

**INTEGRATED MASS BALANCE MODELS FOR
CHEMICAL, PHYSICAL AND BIOLOGICAL
PROCESSES IN WASTEWATER TREATMENT
PLANTS:
PART 1**

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Water Research Commission



**INTEGRATED MASS BALANCE MODELS FOR
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IN WASTEWATER TREATMENT PLANTS:
PART 1**

**Report to the
WATER RESEARCH COMMISSION**

by

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EXECUTIVE SUMMARY **(WRC Project K5/1338)**

TOWARD DEVELOPING INTEGRATED CHEMICAL, PHYSICAL AND BIOLOGICAL PROCESSES MASS BALANCES MODELS OVER WASTEWATER TREATMENT PLANTS

1. INTRODUCTION

Since the activated sludge system produces the effluent that must comply with legislated effluent criteria, it has been well researched and relatively reliable simple steady state design and complex dynamic simulation models have been developed for it, including biological N and/or P removal. However, little attention has been focussed on modelling the wastewater treatment plant (WWTP) as a whole, where the outflow from one unit operation becomes inflow to downstream or upstream unit operations. The interconnection of individual unit operations of a WWTP means that design and operation optimisation of one unit operation can have unexpected and often unforeseen consequences on the performance of both upstream and downstream unit operations, and hence on the WWTP performance as a whole. For example, the recycling of nutrient rich liquors from sludge treatment unit operations to the activated sludge system has a significant impact on the WWTP effluent quality (e.g. Pitman et al., 1991; Wild and Siegrist, 1999), contributing up to 25% of the total N load to the activated sludge system (Janus and van der Roest, 1997).

Accordingly, this project was initiated in April 2002 with overall objective of developing mass balance models for the entire WWTP. Unit operations in which transformations of the materials take place and hence to be modelled were primary sedimentation, biological wastewater treatment in activated sludge systems, including or excluding biological N and P removal, aerobic and anaerobic stabilization of primary and secondary sludges and generic sludge thickening. This WWTP model would be developed for both steady state and dynamic simulation conditions.

2. RESEARCH OBJECTIVES AND AIMS

The overall long term objective of this research project was to develop a COD (electron), carbon (C), nitrogen (N), phosphorus (P), alkalinity (proton), calcium (Ca) and magnesium (Mg) and inorganic suspended solids (ISS) concentrations mass balances model for municipal WWTPs comprising primary sedimentation, secondary treatment with activated sludge and aerobic and anaerobic sludge stabilization of primary (PS) and secondary (waste activated, WAS) sludges.

To achieve this objective a number of specific aims were set for the project:

- (1) To develop steady state and dynamic simulation predictive models for ISS, to enable the ISS to be tracked through the WWTP.
- (2) To develop a simple COD, N and P balances steady state WWTP models with primary sedimentation, N removal activated sludge and aerobic digestion of PS and WAS.
- (3) To extend the activated sludge simulation models to incorporate pH as a predictive

parameter; this required incorporating chemical (weak acid/base aqueous chemistry) and physical (gas exchange) processes and integrating these with the biological processes. This extension would be restricted to aerobic and anoxic/aerobic activated sludge systems.

- (4) To develop an integrated mixed weak acid/base chemical, physical and biological processes model in three phases (liquid, gas and solid) for anaerobic digestion (AD) of sewage sludge.
- (5) To develop a scheme for PS and WAS characterization for the AD model, in conformity with the wastewater and activated sludge characterization schemes.
- (6) To develop an steady state model for anaerobic digestion (AD) of PS and WAS for incorporation into (2) above.
- (7) To develop a biological nutrient removal (BNR) activated sludge model for sequencing batch reactors (SBR) to compare BNR in SBR with BNR in multi-reactor systems applied in South Africa.

Completion of aims 4 and 5 turned out to be too ambitious for this 3 year project (2002-2004). However, a number of significant advances were made towards the overall objective of developing steady state and dynamic simulation mass balance models for the entire WWTP. These advances are outlined below.

3. PROJECT ACHIEVEMENTS

The aims that were achieved in this project towards developing mass balances based (COD, C, N, P and ISS) steady state and dynamic simulation models for the entire WWTP, including aerobic and anaerobic digestion of waste sludges, were:

- (1) Developed a predictive model for the activated sludge reactor inorganic suspended solids (ISS) concentration so that the reactor total (TSS) concentration becomes a model calculated value based on a measured influent ISS concentration and no longer estimated from an empirically selected VSS/TSS ratio for the activated sludge (Aim 1).
- (2) Set up a simple mass balances (COD and N) WWTP steady state and kinetic simulation models with primary sedimentation, anoxic-aerobic activated sludge and aerobic digestion of primary and waste activated sludge. Compare and verify kinetic model with the steady state model calculations (Aim 2).
- (3) Integrate the biological processes of N removal activated sludge (ASM1) into a 2 phase (aqueous-gas) version of the chemical physical processes model (2) above and verify it with the normal single aqueous phase ASM1 and validate it against literature data (Aim 3).
- (4) Refine and further validate against literature data the 3 phase mixed weak acid base chemical physical processes model developed by Musvoto et al. (1997, 2000) (Preliminary work to Aim 4).
- (5) Integrate the biological processes of anaerobic digestion into a 2 phase (aqueous-gas) version of the chemical physical processes model (4) above to construct a mass balances (COD, C, N, O, H) based integrated chemical physical biological processes model capable of predicting digester pH (UCTADM1) and verify it with laboratory and literature data. Included here is input characterisation (Aims 4 and 5).
- (6) Simplify UCTADM1 into a steady state model for initial design of AD systems and integration into the WWTP model (Aim 6).

- (7) Comparison of SBR for BNR with multi-reactor systems as applied in South Africa (Aim 7).

A summary of these developments is given below.

4. MODELLING INORGANIC MATERIAL IN ACTIVATED SLUDGE SYSTEMS

A simple predictive model for the activated sludge reactor inorganic suspended solids (ISS) concentration has been developed. It is based on the accumulation of influent ISS in the reactor and an ordinary heterotrophic organism (OHO) ISS content (f_{iOHO}) of 0.15 mg ISS/mgOHOVSS and a variable phosphate accumulating organism (PAO) ISS content (f_{iPAO}) proportional to their P content (f_{XBGP}). The model is validated with data from 21 investigations conducted over the past 15 years on 30 aerobic and anoxic-aerobic nitrification denitrification (ND) systems and 18 anaerobic-anoxic-aerobic ND biological excess P removal (BEPR) systems variously fed artificial and real wastewater and operated from 3 to 20 days sludge age. The predicted reactor VSS/TSS ratio reflects the observed relative sensitivity to sludge age, which is low, and to BEPR, which is high. To use the model in design requires measurement of the influent ISS concentration, which is not commonly done in wastewater characterization analyses and a method to do this accurately was developed. This model can be readily integrated into the activated sludge simulation models. Also, it provides a framework for tracking the ISS concentrations through the entire WWTP. Incorporation of ISS into the other unit operations within the WWTP still needs to be completed.

5. STEADY STATE MASS BALANCES WWTP MODEL

A steady state WWTP mass balances (COD, N and P) spreadsheet programme was developed capable of:

5.1 *Wastewater characterization:*

From the given (measured) concentrations and component fractions, it characterizes the raw and settled wastewaters and primary sludge COD, TKN, FSA, TP and OP, each into their unbiodegradable and biodegradable soluble and particulate components from mass balances around the PST.

5.2 *Activated sludge system design:*

It calculates the design parameters for the fully aerobic, nitrification denitrification (ND) or ND biological excess P removal (BEPR) activated sludge systems treating the raw and settled WW at long and short sludge ages respectively, i.e. volume of reactor, average and peak oxygen demand, effluent COD, TKN, FSA, TP and OP concentrations and waste activated sludge (WAS) flow and composition.

5.3 *Aerobic digester design:*

It calculates the design parameters for a single reactor aerobic digester by taking the PS and WAS (excluding BEPR systems at this stage) flows and concentrations (including the liquid stream), blending and concentrating them to the selected thickened concentrations and aerobically digesting the blended and thickened sludge to a selected residual biodegradable organic content, taking due account in N and P released during digestion. It calculates the digester volume, oxygen demand and effluent concentrations, and checks material mass balances

(COD, N and P), all for the minimum ($T_{\min}$) and maximum ($T_{\max}$) temperatures.

5.4 Mass balance checks:

It checks the COD, N and P mass balances around the WWTP comprising (i) raw WW treatment in a long sludge age AS system, where the sludge age is selected long enough for sludge stabilization in the reactor and direct discharge of WAS to drying beds (i.e. extended aeration), and (ii) PSTs, short sludge aged activated sludge system, PS and WAS thickening and aerobic digestion of PS and WAS to the same residual biodegradable organics as (i) above (Fig 1). The concentrations of COD (and oxygen demand), N and P in the effluent streams for the AS system, the thickening units and the aerobic digester are added and balance to within 0.5% of the influent raw wastewater COD, TKN and TP for both $T_{\min}$ and $T_{\max}$ temperatures. The carbonaceous oxygen utilised in the raw WW system (AS only), and in the settled WW system (AS and aerobic digester) are within 0.5%.

5.5 Comparison with simulation results:

An Activated Sludge Model No 1 (ASM1, Henze et al., 1985) Aquasim (Reichert, 1998) dynamic simulation model was set up for the raw and settled WW treatment plants above, including thickening and aerobic digestion of PS and WAS (Fig 1). For both systems, the simulation model gives virtually identical results for all the AS and aerobic digestion effluent COD, TKN, FSA, TP, OP, VSS, ISS and TSS concentrations from both systems. There is therefore close correlation between the far more complex dynamic simulation WWTP model in which ASM1 is used to model the AS and aerobic digester systems and the much simpler steady state model programmed into the spreadsheet described here.

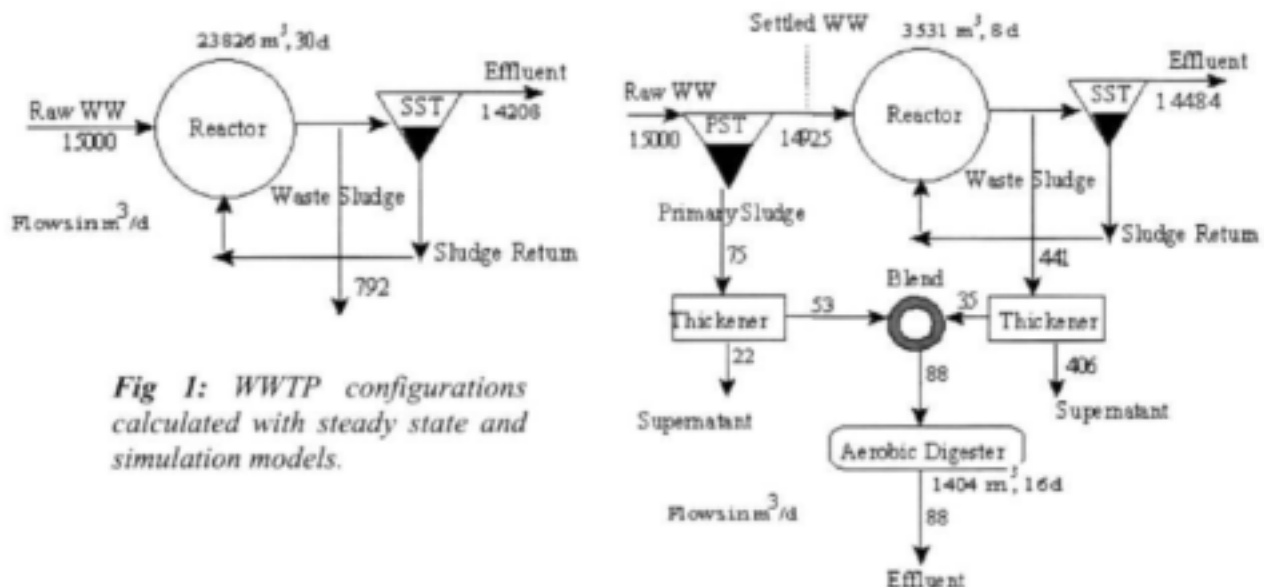


Fig 1: WWTP configurations calculated with steady state and simulation models.

6. INTEGRATED CHEMICAL-PHYSICAL PROCESSES KINETIC MODELLING OF MULTIPLE MINERAL PRECIPITATION PROBLEMS

In a previous research project (K5/692, Musvoto et al., 2002) a three phase (aqueous/gas/solid) mixed weak acid/base chemistry kinetic model was developed. This model formed the framework for the activated sludge and anaerobic digestion kinetic modelling in this project (see

Sections 7 and 8 below). Accordingly, to further validate the model, it was applied to evaluate the processes operative in the aeration treatment of swine wastewater (SWW) and sewage sludge anaerobic digester liquor (ADL). In both applications, with a single set of constants (except for the aeration rates which are situation specific), close correlation could be obtained between predicted and measured data, except for the Ca concentration-time profile in the SWW. For this wastewater, the model application highlighted an inconsistency in the measured Ca data which could not be resolved; this illustrates the value of a mass balance based model in evaluating experimental data. From the model applications, in both wastewaters the dominant minerals precipitating are struvite and amorphous calcium phosphate (ACP), which precipitate simultaneously competing for the same species, P. The absolute and relative masses of the two precipitants are governed by the initial solution state (e.g. total inorganic C (C_T), Mg, Ca and P concentrations), their relative precipitation rates (struvite > ACP) and the system conditions imposed (aeration rates and time applied). It is concluded that the kinetic model is able to correctly predict the time dependent weak acid/base chemistry reactions and final equilibrium state (in terms of the duration of the experimental batch tests, <48h) for situations where multiple minerals competing for the same species precipitate simultaneously or sequentially, a deficiency in traditional equilibrium chemistry based algebraic models. This indicated that the approach developed for mixed phase and process modelling could be accepted for the modelling to be undertaken in this project.

7. INTEGRATED BIOLOGICAL, CHEMICAL AND PHYSICAL PROCESSES KINETIC MODELLING: ANOXIC-AEROBIC C AND N REMOVAL IN THE ACTIVATED SLUDGE SYSTEM

The biological kinetic ASM1 for carbon (C) and nitrogen (N) removal was integrated with the mixed weak acid/base model of Musvoto et al. (1997, 2000) (evaluated above) to extend application of ASM1 to situations where an estimate for pH is important. Because chemical precipitation is generally not significant when treating municipal wastewaters for C and N removal, only gas and liquid phase processes were considered for this integrated model. However, the approach will facilitate ready integration of chemical precipitation processes if required. The biological processes in ASM1 were modified to take into account the effect of the interaction of the weak acid/base species of the ammonia, carbonate and phosphate systems and pH with heterotrophic and autotrophic organism behaviour, which includes generation and utilization CO_2 in metabolism, use of specific weak acid/base species for organism growth and generation and utilization of H^+ . With these modifications, simulations with the model were compared with those of ASM1 and experimental data in the literature; a good correlation was obtained. However, these comparisons are only a preliminary validation, because, despite their inclusion, the weak acid/bases and pH do not have a significant effect on the biological processes in the cases considered (i.e. well buffered wastewater). A difficulty in calibrating this model was selection of the K_{La} value for the aeration system, which affects the pH in the anoxic and aerobic reactors through CO_2 gas exchange. Aerobic reactor outflows from two full-scale wastewater treatment plants with fine bubble aeration systems were found to be around 20% supersaturated with CO_2 , whereas simulations indicated higher supersaturations. The performance of a ND activated sludge system with low influent alkalinity was also evaluated. The developed model extends application of activated sludge simulation models to situations where pH prediction is of importance such as treatment of low alkalinity wastewaters or wastewaters with high N concentrations. This model produces the outputs required for the models of the other unit operations in the WWTP, such as anaerobic digestion of WAS.

