic SRB growth rate constant
	Type:	Constant Variable
	Unit:	/d
	Value:	2.8
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
muMax_ps:	Description:	Maximum specific Propionate degrading SRB growth rate constant
	Type:	Constant Variable
	Unit:	/d
	Value:	0.583
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
MWH2:	Description:	Molecular weight of H2
	Type:	Formula Variable
	Unit:	g
	Expression:	(2*AW_H)
MWH2S:	Description:	Molecular weight of H2S
	Type:	Formula Variable
	Unit:	g
	Expression:	(2*AW_H)+AW_S
MWHS:	Description:	Molecular weight of HS

	Type:	Formula Variable
	Unit:	g
	Expression:	(AW_H)+AW_S
MWHSO4:	Description:	Molecular wight of HSO4
	Type:	Formula Variable
	Unit:	g
	Expression:	AW_H+AW_S+(4*AW_O)
MWS:	Description:	Molecular weight of S
	Type:	Formula Variable
	Unit:	g
	Expression:	AW_S
MWSO4:	Description:	Molecular wight of HSO4
	Type:	Formula Variable
	Unit:	g
	Expression:	AW_S+(4*AW_O)
MW_C5H7O2N:	Description:	Molecular weight of organisms
	Type:	Formula Variable
	Unit:	g
	Expression:	(5*AW_C)+(7*AW_H)+(2*AW_O)+AW_N
MW_CaCO3:	Description:	Molecular weight of CaCO3
	Type:	Formula Variable
	Unit:	g
	Expression:	40.078+(AW_C*1)+(AW_O*3)
MW_CO2:	Description:	Molecular weight of CO2
	Type:	Formula Variable
	Unit:	g
	Expression:	AW_C+(2*AW_O)
MW_Glucose:	Description:	Molecular weight of glucose (C6H12O 6)
	Type:	Formula Variable
	Unit:	g
	Expression:	(6*AW_C)+(12*AW_H)+(6*AW_O)
MW_HAc:	Description:	Molecular weight of Hac
	Type:	Formula Variable
	Unit:	g
	Expression:	(AW_C*2)+(AW_H*4)+(AW_O*2)
MW_HPr:	Description:	Molecular weight of HPr
	Type:	Formula Variable
	Unit:	g
	Expression:	(AW_C*3)+(AW_H*6)+(AW_O*2)
MW_NH3:	Description:	Molecular weight of NH3
	Type:	Formula Variable
	Unit:	g
	Expression:	AW_N+(3*AW_H)
MW_NH4:	Description:	Molecular weight of NH4
	Type:	Formula Variable
	Unit:	g
	Expression:	AW_N+(4*AW_H)
NH3mol:	Description:	stoichiometry for endogenous respir ation for all organisms groups
	Type:	Formula Variable
	Unit:	mol
	Expression:	(in_PscHon+4*in_PsChon-2*in_PschOn-23*in_PschoN)/(in_PscHon+4*in_PscHon-2*in_PschOn-3*in_PschoN)
NT:	Description:	Total dissolved nitrogen species co ncentration in digester
	Type:	Formula Variable

	Unit:	mol/l
	Expression:	C2_NH3+C1_B10_NH4
outALK:	Description:	H2CO3* alkalinity in effluent
	Type:	Formula Variable
	Unit:	mg/l as CaCO3
	Expression:	(ALKmol*MW_CaCO3*1000)/2
outALKmol:	Description:	H2CO3* alkalinity in effluent
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	ALKmol
outCODbp:	Description:	CODbp converted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	(D1_Sbp*(AW_C*in_PsChon+AW_H*in_PscHon+AW_O*in_PschOn+AW_N*in_PschoN))*1000*in_f_CODPS
outCODbs:	Description:	CODbs converted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	D2_B2_Sbsf*MW_Glucose*1000*in_f_GlucCOD
outCODsol_H2S_HS:		
	Description:	COD of H2S/HS
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	(out_H2S+out_HS)*1.996
outCODsol_organic:		
	Description:	Total soluble COD out
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	outCODbs+outCODus+outHAc_Ac+outHPr_Pr
outCODtot:	Description:	Total COD out
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	outCODtotpart+outCODtotsol
outCODtotpart:	Description:	Total particulate COD out
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	outCODbp+outCODup+out_ZAC+out_ZAD+out_ZAM+out_ZHM+Xa_ps_out+Xa_hs_out+Xa_as_out
outCODtotsol:	Description:	Total soluble COD out
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	outCODbs+outCODus+outHAc_Ac+outHPr_Pr+outCODsol_H2S_HS
outCODup:	Description:	CODup converted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	B3_CODup*1000
outCODup_mol:	Description:	CODup converted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	(((B3_CODup*1000)/in_f_CODPS)/1000)/(AW_C*in_PsChon+AW_H*in_PscHon+AW_O*in_PschOn+AW_N*in_PschoN)
outCODus:	Description:	CODus converted to mgCOD/l
	Type:	Formula Variable

	Unit:	mgCOD/l
	Expression:	B1_CODus*1000
outFSA:	Description:	Total effluent ammonia system converted to mgN/l
	Type:	Formula Variable
	Unit:	mgN/l
	Expression:	((C2_NH3*MW_NH3)+(C1_B10_NH4*MW_NH4))*1000
outHAc_Ac:	Description:	Total effluent acetate system converted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	(C13_HAc*MW_HAc*1000*in_f_HAcCOD)+(C14_Ac*(MW_HAc-AW_H)*1000*in_f_HAcCOD)
outHPr_Pr:	Description:	Total effluent propionate system converted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	(C28_HPr*MW_HPr*1000*in_f_HPrCOD)+(C29_Pr*(MW_HPr-AW_H)*1000*in_f_HPrCOD)
out_CH4_Volume:	Description:	Convert mol/l CH4 to l/linfluent
	Type:	Formula Variable
	Unit:	l/l influent
	Expression:	(P4_CH4*R*Tk_Gas)/pATM
out_CO2_Volume:	Description:	Convert mol/l CO2 to l/linfluent
	Type:	Formula Variable
	Unit:	l/l influent
	Expression:	(P1_C6_CO2gas*R*Tk_Gas)/pATM
out_Gas_PerMethane:		
	Description:	% Methane Gas
	Type:	Formula Variable
	Unit:	%
	Expression:	(out_CH4_Volume*100)/out_Gas_Volume
out_Gas_Volume:	Description:	Total gas volume produced
	Type:	Formula Variable
	Unit:	l gas / l influent
	Expression:	out_CH4_Volume+out_CO2_Volume+out_H2S_Volume
out_H2S:	Description:	Effluent H2S Concentration
	Type:	Formula Variable
	Unit:	mg/l
	Expression:	C32_H2S*1000*34.0818
out_H2S_Volume:	Description:	Convert mol/l H2S to l/linfluent
	Type:	Formula Variable
	Unit:	l/l influent
	Expression:	(C33_H2Sgas*R*Tk_Gas)/pATM
out_HS:	Description:	Effluent HS Concentration
	Type:	Formula Variable
	Unit:	mg/l
	Expression:	C34_HS*1000*33.0739
out_HSO4:	Description:	Effluent HSO4 Concentration
	Type:	Formula Variable
	Unit:	mg/l
	Expression:	C30_HSO4*1000*97.0705
out_pH:	Description:	pH of effluent
	Type:	Formula Variable
	Unit:	

	Expression:	pH
out_SO4:	Description:	Effluent SO4 Concentration
	Type:	Formula Variable
	Unit:	mg/l
	Expression:	C31_SO4*1000*96.062
out_ZAC:	Description:	Z_AC converted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	D5_Z_AC*MW_C5H7O2N*1000*f_C5H7O2NCOD
out_ZAD:	Description:	Z_ADconverted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	D4_Z_AD*MW_C5H7O2N*1000*f_C5H7O2NCOD
out_ZAM:	Description:	Z_AM converted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	D6_Z_AM*MW_C5H7O2N*1000*f_C5H7O2NCOD
out_Zas:	Description:	Z_as converted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	S2_Zas*MW_C5H7O2N*1000*f_C5H7O2NCOD
out_ZHM:	Description:	Z_HM converted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	D7_Z_HM*MW_C5H7O2N*1000*f_C5H7O2NCOD
out_Zhs:	Description:	Z_hs converted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	S3_Zhs*MW_C5H7O2N*1000*f_C5H7O2NCOD
out_Zps:	Description:	Z_ps converted to mgCOD/l
	Type:	Formula Variable
	Unit:	mgCOD/l
	Expression:	S1_Zps*MW_C5H7O2N*1000*f_C5H7O2NCOD
P1_C6_CO2gas:	Description:	Gaseous carbon dioxide concentration
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
P4_CH4:	Description:	Methane gas concentration
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
pATM:	Description:	Atmospheric pressure at sea level
	Type:	Formula Variable
	Unit:	atm
	Expression:	0.9869
pCO2:	Description:	Partial pressure of CO2
	Type:	Formula Variable
	Unit:	atm
	Expression:	P1_C6_CO2gas/(P4_CH4+P1_C6_CO2gas+C33_H2Sgas)
pH:	Description:	pH of the solution

	Type:	Formula Variable
	Unit:	
	Expression:	-log10(C7_H*fm)
pH2S:	Description:	Partial pressure of H2S
	Type:	Formula Variable
	Unit:	atm
	Expression:	C33_H2Sgas/(P4_CH4+P1_C6_CO2gas+C33_H2Sgas)
pKa:	Description:	pK constant for Hac <-> Ac + H
	Type:	Formula Variable
	Unit:	
	Expression:	(1170.5/Tk)-3.165+(0.0134*Tk)
pKc1:	Description:	pK constant for H2CO3 <-> HCO3 + H
	Type:	Formula Variable
	Unit:	
	Expression:	(3404.7/Tk)-14.8435+(0.03279*Tk)
pKc2:	Description:	pK constant for HCO3 <-> CO3 + H
	Type:	Formula Variable
	Unit:	
	Expression:	(2902.4/Tk)-6.498+(0.02379*Tk)
pKH2S:	Description:	pk constant for H2S <-> HS + H
	Type:	Formula Variable
	Unit:	
	Expression:	7+(1132.18/Tk)-3.7993
pKHCO2:	Description:	pK constant for the dissolution of CO2
	Type:	Formula Variable
	Unit:	
	Expression:	-(2025.3/Tk)-(0.0104*Tk)+11.365
pKHSO4:	Description:	pK constant for HSO4 <-> H +SO4
	Type:	Formula Variable
	Unit:	
	Expression:	1.99
pKn:	Description:	pK constant for NH4 <-> NH3 + H
	Type:	Formula Variable
	Unit:	
	Expression:	(2835.8/Tk)-0.6322+(0.00123*Tk)
pKp1:	Description:	pK constant for H3PO4 <-> H2PO4 + H
	Type:	Formula Variable
	Unit:	
	Expression:	(799.3/Tk)-4.5535+(0.01349*Tk)
pKp2:	Description:	pK constant for H2PO4 <-> HPO4 + H
	Type:	Formula Variable
	Unit:	
	Expression:	(1979.5/Tk)-5.3541+(0.01984*Tk)
pKp3:	Description:	pK constant for HPO4 <-> PO4 + H
	Type:	Formula Variable
	Unit:	
	Expression:	12.023
pKPr:	Description:	pK constant for HPr <-> Pr + H
	Type:	Formula Variable
	Unit:	
	Expression:	(1170.5/Tk)-3.165+(0.0134*Tk)
pKW:	Description:	pK constant for dissociation of water
	Type:	Formula Variable
	Unit:	
	Expression:	14

Pr_init:	Description:	Initial Pr concentration in the reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(PT_init*Kp)/(vinit_H+Kp)
PT_init:	Description:	Initial concentration of propionate in the anaerobic reactor
	Type:	Constant Variable
	Unit:	mol/l
	Value:	0.029
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Qi:	Description:	Influent flow
	Type:	Formula Variable
	Unit:	l/d
	Expression:	Vr/Rs
Qin:	Description:	Influent flow for H+ dose
	Type:	Formula Variable
	Unit:	l/d
	Expression:	0.001
R:	Description:	Universal gas constant
	Type:	Constant Variable
	Unit:	l.atm/K.mol
	Value:	0.0820575
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Rs:	Description:	Retention time in the reactor
	Type:	Constant Variable
	Unit:	d
	Value:	10
	Standard Deviation:	1
	Minimum:	0
	Maximum:	70
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
S1_Zps:	Description:	Prorionate Degrading SRB biomass concentration
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
S2_Zas:	Description:	Acetotrophic biomass concentration
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
S3_Zhs:	Description:	Hydrogenotrophic SRB biomass concentration
	Type:	Dyn. Volume State Var.
	Unit:	mol/l
	Relative Accuracy:	1e-006
	Absolute Accuracy:	1e-006
Sbp:	Description:	Stoichiometry for the endogenous respiration af all organism groups
	Type:	Formula Variable

	Unit:	mol
	Expression:	20/(in_PscHon+4*in_PsChon-2*in_Psch On-3*in_PschoN)
SC:	Description:	Specific conductivity
	Type:	Formula Variable
	Unit:	mS/m
	Expression:	inSC
SO4_in:	Description:	Influent SO4
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(KHSO4*(SulphateT_in/1000/MWSO4))/(inH+KHSO4)
SO4_init:	Description:	Initial SO4 consentration in the re actor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(SulphateT_init*KHSO4)/(vinit_H+KHS O4)
St:	Description:	Total sulphate species
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	C32_H2S+C34_HS
SulphateT_in:	Description:	Total influent Sulphate species
	Type:	Constant Variable
	Unit:	mgSO4/l
	Value:	2000
	Standard Deviation:	1
	Minimum:	0
	Maximum:	100000
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
SulphateT_init:	Description:	Initial sSulpahte concentration in the reactor
	Type:	Constant Variable
	Unit:	molSO4/l
	Value:	0.048
	Standard Deviation:	1
	Minimum:	0
	Maximum:	100
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
SulphideT_in:	Description:	Total influenty Sulphide species
	Type:	Constant Variable
	Unit:	mgS/l
	Value:	0
	Standard Deviation:	1
	Minimum:	0
	Maximum:	100
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
SulphideT_init:	Description:	Initial Sulphide concentration in t he reactor
	Type:	Constant Variable
	Unit:	molS/l
	Value:	0.01
	Standard Deviation:	1
	Minimum:	0
	Maximum:	100
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Tc:	Description:	Temperature in degrees Celsius
	Type:	Constant Variable

	Unit:	deg. C
	Value:	35
	Standard Deviation:	1
	Minimum:	0
	Maximum:	50
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Tc_Gas:	Description:	Temperature of gas environment
	Type:	Constant Variable
	Unit:	Deg. Celsius
	Value:	20
	Standard Deviation:	1
	Minimum:	0
	Maximum:	100
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Tk:	Description:	Deg. Celsius temperature conversion to deg. Kelvin
	Type:	Formula Variable
	Unit:	deg. K
	Expression:	Tc+273.15
Tk_Gas:	Description:	Deg. Celsius temperature conversion to deg. Kelvin
	Type:	Formula Variable
	Unit:	deg. K
	Expression:	Tc_Gas+273.15
vinit_Ac:	Description:	Initial concentration of Ac species in reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(vinit_AT*Ka)/(vinit_H+Ka)
vinit_ALK:	Description:	Initial alkalinity in reactor
	Type:	Formula Variable
	Unit:	mg/l as CaCO3
	Expression:	(vinit_ALKmol*MW_CaCO3*1000)/2
vinit_ALKmol:	Description:	Initial alkalinity in reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(2*vinit_CO3)+vinit_HCO3+vinit_OH-vinit_H
vinit_AT:	Description:	Initial total At species
	Type:	Constant Variable
	Unit:	mol/l
	Value:	0.029
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
vinit_CH4:	Description:	Initial methane value
	Type:	Constant Variable
	Unit:	mol/l
	Value:	0.22
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
vinit_CO2gas:	Description:	Initial CO2 gas value
	Type:	Constant Variable
	Unit:	mol/l
	Value:	0.2333