8. INTEGRATED CHEMICAL/PHYSICAL AND BIOLOGICAL PROCESSES MODELING PART 2 - ANAEROBIC DIGESTION OF SEWAGE SLUDGES

A two phase (aqueous-gas) integrated mixed weak acid/base chemistry, physical and biological processes kinetic model for anaerobic digestion (AD) of sewage sludge was developed and validated. The biological kinetic processes for AD are integrated into a two phase subset of the three phase mixed weak acid/base chemistry kinetic model of Musvoto et al. (1997, 2000). The approach of characterising sewage sludge into carbohydrates, lipids and proteins, as is done in the International Water Association (IWA) AD model No 1 (ADM1), requires measurements that are not routinely available on sewage sludges. Instead, the sewage sludge is characterized with the COD, carbon, hydrogen, oxygen and nitrogen (CHON) composition. The model is formulated in mole units, based on conservation of C, N, O, H and COD. The model is calibrated and validated with data from laboratory mesophilic anaerobic digesters operating from 7 to 20 days sludge age and fed a sewage primary and humus sludge mixture. These digesters yielded COD mass balances between 107-109% and N mass balances between 91-99%, and hence the experimental data are accepted as reasonable. The sewage sludge is found to be 64 - 68% biodegradable (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 of surface mediated reaction (Contois), with a single set of kinetic and stoichiometric constants, for all retention times good correlation is obtained between predicted and measured results 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 (Fig 2). The measured composition of primary sludge from two local 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 is therefore within 5% of the average measured composition providing persuasive validation of the model. This anaerobic digestion model can serve as a stand alone model for simulation of anaerobic digesters treating sewage sludges, or can be integrated into the dynamic simulation model for the entire WWTP, a long term aim for this research project.

9. A STEADY STATE MODEL FOR ANAEROBIC DIGESTION OF SEWAGE SLUDGES

A steady state model for anaerobic digestion of sewage sludge was developed that comprises three sequential parts - (i) a kinetic part from which the % COD removal and methane production are determined for a given retention time, (ii) a stoichiometry part from which the gas composition (or partial pressure of CO_2), ammonia released and alkalinity generated are calculated from the %COD removal and (iii) a carbonate system weak acid/base chemistry part from which the digester pH is calculated from the partial pressure of CO_2 and alkalinity generated. From the stoichiometry and weak acid base chemistry parts of the model, for a given % COD removal, the digester gas composition, ammonia released, alkalinity generated and digester pH are completely defined by the influent (i) sludge composition, i.e. X, Y, Z and A in $C_XH_YO_ZN_A$ of the hydrolysable organics, (ii) volatile fatty acid (VFA) concentration and (iii) pH. For the kinetic part of the model, four hydrolysis kinetic equations were calibrated against 7 to 60 day retention time anaerobic digesters treating two different sewage sludge types, viz. (i) first order, (ii) first order specific, (iii) Monod and (iv) Contois (saturation). Once calibrated against the two sludge type data sets and taking into account experimental error in effluent COD concentrations and gas productions (i.e. COD mass balance error), each of the four hydrolysis

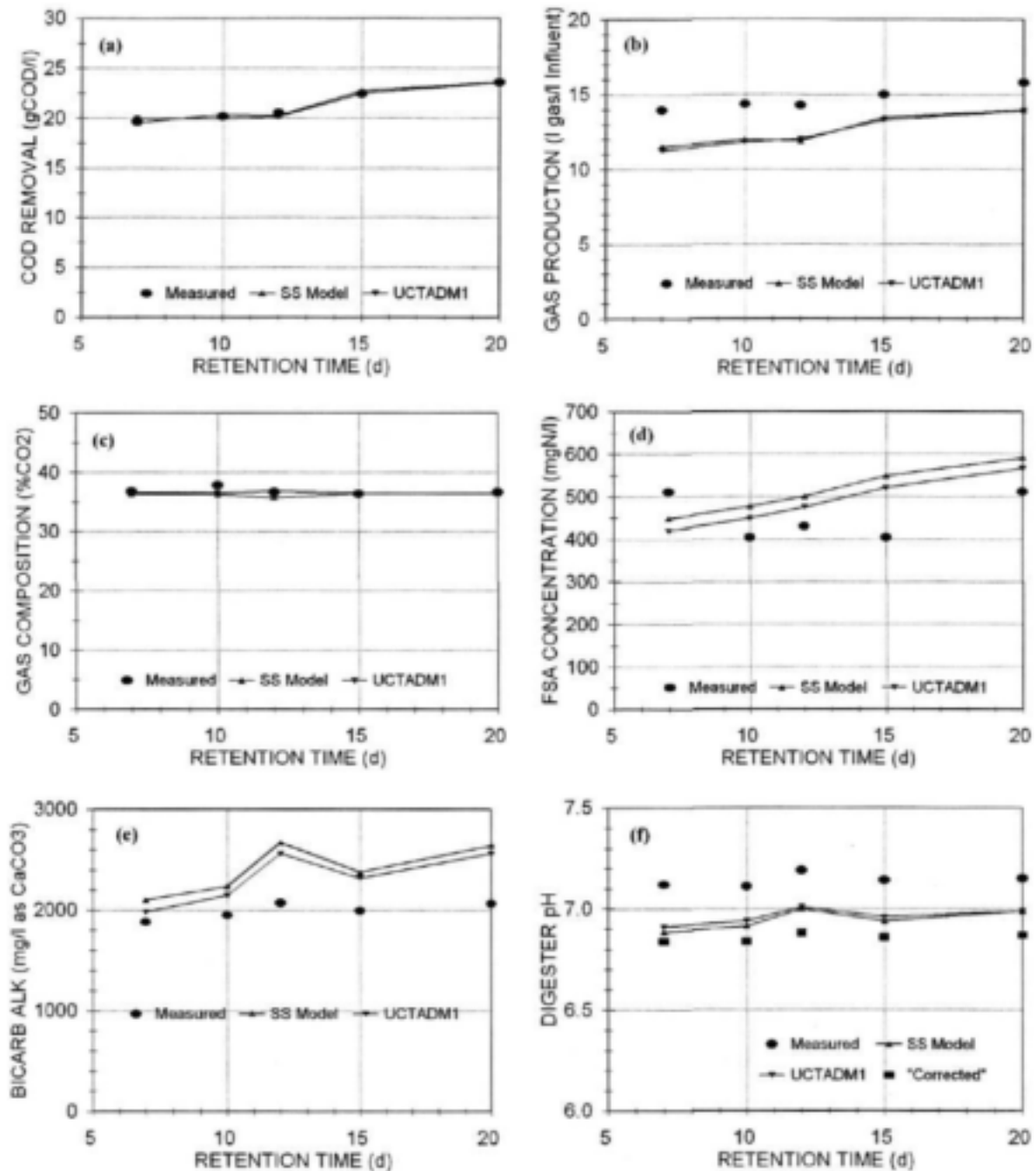


Fig 2: Comparison between kinetic simulation model (UCTADM1) predicted (lines) and measured (points) (a) COD removal, (b) gas production, (c) gas composition, (d) free and saline ammonia, (e) H_2CO_3^* alkalinity and (f) digester pH versus retention time for the Izzett et al. (1992) data set; also shown are the predictions of the steady state AD model.

kinetic equations predicted the % COD removal versus retention time equally well, and predicted COD removal and methane production compared well with measured data. For the different sewage sludge types, viz. (i) a primary and humus sludge mixture from a trickling filter plant and (ii) a "pure" primary sludge, different kinetic rate constants were obtained indicating that the "pure" primary sludge hydrolysed faster and had a lower unbiodegradable particulate COD fraction ($f_{ps-up} = 0.33$) than the primary and humus sludge mixture (0.36). With the %COD removal known from the hydrolysis part of the model, and again taking experimental error into account (i.e. C and N mass balances error), the stoichiometry and weak acid/base chemistry parts of the model predicted the gas composition, effluent free and saline ammonia (FSA) concentration, alkalinity generated and digester pH well for a primary and humus sludge composition of $C_{3.5}H_7O_2N_{0.196}$ (Fig 2). From independent measurement of primary sludge CHON composition, this model estimated composition is within 96%, 100%, 95% and 99% of the average measured composition of $C_{3.65}H_7O_{1.97}N_{0.190}$ lending strong support to the developed steady state model. This steady state anaerobic digestion model will be an invaluable aid for the design of anaerobic digesters treating sewage sludges. Further, the model can be readily integrated into the steady state mass balances model for the entire WWTP, which is still to be completed.

10. COMPARISON OF SBR FOR BNR WITH CONVENTIONAL MULTI-REACTOR SYSTEMS FOR APPLICATION IN SOUTH AFRICA

Sequencing batch reactor (SBR) technology is widely applied in many countries, in particular Australia. However, it has not found much application in South Africa. SBRs are essentially batch reactors that combine various treatment steps (aerobic, anoxic and anaerobic processes) as well as the solid-liquid separation (sludge settling) into one reactor. This is achieved by sequential cycles of (i) batch feeding, (ii) aerobic conditions (aeration), (iii) anoxic conditions (non-aeration but mixing), (iv) sludge settling (no aeration and no mixing), (v) effluent withdrawal (decanting) and (vi) re-filling with a new batch of feed. These cycles are carefully engineered to achieve either full or partial nutrient removal as required (i.e. COD, nitrogen (N), phosphorus (P) removal). This approach has claimed cost savings (in terms of initial capital costs) as multiple separate reactors with inter-reactor recycles and settling tanks are combined into one single reactor. However, it requires expensive and complex decanting equipment, skilled staff for operation and a strict operating schedule to achieve the anticipated biological nutrient removal.

The biological processes coupled with the complexity of the SBR hydraulics and operation make it difficult to apply steady state models to SBRs and hence, in order to predict SBR behaviour, a kinetic mathematical model needs to be applied. A dynamic kinetic model for SBR systems was developed in AQUASIM based on the activated sludge model of van Haandel et al (1981) (UCTOLD, similar to IWA Activated Sludge model ASM1). The simulation results were compared with those of an equivalent MLE multi-reactor system.

This investigation showed that it is possible to simulate SBR type systems in AQUASIM. The comparison with a MLE system with similar design and operating parameters showed that the two systems produce virtually identical mixed liquor concentrations and effluent COD and ammonia concentrations. The main difference was in the denitrification performance - the MLE system effluent nitrate concentration was considerably lower than that of the SBR system. In the SBR system, selection of different aeration and non-aeration cycle times could reduce the

effluent nitrate concentration but when the non-aeration period became too long, the ammonia (FSA) concentration increased. The SBR system effluent quality (FSA, NO_3) therefore is very sensitive to the cycle time and duration. Depending on the influent TKN/COD ratio, it was possible to find an optimum cycle time and duration so that the N removal performance of the SBR system moved closer to that of the MLE system, but it never equalled it. This is because in the MLE system, all the influent readily biodegradable COD was utilized in the anoxic reactor; in SBRs this was not found possible with different sequencing of aeration and non-aeration periods.

Due to time constraints in the project, biological excess P removal was not investigated. This can be done in the follow-on project with a BioP removal kinetic model, e.g. UCTPHO, to investigate P removal in SBR systems and how this compares with that of a conventional P removal system (e.g. a UCT configuration).

11. CONCLUSIONS AND FURTHER RESEARCH

This project made some significant advances towards developing mass balances based integrated WWTP models for steady state and diurnal flow and load conditions which links primary sedimentation, activated sludge and aerobic or anaerobic digestion of primary and waste activated sludges. The most significant of these are development of (i) the ISS model, which provides a framework for tracking the ISS concentrations through the WWTP, (ii) the two phase mixed weak acid base chemical, physical and biological processes simulation model for anaerobic digestion (AD) of primary sludge (PS) and (iii) the steady state simplification of the two phase AD model.

In a two-year follow-up research project (K5/1620), the four main links between common unit operations of WWTPs will be considered using mass balances based steady state models for the activated sludge system and aerobic and anaerobic digestion: (1) the primary settling tank (PST) - anaerobic digester (AD) link, (2) the activated sludge (AS) system - aerobic digester link, (3) the AS system - AD link and (4) the PST - aerobic digester link. In this development, biological N and P removal AS systems will be considered and where required, steady state models will be developed or extended to allow integrated design of the different unit operations making up the WWTP. Only unit operations in which the biological processes dominate will be considered, viz. N and P removal activated sludge, aerobic digestion and anaerobic digestion. Unit operations in which physical processes dominate, such as primary sedimentation, sludge thickening before and dewatering after sludge digestion will be regarded as solid/liquid separators and solids concentrators only. Several complex issues which require further experimental research remain around aerobic and anaerobic digestion of activated sludge including the polyphosphate accumulating organisms (PAOs), and these biological excess phosphorus removal (BEPR) activated sludge systems need to be considered in the follow-up project.

In particular, specific tasks for the follow up project for the steady state WWTP model will include:

- (1) The modelling of inorganics (ISS) within the activated sludge system has been completed (Section 4 above). However, tracking the ISS through the other unit operations needs to be addressed, in particular through aerobic and anaerobic digestion of primary (PS) and

- waste activated (WAS) sludges.
- (2) The steady state anaerobic digestion model needs to be incorporated into the steady state WWTP mass balances tracking model developed so far. This will require that the inputs for the AD model (i.e. the feed sludge characteristics) be included in the upstream unit operations. In addition to the parameters already in the mass balances model, this will include C, alkalinity, possible SCFA production in the PST. Also, and very importantly, it needs to be established whether or not the unbiodegradable particulate organics from the influent wastewater and generated in the activated sludge reactor (endogenous residue) as defined by the activated sludge (aerobic) system, are unbiodegradable also under anaerobic digester conditions.
 - (3) Recycling of various liquors (e.g. sludge thickening liquors) from downstream unit operations to upstream ones, and the characteristics of these recycle stream would have to be included.
 - (4) The steady state mass balances WWTP model needs to be extended to include biological P removal. This is not a simple task. In the activated sludge system, the ordinary heterotrophic (OHO) and polyphosphate accumulating (PAO) organisms have different endogenous respiration/die off rates, the former high ($b_{H20} = 0.24$ /d at 20 °C) and the latter low ($b_{G20} = 0.04$ /d at 20°C). These b rates influence the rates at which the nutrients N and P bound in the cell mass are released in aerobic (and anaerobic) digestion. The release rates of N and P from the cell bound phase to the dissolved phase under aerobic and anaerobic digestion conditions also needs to be investigated.
 - (6) Due to time constraints in the project, biological excess P removal was not investigated in the sequencing batch reactor (SBR) study. If time allows, this can be done with a BioP removal kinetic model, e.g. UCTPHO, to investigate P removal in SBR systems and how this compares with that of a conventional P removal system (e.g. a UCT configuration).

Accomplishing these tasks is very ambitious for the two year follow-up project (2005-2006), but they will be tackled with all the resources and expertise of the Water Research Group to advance the development of a mass balance WWTP model for steady state and cyclic flow and load conditions as fast as possible.