	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
vinit_CO3:	Description:	Initial concentration of CO3 species in reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	vinit_CT/(((vinit_H^2)/(Kc1*Kc2))+(vinit_H/Kc2)+1)
vinit_CODbp:	Description:	Initial concentration of CODbp species in reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	inSbpi_mol
vinit_CODbs:	Description:	Initial glucose concentration in reactor
	Type:	Constant Variable
	Unit:	mol/l
	Value:	0.1237
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
vinit_CT:	Description:	Initial total dissolved carbon species
	Type:	Constant Variable
	Unit:	mol/l
	Value:	0.0133
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
vinit_H:	Description:	Initial H species concentration
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(10^(-vinit_pH))/fm
vinit_H2:	Description:	Initial H2 conc. in anaerobic reactor
	Type:	Constant Variable
	Unit:	mol/l
	Value:	0.01
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
vinit_H2CO3:	Description:	Initial concentration of H2CO3 species in reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	vinit_CT/(1+(Kc1/vinit_H)+((Kc1*Kc2)/(vinit_H)^2))
vinit_H2Sgas:	Description:	Initial H2S gas value
	Type:	Constant Variable
	Unit:	mol/l
	Value:	0.2333
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10

	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
vinit_HAc:	Description:	Initial concentration of HAc species in reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(vinit_AT*vinit_H)/(vinit_H+Ka)
vinit_HCO3:	Description:	Initial concentration of HCO3 species in reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	vinit_CT/((vinit_H/Kc1)+1+(Kc2/vinit_H))
vinit_NH3:	Description:	Initial concentration of NH3 species in reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(vinit_NT*Kn)/(vinit_H+Kn)
vinit_NH4:	Description:	Initial concentration of NH4 species in reactor
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(vinit_NT*vinit_H)/(vinit_H+Kn)
vinit_NT:	Description:	Initial total dissolved nitrogen species
	Type:	Constant Variable
	Unit:	mol/l
	Value:	0.0109
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
vinit_OH:	Description:	Initial OH species concentration
	Type:	Formula Variable
	Unit:	mol/l
	Expression:	(10^(-(14-vinit_pH)))/fm
vinit_pH:	Description:	Initial pH in the digester
	Type:	Formula Variable
	Unit:	
	Expression:	inpH
vinit_ZAC:	Description:	Initial acetogen conc. in anaerobic reactor
	Type:	Constant Variable
	Unit:	mol/l
	Value:	0.0001778
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
vinit_ZAD:	Description:	Initial acidogen conc. in anaerobic reactor
	Type:	Constant Variable
	Unit:	mol/l
	Value:	0.008317
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive

	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Xa_ps_out:	Description:	Xa_ps converted to mg COD/l
	Type:	Formula Variable
	Unit:	mg COD/l
	Expression:	S1_Zps*MW_C5H7O2N*1000*f_C5H7O2NCOD
Y_AC:	Description:	Acetogen yield coefficient
	Type:	Constant Variable
	Unit:	mol organism/mol substrate
	Value:	0.0278
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Y_AD:	Description:	Acidogenic yield coefficient
	Type:	Constant Variable
	Unit:	mol org/mol substrate
	Value:	0.1074
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Y_AM:	Description:	Acetoclastic methanogen yield coefficient
	Type:	Constant Variable
	Unit:	mol organism/mol substrate
	Value:	0.0157
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Y_as:	Description:	Acetotrophic SRB Yield coefficient
	Type:	Constant Variable
	Unit:	mol org/mol substrate
	Value:	0.0188
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Y_HM:	Description:	Hydrogenotrophic methanogen yield coefficient
	Type:	Constant Variable
	Unit:	mol organism/mol substrate
	Value:	0.004
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive
	Parameter Estimation:	inactive
Y_hs:	Description:	Hydrogenotrophic SRB Yield coefficient
	Type:	Constant Variable
	Unit:	mol org/mol substrate
	Value:	0.0070719
	Standard Deviation:	1
	Minimum:	0
	Maximum:	10
	Sensitivity Analysis:	inactive

Parameter Estimation: inactive

Y_ps: Description: Prorionate Degrading SRB Yield coef ficient
Type: Constant Variable
Unit: mol org/mol substrate
Value: 0.02688
Standard Deviation: 1
Minimum: 0
Maximum: 10
Sensitivity Analysis: inactive
Parameter Estimation: inactive

****

****

Processes

****

C10_RevDissH3PO4:
Description: Reverse dissociation of phosphoric acid
Type: Dynamic Process
Rate: Krp1*C10_H2PO4*C7_H
Stoichiometry:
Variable : Stoichiometric Coefficient
C9_H3PO4 : 1
C10_H2PO4 : -1
C7_H : -1

C11_ForDissH2PO4:
Description: Forward dissociation of H2PO4
Type: Dynamic Process
Rate: Kfp2*C10_H2PO4
Stoichiometry:
Variable : Stoichiometric Coefficient
C10_H2PO4 : -1
C11_HPO4 : 1
C7_H : 1

C12_RevDissH2PO4:
Description: Reverse dissociation of H2PO4
Type: Dynamic Process
Rate: Krp2*C11_HPO4*C7_H
Stoichiometry:
Variable : Stoichiometric Coefficient
C10_H2PO4 : 1
C11_HPO4 : -1
C7_H : -1

C13_ForDissHPO4:
Description: Forward dissociation of HPO4
Type: Dynamic Process
Rate: Kfp3*C11_HPO4
Stoichiometry:
Variable : Stoichiometric Coefficient
C11_HPO4 : -1
C12_PO4 : 1
C7_H : 1