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LIST OF SYMBOLS AND ABBREVIATIONS

Abbreviation	Description
Ac	Acetate
ACP	Amorphous calcium phosphate
AD	Anaerobic digestion
ADL	Anaerobic digester liquor
Alk	Alkalinity
ADWF	Average dry weather flow
ANO	Autotrophic nitrifier organism
AS	Activated sludge
ASM1	Activated Sludge Model No. 1
ASM2	Activated Sludge Model No. 2
ATP	Adenosine triphosphate
BEPR	Biological excess phosphorus removal
BNR	Biological nutrient removal
C	Carbon
Ca	Calcium
CED	Chemical equilibrium dissociation
CF	Cape Flats
CIP	Chemical ion pairing
COD	Chemical oxygen demand
CP	Chemical / physical
CPB	Chemical / physical / biological
DO	Dissolved oxygen
FA	Fully aerobic
FSA	Free and saline ammonia
Fe	Iron
H	Hydrogen
HAc	Acetic acid
HAP	Hydroxyapatite
HPr	Propionic acid
IDS	Inorganic dissolved solids
ISS	Inert suspended solids
IWA	International Water Association
K	Potassium
Mg	Magnesium
MLE	Modified Ludzack Ettinger
MW	Molecular weight
N	Nitrogen
Na	Sodium
ND	Nitrifying / denitrifying
O	Oxygen
OHO	Ordinary heterotrophic organism
oP	Ortho phosphorus

OrgN	Organic nitrogen
OrgP	Organic phosphorus
OUR	Oxygen utilisation rate
P	Phosphorus
PAO	Polyphosphate accumulating organism
PGE	Physical gas exchange
PMP	Physical mineral precipitation
Pr	Propionate
PS	Primary sludge
PST	Primary settling tank
Q	Flow
R	Hydraulic retention time or sludge age for anaerobic digester
RBCOD	Readily biodegradable COD
SBCOD	Slowly biodegradable COD
SBR	Sequencing batch reactor
SCFA	Short chain fatty acid
SS	Settleable solids
SSADL	Blended PS and WAS digester liquor
SST	Secondary settling tank
SWW	Swine wastewater
T	Temperature
TDS	Total dissolved solids
TKN	Total Kjeldahl nitrogen
TOC	Total organic carbon
TP	Total phosphorus
TSS	Total suspended solids
UASB	Upflow anaerobic sludge bed
UASBDL	Upflow anaerobic sludge bed digester liquor
UCT	University of Cape Town
UCTADM1	University of Cape Town anaerobic digester model 1
V	Volume
VFA	Volatile fatty acid
VSS	Volatile suspended solids
WAS	Waste activated sludge
WRC	Water Research Commission
WW	Wastewater
WWTP	Wastewater treatment plant

Symbol**Description**

b	Death rate
C_{Hgas}	Head space gas concentration
C_T	Total inorganic carbon
C_{var}	Coefficient of variation
E	Fraction of hydrolysed COD utilised that is converted to biomass
f_{IOHO}	Inorganic content of ordinary heterotrophic organisms
f_{IPAO}	Inorganic content of polyphosphate accumulating organisms
f_m	Monovalent ion activity coefficient

f_{pr}	Fraction of COD removed by primary sedimentation
$f_{\text{PS'up}}$	Fraction of unbiodegradable COD in the sewage sludge
$f_{\text{Sb's}}$	Influent RBCOD fraction with respect to the biodegradable COD
$f_{\text{S'up}}$	Particulate unbiodegradable COD fraction
$f_{\text{S'us}}$	Soluble unbiodegradable COD fraction
f_{XBGP}	Phosphorus content of PAOs
$f_{\text{ZB,N}}$	N content of the OHOs
$f_{\text{ZB,P}}$	P content of the OHOs
f_{xm}	Unaerated sludge mass fraction
H_c	Dimensionless Henry's law constant
k_G	Gas phase individual mass transfer coefficient
K_h	First order hydrolysis rate constant
K_H	First order specific hydrolysis rate constant
K_I	Inhibition constant (hydrogen ion concentration at which the growth of acetoclastic methanogens is half the normal rate)
k_L	Liquid phase individual mass transfer coefficient
K_{La}	Overall liquid phase mass transfer rate coefficient
$k_{\text{max,HYD}}$	Maximum specific hydrolysis rate
K_{ppt}	Mineral precipitation rate constant
K_m	Weak acid/base kinetic rate constant
K_{rG}	Gas stripping rate constant
K_{rIP}	Ion pair kinetic rate constant
K_S	Half saturation coefficient
μ_A	ANO maximum specific growth rate
μ_{max}	Maximum specific growth rate
N_{obui}	Influent organic biodegradable soluble N
P_{atm}	Atmospheric pressure
p_{CO_2}	Partial pressure of CO_2
p_{H_2}	Partial pressure of hydrogen
p_{N_2}	Partial pressure of nitrogen
p_{O_2}	Partial pressure of oxygen
pK	Weak acid/base equilibrium constant
pK_{ST}	Ion pair kinetic rate constant
P_T	Total phosphorus
P_{tot}	Total gas pressure in head space
q_{gas}	Vent gas flow rate from the head space
Q_{gas}	Total gas production
r_h	Volumetric hydrolysis/acidogenesis rate
R_{hn}	Hydraulic retention time
R_s	Sludge age
R_{min}	Minimum sludge age for nitrification
r_{ZAC}	Growth rate of acetogens
r_{ZAD}	Growth rate of acidogens
r_{ZAM}	Growth rate of acetoclastic methanogens
r_{ZHM}	Growth rate of hydrogenotrophic methanogens
R^2	Correlation coefficient
S_{bp}	Biodegradable particulate organics concentration

S_{bpi}	Influent biodegradable particulate organics concentration
S_{bpr}	Biodegradable COD removal
S_{bs}	Biodegradable soluble COD concentration
S_{bsi}	Influent biodegradable soluble COD concentration
S_{bsa}	Soluble COD that is SCFA concentration
S_{bsai}	Influent soluble COD that is SCFA concentration
S_{bsACi}	Influent acetate concentration
S_{bsf}	Soluble COD that is glucose concentration
S_{bsfi}	Influent soluble COD that is glucose concentration
S_{bsfACi}	Influent acetic acid concentration
S_m	Methane concentration
S_{te}	Total effluent COD concentration
S_{ti}	Total influent COD concentration
S_{up}	Unbiodegradable particulate COD concentration
S_{upi}	Influent unbiodegradable particulate COD concentration
S_{us}	Unbiodegradable soluble COD concentration
S_{usi}	Influent unbiodegradable soluble COD concentration
X_{IO}	Accumulated inert suspended solids in the reactor
X_{Ioi}	Influent inert suspended solids
Y_{ZA}	ANO yield coefficient
Y	Yield coefficient
Y_{ZH}	OHO yield coefficient
Y_{ac}	Anabolic yield of acetogens
Y_{ad}	Anabolic yield of acidogens
Y_{am}	Anabolic yield of acetoclastic methanogens
Y_{hm}	Anabolic yield of hydrogenotrophic methanogens
Y_{AC}	True acetogen yield
Y_{AD}	True acidogen yield
Y_{AM}	True acetoclastic methanogen yield
Y_{HM}	True hydrogenotrophic methanogen yield
Z_{AC}	Growth of acetogenic organisms
Z_{AD}	Growth of acidogenic organisms
Z_{AM}	Growth of acetoclastic methanogenic organisms
Z_{HM}	Growth of hydrogenotrophic methanogenic organisms

Note: Only symbols and abbreviations used in the text are included, those in equations are defined below the appropriate equations.

CHAPTER 1

TOWARD DEVELOPING INTEGRATED MASS BALANCE MODELS FOR CHEMICAL, PHYSICAL AND BIOLOGICAL PROCESSES IN WASTEWATER TREATMENT PLANTS

1. INTRODUCTION

To aid the design and operation of, and research into conventional biological wastewater treatment systems, a variety of mathematical models have been developed. For these models the primary focus has been on the individual unit operation of the activated sludge system, since this is the unit operation that produces the effluent that must comply with legislated effluent criteria (Wild and Siegrist, 1999). As a consequence the activated sludge system has been well researched and relatively reliable simple steady state design (e.g. WRC, 1984; Wentzel *et al.*, 1990; Maurer and Gujer, 1994) and complex dynamic simulation models (e.g. Dold *et al.*, 1980, 1991; Wentzel *et al.*, 1992; Henze *et al.*, 1987, 1995) have been developed for the system, including biological N and/or P removal, or not. However, little attention has been focussed on modelling the wastewater treatment plant (WWTP) as a whole, in an integrated fashion.

The WWTP comprises a sequence of individual unit operations (e.g. primary settling, activated sludge, anaerobic digestion). These individual unit operations are interconnected through a web of flows: The outputs from upstream unit operations become inputs to downstream unit operations; further, common practise at WWTPs is to recycle various liquors (e.g. sludge thickening and anaerobic digestion supernatants) from downstream unit operations to upstream ones. This interconnection of individual unit operations means that design and operation optimisation of one unit operation can have unexpected and often unforeseen consequences on the performance of both upstream and downstream unit operations, and hence on the WWTP performance as a whole. For example, the recycling of nutrient rich liquors from sludge treatment unit operations to the activated sludge system has a significant impact on the WWTP effluent quality (e.g. Pitman *et al.*, 1991; Wild and Siegrist, 1999), contributing up to 25% of the total N load to the activated sludge system (Janus and van der Roest, 1997).

To assess and quantify the interdependencies of the various unit operations making up the WWTP, models that track materials of importance through the WWTP on a mass balance basis are required. Such models will be termed materials mass balance ones. Materials mass balance based models of the entire WWTP would be a valuable tool to aid optimisation of WWTP design and performance. Potential advantages of mass balance based models of the entire WWTP are that they allow for design and operation:

- (1) Tracking compounds through the WWTP - currently little more than total settleable solids (TSS) is used mostly manually to assess loads and capacities on different unit operations in a WWTP sequence; TSS is not mass conservative and provides no assessment of mass balances and continuity for the sequence of unit operations at the WWTP.
- (2) Identifying characteristics of streams from one unit operation (e.g. primary settling) to a downstream one (e.g. aerobic/anaerobic digestion); this will assist in design and

- performance assessment and optimisation of the various unit operations in the WWTP.
- (3) Assessing impact of recycling sludge thickening and dewatering liquors from downstream operations on upstream operations.
 - (4) Identifying bottlenecks and overloaded unit operations which limit the capacity of the WWTP.
 - (5) Optimizing unit operations for maximum unit operation throughput and minimum impact on effluent quality and upstream units.
 - (6) Assessing the impact of interventions such as including additional unit operations in the sequence like phosphorus precipitation or nitrification of recycling liquors.
 - (7) Identifying WWTP operational and analytical data that do not conform to mass balance and continuity principles - from the writers' experience something as basic as flow measurement can have significant errors up to 50% leading to inefficient and uneconomical operation of the WWTP.

Accordingly, this project was initiated in April 2002 with overall objective of developing mass balance models for the entire WWTP. A WWTP mass balances model would have to ensure that materials of importance in any of the individual unit operations are included, so that materials are common at the interconnections between unit operations. This may require modelling of parameters in an individual unit operation that may not be of significance to that unit operation, but may crucial to a unit operation that receives the output. For example, in activated sludge models carbon (C) is not usually included as a compound, but C is of importance in the anaerobic digestion of sewage sludges, because in this unit operation it determines gas production and composition, and influences the pH established through the weak acid/base chemistry (C also becomes important in the activated sludge system when pH is included, a necessity for a proton balance).

From the above, the major (but long term) objective of this project was to:

- Develop a materials mass balances model for the entire municipal waste water treatment plant (WWTP). Materials identified as of importance and to be included in the model were COD (electron), carbon (C), nitrogen (N), phosphorus (P), alkalinity (proton), calcium (Ca) and magnesium (Mg). Also, because of its importance in accepted design procedures for the various unit operations (e.g. secondary settling tanks), the inorganic concentrations were to be included.

Unit operations in which transformations of the materials take place and hence to be modelled were primary sedimentation, biological wastewater treatment in activated sludge systems, including or excluding biological N and P removal, aerobic and anaerobic stabilization of primary and secondary sludges and generic sludge thickening. This WWTP model would be developed for both steady state and dynamic simulation conditions.

Steady state models are based on the slowest process kinetic rate that governs the overall behaviour of a WWTP unit operation and relates this process rate to the unit operation's design and operating parameters. Therefore, steady state models allow the individual unit operations design and operating parameters, such as reactor volume and recycle ratios, to be estimated reasonably simply and quickly from system performance criteria specified for the design, such as effluent quality. For example, a steady state aerobic or anaerobic digestion model would be useful to (i) estimate retention time, reactor volume, gas production and composition for a

required system performance like COD (or VSS) removal (degree of sludge stabilization), (ii) investigate the sensitivity of the system performance to changes in the design and operation parameters, (iii) provide a basis for cross-checking simulation model results, and (iv) estimate product stream concentrations for design and operation of down- (or up-) stream unit operations of the wastewater treatment plant, e.g. assess the impact of ammonia, nitrate or phosphate return with recycling of digestion liquors. Since the outflow(s) from one unit operation become the inflow(s) to downstream and/or upstream unit operations, it makes sense to link all the selected unit operations and design each unit operation in its integrated context of the entire WWTP for the particular influent wastewater characteristics. Once approximate design and operating parameters are known, these can serve as input to the more complex simulation models to investigate dynamic behaviour of the unit operation and refine the design and operating parameters.

Development of materials mass balance models for the entire WWTP requires that steady state and dynamic simulation models be developed for those unit operations where these are not available or inadequate. In these developments the main focus was to be on the unit operations that are not simply physical separations (e.g. settling tanks, dissolved air flotation), but include biologically mediated transformations. In assessing the level of modelling of the various unit operations, one unit operation immediately apparent to require intensive modelling effort was that of anaerobic digestion of sewage sludges. Steady state and dynamic simulation modelling of even the biologically mediated reactions in this unit operation had not progressed to the same extent as for activated sludge. Hence, this was identified as a priority in this research project, *and was the first main aim.*

To develop models for anaerobic digestion of sewage sludges, the models need to be considerably more complex than existing models for the activated sludge system. In activated sludge systems, generally it can be accepted that the biological processes dominate, and hence physical (e.g. gas exchange) and chemical (e.g. precipitation) processes are of minor importance and hence can be neglected. Further, in most cases it also can be accepted that the biological processes take place within a regime of constant pH, that is, weak acid/base chemistry and its interactions with the biological processes do not need to be included. For the activated sludge system treating municipal wastewaters, where the concentrations of compounds that cause changes in reactor pH are low relative to the alkalinity of the wastewater, these assumptions usually are valid. However, in anaerobic digestion physical processes are of importance in that considerable gas production of CO_2 and CH_4 takes place, and in the digestion of biological P removal sludges chemical processes play an important role in that significant precipitation can occur within the digester or in the liquors leaving the digester. This strongly suggested that the models for anaerobic digestion would have to include in addition to the biological processes, chemical and physical processes, and interactions between all these groups of processes. To include chemical and physical processes requires that the pH parameter/compound is incorporated directly in the models and accurately determined, as pH is of fundamental importance in the chemical and physical processes, significantly influencing them. Furthermore, in anaerobic digestion pH itself is a crucial parameter, as the biological processes are particularly pH sensitive, and produce and consume weak acid/base species (e.g. short-chain fatty acids, SCFA) that can significantly influence the pH, i.e. it is no longer reasonable to accept that the biological processes take place within a regime of constant pH. Hence, inclusion of pH directly within the models for anaerobic digestion is fundamental. Including pH will require that all the weak acid/base systems present that influence the pH (e.g. carbonate, SCFA, free and saline

ammonia, FSA and phosphate systems) also be included in some fashion, i.e. aqueous chemical processes require inclusion. That is, the weak acid/base chemistry "background" in which the biological processes operate needs to be brought to the "foreground" and must form an integral part of the models.

In a previous WRC research project (K5/692 "Treatment of wastewaters with high nutrients (N and P) but low organic (COD) contents", Musvoto *et al.*, 2002), a novel approach to kinetic modelling of weak acid/base chemistry and incorporating pH directly into kinetic models was developed (Musvoto *et al.*, 1997, 2000). This approach was recognised to facilitate integrating chemical and physical processes with biological process based models, a requirement in the current research project. Hence, this approach will be followed here and extended to anaerobic digestion of sewage sludges.

Development of steady state and dynamic simulation models for anaerobic digestion requires that the inputs to the digester (i.e. the sewage sludge) be well defined. Accordingly, primary and secondary sewage sludge characterisation formed the basis for ***the second aim in the project***. In this regard, of particular importance are COD, weak acid/base chemistry and species (and associated pH), and C and N contents of the input. These parameters would have to be predictable in the outputs from upstream unit operations (see below).

In the materials mass balances model, the activated sludge system unit operation has received considerable modelling attention in the past (e.g. Dold *et al.*, 1980, 1991; Henze *et al.*, 1987, 1995). In South Africa, application of these models has been largely restricted to continuous flow-through type systems with secondary settling tanks (SSTs), since this is the system almost universally implemented. As alternative, sequencing batch reactor (SBR) activated sludge systems have been developed and implemented quite widely in Australia for small WWTPs (< 20 Mt/d). The SBR offers certain potential advantages, for example, SSTs are not required, because the final settling step is conducted within the bioreactor. Due to the apparent success of the SBR in Australia, interest in these systems has developed in South Africa. Accordingly, a process performance evaluation of the system in comparison with the conventional continuous flow-through type system was conducted. This required the implementation of the available activated sludge models in the SBR configuration for South African municipal wastewaters. This implementation would also provide the materials mass balances models with an alternative for the conventional activated sludge unit operation, and ***formed the third main aim of the project***.

As the project progressed, two aspects not included in the original project aims were identified to be important and hence received attention:

- (1) In the anaerobic digestion model, the characteristics of the input (i.e. the sludges) are important for reasonable simulations and calculations, including *inter alia* the pH and associated weak acid/base species (e.g. carbonate, ammonia) and C and N contents. The anaerobic digester input is derived in part from the activated sludge unit operation (the secondary sludge), and hence these inputs would need to be predictable parameters in this unit operation: Current activated sludge models do not include these parameters, and hence would have to be extended to include them. This requires that the physical processes (for CO₂ loss via gas stripping) and pH be incorporated directly in the activated sludge models in some fashion. Initially, this would be restricted to aerobic COD

removal and nitrification, and anoxic/aerobic COD removal, nitrification and denitrification activated sludge systems. This was added to the original aims and formed the basis for the *fourth main aim in the project*.

- (2) In tracking materials through the WWTP, it became apparent that the inorganics were of significance, in that conventional design procedures for a number of the physical separation unit operations are based on total suspended solids (TSS) concentrations which include the inorganics. Reliable steady state design and dynamic simulation predictive models for the organic (volatile) suspended solids (VSS) concentrations in activated sludge systems are available. In contrast, predictive models for the reactor inorganic suspended solids (ISS), and hence the total suspended solids ($TSS = VSS + ISS$) concentrations have not received the same attention or general acceptance. Accordingly, attention was focussed on developing a reliable model for prediction of ISS, and hence TSS. This was the *fifth main aim in this research project*.

1.2 RESEARCH OBJECTIVES AND AIMS

From the discussion above, the overall long term objective of this research project was to:

- To develop a COD (electron), carbon (C), nitrogen (N), phosphorus (P), alkalinity (proton), calcium (Ca) and magnesium (Mg) mass balances model including inorganic concentrations for municipal waste water treatment plants (WWTP) including primary, secondary and sludge treatment.

To achieve this objective a number of specific aims were originally identified for the project:

- (1) To develop an integrated mixed weak acid/base chemical, physical and biological processes model in three phases (liquid, gas and solid) for anaerobic digestion (AD) of sewage sludge.
- (2) To develop a scheme for sewage sludge primary and secondary sludge characterization for the AD model (in conformity with the wastewater and activated sludge characterization schemes).
- (3) To develop a biological nutrient removal (BNR) activated sludge model for sequencing batch reactors (SBR) to compare BNR in SBR with BNR in multi-reactor systems applied in South Africa.

During the course of the project, two additional aims were identified that were not part of the original proposal:

- (4) To extend the activated sludge simulation models to incorporate pH as a predictive parameter; this required incorporating chemical (weak acid/base aqueous chemistry) and physical (gas exchange) processes and integrating these with the biological processes. These extensions were to be restricted to aerobic and anoxic/aerobic activated sludge systems.
- (5) To develop steady state and dynamic simulation predictive models for ISS, to enable inorganics to be tracked through the WWTP.

The products emerging from these objectives were envisaged to be (1) a simple steady state material mass balance model and computer program and a kinetic simulation model for

municipal WWTPs. From input influent wastewater characteristics, the program will track the materials (and water) through the various unit operations of the WWTP such as primary sedimentation, activated sludge (in- or excluding biological N and/or P removal) as well as aerobic and/or anaerobic digestion of primary and/or secondary sludge (Overall Objective) and (2) an integrated chemical, biological and physical processes kinetic model for anaerobic digestion wherein the biological processes interact with the weak acid/base chemistry of the liquid phase in which they take place so that the model will be able to predict operating pH, bioprocess stability and mineral precipitation (Aim 1). Outputs from the material mass balance model (1 above) will help define the input influent characteristics of the sludge to be digested from the influent wastewater characteristics and the performance and type of primary and secondary treatment (Aim 3). These objectives and outputs turned out to be too ambitious for this 3 year project (2002-2004). However, a number of significant advances were made towards this overall objective of developing steady state and dynamic simulation mass balance models for the entire WWTP. These advances are outlined in this report.

1.3 RESEARCH APPROACH AND REPORT LAYOUT

This report sets out the development of mass balance based kinetic models that can simulate quantitatively

- (1) 3 phase (aqueous-gas-solid) mixed weak acid/base chemical physical processes of multiple mineral precipitation of calcium, magnesium phosphate and carbonate based minerals and gas exchange,
- (2) 2 phase (aqueous-gas) mixed weak acid/base chemical, physical biological processes of nitrogen removal activated sludge systems and
- (3) 2 phase (aqueous-gas) mixed weak acid/base chemical, physical biological processes of anaerobic digestion of sewage sludges.

In the development of these models, requirements were (i) that they should be as far as possible combinations of the existing biological models and the mixed weak acid base chemistry so that the chemical physical processes within which the biological processes take place are modeled as well as the biological processes themselves, (ii) that the integration between the biological and chemical physical processes is seamless with the hydrogen ion (i.e. pH) being modeled as a process compound like all the others, and (iii) that the models of the different unit operations such as N removal activated sludge, anaerobic digestion, primary sedimentation etc. can be readily combined to form a mass balances based kinetic model for the entire wastewater treatment plant.

Although the development of mass balances based (COD, C, N and P) steady state and dynamic simulation models for the entire WWTP, including aerobic and anaerobic digestion of waste sludge, turned out to be a task greater than could be accomplished on this 3 years project, this report describes a number of significant steps that were achieved towards this greater objective, viz.

- (1) Develop a predictive model for the activated sludge reactor inorganic suspended solids (ISS) concentration so that the reactor total (TSS) concentration becomes a model calculated value based on a measured influent ISS concentration and no longer estimated

- from an empirically selected VSS/TSS ratio for the activated sludge (Aim 5; Chapter 2).
- (2) Set up a simple mass balances (COD and N) WWTP steady state and kinetic simulation models with primary sedimentation, anoxic aerobic activated sludge and aerobic digestion of primary and waste activated sludge. Compare and verify kinetic model with the steady state model calculations (Overall objective, Chapter 3).
 - (3) Refine and further validate against literature data the 3 phase mixed weak acid base chemical physical processes model developed by Musvoto et al. (1997, 2000) and van Rensburg et al. (2003) (Prelim to Aim 1, Chapter 4).
 - (4) Integrate the biological processes of N removal activated sludge (ASM1) into a 2 phase (aqueous-gas) version of the chemical physical processes model (2) above and verify it with the normal single aqueous phase ASM1 and validate it against literature data (Aim 4, Chapter 5).
 - (5) Integrate the biological processes of anaerobic digestion into a 2 phase (aqueous-gas) version of the chemical physical processes model (2) above to construct a mass balances (COD, C, N, O, H) based integrated chemical physical biological processes model capable of predicting digester pH (UCTADM1) and verify it with laboratory and literature data. Included here is input characterisation. (Aims 1 and 2, Chapter 6).
 - (6) Simplify UCTADM1 into a steady state model for initial design of AD systems and integration into the WWTP model (Aim 1, Chapter 7).
 - (7) Comparison of SBR for BNR with multi-reactor systems as applied in South Africa (Aim 3, Chapter 8).

Detail of these developments are presented in the subsequent chapters as indicated above.

1.4 CONCLUSION

This report encompasses a comprehensive range of steady state and kinetic models:

Steady state models:

1. Mass balances (COD, N and P) steady state model with primary sedimentation, anoxic aerobic activated sludge and aerobic digestion of primary and waste activated sludge.
2. Steady state anaerobic digestion (COD, C, N, O, H) model.
3. A steady state model for calculating the reactor ISS concentration for biological nutrient (N and P) removal activated sludge systems.

Kinetic simulation models:

- (i) Including prediction of the reactor ISS concentration can be readily accomplished from the principles of the steady state ISS model with minor modification of existing kinetic simulation models for biological nutrient removal systems.
- (ii) Integrated 2 phase (aqueous-gas) N removal activated sludge (ASM1) kinetic model.
- (iii) Integrated 2 phase (aqueous-gas) chemical, physical and biological anaerobic processes model.
- (iv) Kinetic model for the SBR BNR system as would applied in South Africa

The original objectives of the project required that phosphorus (P) be included in the steady state and kinetic models as well as the inclusion of the third (solid) phase in the kinetic models. This was not achieved in the timescale of this project and forms part of the objectives of a follow-up

project (K5/1620) which continues the research commenced in this project of developing mass balances based models of the entire WWTP. Furthermore, it was agreed that the mass balances steady state WWTP model computer program based on the research conducted in this project and which formed part of the objectives of this project, would be outsourced to an external specialist company, because the Water Research Group does not possess the necessary computer programming skills to develop such a program.

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CHAPTER 2

A MODEL FOR CALCULATING THE REACTOR INORGANIC SUSPENDED SOLIDS CONCENTRATION IN ACTIVATED SLUDGE SYSTEMS

2.1 INTRODUCTION

Reliable steady state and dynamic simulation predictive models for the organic (volatile) suspended solids (VSS) concentration in activated sludge (AS) reactors have been developed over the past two decades. In contrast, predictive models for the reactor inorganic suspended solids (ISS), and hence the total suspended solids ($TSS = VSS + ISS$) concentrations have not received the same attention or general acceptance. Reasonably accurate estimates of the TSS concentration are important for the design and operation of the down-stream unit operations, such as secondary settling tanks and sludge treatment systems. In this chapter, a new predictive model for the ISS concentration in the AS reactor (excluding that from chemical precipitant dosing) is presented.

2.2 MODEL DEVELOPMENT

In this model the ISS content of the organics is not conceptualized as actual inorganics structurally part of the VSS itself as it exists in the reactor, but rather as inorganics that are formed in the TSS test procedure. When the mixed liquor organics are in the activated sludge reactor, in particular the active organisms, they include intracellular and/or bound water, which contains inorganic dissolved solids. When the mixed liquor is dried in the TSS test procedure, these inorganic dissolved solids precipitate to form ISS. It is mainly for this conceptual reason that only active organisms are accepted to have an ISS/VSS ratio; the unbiodegradable organic components of the mixed liquor clearly cannot contain intracellular water and the bound water is accepted to be negligible.

Experimental data measured in UCT's Water Research Laboratory over the past 15 years forms the basis for the model development and validation. Altogether 22 investigations (I1 to I22) were considered, some of which ran concurrently (Ekama and Wentzel, 2004). In these investigations, artificial or real wastewater was feed to 30 FA or ND and 18 NDBEPR systems operated over a range of sludge ages (3 to 20d) and nominal hydraulic retention times (8.9 to 48h).

2.2.1 Conceptual Model

Conceptually the reactor ISS concentration model is based on the following principles;

- 1) ISS in the influent (X_{iss} , mgISS/l) accumulates in the reactor (X_{io}). From a mass balance, this accumulation is proportional to the sludge age (R_s) and inversely proportional to the nominal hydraulic retention time (R_{ho}). This is in agreement with Gujer (1993).
- 2) Precipitation of minerals in the biological reactor (unless stimulated by chemical precipitant dosing, which is not considered in this report), and dissolution of influent ISS, are considered negligible.
- 3) In contrast to the inorganic models of ASM2, 2d and Gujer (1993), but in agreement with Wentzel et al. (2002), slowly biodegradable particulate substrate does not contain an inorganic component.
- 4) The ordinary heterotrophic organisms (OHOs) and the phosphate accumulating organisms (PAOs) take up inorganic dissolved solids (IDS) as part of their intra-cellular cell mass which, when sludge samples are dried and incinerated in the TSS-VSS test procedure, precipitate as inorganic solids. Insofar as suspended solids (organic and inorganic) accumulation in the reactor is concerned, the autotrophic nitrifying organisms make a negligible contribution (<2%).

- 5) Additionally, the PAOs take up inorganic dissolved solids (IDS) and store it as polyphosphate with associated counter ions, in conformity with ASM2 and 2d.
- 6) Although in ASM2, 2d, Gujer (1993) and Wentzel et al. (2002) inorganics are included in the endogenous residue fraction, Wentzel et al. (2002) noted that there is no information in the literature on the validity of this assumption. In the model developed here, it is assumed that there are no inorganics associated with unbiodegradable particulate organics, which includes endogenous residue. This assumption was validated in the model development (Ekama and Wentzel, 2004).