C14_RevDissHPO4:
Description: Reverse dissociation of HPO4
Type: Dynamic Process
Rate: Krp3*C12_PO4*C7_H
Stoichiometry:
Variable : Stoichiometric Coefficient
C11_HPO4 : 1
C12_PO4 : -1
C7_H : -1

```
C15_ForDissHAc:Description:          Forward dissociation of acetic acid
               Type:                 Dynamic Process
               Rate:                 Kfa*C13_HAc
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C7_H : 1
                 C13_HAc : -1
                 C14_Ac : 1
-------------------------------------------------------------------------
C16_RevDissHAc:Description:          Reverse dissociation of acetic acid
               Type:                 Dynamic Process
               Rate:                 Kra*C14_Ac*C7_H
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C7_H : -1
                 C13_HAc : 1
                 C14_Ac : -1
-------------------------------------------------------------------------
C17_ForDissH2O:Description:          Forward dissociation of water
               Type:                 Dynamic Process
               Rate:                 KfW
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C7_H : 1
                 C8_OH : 1
-------------------------------------------------------------------------
C18_RevDissH2O:Description:          Reverse dissociation of water
               Type:                 Dynamic Process
               Rate:                 KrW*C7_H*C8_OH
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C7_H : -1
                 C8_OH : -1
-------------------------------------------------------------------------
C1_ForDissNH4: Description:          Forward dissociation of ammonium io
                                     n
               Type:                 Dynamic Process
               Rate:                 Kfn*C1_B10_NH4
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C1_B10_NH4 : -1
                 C2_NH3 : 1
                 C7_H : 1
-------------------------------------------------------------------------
C2_RevDissNH4: Description:          Reverse dissociation of ammonium io
                                     n
               Type:                 Dynamic Process
               Rate:                 Krn*C2_NH3*C7_H
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C1_B10_NH4 : 1
                 C2_NH3 : -1
                 C7_H : -1
-------------------------------------------------------------------------
C3_ForDissH2CO3:
               Description:          Forward dissociation of carbonic ac
                                     id plus dissolved CO2
               Type:                 Dynamic Process
               Rate:                 Kfc1*C3_H2CO3
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C3_H2CO3 : -1
                 C4_HCO3 : 1
                 C7_H : 1
-------------------------------------------------------------------------
C46_ForDissHPr:Description:          Forward dissociation of propionic a
                                     cid
               Type:                 Dynamic Process
               Rate:                 KfPr*C28_HPr
               Stoichiometry:
```

```
                Variable : Stoichiometric Coefficient
                C28_HPr : -1
                C7_H : 1
                C29_Pr : 1
-------------------------------------------------------------------------
C47_RevDissHPr:Description:          Reverse dissociation of propionic a
                                     cid
               Type:                 Dynamic Process
               Rate:                 KrPr*C29_Pr*C7_H
               Stoichiometry:
                Variable : Stoichiometric Coefficient
                C28_HPr : 1
                C7_H : -1
                C29_Pr : -1
-------------------------------------------------------------------------
C48_forwdissHSO4:
               Description:          forward dissociation of HSO4
               Type:                 Dynamic Process
               Rate:                 KfHSO4*C30_HSO4
               Stoichiometry:
                Variable : Stoichiometric Coefficient
                C7_H : 1
                C30_HSO4 : -1
                C31_SO4 : 1
-------------------------------------------------------------------------
C49revdissHSO4:Description:          Reverse dissociation of HSO4
               Type:                 Dynamic Process
               Rate:                 KrHSO4*C7_H*C31_SO4
               Stoichiometry:
                Variable : Stoichiometric Coefficient
                C7_H : -1
                C30_HSO4 : 1
                C31_SO4 : -1
-------------------------------------------------------------------------
C4_RevDissH2CO3:
               Description:          Reverse dissociation of carbonic ac
                                     id plus dissolved CO2
               Type:                 Dynamic Process
               Rate:                 Krc1*C4_HCO3*C7_H
               Stoichiometry:
                Variable : Stoichiometric Coefficient
                C3_H2CO3 : 1
                C4_HCO3 : -1
                C7_H : -1
-------------------------------------------------------------------------
C50forwdissH2S:Description:          Forward dissociation of H2S
               Type:                 Dynamic Process
               Rate:                 KfH2S*C32_H2S
               Stoichiometry:
                Variable : Stoichiometric Coefficient
                C7_H : 1
                C32_H2S : -1
                C34_HS : 1
-------------------------------------------------------------------------
C51revdissH2S: Description:          Reverse dissociation of H2S
               Type:                 Dynamic Process
               Rate:                 KrH2S*C34_HS*C7_H
               Stoichiometry:
                Variable : Stoichiometric Coefficient
                C7_H : -1
                C32_H2S : 1
                C34_HS : -1
-------------------------------------------------------------------------
C5_ForDissHCO3:Description:          Forward dissociation of bicarbonate
                                      ions
               Type:                 Dynamic Process
               Rate:                 Kfc2*C4_HCO3
               Stoichiometry:
                Variable : Stoichiometric Coefficient
                C4_HCO3 : -1
                C5_CO3 : 1
```

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                C7_H : 1
-------------------------------------------------------------------------
C6_RevDissHCO3:Description:          Reverse dissociation of bicarbonate
                                      ion
               Type:                 Dynamic Process
               Rate:                 Krc2*C5_CO3*C7_H
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C4_HCO3 : 1
                 C5_CO3 : -1
                 C7_H : -1
-------------------------------------------------------------------------
C9_ForDissH3PO4:
               Description:          Forward dissociation of phosphoric
                                     acid
               Type:                 Dynamic Process
               Rate:                 Kfp1*C9_H3PO4
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C9_H3PO4 : -1
                 C10_H2PO4 : 1
                 C7_H : 1
-------------------------------------------------------------------------
D10_EndRespHydrogenotrophicMethanogens:
               Description:          Death of hydrogenotrophic methanoge
                                     ns
               Type:                 Dynamic Process
               Rate:                 b_HM*D7_Z_HM
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 D7_Z_HM : -1
                 C3_H2CO3 : (5*(in_PscHon-2*in_PschOn-3*in_PschoN))/Hydr
                   olysisProt
                 C2_NH3 : (in_PscHon+4*in_PsChon-2*in_PschOn-23*in_Pscho
                   N)/HydrolysisProt
                 D1_Sbp : 20/HydrolysisProt
-------------------------------------------------------------------------
D1_Hydrolysis: Description:          Conversion of CODbp to CODbs (=gluc
                                     ose)
               Type:                 Dynamic Process
               Rate:                 ((Kmax_Hyd*(D1_Sbp/D4_Z_AD))/(Ks_Hy
                                     d+(D1_Sbp/D4_Z_AD)))*D4_Z_AD
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 D1_Sbp : -1
                 C3_H2CO3 : -((in_PscHon-2*in_PschOn-3*in_PschoN)/4)
                 D2_B2_Sbsf : HydrolysisProt/24
                 C2_NH3 : in_PschoN
-------------------------------------------------------------------------
D2_Acidogenisis_lowpH2:
               Description:          Acidogenisis under both high and lo
                                     w hydrogen partial pressures
               Type:                 Dynamic Process
               Rate:                 ((muMax_AD*D2_B2_Sbsf)/(Ks_AD+D2_B2
                                     _Sbsf))*(1-(D3_H2/(KH2+D3_H2)))*D4_
                                     Z_AD
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 D2_B2_Sbsf : -1/Y_AD
                 C13_HAc : (2*(1-((5*Y_AD)/6)))/Y_AD
                 D3_H2 : (4*(1-((5*Y_AD)/6)))/Y_AD
                 C3_H2CO3 : (2*(1-((5*Y_AD)/6)))/Y_AD
                 C1_B10_NH4 : -1
                 C7_H : 1
                 D4_Z_AD : 1
-------------------------------------------------------------------------
D3_Acidogenisis_highpH2:
               Description:          Acidogenisis under high hydrogen pa
                                     rtial pressure only
               Type:                 Dynamic Process
               Rate:                 ((muMax_AD*D2_B2_Sbsf)/(Ks_AD+D2_B2
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                                    _Sbsf))*(D3_H2/(KH2+D3_H2))*D4_Z_AD
              Stoichiometry:
                Variable : Stoichiometric Coefficient
                D2_B2_Sbsf : -(1/Y_AD)
                C13_HAc : (1-((5*Y_AD)/6))/Y_AD
                D3_H2 : (1-((5*Y_AD)/6))/Y_AD
                C28_HPr : (1-((5*Y_AD)/6))/Y_AD
                C1_B10_NH4 : -1
                C7_H : 1
                D4_Z_AD : 1
                C3_H2CO3 : (1-((5*Y_AD)/6))/Y_AD
-------------------------------------------------------------------------
D4_EndRespAcidogens:
              Description:          Death of Acidogens
              Type:                 Dynamic Process
              Rate:                 b_AD*D4_Z_AD
              Stoichiometry:
                Variable : Stoichiometric Coefficient
                D4_Z_AD : -1
                C3_H2CO3 : (5*(in_PscHon-2*in_PschOn-3*in_PschoN))/Hydr
                  olysisProt
                C2_NH3 : (in_PscHon+4*in_PsChon-2*in_PschOn-23*in_Pscho
                  N)/HydrolysisProt
                D1_Sbp : 20/HydrolysisProt
-------------------------------------------------------------------------
D5_Acetogenisis:
              Description:
              Type:                 Dynamic Process
              Rate:                 ((muMax_AC*C29_Pr)/(Ks_AC+C29_Pr))*
                                    (1-(D3_H2/(KH2+D3_H2)))*D5_Z_AC
              Stoichiometry:
                Variable : Stoichiometric Coefficient
                C28_HPr : -(1/Y_AC)
                C13_HAc : (1-((3*Y_AC)/2))/Y_AC
                D3_H2 : (3-4*Y_AC)/Y_AC
                C1_B10_NH4 : -1
                D5_Z_AC : 1
                C7_H : 1
                C3_H2CO3 : (1-2*Y_AC)/Y_AC
-------------------------------------------------------------------------
D6_EndRespAcetogens:
              Description:          Death of Acetogens
              Type:                 Dynamic Process
              Rate:                 b_AC*D5_Z_AC
              Stoichiometry:
                Variable : Stoichiometric Coefficient
                D5_Z_AC : -1
                C3_H2CO3 : (5*(in_PscHon-2*in_PschOn-3*in_PschoN))/Hydr
                  olysisProt
                C2_NH3 : (in_PscHon+4*in_PsChon-2*in_PschOn-23*in_Pscho
                  N)/HydrolysisProt
                D1_Sbp : 20/HydrolysisProt
-------------------------------------------------------------------------
D7_AcetoclasticMethanogenesis:
              Description:
              Type:                 Dynamic Process
              Rate:                 ((muMax_AM*C13_HAc)/(Ks_AM+C13_HAc)
                                    )*D6_Z_AM
              Stoichiometry:
                Variable : Stoichiometric Coefficient
                C13_HAc : -(1/Y_AM)
                C3_H2CO3 : (1-((5*Y_AM)/2))/Y_AM
                C1_B10_NH4 : -1
                C7_H : 1
                D6_Z_AM : 1
                P4_CH4 : (1-((5*Y_AM)/2))/Y_AM
-------------------------------------------------------------------------
D8_EndRespAcetoclasticMethanogens:
              Description:          Death of acetoclastic methanogens
              Type:                 Dynamic Process
              Rate:                 b_AM*D6_Z_AM
```

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                Stoichiometry:
                  Variable : Stoichiometric Coefficient
                  D6_Z_AM : -1
                  C3_H2CO3 : (5*(in_PscHon-2*in_PschOn-3*in_PschoN))/Hydr
                    olysisProt
                  C2_NH3 : (in_PscHon+4*in_PsChon-2*in_PschOn-23*in_Pscho
                    N)/HydrolysisProt
                  D1_Sbp : 20/HydrolysisProt
-------------------------------------------------------------------------
D9_HydrogenotrophicMethanogenesis:
                Description:
                Type:                   Dynamic Process
                Rate:                   ((muMax_HM*D3_H2)/(Ks_HM+D3_H2))*D7
                                        _Z_HM
                Stoichiometry:
                  Variable : Stoichiometric Coefficient
                  D3_H2 : -(1/Y_HM)
                  C3_H2CO3 : -((1+10*Y_HM)/(4*Y_HM))
                  C1_B10_NH4 : -1
                  C7_H : 1
                  D7_Z_HM : 1
                  P4_CH4 : ((1-10*Y_HM)/(4*Y_HM))
-------------------------------------------------------------------------
P12_DissolutionH2S:
                Description:            Dissolution of gaseous H2S into the
                                         liquid
                Type:                   Dynamic Process
                Rate:                   KrH2Sgas*pH2S*KH2Sgas
                Stoichiometry:
                  Variable : Stoichiometric Coefficient
                  C32_H2S : 1
                  C33_H2Sgas : -1
-------------------------------------------------------------------------
P13_ExpulsionH2S:
                Description:            Expulsion of dissolved H2S from the
                                         liquid
                Type:                   Dynamic Process
                Rate:                   KrH2Sgas*C32_H2S
                Stoichiometry:
                  Variable : Stoichiometric Coefficient
                  C32_H2S : -1
                  C33_H2Sgas : 1
-------------------------------------------------------------------------
P6_C7_DissolutionCO2:
                Description:            Dissolution of gaseous CO2 into the
                                         liquid
                Type:                   Dynamic Process
                Rate:                   KrCO2*pCO2*KHCO2
                Stoichiometry:
                  Variable : Stoichiometric Coefficient
                  C3_H2CO3 : 1
                  P1_C6_CO2gas : -1
-------------------------------------------------------------------------
P7_C8_ExpulsionCO2:
                Description:            Expulsion of dissolved carbon dioxi
                                        de from the liquid
                Type:                   Dynamic Process
                Rate:                   KrCO2*C3_H2CO3
                Stoichiometry:
                  Variable : Stoichiometric Coefficient
                  C3_H2CO3 : -1
                  P1_C6_CO2gas : 1
-------------------------------------------------------------------------
S1_Zps_decay:   Description:            Endogenous decay of propionate degr
                                        ading SRB
                Type:                   Dynamic Process
                Rate:                   bps*S1_Zps
                Stoichiometry:
                  Variable : Stoichiometric Coefficient
                  C2_NH3 : NH3mol
                  C3_H2CO3 : H2CO3mol
```

```
                D1_Sbp : Sbp
                S1_Zps : -1
-------------------------------------------------------------------------
S2_Zps_growth: Description:          Growth of propionate degrading SRB
               Type:                 Dynamic Process
               Rate:                 ((muMax_ps*C28_HPr)/((KSmol_ps*(C28
                                     _HPr/(C28_HPr+C29_Pr)))+C28_HPr))*(
                                     C31_SO4/(KNmol_ps+C31_SO4))*(C1_B10
                                     _NH4/(K_NH4+C1_B10_NH4))*S1_Zps
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C1_B10_NH4 : -1
                 C3_H2CO3 : ((1/Y_ps)-2)
                 C7_H : (13/4-(3/(2*Y_ps)))
                 C13_HAc : ((1/Y_ps)-3/2)
                 C28_HPr : -(1/Y_ps)
                 D3_H2 : 1/2
                 C31_SO4 : -((3/(4*Y_ps))-9/8)
                 C32_H2S : ((3/(4*Y_ps))-9/8)
                 S1_Zps : 1
-------------------------------------------------------------------------
S3_Zas_growth: Description:          Growth of Acetotrophic SRB
               Type:                 Dynamic Process
               Rate:                 ((muMax_as*C13_HAc)/((KSmol_as*(C13
                                     _HAc/(C13_HAc+C14_Ac)))+C13_HAc))*(
                                     C31_SO4/(KNmol_as+C31_SO4))*(C1_B10
                                     _NH4/(K_NH4+C1_B10_NH4))*S2_Zas
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C1_B10_NH4 : -1
                 C3_H2CO3 : ((2/(Y_as))-5)
                 C7_H : (6-(2/(Y_as)))
                 C13_HAc : -(1/Y_as)
                 C31_SO4 : -((1/(Y_as))-(5/2))
                 C32_H2S : ((1/(Y_as))-(5/2))
                 S2_Zas : 1
-------------------------------------------------------------------------
S4_Zas_decay:  Description:          Endogenous decay of acetotrophic SR
                                     B
               Type:                 Dynamic Process
               Rate:                 bas*S2_Zas
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C2_NH3 : NH3mol
                 D1_Sbp : Sbp
                 C3_H2CO3 : H2CO3mol
                 S2_Zas : -1
-------------------------------------------------------------------------
S5_Zhs_growth: Description:          growth of Hydrogenotrophic SRB
               Type:                 Dynamic Process
               Rate:                 ((muMax_hs*D3_H2)/(KSmol_hs+D3_H2))
                                     *(C31_SO4/(KNmol_hs+C31_SO4))*(C1_B
                                     10_NH4/(K_NH4+C1_B10_NH4))*S3_Zhs
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C1_B10_NH4 : -1
                 C3_H2CO3 : -5
                 C7_H : (6-(1/(2*Y_hs)))
                 D3_H2 : -(1/Y_hs)
                 C31_SO4 : -((1/(4*Y_hs))-5/2)
                 C32_H2S : ((1/(4*Y_hs))-5/2)
                 S3_Zhs : 1
-------------------------------------------------------------------------
S6_Zhs_decay:  Description:          Endogenous decay of Hydrogenotrophi
                                     c SRb
               Type:                 Dynamic Process
               Rate:                 bhs*S3_Zhs
               Stoichiometry:
                 Variable : Stoichiometric Coefficient
                 C2_NH3 : NH3mol
                 C3_H2CO3 : H2CO3mol
```