Integrating the above into the Wentzel et al. (1990) steady state NDBEPR AS model, the masses of VSS, ISS and TSS in the reactor, and the VSS/TSS ratio (f_i), are given by:

$$\frac{MX_v}{MS_B} = (1 - f_{S'us} - f_{S'up}) \left[\left(1 - \frac{\% f_{Sb's}}{100} \right) \frac{Y_H R_s}{(1 + b_{HT} R_s)} (1 + f_{EH} b_{HT} R_s) + \frac{\% f_{Sb's}}{100} \frac{Y_G R_s}{(1 + b_{GT} R_s)} (1 + f_{EG} b_{GT} R_s) \right] + \frac{f_{S'up}}{f_{cv}} R_s \quad \text{kgVSS/(kgCOD load/d)} \quad (1)$$

$$\frac{MX_{io}}{MS_B} = (1 - f_{S'us} - f_{S'up}) \left[\left(1 - \frac{\% f_{Sb's}}{100} \right) \frac{Y_H R_s}{(1 + b_{HT} R_s)} f_{iOHO} + \frac{\% f_{Sb's}}{100} \frac{Y_G R_s}{(1 + b_{GT} R_s)} f_{iPAO} \right] + \frac{X_{iol}}{S_B} R_s \quad \text{kgISS/(kgCOD load/d)} \quad (2)$$

$$\frac{MX_t}{MS_B} = (1 - f_{S'us} - f_{S'up}) \left[\left(1 - \frac{\% f_{Sb's}}{100} \right) \frac{Y_H R_s}{(1 + b_{HT} R_s)} (1 + f_{EH} b_{HT} R_s + f_{iOHO}) + \frac{\% f_{Sb's}}{100} \frac{Y_G R_s}{(1 + b_{GT} R_s)} (1 + f_{EG} b_{GT} R_s + f_{iPAO}) \right] + \left[\frac{f_{S'up}}{f_{cv}} + \frac{X_{iol}}{S_B} \right] R_s \quad \text{kgTSS/(kgCOD load/d)} \quad (3)$$

$$f_i = \frac{MX_v}{MX_t} \quad \text{kgVSS/kgTSS} \quad (4)$$

where

b_{HT}, b_{GT} = endogenous respiration rate for OHOs and PAOs at T °C
= 0.24/d and 0.04/d respectively at 20°C ($\theta_b = 1.029$ for both)

f_{cv} = COD/VSS ratio of organics = 1.48 mgCOD/mgVSS

f_{EH}, f_{EG} = endogenous residue fraction of the OHOs and PAOs
= 0.20 and 0.25 respectively

f_i = VSS/TSS ratio of reactor sludge mass

f_{iOHO} = inorganic content of OHO cell mass = 0.15 mgISS/mgOHOVSS

f_{iPAO} = total inorganic solids content of PAOs (mgISS/mgPAOVSS)

$f_{S'up}$ = influent unbiodegradable particulate COD fraction

$f_{S'us}$ = influent unbiodegradable soluble COD fraction

$f_{Sb's}$ = influent readily biodegradable (RB)COD fraction with respect to biodegradable COD.

MS_B = COD mass load on reactor (kgCOD/d) = $Q_i S_B$

MX_{io} = mass of ISS in reactor (kgTSS)

MX_t = mass of TSS in reactor (kgTSS)

MX_v = VSS mass in reactor (kgVSS)

- Q_i = average dry weather flow (ADWF, Mt/d)
 R_s = system sludge age (days)
 S_{ii} = flow weighted average influent COD concentration entering biological reactor (mgCOD/l)
 X_{io} = ISS concentration in biological reactor (mgISS/l)
 X_{loi} = influent ISS concentration entering biological reactor (mgISS/l)
 X_v = VSS concentration in the reactor (mgVSS/l)
 Y_H, Y_G = yield coefficient for OHOs and PAOs = 0.45 mgVSS/mgCOD
 $\%$ = Percentage of influent readily biodegradable COD taken up by PAOs

In the ISS model (Eq 2), there are 3 unknown parameters which need to be determined, i.e. the influent ISS concentration (X_{loi}), which may be directly measured, and the inorganic contents of the OHOs and PAOs (f_{iOHO} and f_{iPAO}), which cannot be measured directly, only calculated indirectly by matching measured and model predicted reactor ISS concentrations. However, because in the 21 investigations (I1 to I21) the influent ISS concentration was not measured except in I11, I12, and I18 and in two 24 hour tests at the source WWTP (I22) (see Table 1), the values for all three parameters had to be determined from model application to the 48 experimental systems. Details of the 22 experimental investigations are given by Ekama and Wentzel (2004).

Table 1: Mitchells Plain wastewater influent ISS/COD concentration ratios (mg/mg) measured at the treatment plant before (raw) and after (settled) primary settling (Investigations I22 and I18) and in the laboratory on the collected raw wastewater from the same plant (Investigations I11 and I12).

At the Mitchells Plain wastewater treatment plant			In the laboratory	
Investigation	Raw	Settled	Investigation	Raw
I18 ^a	-	0.041	I11 ^a	0.031
I22: Test 1 ^b	0.041	0.039	I12 ^a	0.087-0.096
I22: Test 2 ^b	0.050	0.043		

^a Determined by filtration through Whatman's No 1 ashless filter papers of known dry mass, drying at 105°C for 24h and incineration in a crucible of known dry mass at 600°C for 20 minutes.

^b Determined by filtration through pretreated glass fibre membranes of known dry mass, drying at 105°C for 24h and incineration at 600°C for 20 minutes. Filter pretreatment comprises incineration at 600°C for 6h to stabilize its mass before subsequent heating.

2.3 MODEL APPLICATION

In application of the model (Eq 2) to the various experimental systems, the following approach was adopted: (1) Systems fed artificial wastewater received zero or very low influent ISS ($X_{loi} \approx 0$). The ISS measured in the reactor is therefore predominantly the ISS content of the OHOs or PAOs. The 6 systems (2 ND and 4 NDBEPR) fed artificial wastewater formed the starting point for determining the initial estimates for the OHO and PAO ISS contents (f_{iOHO} and f_{iPAO}). (2) Because the influent ISS concentrations (X_{loi}) were not measured except in 3 investigations, this concentration was calculated with Eq (2) from the measured reactor ISS concentration (X_{io}) and the initial estimates of f_{iOHO} and f_{iPAO} for each sewage batch or steady state period of each system in each investigation. Because different influent COD concentrations were fed to the different systems by diluting the collected wastewater with tap water to a target feed COD concentration, this calculated influent ISS concentration was expressed as a ratio of the feed COD concentration (S_{ii}), i.e. X_{loi}/S_{ii} mgISS/mgCOD (as in Eq 2), to make the influent ISS comparable between systems and investigations. Consistency of the influent X_{loi}/S_{ii} ratio over a range of sludge ages and retention times in the same investigation and between investigations allowed refinement of the initial f_{iOHO} estimate from the artificial wastewater systems.

2.3.1 Calculation Method

For each sewage batch or steady state period of a system in an investigation, the mass of VSS for FA, ND or NDBEPR systems were calculated iteratively with Eq 1. The measured values for the influent COD concentration, RBCOD fraction and unbiodegradable soluble COD fraction ($f_{s,us}$ = filtered effluent COD/ S_0) were input to the equation together with the known sludge age. The particulate unbiodegradable COD fraction ($f_{s,up}$) was varied until the calculated system VSS mass, comprising active and endogenous PAO and/or OHO components and unbiodegradable particulate VSS from the influent, matched that measured. For the NDBEPR systems, when the correct $f_{s,up}$ had been found, the calculated P removal was matched to that measured by decreasing the PAO P content (f_{XBGP}) from the standard value of 0.38 mgP/mgPAOVSS to a lower value (Ekama and Wentzel, 1999). Generally, when the P uptake was predominantly aerobic (>90% of total P uptake), the calculated f_{XBGP} was close to the 0.38 mgP/mgPAOVSS value for the enhanced PAO cultures of Wentzel et al. (1989). However, when significant anoxic P uptake took place (>20%), the calculated f_{XBGP} was lower than 0.38 mgP/mgPAOVSS (Hu et al., 2002). For the FA and ND systems, the % factor in Eq 3 was set to zero, which in the model stops PAOs, and their associated endogenous VSS, from forming. For the enhanced PAO cultures of Wentzel et al. (1989), the % factor was set to 100 and the influent RBCOD fraction with respect to biodegradable COD, f_{bs} , was set to 1.0 because all the influent COD was in the RBCOD (SCFA) form, which in the model, stops OHOs and their associated endogenous VSS from forming.

With $f_{s,up}$ known for each sewage batch or steady state period of a system in an investigation, Eq 2 was used with the measured reactor ISS concentration (X_{I0}) and initial estimates for the ISS contents of the OHOs and PAOs (f_{iOHO} and f_{iPAO}) to calculate the influent ISS concentration (X_{I0i}) for each sewage batch or steady state period of a system in an investigation. For each system in an investigation, the weighted mean influent ISS concentration (X_{I0i}) was determined by multiplying the sewage batch or steady state period average X_{I0i} values by the number of tests in the sewage batch or steady state period, adding these over the whole investigation and dividing by the total number of tests on the system in the investigation. For investigations with more than one system, a weighted investigation mean X_{I0i} was calculated from the weighted system X_{I0i} means. The investigation weighted mean X_{I0i} and selected f_{iOHO} and f_{iPAO} were then applied in Eq 2 to the sewage batch or steady state period average data to determine the calculated reactor ISS concentrations (X_{I0}) for each sewage batch or steady state period, which were then compared with the corresponding measured sewage batch or steady state period ISS concentrations on each system. For those investigations where the influent ISS was not measured, the final f_{iOHO} and f_{iPAO} values accepted were those that gave the most consistent comparison between calculated and measured reactor ISS concentrations over all the sewage batches or steady state periods of the different systems of an investigation and between investigations. For those investigations where the influent ISS (X_{I0i}) was measured, the calculated influent ISS/COD ratio (X_{I0i}/S_0) was compared with the measured value.

2.4 RESULTS

From the enhanced PAO cultures investigation (Wentzel et al., 1989, I1), the PAO ISS content (f_{iPAO}) for 100% aerobic P uptake BEPR was calculated to be 1.30 mgISS/mgPAOVSS, which gave a very good correlation with experimental data (Fig 1). From the ND systems fed artificial or real wastewater over 3 to 20 days sludge age, the OHO ISS content (f_{iOHO}) was estimated to be around 0.15 mgISS/mgOHOVSS. These calibrated OHO and PAO ISS contents were then applied to NDBEPR systems. For the systems exhibiting > 90% aerobic P uptake BEPR, the predicted ISS correlated well with that measured (Fig 2). However, for systems exhibiting significant anoxic P uptake BEPR, for which the P content of the PAOs was lower, the correlation was very poor.

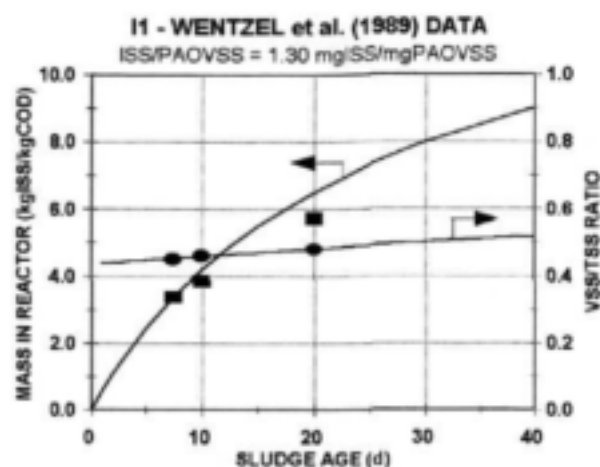


Fig 1: Model predicted (lines) and experimentally measured reactor ISS mass in kgISS/kgCOD load (■) and VSS/TSS ratio (●) versus sludge age for the four acetate fed enhanced PAO culture systems of Wentzel et al. (1989) (I1) accepting PAO ISS content $f_{PAO} = 1.30$ mgISS/mgVSS (> 90% aerobic P uptake BEPR).

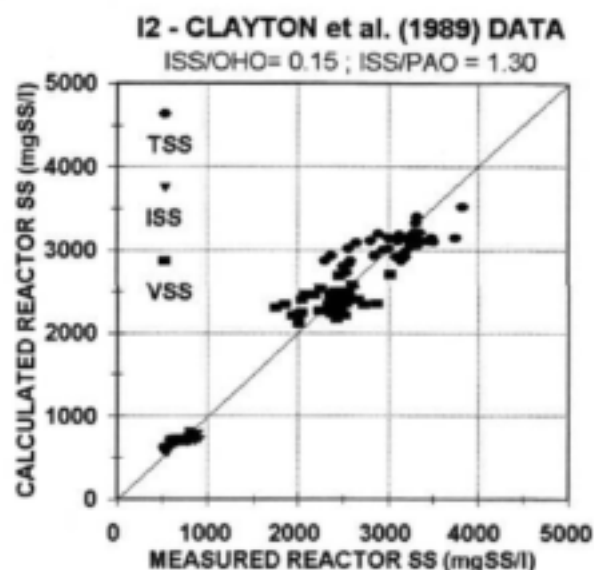


Fig 2: Model predicted versus experimentally measured sewage batch average reactor ISS (▼), VSS (■) and TSS (●) concentrations for OHO and PAO ISS content (f_{OHO} and f_{PAO}) of 0.15 and 1.30 mgISS/mgVSS for the > 90% aerobic P uptake BEPR MUCT system of Clayton et al. (1989) at 18 days sludge age.

Because the P content of the PAOs was lower, it seemed reasonable to accept that the ISS content also would be lower. Hence, a linear relationship between the P and ISS contents of the PAOs was established with the enhanced PAO cultures polyphosphate content at the one extreme and zero polyphosphate content (equivalent to OHOs) at the other extreme, viz.

$$f_{PAO} = f_{PAO_{BM}} + 3.286 (f_{XBGP} - f_{XBGP_{BM}}) \quad \text{mgISS/mgPAOVSS} \quad (5)$$

$f_{PAO_{BM}}$ = inorganic solids content of the PAO active biomass (mgISS/mgVSS)
= 0.15 mgISS/mgPAOVSS (without polyphosphate)

f_{XBGP} = total P content of PAOs (= $f_{XBGP_{BM}} + f_{XBGP_{PP}}$)

$f_{XBGP_{BM}}$ = P content of the PAO cell mass = 0.03 mgP/mgPAOVSS.

The implications of Eq 5 are that (1) the PAO P and ISS contents without polyphosphate are the same as OHOs (i.e. $f_{XBGP_{BM}} = f_P = 0.03$ mgP/mgPAO or OHO VSS and $f_{PAO_{BM}} = f_{OHO} = 0.15$ mgISS/mgPAO or OHO VSS) and (2) the 3.286 factor is the ISS content of the PAO intracellular polyphosphate. This value correlates very closely with the 3.19 mgISS/mgP value estimated from the composition of polyphosphate (Fukase et al., 1982, Wentzel et al., 1989) and the 3.23 value included in ASM2 and 2d by Gujer (1993). It is not clear where Gujer (1993) obtained the 3.23 value - it is possible that he calculated it from the enhanced PAO cultures of Wentzel et al. (1989) so the close correspondence with his value should not be regarded as independent validation. Incorporation of Eq 5 for f_{PAO} in Eq 2 significantly improved the correlation between the calculated and measured reactor ISS concentrations for NDBEPR systems. A plot of Eq 5 and the f_{PAO} calculated from the PAO P content (f_{XBGP}) determined from the observed P removal (see above) for the 18 NDBEPR systems is shown in Fig 3. Despite the large variation in f_{PAO} in the 18 systems evident in Fig 3, the correlation between calculated and measured reactor ISS concentration in the different systems was good.