D1_Sbp : Sbp
S3_Zhs : -1

****

****
Compartments
****

Reactor: Description:
Type: Mixed Reactor Compartment
Compartment Index: 0
Active Variables: C14_Ac, ALK, ALKmol, AW_C, AW_H, AW_N, AW_O, b_AD, b_AC, b_AM, b_HM, P4_CH4, P1_C6_CO2gas, C5_CO3, D1_Sbp, D2_B2_Sbsf, B3_CODup, B1_CODus, CT, EndogenousProt, fd, fm, ft, f_C5H7O2NCOD, C7_H, D3_H2, C3_H2CO3, C13_HAc, C4_HCO3, C28_HPr, Kmax_Hyd, HydrolysisProt, inALK, inALKmol, inCO3, inCO3acidity, inCT, inNai, inH, inH2CO3, inHCO3, inNH3, inNH4, inOH, inSbpi, inSpi, inSupi, inSbsfi, inSbsaAi, inSbsaPi, inSsi, inSbsai, inSusi, inSti, inSC, in_f_GlucCOD, in_f_HAc, in_f_HAcCOD, in_f_HPr, in_f_HPrCOD, in_f_Sup, in_f_Sus, inpH, Kc1, Kc2, Kfa, Kfc1, Kfc2, Kfn, Kfp1, Kfp2, Kfp3, KfPr, KfW, KH2, KHCO2, Kn, Kra, Krc1, Krc2, KrCO2, Krn, Krp1, Krp2, Krp3, KrPr, KrW, Ks_AD, Ks_AC, Ks_AM, Ks_HM, Ks_Hyd, Kw, muMax_AD, muMax_AC, muMax_AM, muMax_HM, MW_C5H7O2N, MW_CaCO3, MW_CO2, MW_Glucose, MW_HAc, MW_HPr, MW_NH3, C2_NH3, C1_B10_NH4, NT, C8_OH, outALK, outALKmol, outCODbp, outCODbs, outCODtot, outCODtotpart, outCODtotsol, outCODup, outCODus, outFSA, outHAc_Ac, outHPr_Pr, out_ZAC, out_ZAD, out_ZAM, out_ZHM, out_pH, pCO2, pH, pKa, pKc1, pKc2, pKHCO2, pKn, pKp1, pKp2, pKp3, pKPr, pKW, C12_PO4, C29_Pr, in_PsChon, in_PscHon, in_PschoN, in_PschOn, Qi, R, Rs, SC, Tc, Tk, vinit_ALK, vinit_ALKmol, vinit_CO3, vinit_CODbs, vinit_CT, vinit_H, vinit_H2CO3, vinit_HCO3, vinit_Ac, vinit_NH4, vinit_NT, vinit_OH, vinit_pH, vinit_ZAC, vinit_ZAD, vinit_ZAM, vinit_ZHM, Vr, D5_Z_AC, D4_Z_AD, D6_Z_AM, D7_Z_HM, Y_AD, Y_AC, Y_AM, Y_HM, AW_P, AW_S, bas, bhs, bps, C10_H2PO4, C11_HPO4, C31_SO4, C32_H2S, C9_H3PO4, H2CO3mol, H2S_in, H2S_init, H2_in, C34_HS, C30_HSO4, HSO4_in, HSO4_init, HS_in, HS_init, inSbpi_mol, inSbsaAAc_mol, inSbsaAHAc_mol, inSbsaAi_mol, inSbsaPHPr_mol, inSbsaPi_mol, inSbsaPPr_mol, in_f_CODPS, Ka, KfH2S, KfHSO4, KH2S, KHSO4, KImol_as, KImol_hs, KImol_ps, KI_as, KI_hs, KI_ps, KNmol_as, KNmol_hs, KNmol_ps, KN_as, KN_hs, KN_ps, Kp, KrH2S, KrHSO4, KSmol_as, KSmol_hs, KSmol_ps, KS_as, KS_hs, KS_ps, K_NH4, muMax_as, muMax_hs, muMax_ps, MWH2, MWH2S, MWHSO4, NH3mol, out_CH4_Volume, out_CO2_Vol

ume, out_Gas_PerMethane, out_Gas_Volume, pATM, pKH2S, pKHSO4, S1_Zps, S2_Zas, S3_Zhs, Sbp, SO4_in, SO4_init, St, SulphateT_in, SulphateT_init, SulphideT_in, SulphideT_init, Tc_Gas, Tk_Gas, vinit_AT, vinit_CH4, vinit_CO2gas, vinit_CODbp, vinit_H2, vinit_HAc, vinit_NH3, Xa_as_init, Xa_as_out, Xa_hs_init, Xa_hs_out, Xa_ps_init, Xa_ps_out, Y_as, Y_hs, Y_ps, C33_H2Sgas, HPr_init, in_f_H2COD, KH2Sgas, KrH2Sgas, out_H2S_Volume, out_SO4, pH2S, Pr_init, PT_init, vinit_H2Sgas, MWS, MWSO4

Active Processes: P6_C7_DissolutionCO2, P7_C8_ExpulsionCO2, C3_ForDissH2CO3, C17_ForDissH2O, C15_ForDissHAc, C5_ForDissHCO3, C46_ForDissHPr, C1_ForDissNH4, C4_RevDissH2CO3, C18_RevDissH2O, C12_RevDissH2PO4, C10_RevDissH3PO4, C16_RevDissHAc, C6_RevDissHCO3, C14_RevDissHPO4, C47_RevDissHPr, C2_RevDissNH4, D7_AcetoclasticMethanogenesis, D5_Acetogenisis, D3_Acidogenisis_highpH2, D2_Acidogenisis_lowpH2, D8_EndRespAcetoclasticMethanogens, D6_EndRespAcetogens, D4_EndRespAcidogens, D10_EndRespHydrogenotrophicMethanogens, D9_HydrogenotrophicMethanogenesis, D1_Hydrolysis, C11_ForDissH2PO4, C13_ForDissHPO4, C51revdissH2S, C48_forwdissHSO4, C49revdissHSO4, C50forwdissH2S, C9_ForDissH3PO4, S1_Zps_decay, S3_Zas_growth, S4_Zas_decay, S5_Zhs_growth, S2_Zps_growth, S6_Zhs_decay, P12_DissolutionH2S, P13_ExpulsionH2S

Initial Conditions:

Variable(Zone)	Initial Condition
C7_H(Bulk Volume)	vinit_H
C8_OH(Bulk Volume)	vinit_OH
D4_Z_AD(Bulk Volume)	vinit_ZAD
D5_Z_AC(Bulk Volume)	vinit_ZAC
C33_H2Sgas(Bulk Volume)	vinit_H2Sgas
C29_Pr(Bulk Volume)	Pr_init
D6_Z_AM(Bulk Volume)	vinit_ZAM
C28_HPr(Bulk Volume)	HPr_init
D7_Z_HM(Bulk Volume)	vinit_ZHM
C3_H2CO3(Bulk Volume)	vinit_H2CO3
C4_HCO3(Bulk Volume)	vinit_HCO3
C5_CO3(Bulk Volume)	vinit_CO3
D2_B2_Sbsf(Bulk Volume)	vinit_CODbs
C2_NH3(Bulk Volume)	vinit_Ac
C1_B10_NH4(Bulk Volume)	vinit_NH4
P4_CH4(Bulk Volume)	vinit_CH4
P1_C6_CO2gas(Bulk Volume)	vinit_CO2gas
C14_Ac(Bulk Volume)	vinit_Ac
C13_HAc(Bulk Volume)	vinit_HAc
D1_Sbp(Bulk Volume)	vinit_CODbp
D3_H2(Bulk Volume)	vinit_H2
C31_SO4(Bulk Volume)	SO4_init
C32_H2S(Bulk Volume)	H2S_init
S1_Zps(Bulk Volume)	Xa_ps_init
S2_Zas(Bulk Volume)	Xa_as_init
S3_Zhs(Bulk Volume)	Xa_hs_init
C34_HS(Bulk Volume)	HS_init
C30_HSO4(Bulk Volume)	HSO4_init

Inflow: Qi

Loadings:

Variable	Loading
D1_Sbp	inSbpi_mol*Qi

```
    B3_CODup : (inSupi/1000)*Qi
    B1_CODus : (inSusi/1000)*Qi
    D2_B2_Sbsf : (((inSbsfi/in_f_GlucCOD)/1000)/MW_Glucose)
      *Qi
    C7_H : inH*Qi+Qin*Hin
    C13_HAc : inSbsaAHAc_mol*Qi
    C28_HPr : inSbsaPHPr_mol*Qi
    C2_NH3 : inNH3*Qi
    C1_B10_NH4 : inNH4*Qi
    C5_CO3 : inCO3*Qi
    C4_HCO3 : inHCO3*Qi
    C3_H2CO3 : inH2CO3*Qi
    C8_OH : inOH*Qi
    C14_Ac : inSbsaAAc_mol*Qi
    C29_Pr : inSbsaPHPr_mol*Qi
    D3_H2 : H2_in*Qi
    C32_H2S : Qi*H2S_in
    C31_SO4 : Qi*SO4_in
  Volume:                16
  Accuracies:
    Rel. Acc. Q:         0.001
    Abs. Acc. Q:         0.001
    Rel. Acc. V:         0.001
    Abs. Acc. V:         0.001
*************************************************************************
```

```
*************************************************************************
Definitions of Calculations
*************************************************************************
Simulation:    Description:
               Calculation Number:   0
               Initial Time:         0
               Initial State:        given, made consistent
               Step Size:            0.0166666
               Num. Steps:           1440
               Status:               inactive for simulation
                                     inactive for sensitivity analysis
-------------------------------------------------------------------------
Test:          Description:
               Calculation Number:   0
               Initial Time:         0
               Initial State:        given, made consistent
               Step Size:            1
               Num. Steps:           300
               Status:               active for simulation
                                     inactive for sensitivity analysis
*************************************************************************
```

```
*************************************************************************
Plot Definitions
*************************************************************************
Alkalinity_mgCaCO3:
               Description:
               Abscissa:             Time
               Title:                H2CO3* Alkalinity
               Abscissa Label:       Time (d)
               Ordinate Label:       mg/l as CaCO3
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : outALK [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
Alkalinity_mol:Description:
               Abscissa:             Time
```

```
                Title:                  H2CO3* Alkalinity
                Abscissa Label:         Time (d)
                Ordinate Label:         mol/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : ALKmol [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
Biomass_mol:    Description:
                Abscissa:               Time
                Title:                  Biomasses in mol units
                Abscissa Label:         Time (days)
                Ordinate Label:         mol/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : D4_Z_AD [0,Reactor,Bulk Volume,0]
                  Value : D5_Z_AC [0,Reactor,Bulk Volume,0]
                  Value : D6_Z_AM [0,Reactor,Bulk Volume,0]
                  Value : D7_Z_HM [0,Reactor,Bulk Volume,0]
                  Value : S1_Zps [0,Reactor,Bulk Volume,0]
                  Value : S2_Zas [0,Reactor,Bulk Volume,0]
                  Value : S3_Zhs [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
Carbonate_mol:  Description:
                Abscissa:               Time
                Title:                  Carbonate system in mol units
                Abscissa Label:         Time (days)
                Ordinate Label:         mol/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : C3_H2CO3 [0,Reactor,Bulk Volume,0]
                  Value : C4_HCO3 [0,Reactor,Bulk Volume,0]
                  Value : C5_CO3 [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
CODpart_biomass:
                Description:
                Abscissa:               Time
                Title:                  Biomasses in mgCOD units
                Abscissa Label:         Time (days)
                Ordinate Label:         mgCOD/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : out_ZAD [0,Reactor,Bulk Volume,0]
                  Value : out_ZAC [0,Reactor,Bulk Volume,0]
                  Value : out_ZAM [0,Reactor,Bulk Volume,0]
                  Value : out_ZHM [0,Reactor,Bulk Volume,0]
                  Value : out_Zas [0,Reactor,Bulk Volume,0]
                  Value : out_Zhs [0,Reactor,Bulk Volume,0]
                  Value : out_Zps [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
CODpart_bpup:   Description:
                Abscissa:               Time
                Title:                  Biodeg & Unbiodeg particulate COD i
                                        n mgCOD/l units
                Abscissa Label:         Time (d)
                Ordinate Label:         mgCOD/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : outCODbp [0,Reactor,Bulk Volume,0]
                  Value : outCODup [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
CODpart_bpup_mol:
                Description:
                Abscissa:               Time
                Title:                  Biodeg & Unbiodeg particulate COD i
                                        n mgCOD/l units
                Abscissa Label:         Time (d)
                Ordinate Label:         mgCOD/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : D1_Sbp [0,Reactor,Bulk Volume,0]
                  Value : outCODup_mol [0,Reactor,Bulk Volume,0]
```

```
CODpart_total: Description:
               Abscissa:              Time
               Title:                 Total particulate COD in mgCOD/l un
                                      its
               Abscissa Label:        Time (d)
               Ordinate Label:        mgCOD/l
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : outCODtotpart [0,Reactor,Bulk Volume,0]
---------------------------------------------------------------------
CODsol_bsf:    Description:
               Abscissa:              Time
               Title:                 Biodeg. soluble COD
               Abscissa Label:        Time (d)
               Ordinate Label:        mgCOD/l
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : outCODbs [0,Reactor,Bulk Volume,0]
---------------------------------------------------------------------
CODsol_bsf_mol:Description:
               Abscissa:              Time
               Title:                 Glucose concentration in mol units
               Abscissa Label:        Time (d)
               Ordinate Label:        mol/l
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : D2_B2_Sbsf [0,Reactor,Bulk Volume,0]
---------------------------------------------------------------------
CODsol_H2S_HS: Description:
               Abscissa:              Time
               Title:                 H2S/HS as COD
               Abscissa Label:        Time (d)
               Ordinate Label:        mgCOD/l
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : outCODsol_H2S_HS [0,Reactor,Bulk Volume,0]
---------------------------------------------------------------------
CODsol_organic:Description:
               Abscissa:              Time
               Title:                 Total soluble organic COD in mgCOD/
                                      l units
               Abscissa Label:        Time (d)
               Ordinate Label:        mgCOD/l
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : outCODsol_organic [0,Reactor,Bulk Volume,0]
---------------------------------------------------------------------
CODsol_total:  Description:
               Abscissa:              Time
               Title:                 Total soluble COD in mgCOD/l units
               Abscissa Label:        Time (d)
               Ordinate Label:        mgCOD/l
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : outCODtotsol [0,Reactor,Bulk Volume,0]
---------------------------------------------------------------------
CODsol_us:     Description:
               Abscissa:              Time
               Title:                 Unbiodegradable soluble COD
               Abscissa Label:        Time (d)
               Ordinate Label:        g/l
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : B1_CODus [0,Reactor,Bulk Volume,0]
---------------------------------------------------------------------
CODsol_VFA:    Description:
               Abscissa:              Time
               Title:                 VFA concentration in mgCOD/l units
               Abscissa Label:        Time (d)
               Ordinate Label:        mgCOD/l
```

```
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : outHAc_Ac [0,Reactor,Bulk Volume,0]
                  Value : outHPr_Pr [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
CODsol_VFAAc_mol:
                Description:
                Abscissa:             Time
                Title:                Acetate system in mol units
                Abscissa Label:       Time (days)
                Ordinate Label:       mol/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : C13_HAc [0,Reactor,Bulk Volume,0]
                  Value : C14_Ac [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
CODsol_VFAPr_mol:
                Description:
                Abscissa:             Time
                Title:                Propionate system in mol units
                Abscissa Label:       Time (days)
                Ordinate Label:       mol/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : C28_HPr [0,Reactor,Bulk Volume,0]
                  Value : C29_Pr [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
CODtotal:       Description:
                Abscissa:             Time
                Title:                Total COD in mgCOD/l units
                Abscissa Label:       Time (d)
                Ordinate Label:       mgCOD/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : outCODtot [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
FSA_mgN:        Description:
                Abscissa:             Time
                Title:                Dissolved N in mgN/l
                Abscissa Label:       Time (d)
                Ordinate Label:       mgN/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : outFSA [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
Gas_CH4_lperl_infl:
                Description:
                Abscissa:             Time
                Title:                Methane gas production
                Abscissa Label:       Time (d)
                Ordinate Label:       l gas / l influent
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : out_CH4_Volume [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
Gas_CH4_mol:    Description:
                Abscissa:             Time
                Title:                Methane gas production
                Abscissa Label:       Time (d)
                Ordinate Label:       mol/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : P4_CH4 [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
Gas_CO2_lperl_infl:
                Description:
                Abscissa:             Time