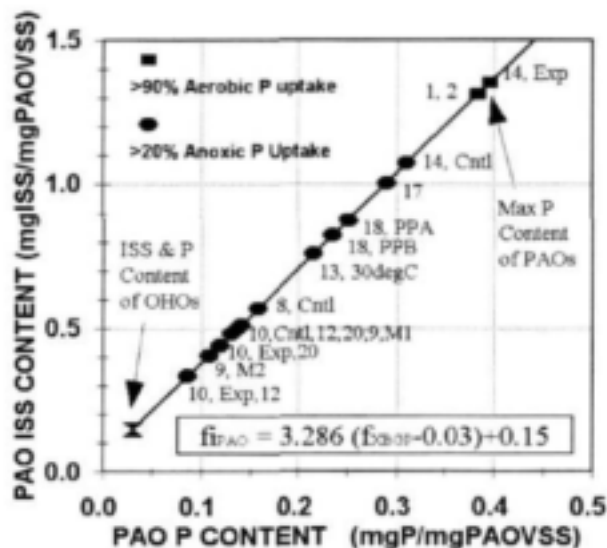


Fig 3: Predicted PAO inorganic solids (ISS) content (f_{IPAO}) (Eq 5) versus PAO P content (f_{XBP}) for > 90% aerobic P uptake BEPR (■) and variable anoxic-aerobic P uptake BEPR (●) in the 18 NDBEPR systems of investigations I1, I2, I8, I9, I10, I13, I14, I17 and I18 based on the measured f_{IPAO} value in the four enhanced PAO culture systems (I1) on one extreme ($f_{IPAO} = 1.30$, $f_{XBP} = 0.38$, ■) and the P content of OHOs on the other ($f_{IPAO} = 0.15$, $f_{XBP} = 0.03$, ●).

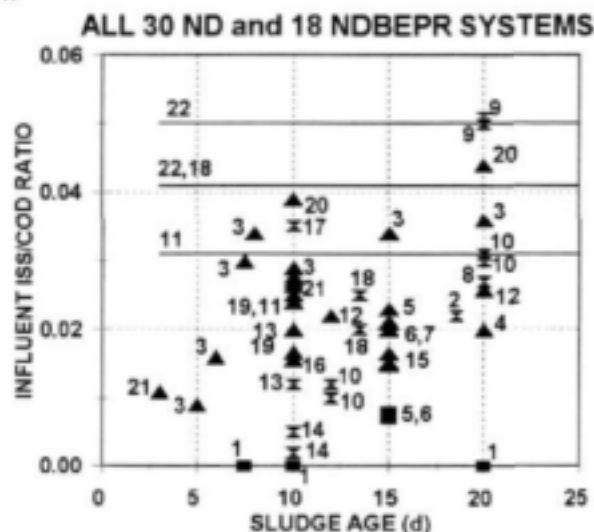


Fig 4: Model predicted system average influent ISS concentration (as a ratio of the influent COD concentration) versus sludge age for the 30 ND and 18 NDBEPR systems fed artificial (■, 5 and 6 ND, 1 NDBEPR) and real (▲ ND, 1 NDBEPR) wastewater with ratios measured in the laboratory (line, I11) and at the source WWTP (lines, I18, I22).

With the ISS contents of the OHO and PAOs established, the influent ISS concentration to account for the measured reactor ISS concentration was calculated as a ratio of the influent COD concentration ($X_{\text{tot}}/S_{\text{g}}$). For artificial feed systems, as expected, this ratio was very low (0.000 to 0.007) and for the real wastewater systems, it varied between 0.01 and 0.05 for both ND and BEPR systems (Fig 4). Because the influent ISS concentrations were not measured in 18 of the 22 investigations, it is not possible to validate this variation in influent ISS concentration. In 1 of the 3 investigations in which the influent ISS concentration was measured (I11), a reasonably close correlation between calculated and measured influent ISS/COD ratio was obtained, i.e. 0.0267 (28.1 mgISS/t) versus 0.0308 (32.5 mg ISS/t) on a fully aerobic laboratory system. In the 2nd (I12) and 3rd (I18) investigations, the difference between calculated and measured influent ISS/COD ratio was much larger, i.e. on two 2Mt/d NDBEPR plants 0.0213 (13.1 mgISS/t) versus 0.0413 (25.3 mgISS/t) and on two laboratory ND systems, 0.0248 (12.2 mgISS/t) versus 0.0915 (47.0 mgISS/t) (Wentzel et al., 2002). This large error in an investigation focussed on ISS model development cast doubt on the conventional method of measuring the influent ISS concentration (see below). Because influent ISS concentrations measured at the source WWTP with the improved analytical procedure (I22) yielded values in the range 0.040 to 0.050 (Table 1), the very high measured value of Wentzel et al. (2002) was almost certainly affected by bias resulting from the analytical procedure. The improved procedure reduced bias and increased precision of the measured influent ISS concentration.

2.5 MEASUREMENT OF INFLUENT ISS CONCENTRATION

A source of bias in the ISS concentration measurement is from the inorganic dissolved solids (IDS) of the residual water before drying. The IDS of the sample, the sample size, solid/liquid separation

method and the solids concentration can significantly bias the ISS concentration upwards, causing a considerable loss of accuracy. Precision is also a problem. The ash residue in the crucible is the ISS, which is the difference between two large masses around 1000 times greater than the ISS mass. This causes large variance in the measured ISS concentration.

To try to overcome these problems of accuracy and precision in the influent ISS measurement, various filtration media were tested. Glass fibre filters (GF/C Schleicher & Schüll GF52) proved best because (i) their pore size was small enough ($<1.0\mu$) to retain even very fine clay - tests with kaolin yielded $>99\%$ recovery; (ii) precision improved significantly because the glass fibre filters acted as very light mass crucibles - however, they needed to be pre-treated by incineration for >6 h prior to use to stabilize their mass, and (iii) their moisture retention was negligible. This method was therefore used to measure the influent ISS/COD ratio of raw and settled wastewater at the Mitchell Plain WWTP (I22, Table 1) and corresponds reasonably well with the model estimated values (Fig 4) for the 48 ND and NDBEPR systems. It is recommended that this method be adopted for measurement of the influent ISS concentration to build up a database for this wastewater characteristic for design.

2.6 MODEL VALIDATION

In application of the model to the 48 experimental systems above, the system average influent ISS/COD ratio required to obtain the best fit between predicted and measured system reactor ISS concentration was determined for each system. Since in 18 of the 22 investigations, the influent ISS concentration was not measured, the corresponding predicted values could not be validated for each investigation. Of the 3 investigations in which the influent ISS concentration was measured (I11, I12 and I18), only one yielded a reasonable correspondence between measured and predicted influent ISS/COD ratios. Thus comparison of predicted and measured influent ISS/COD ratio of individual experimental systems did not produce acceptable validation of the proposed ISS model. However, sufficient validation of the proposed ISS model for BNR system design and modelling is provided by (1) independent determination of the f_{IHO} and f_{IPAO} from the ND and enhanced PAO culture systems fed artificial wastewater (i.e. zero influent ISS, Fig 1) and using these virtually unchanged in combination for the real wastewater systems (Fig 2), (2) relative consistency between the predicted influent ISS/COD concentration ratio across the very large experimental data base comprising 30 ND and 18 NDBEPR systems over a wide range of sludge ages from 3 to 20 days and hydraulic retention times of 9 to 48h and that measured with the improved method at the source WWTP, (I22, Fig 4) and (3) with the predicted influent ISS/COD ratio fixed for a particular investigation close correlation between predicted and measured reactor ISS concentrations for all sewage batches and steady state periods for that investigation. General adoption of the improved ISS measurement method is required to further substantiate validation of the proposed model.

2.7 CONCLUSIONS

A simple predictive model for estimating activated sludge reactor ISS (and hence TSS) concentration (excluding that from chemical precipitant dosing) has been developed. It is based on (i) the accumulation of influent ISS in the reactor and (ii) an uptake of inorganic dissolved solids (IDS) from the bulk liquid by ordinary heterotrophic organism (OHO) with a fixed ISS content ($f_{\text{IHO}} = 0.15$ mgISS/mgOHOVSS) and by phosphate accumulating organisms (PAO) with a variable ISS content (f_{IPAO}) proportional to their P content ($f_{\text{XBGP}}, f_{\text{IPAO}} = 0.15 + 3.286[f_{\text{XBGP}} - 0.03]$ mgISS/mgPAOVSS). The model was validated with data measured on 48 aerobic, anoxic-aerobic nitrification denitrification (ND) and anaerobic-anoxic-aerobic ND biological excess phosphorus removal (BEPR) systems operated in 22 investigations conducted in the Water Research Laboratory at the University of Cape Town over the past 15 years. These systems had sludge ages varying from 3 to 20 days, nominal

hydraulic retention times from 9 to 48h and were fed artificial or real wastewater from the same Mitchells Plain wastewater treatment plant. Validation of the model is not based on a good correlation between predicted and measured influent ISS concentrations, because the influent ISS concentrations were not measured for the majority of investigations, and where it was measured, the method was found to be unreliable. Rather, validation of the model is based on (1) consistency of predicted and measured reactor ISS concentrations over the 48 investigations and (2) reasonable correspondence between predicted influent ISS/COD ratio for the 48 investigations and that measured with an improved method at the Mitchells Plain WWTP. This improved method requires more extensive application to further validate the proposed ISS model and to determine the influent ISS/COD ratio of various wastewaters.

The ISS model can be readily integrated into existing steady state or dynamic simulation activated sludge models because (i) these models formed the basis for determining the OHO and PAO ISS contents and (ii) the OHO and PAO VSS concentrations in these models are known from the predictions. This will eliminate having to guess the reactor VSS/TSS ratio for design, but will require the influent ISS concentration to be known. Currently, this concentration is not measured as part of typical wastewater characterization analyses. It is recommended that in future this be done with the glass fibre filtration and incineration method suggested.

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CHAPTER 3

THE STEADY STATE MASS BALANCES (COD, ISS, VSS, TSS, N AND P) WWTP MODEL

3.1 INTRODUCTION

Steady state models are relatively simple (stoichiometric) models that utilise constant flows and loads as input to determine the system design parameters. They are based on the slowest process kinetic rate that governs the overall behaviour of the system and relate this process rate to the system design and operating parameters. Therefore a steady state model allows the system design and operating parameters (e.g. reactor volumes, sludge recycle ratios) to be estimated reasonably simply and quickly from the performance criteria for the design, such as effluent quality. For example, for an activated sludge steady state model the system sludge age, wastewater characteristics and average dry weather flow as well as summer/winter temperatures are required as input. From this input the steady state model generated the following information:

- 1.1 Mass of organism, endogenous residue, inorganic and inert material contained in the reactor(s) and hence the
- 1.2 Required reactor volume(s) for a chosen sludge age.
- 1.3 Daily sludge production.
- 1.4 Effluent COD, TKN, FSA, nitrate and P concentrations.
- 1.5 System carbonaceous and nitrification oxygen requirements.

Individual unit operations in wastewater treatment such as the activated sludge system have been thoroughly investigated in earlier research and relatively reliable simple steady state models for the system, including biological N and/or P removal, have been developed over the past years. However little attention has been focussed on the WWTP as a whole in an integrated fashion, where the inputs of the upstream unit processes of the WWTP become inputs to the downstream unit operations based on material mass balances around the sequence of unit operations. Of course in WWTP design, such an integrated approach has been followed by designers but this is done either manually or with very simple mass balance spreadsheets of only a few material components (COD, TSS and perhaps N and P) without due recognition of the interrelationships and changes between the materials.

Therefore an integrated materials mass balance steady state model for the entire wastewater treatment plant including

1. COD, TKN, and total P (TP), each in their biodegradable and unbiodegradable and dissolved and particulate forms, free and saline ammonia (FSA), dissolved Ortho P (oP), nitrate, Alkalinity (Alk).
- (ii) Primary sedimentation.
- (iii) Activated sludge including in- or excluding nitrification, denitrification and/or biological excess P removal (BEPR).
- (iv) Waste activated sludge (secondary) and/or primary sludge thickening.

(v) Aerobic and/or anaerobic treatment of primary and/or secondary sludge.

will for example help define for design and operation.....

- the correct relationship between the raw (unsettled) and settled wastewater characteristics and the composition of the primary sludge (eg % biodegradable materials formed in primary settling tanks). Currently raw and settled wastewater and primary sludge characteristics are selected based on experience which are often inconsistent with mass balances. A good estimate of the % biodegradable material in the primary sludge is required for design of the primary sludge treatment system whether it be aerobic or anaerobic digestion.
- (ii) the concentrations of the input materials COD, VSS, TKN, FSA, OrgN, TP, oP and Alk to the anaerobic digester model (if selected) from the primary and/or secondary sludge characteristics. From the transformations in the anaerobic digester (from a simplified steady state model derived from the complex kinetic one described below, see Chapter 6), the gas volume and composition, heat requirements and generation, %COD and VSS removal and concentrations of mineral precipitation during or after digestion can be predicted.
- (iii) the expected loads on the various unit operations of the sequence from estimated loads on the WWTP and the operating conditions in the upstream unit operations. This will help to find bottlenecks i.e. unit operations which limit the capacity of the WWTP under different organic and hydraulic loading conditions.

3.2 THE STEADY STATE MASS BALANCES SPREADSHEET

The steady state design and operation WWTP mass balances spreadsheet (in Corel Quattro Pro 8), comprises 15 sheets:

1. Input: WW and PS fractions from WW characterization tests (Imhoff cone settling, membrane filtration). Kinetic and stoichiometric metric constants for the AS models for BNR.
2. Loads: Input diurnal variation in flows and COD, TKN, FSA, TP, OP and settleable solids (SS) concentrations. Estimates COD, OrgN, OrgP, VSS, ISS and TSS removal in primary settling, from which are calculated the diurnal variation in settled WW COD, TKN, FSA, TP, OP concentrations. Estimates of COD, TKN, FSA, TP and OP loads on the biological reactor for raw and settled WWS. Characterizes the PS composition (COD, VSS, ISS, TSS, OrgN, OrgP, each into their unbiodegradable and biodegradable soluble and particulate components) from mass balances around the PST.
3. Char: Characterizes the raw and settled WWS COD, TKN, FSA, TP and OP, each into their unbiodegradable and biodegradable soluble and particulate components, from the concentrations and fractions.
4. ASTmin, 5 ASTmax: Calculates the design parameters for the fully aerobic raw and settled WW activated sludge (AS) systems are long and short sludge ages respectively, (i.e. volume of reactor, average and peak oxygen demand, effluent COD, TKN, FSA, TP and OP concentrations and waste activated sludge (WAS) flow and composition.

6. **AerDigSgl:** Single reactor aerobic digester. Takes PS and WAS flows and concentrations (including the liquid stream), blends and concentrates them to the selected thickened concentration. Aerobically digests blended and thickened sludge to a selected residual biodegradable organic content, taking due account in N and P released during digestion. Calculates digester volume, oxygen demand and effluent concentrations. Checks material mass balances (COD, N and P) over the aerobic digester. It does this for WAS from fully aerobic, N removal (MLE) and N&P removal (UCT) at T_{min} and T_{max} temperatures.
7. **AerDTmin, 8. AerDTmax:** Explores aerobic digestion of fully aerobic and ND WAS sludge in single, double and triple compartment digesters with and without PS and with separate PS and WAS thickening before blending, where the degree of thickening is governed by (i) selected upper limits of PS and WAS thickening by gravity sedimentation and flotation respectively or (ii) selected maximum OUR in the digester. This study showed that (1) compartmentalizing the aerobic digester is only beneficial (smaller volume) for WAS digestion. Only for WAS can the digester volume be reduced by compartmentalization (as a result of the first ordered digestion rate) due to reduction in retention time, compared with a single completely mixed digester. For WAS only digester volume is governed by flotation thickening limitations, not by oxygen transfer limitations in the digester. Compartmentalizing the digester for PS and PA/WAS blends is not beneficial. The high OUR stimulated by the PS biodegradable organics limits the thickened feed sludge concentration to the first compartment to well below PS thickening capacity of gravity thickening. (2) Step feeding PS and PA/WAS blends in proportion to the digester compartment volumes equalizes the OUR in the compartments but the retention time is then not long enough to achieve the required residual biodegradable organics in the effluent (i.e. reduced sludge stabilization). Only if the digester retention time is increased to that for the single reactor digester, is the required degree of stabilization achieved with step feeding. Therefore for PS and PS/WAS blends, it is the OUR in the digester that governs the digester volume and the degree of sludge thickening of required. (See Appendix 4).
9. **MBalAE:** Checks the COD, N and P mass balances around the WWTP comprising (i) raw WW treatment in a long sludge age AS system, where the sludge age is selected long enough for sludge stabilization in the reactor and direct discharge of WAS to drying beds, and (ii) PSTs, short sludge aged activated sludge system, PS and WS thickening and aerobic digestion of PS and WAS to the same residual biodegradable organics as (i) above. The concentrations of COD (and oxygen demand), N and P in the effluent streams for the AS system the thickening units and the aerobic digester are added and balance to within 0.5% of the influent raw wastewater CCOD, TKN and TP for both T_{min} and T_{max} temperatures. Also the carbonaceous oxygen utilised in the raw WW system (AS only), and in the settled WW system (AS and aerobic digester) are within 0.5%. The total oxygen demand also is close but can't be used as a mass balance check because the effluent FSA concentration from the short sludge aged system is higher than that from the long sludge age, resulting in somewhat lower nitrification oxygen demand in the settled WW system.
10. **MLEUCTConst:** Collects the required input data for a MLE N removal and UCT N&P removal AS system design and makes the necessary temperature adjustments to the kinetic constants.
11. **MLESys, 12 UCTSys:** Does the complete design for the MLE and UCT systems at t_{min} and

Tmax for raw and settled WW. Calculates anaerobic, anoxic and aerobic reactor volumes, recycles ratios, oxygen demand, effluent concentrations and WAS flow and composition.

13. MLEBal, 14 UCTBal: Calculates the COD, N and P mass balances over the WWTP treating the raw and settled WW in MLE and UCT systems as 8 above for the fully aerobic system. COD, N and P mass balances over both raw and settled WWTPs are within 0.2%.
15. Tables, 16. Summary: Tabulates and summarises the results calculated in the various spreadsheet pages above.

Denitrification kinetics in WAS anoxic aerobic digesters have been measured experimentally and the simulation model UCTOLD (similar to ASM#1 (Henze *et al.*, 1987)) simulated the dynamic behaviour very well (Warner *et al.*, 1986). A much simpler steady state model has also been developed for anoxic aerobic digesters, but this has not been integrated into the spreadsheet, which so far is for fully aerobic digesters only.

3.3 COMPARISON OF THE RESULTS CALCULATED BY THE STEADY STATE MASS BALANCES SPREADSHEET AND ASM#1

An ASM#1 (Henze *et al.*, 1987) Aquasim (Reichert, 1998) dynamic simulation model has been set up for the raw and settled WW treatment plants shown in Fig. 5, including thickening and aerobic digestion of PS and WAS to compare the results with the output from the steady state mass balances spreadsheet. The raw wastewater entering the primary settling tank (PST) exits the PST as settled wastewater, which subsequently flows into the AS reactor and primary sludge, which is thickened, blended with the thickened waste activated sludge and the blend flows into the aerobic digester for sludge stabilisation. The influent (raw) and settled wastewater characteristics and the design and operating parameters are listed in Tables 2 and 3 respectively.

From the wastewater characteristics and the design and operating parameters, the steady state spreadsheet calculates the following parameters for the treatment plant:

Primary Sludge (settled WW):

- (i) Primary settling tank desludging flow 75 m³/d
- (ii) Flow from PS thickener 52.4 m³/d for 6% primary sludge TSS concentration
- (iii) Supernatant flow from PS thickener 22.6 m³/d

Activated sludge:

- Sludge age: Raw WW 30d; Settled WW 8d.
- Reactor volume: Raw WW 23826 m³; Settled WW 3531 m³
- Waste flow: Raw WW 794 m³/d; Settled WW 441 m³/d
- Flow from WAS thickener 35.3 m³/d for 5% waste activated sludge concentration (settled WW)
- Supernatant flow from WAS thickener 405.7 m³/d (settled WW)

Aerobic digester (settled WW):

- Influent flow of blended thickened sludge 87.7 m³/d
- Retention time for required effluent active fraction of 0.235 is 16d
- Reactor volume 1404 m³

The above parameters are required to set up the kinetic ASM#1 (Henze *et al.*, 1987) model for the treatment plant.

Table 2: Raw and settled wastewater characteristics.

	Influent wastewater (WW) concentration	Raw WW	Settled WW
	Influent flow (Ml/d)	15.000	14.925
C O D	Total - S_t (mgCOD/l)	750.0	450.0
	Soluble biodeg - S_{bsi} (mgCOD/l)	146.0	146.0
	Particulate biodeg - S_{bpi} (mgCOD/l)	439.0	233.5
	Soluble unbiodeg - S_{usi} (mgCOD/l)	52.5	52.5
	Particulate unbiodeg S_{upi} (mgCOD/l)	112.5	18.0
T K N	Total TKN - N_t (mgN/l)	60.0	51.0
	Free and saline - FSA - N_{si} (mgN/l)	45.0	45.0
	Soluble biodeg OrgN - N_{bsi} (mgN/l)	1.7	1.7
	Particulate biodeg OrgN - N_{bpi} (mgN/l)	3.9	1.3
	Soluble unbiodeg OrgN - N_{usi} (mgN/l)	1.8	1.8
	Particulate unbiodeg OrgN- N_{upi} (mgN/l)	7.6	1.2
	Inorganic Suspended solids (mgISS/l)	47.7	9.5

Table 3: System design and operating parameters.

	WASTEWATER
Min. Temperature (°C)	14°
Max. Temperature (°C)	22°
Characteristics	See Table 2
	ACTIVATED SLUDGE SYSTEM
Influent flow (Ml/d)	14.925
Sludge age (d)	8
Design reactor concentration (gTSS/l)	4.0
Aeration power (kWh/kgO)	1.20
	AEROBIC DIGESTER
Effluent active fraction	0.235
Aeration power (kWh/kgO)	1.20
	PS THICKENER
Effluent sludge concentration (gTSS/l)	60.0
	WAS THICKENER
Effluent sludge concentration (gTSS/l)	50.0

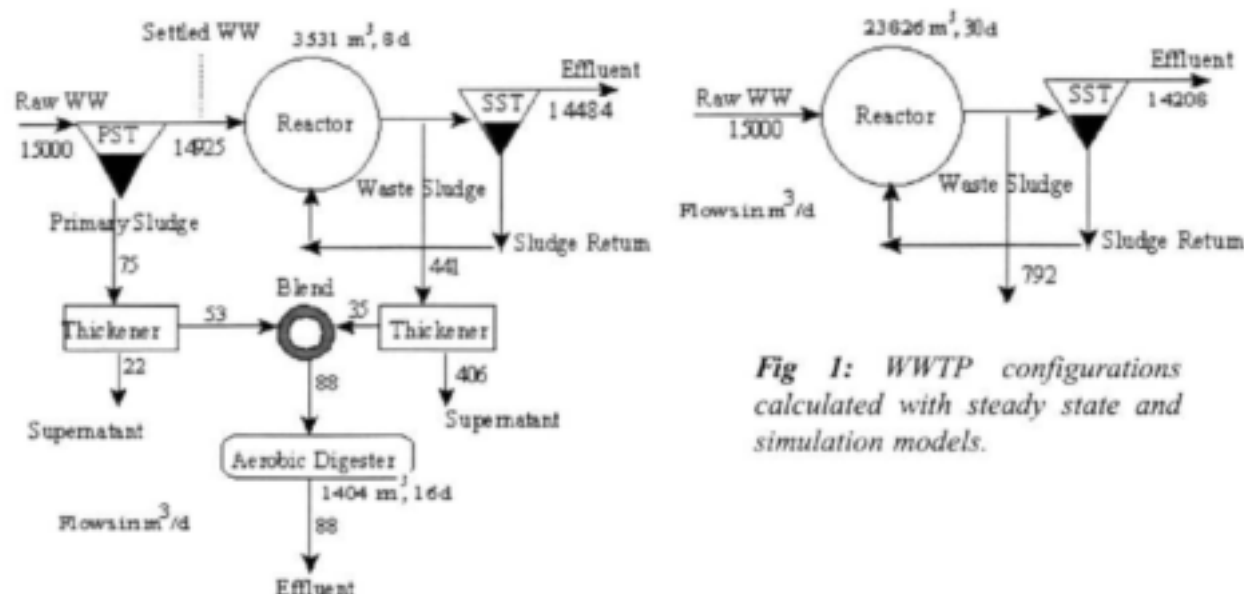


Fig 1: WWTP configurations calculated with steady state and simulation models.

With the given wastewater characteristics and design and operating parameters and using the reactor sizes as well as the flow data obtained from the steady state mass balances spreadsheet, a ASM#1 (Henze *et al.*, 1987) dynamic model of the wastewater treatment plant (Fig 5) was set up in Aquasim (Reichert, 1998). This model was used to simulate the performance of the wastewater treatment plant (Fig 5) for constant flow and load conditions, to enable the results to be compared directly with the results obtained from the steady state mass balances spreadsheet. Table 4 shows the results from the steady state mass balances spreadsheet and the results obtained from the dynamic ASM#1 (Henze *et al.*, 1987) Aquasim (Reichert, 1998) model.

From Table 4 it can be seen that the dynamic model gives virtually identical results for all the effluent AS and AD COD, TKN, FSA, TP, OP, VSS, ISS and TSS concentrations from both systems. Small differences are evident, for example the slightly lower carbonaceous OUR of the dynamic model (43.5 vs. 44.4 mgO/lreactor/hr). The lower OUR result from the dynamic model can be attributed to the fact that in the dynamic model, not all biodegradable COD is utilised: A fraction remains as adsorbed COD on the organisms, while another small fraction remains enmeshed in the sludge. This is in contrast with the steady state model, where it is assumed that all biodegradable COD is utilised, resulting in a higher carbonaceous OUR. This difference can be expected to increase with decreasing sludge age, because the lower the sludge age, the less time is available to the organisms in the dynamic model to utilize the available COD, hence more COD will remain enmeshed in the sludge.

A further difference in the results of the steady state model and the dynamic ASM#1 model can be seen in the effluent nitrogen compounds. The effluent TKN from the dynamic model is higher than that from the steady state mass balances model, while the converse is true for the nitrate; which is expected. The higher effluent TKN from the dynamic model is a result from a higher effluent FSA and a higher effluent soluble biodegradable organic N, compared to the effluent from the steady state model. As for the COD, the assumption in the steady state model is that all biodegradable material is utilised, and this is not the case for the dynamic model. Therefore in the dynamic model, there is an effluent soluble biodegradable organic N, which in the steady state model is zero. This, combined with the fact that for the dynamic model there is residual biodegradable particulate COD, which contains N, enmeshed in the sludge and adsorbed on the organisms, results less N being nitrified in the dynamic model, which leads to a lower effluent nitrate concentration.

Table 4: Results from the simulations of the wastewater treatment plant shown in Fig. 5 using the steady state mass balances spreadsheet and the dynamic ASM#1 (Henze et al., 1987) Aquasim ((Reichert, 1998) model.

COMPOUND	UNITS	STEADY STATE MODEL	ASM#1
<i>Activated Sludge (14°C)</i>			
Reactor active organism conc.	mgVSS/l	2207	2273
Reactor endogenous residue conc.	mgVSS/l	714	729
Reactor inert organic conc.	mgVSS/l	411	411
Reactor volatile solids conc.	mgVSS/l	3333	3413
Reactor inorganic solids conc.	mgISS/l	667	667
Reactor total solids conc.	mgTSS/l	4000	4080
Active fraction (w.r.t. VSS)	-	0.662	0.666
Effluent soluble COD	mgCOD/l	52.50	52.50
Effluent soluble biodegradable organic N	mgN/l	0.00	1.20
Effluent soluble unbiodegradable organic N	mgN/l	1.80	1.80
Effluent FSA	mgN/l	0.01	1.21
Effluent TKN	mgN/l	1.81	4.21
Effluent NO ₃	mgN/l	42.30	36.30
Carbonaceous OUR	mgO/feactor/h	44.4	43.5
Nitrification OUR	mgO/feactor/h	31.7	28.4
Total OUR	mgO/feactor/h	76.1	71.9
<i>Aerobic Digester (14°C)</i>			
Effluent active organism conc.	mgVSS/l	6382	6652
Effluent endogenous residue conc.	mgVSS/l	4132	4435
Effluent inert organic conc.	mgVSS/l	16630	16630
Effluent volatile solids conc.	mgVSS/l	27144	27717
Effluent inorganic solids conc.	mgISS/l	10316	10316
Effluent total solids conc.	mgTSS/l	37460	38033
Active fraction (w.r.t. VSS)	-	0.235	0.239
Effluent soluble COD	mgCOD/l	52.50	52.50
Effluent soluble biodegradable organic N	mgN/l	0.00	1.20
Effluent soluble unbiodegradable organic N	mgN/l	1.80	1.80
Effluent FSA	mgN/l	0.00	0.05
Effluent soluble TKN	mgN/l	1.80	3.05
Effluent NO ₃	mgN/l	536.00	528.20
Carbonaceous OUR	mgO/feactor/h	94.4	94.8
Nitrification OUR	mgO/feactor/h	6.2	6.0
Total OUR	mgO/feactor/h	100.6	100.8

In nitrifying aerobic digestion of waste activated sludge, nitrate utilization for OHO growth can occur even when there is sufficient ammonia available. This happens because the rate of nitrification is faster than the rate of OHO growth, which is limited by the supply rate of SBCOD from the OHO death process. This leads to uptake of nitrate for OHO growth but the release of ammonia in OHO death. This released ammonia is then nitrified with an associated OUR for nitrification. The consequence is an artificially high nitrification OUR from the continual supply of ammonia nitrogen from the death process, nitrogen that was taken up by the OHOs as nitrate. This problem can be eliminated in the model by reducing the switching function K value which controls the switch from ammonia to nitrate uptake for OHO growth to a very low value (0.0001). This stops the OHO growth process from slowing down when the ammonia concentration gets low, allowing it to successfully "compete" for ammonia against the nitrification process. In aerobic digestion of waste activated sludge, there is always sufficient ammonia for growth because the ammonia released in OHO death is always greater than that taken up for OHO growth on the SBCOD released in OHO death. The same problem can happen with aerobic digestion of primary sludge, even when sufficient ammonia is dosed for sludge production from the primary sludge particulate biodegradable organics. This problem therefore has nothing to do with ammonia deficiency but everything to do with the relative rates of processes competing for the same compounds, in this case ammonium (NH_4^+). *K values of switching functions on processes competing for the same compounds are therefore very import to watch.*

There is therefore close correlation between the formal complex dynamic simulation WWTP model in which ASM#1 (Henze *et al.*, 1987) is used to model the AS and AD systems and the much simpler steady state model programmed into the spreadsheet described here.