                Title:                CO2 gas production
                Abscissa Label:       Time (d)
                Ordinate Label:       l gas / l influent
                Curves:
```

```
                Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                Value : out_CO2_Volume [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
GAS_CO2_mol:    Description:
                Abscissa:               Time
                Title:                  CO2 gas production
                Abscissa Label:         Time (d)
                Ordinate Label:         mol/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : P1_C6_CO2gas [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
Gas_H2S_lperl_infl:
                Description:
                Abscissa:               Time
                Title:                  H2S gas production
                Abscissa Label:         Time (d)
                Ordinate Label:         l gas / l influent
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : out_H2S_Volume [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
GAS_H2S_mol:    Description:
                Abscissa:               Time
                Title:                  H2S gas production
                Abscissa Label:         Time (d)
                Ordinate Label:         mol/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : C33_H2Sgas [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
Gas_perMethane:Description:
                Abscissa:               Time
                Title:                  % methane
                Abscissa Label:         Time (d)
                Ordinate Label:         %
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : out_Gas_PerMethane [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
Gas_Total_lperl_infl:
                Description:
                Abscissa:               Time
                Title:                  Total gas production
                Abscissa Label:         Time (d)
                Ordinate Label:         l gas / l influent
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : out_Gas_Volume [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
H2S_HS:         Description:            Undissociated hydrogen sulphide con
                                        centration over time
                Abscissa:               Time
                Title:                  H2S&HS
                Abscissa Label:         Time (d)
                Ordinate Label:         Conc (mol/l)
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : C32_H2S [0,Reactor,Bulk Volume,0]
                  Value : C34_HS [0,Reactor,Bulk Volume,0]
                  Value : St [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
H2S_HSmg:       Description:             sulphide species concentration ove
                                        r time
                Abscissa:               Time
                Title:                  sulphide species concentration
                Abscissa Label:         Time (d)
                Ordinate Label:         Conc (mg/l)
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : out_H2S [0,Reactor,Bulk Volume,0]
```

```
                Value : out_HS [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
H2_mol:         Description:
                Abscissa:               Time
                Title:                  Dissolved hydrogen in mol units
                Abscissa Label:         Time (d)
                Ordinate Label:         mol/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : D3_H2 [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
HSO4_in:        Description:            Influent HSO4 concentration
                Abscissa:               Time
                Title:
                Abscissa Label:
                Ordinate Label:
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : HSO4_in [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
HSO4_SO4:       Description:            Molar concentration of sulphate spe
                                        cies
                Abscissa:               Time
                Title:                  concentration of sulphate species
                Abscissa Label:         Time (d)
                Ordinate Label:         Conc (mol/l)
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : C31_SO4 [0,Reactor,Bulk Volume,0]
                  Value : C30_HSO4 [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
HSO4_SO4_mg:    Description:            concentration of sulphate species
                Abscissa:               Time
                Title:                  concentration of sulphate species
                Abscissa Label:         Time (d)
                Ordinate Label:         Conc (mg/l)
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : out_SO4 [0,Reactor,Bulk Volume,0]
                  Value : out_HSO4 [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
H_mol:          Description:
                Abscissa:               Time
                Title:                  Dissolved H species in mol units
                Abscissa Label:         Time (d)
                Ordinate Label:         mol/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : C7_H [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
inCarbonate_mol:
                Description:
                Abscissa:               Time
                Title:                  Carbonate species in influent
                Abscissa Label:         Time (days)
                Ordinate Label:         mol/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : inH2CO3 [0,Reactor,Bulk Volume,0]
                  Value : inHCO3 [0,Reactor,Bulk Volume,0]
                  Value : inCO3 [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
inCODpart_mgCOD:
                Description:
                Abscissa:               Time
                Title:                  Particulate COD in Influent
                Abscissa Label:         Time (days)
                Ordinate Label:         mg COD/l
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : inSti [0,Reactor,Bulk Volume,0]
```

```
                Value : inSpi [0,Reactor,Bulk Volume,0]
                Value : inSupi [0,Reactor,Bulk Volume,0]
                Value : inSbpi [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
inCODsol_mgCOD:Description:
               Abscissa:              Time
               Title:                 Soluble COD in Influent
               Abscissa Label:        Time (days)
               Ordinate Label:        mg COD/l
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : inSti [0,Reactor,Bulk Volume,0]
                 Value : inSsi [0,Reactor,Bulk Volume,0]
                 Value : inSbsfi [0,Reactor,Bulk Volume,0]
                 Value : inSusi [0,Reactor,Bulk Volume,0]
                 Value : inSbsaAi [0,Reactor,Bulk Volume,0]
                 Value : inSbsaPi [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
inH2SHS:       Description:           Influent Concentration
               Abscissa:              Time
               Title:
               Abscissa Label:        Time(d)
               Ordinate Label:
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : HS_in [0,Reactor,Bulk Volume,0]
                 Value : H2S_in [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
inHSO4SO4:     Description:           Influent SO4 Concentration
               Abscissa:              Time
               Title:
               Abscissa Label:        Time(d)
               Ordinate Label:
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : SO4_in [0,Reactor,Bulk Volume,0]
                 Value : HSO4_in [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
inNH3NH4_mol:  Description:
               Abscissa:              Time
               Title:                 NH3/NH4 in Influent
               Abscissa Label:        Time (days)
               Ordinate Label:        mol/l
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : inNH3 [0,Reactor,Bulk Volume,0]
                 Value : inNH4 [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
NH3NH4_mol:    Description:
               Abscissa:              Time
               Title:                 NH3/NH4 system in mol units
               Abscissa Label:        Time (days)
               Ordinate Label:        mol/l
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : C2_NH3 [0,Reactor,Bulk Volume,0]
                 Value : C1_B10_NH4 [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
OH_mol:        Description:
               Abscissa:              Time
               Title:                 Dissolved OH species in mol units
               Abscissa Label:        Time (d)
               Ordinate Label:        mol/l
               Curves:
                 Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                 Value : C8_OH [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
pH:            Description:
               Abscissa:              Time
               Title:                 pH in bulk liquid
               Abscissa Label:        Time (d)
```

```
                Ordinate Label:       pH
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : pH [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
SO4_HSO4:       Description:          Molar concentration of sulphate spe
                                      cies
                Abscissa:             Time
                Title:                Concentration of sulphate species
                Abscissa Label:       Time (d)
                Ordinate Label:        Conc (mol/l)
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : C31_SO4 [0,Reactor,Bulk Volume,0]
                  Value : C30_HSO4 [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
SO4_in:         Description:          Influent SO4 concentration
                Abscissa:             Time
                Title:
                Abscissa Label:
                Ordinate Label:
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : SO4_in [0,Reactor,Bulk Volume,0]
-------------------------------------------------------------------------
SO4_mg:         Description:          sulphate species concentration
                Abscissa:             Time
                Title:                Sulphate species concentration
                Abscissa Label:       Time (d)
                Ordinate Label:        Conc (mg/l)
                Curves:
                  Type : Variable [CalcNum,Comp.,Zone,Time/Space]
                  Value : out_SO4 [0,Reactor,Bulk Volume,0]
*************************************************************************




*************************************************************************
Calculation Parameters
*************************************************************************
Numerical Parameters:    Maximum Int. Step Size:  1
                         Maximum Integrat. Order: 5
                         Number of Codiagonals:   1000
                         Maximum Number of Steps: 1000
-------------------------------------------------------------------------
                         Fit Method:              secant
                         Max. Number of Iterat.:  100
*************************************************************************
```