3.4 CONCLUSIONS

The steady state spreadsheet described in this chapter is capable of the following:

- Characterizes the raw and settled WWS COD, TKN, FSA, TP and OP, each into their unbiodegradable and biodegradable soluble and particulate components, from the given (measured) concentrations and fractions and the primary sludge (PS) COD, VSS, ISS, TSS, OrgN, OrgP, also each into their unbiodegradable and biodegradable soluble and particulate components from mass balances around the PST.
- (2) Calculates the design parameters for the fully aerobic, nitrification denitrification (ND) or ND biological excess P removal (BEPR) systems treating the raw and settled WW at long and short sludge ages respectively, i.e. volume of reactor, average and peak oxygen demand, effluent COD, TKN, FSA, TP and OP concentrations and waste activated sludge (WAS) flow and composition.
- (3) Calculates the design parameters for a single reactor aerobic digester by taking the PS and WAS flows and concentrations (including the liquid stream), blending and concentrating them to the selected thickened concentrations, aerobically digesting the blended and thickened sludge to a selected residual biodegradable organic content, taking due account in N and P released during digestion. Calculates digester volume, oxygen demand and effluent concentrations. Checks material mass balances (COD, N and P) over the aerobic digester. WAS can be from fully aerobic, N removal (MLE) and N&P removal (UCT) at $T_{\min}$ and $T_{\max}$ temperatures.
- (4) Explores aerobic digestion of fully aerobic and ND WAS sludge in single, double and triple compartment digesters with and without PS and with separate PS and WAS thickening before blending, where the degree of thickening is governed by (i) selected upper limits of PS and WAS thickening by gravity sedimentation and flotation respectively or (ii) selected maximum OUR in the digester. This study showed that (1) compartmentalizing the aerobic digester is only beneficial

(smaller volume) for WAS digestion. Only for WAS can the digester volume be reduced by compartmentalization (as a result of the first order digestion rate) due to reduction in retention time, compared with a single completely mixed digester. For WAS only the digester volume is governed by flotation thickening limitations, not by oxygen transfer limitations in the digester. Compartmentalizing the digester for PS and PS/WAS blends is not beneficial. The high OUR stimulated by the PS biodegradable organics limits the thickened feed sludge concentration to the first compartment to well below PS thickening capacity of gravity thickening. (2) Step feeding PS and PS/WAS blends in proportion to the digester compartment volumes equalizes the OUR in the compartments but the retention time is then not long enough to achieve the required residual biodegradable organics in the effluent (i.e. reduced sludge stabilization). Only if the digester retention time is increased to that for the single reactor digester, is the required degree of stabilization achieved with step feeding. Therefore for PS and PS/WAS blends, it is the OUR in the digester that governs the digester volume and the degree of sludge thickening required.

- (5) Checks the COD, N and P mass balances around the WWTP comprising (i) raw WW treatment in a long sludge age AS system, where the sludge age is selected long enough for sludge stabilization in the reactor and direct discharge of WAS to drying beds (i.e. extended aeration), and (ii) PSTs, short sludge aged activated sludge system, PS and WAS thickening and aerobic digestion of PS and WAS to the same residual biodegradable organics as (i) above. The concentrations of COD (and oxygen demand), N and P in the effluent streams for the AS system, the thickening units and the aerobic digester are added and balance to within 0.5% of the influent raw wastewater COD, TKN and TP for both T_{min} and T_{max} temperatures. Also the carbonaceous oxygen utilised in the raw WW system (AS only), and in the settled WW system (AS and aerobic digester are within 0.5%). The total oxygen demand also is close, but can't be used as a mass balance check because the effluent FSA concentration from the short sludge aged system is higher than that from the long sludge age, resulting in somewhat lower nitrification oxygen demand in the settled WW system.

Still required to be integrated into the steady state mass balances model are:

- (1) The inorganics: The modelling of inorganics within the activated sludge system has been completed (see Chapter 2). However, tracking the inorganics through the other unit operations needs to be addressed, in particular through aerobic and anaerobic digestion of the various sludges.
- (2) The anaerobic digestion of the sewage sludges needs to be incorporated: A steady state model for anaerobic digestion of sewage sludges has been developed (see Chapter 7), and this needs to be included in the mass balances tracking model. This will require that the inputs required for the anaerobic digestion model (i.e. the sludge characteristics) be included in the upstream unit operations. In addition to the parameters already in the mass balances model, this will include C, alkalinity, possible SCFA production in the PST.
- (3) Recycling of various liquors (e.g. sludge thickening liquors) from downstream unit operations to upstream ones, and the characteristics of these recycle stream would have to be included.
- (4) The steady state mass balances WWTP model needs to be extended to include biological P removal.

This Chapter shows further, that there is a close correlation between the formal complex dynamic simulation WWTP model in which ASM#1 (Henze *et al.*, 1987) is used to model the AS and AD systems and the much simpler steady state model programmed into the spreadsheet described here. Only one parameter had to be changed in ASM#1 (Henze *et al.*, 1987), i.e. the K value of the switching function for the nitrogen requirement for aerobic growth from 0.10 to 0.0001 mgN/l. This switching function controls the uptake of FSA for growth, and if insufficient, allows nitrate to be taken up

instead.

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CHAPTER 4

MODELLING PHYSICAL CHEMICAL PROCESS IN 3 PHASES

4.1 INTEGRATED 3 PHASE CHEMICAL PHYSICAL MODELLING OF THE CARBONATE SYSTEM

Musvoto et al. (1997) describe the development of an integrated mass balances based kinetic model to simulate the chemical-physical processes of (i) the carbonate¹ system in three phases (solid-aqueous-gas) and (ii) the mixed water², carbonate, phosphate¹, short chain fatty acid (SCFA) and ammonia weak acid/base systems in single (aqueous) phase. The model was validated for the steady state (time independent) conditions by comparing predicted equilibrium results with predictions from well established equilibrium chemistry based models in the literature, such as (i) Stasoft I (Loewenthal et al., 1988) and Stasoft III (Friend and Loewenthal, 1992) for the three phase carbonate system in pure water and (ii) Loewenthal et al. (1989, 1991) for the single aqueous phase behaviour of the water, carbonate, phosphate, SCFA and ammonia mixed weak acid/base systems.

The model includes H^+ as a compound (and therefore pH), and is based on the kinetics of the forward and reverse reactions for the dissociation of the weak acid/bases. The weak acid/bases included in the model are water, carbonate, ammonium, phosphate and short-chain fatty acids. However, the approach used to develop the model is general, and can be applied to include any other weak acid/bases of importance. Precipitation of $CaCO_3$ and gas exchange of CO_2 also have been included. The model and the approach on which it is based have been validated by comparing model predictions to those obtained from equilibrium chemistry-based models; good correlation was obtained. Compared to the traditional equilibrium chemistry approach to modelling aqueous mixtures of weak acid/bases, the kinetic approach offers several advantages. In particular, the kinetic approach will expedite integration of the weak acid/base model with other kinetic models. For example, the model can be readily integrated with the existing biological kinetic models for waste-water treatment systems, to extend application of these models to situations where the pH does not remain constant and the changes in pH influence the behaviour. Furthermore, by providing an estimation for the pH, the weak acid/base model will greatly simplify the inclusion of chemical (e.g. precipitation/dissolution) and/or physical (e.g. CO_2 and NH_3 gas exchange) processes, either in an independent chemical/physical model, or in the existing biological models. Chemical and physical processes are of increasing importance in waste-water treatment systems; for example, in chemical or combined chemical/biological P removal

¹In this report, as in the earlier publications on the same subject, the term "carbonate system" refers to the inorganic carbon system. The term "carbonate system species" refers to all the species making up the total inorganic carbon (denoted C_T), viz. $H_2CO_3^*$ comprising dissolved CO_2 and H_2CO_3 , bicarbonate HCO_3^- and carbonate CO_3^{2-} , and the term "carbonate species" refers to the CO_3^{2-} species only. The same nomenclature applies to the term "phosphate system", "phosphate system species", denoted P_T , and "phosphate species".

²In aqueous single or mixed weak acid/base systems, the water always is present and acts as an additional weak acid/base system because of its dissociation to H^+ and OH^- . It is included here for completeness. In mixed weak acid/base systems, the water system is one of several weak acid/base systems that contribute to the Total Alkalinity and Acidity mass parameters (Loewenthal et al., 1989).

in activated sludge systems, in treatment of waste waters with compounds that result in pH changes during biological treatment, such as anaerobic digester liquors, sludge dewatering liquors and trickling filter effluents.

4.2 INTEGRATED 3 PHASE CHEMICAL PHYSICAL MODELLING OF THE MIXED WEAK ACID BASE SYSTEMS

Aeration of anaerobic digester liquor (ADL), either deliberate or inadvertent, strips CO_2 from the ADL resulting in an increase in pH; at higher pH various calcium and magnesium phosphates (and possibly carbonates) precipitate and NH_3 stripping occurs. Loss of CO_2 thus can be problematic, with magnesium phosphate precipitants such as struvite causing pipe blockages (e.g. Borgerding, 1972; Mohajit et al., 1989; Mamais et al., 1994; Williams, 1999). However, this process has been exploited as a treatment method for removal of the high concentrations of N and/or P commonly found in ADL, particularly in those from digestion of waste sludge from biological phosphorus removal activated sludge systems (Pitman et al., 1989, 1999; Battistoni et al., 1997; Woods et al., 1999; Stratful et al., 1999). A model that can conveniently handle three phase mixed weak acid/base chemistry will be helpful to optimise the aeration treatment method for ADL and to develop and evaluate alternative treatment methods. Further, such a model will find potential application in a variety of other chemical treatment systems.

The three phase physical-chemical kinetic model developed for the carbonate system (Musvoto et al., 1997) was extended by Musvoto et al. (2000) to include the phosphate, ammonia and short chain fatty acid weak acid/base systems in three phases with multi-mineral precipitation and multi-gas stripping. The specific kinetic model was developed to simulate the physical-chemical reactions which occur in the aeration treatment of ADL. The processes that occur under these conditions are the dissociation of the weak acid/bases, precipitation of solids (struvite, newberyite, amorphous calcium phosphate, ACP, magnesium and calcium carbonate) and stripping of CO_2 and NH_3 gases. Ion pairing effects were also included in the model because the ionic strength of the liquors tested was greater than 0.025. The resultant kinetic model was validated by comparing predictions with (i) equilibrium concentrations from (a) an equilibrium based struvite precipitation algorithm (Loewenthal et al., 1994) coded into a computer programme called Struvite 3.1 by Loewenthal and Morrison (1997) and (b) experimental data available in the literature (Ferguson and McCarty, 1971) and (ii) kinetic (time dependent) and equilibrium (time independent) data obtained from aeration batch tests on anaerobic digester liquors (ADL) from (a) a spent wine upflow anaerobic sludge bed (UASB) digester and (b) a sewage sludge anaerobic digester.

In the kinetic model the dissociation constants, ion pair stability constants and mineral solubility products were regarded as model constants and were not changed (except for ionic strength and temperature adjustments). The specific precipitation rates of the minerals and the specific stripping rates of the gases were regarded as calibration constants and changed to fit predicted to experimental results. The calibration constants are important when simulating time dependent experimental results and when simulating the final equilibrium condition for a solution with precipitation of multiple minerals that compete for common species (e.g. ACP and CaCO_3 competing for Ca species). In these latter solutions the final equilibrium condition may be influenced by the relative rates of precipitation of the competing precipitating minerals. For time independent simulations with non-competing minerals precipitating, when comparing predicted with observed results of only the final steady state conditions, only the model constants are important, not the kinetic mineral precipitation and gas stripping rates.

To check the performance of the model with a single precipitating mineral under time independent conditions, predicted results were compared with the Struvite 3.1 equilibrium based computer program of Loewenthal and Morrison (1997). Since in this situation only a single mineral is precipitating (struvite), only the model constants are of importance. From this comparison it was concluded that the kinetic model can accurately predict equilibrium conditions for single mineral precipitation. To check the performance of the model for multiple mineral precipitation, the experimental results of Ferguson and McCarty (1971) were simulated. In the experiments of Ferguson and McCarty, although only initial and final conditions are available, because multiple minerals are precipitating competing for the same compounds both the model and calibration constants are of importance. From these simulations it was concluded that the model performed well and was sufficiently robust and stable to simulate multiple mineral precipitation.

To validate the time dependent performance of the model and determine the calibration constants, batch experiments were conducted by aerating two anaerobic digester liquors (ADL), viz. three batch tests on liquor from a spent wine UASB digester (UASBDL) and four batch tests on liquor from an anaerobic digester treating a blended primary sludge and waste activated sludge (SSADL). In these batch tests, Ca, Mg, $\text{PO}_4\text{-P}$ (P_T), inorganic C (C_T , via the $\text{H}_2\text{CO}_3^* \text{Alk}$), free and saline ammonia (FSA, N_T) and pH were measured over 24 to 54h. After establishing (i) the minerals most likely to precipitate viz. struvite (MgNH_4PO_4), newberyite (MgHPO_4), amorphous calcium phosphate [ACP, $\text{Ca}_3(\text{PO}_4)_2$], CaCO_3 and MgCO_3 and (ii) their solubility products from the literature, the specific precipitation and gas stripping rate constants were determined by (i) trial and error visual fitting of predicted results to the experimental data and (ii) a parameter estimation facility which searches for the calibration constants that minimize the error between the model predictions and experimental results. A good correlation was obtained between model predictions and experimental results with both methods for six of the seven batch tests and while the second method may be superior, visually there was no discernable difference between the predicted results of the two methods. The good correlation indicated that no mineral that precipitated significantly in the ADL were omitted from the model.

The same minerals were found to precipitate in the two liquors and in similar proportions, viz. in decreasing proportion of precipitate mass formed struvite (MgNH_4PO_4) (82-89%), amorphous calcium phosphate (ACP) (5-15%), calcium carbonate (CaCO_3) (0-6%), magnesium carbonate (MgCO_3) (0-5%) and newberyite (MgHPO_4) (0.1-0.3%). Unfortunately no experimental tests were conducted to measure the concentration of precipitate formed. Comparing the mineral precipitation rates in the UASBDL and SSADL, it was found that (i) the rates of struvite and ACP precipitation were 9 and 2 times faster respectively in the UASBDL than in the SSADL, (ii) in contrast, the rate of CaCO_3 precipitation was 140 times faster in the SSADL than in the UASBDL, (iii) the rates of MgCO_3 and MgHPO_4 precipitation were approximately the same in both liquors. No meaningful comparison could be made for the gas stripping rates because the aeration rate was different in each batch test and were not measured. This is the weakest part of the batch tests and is, in hindsight, an omission; if the aeration rate had been measured, a comparison could have been made between the airflow rate and CO_2 and NH_3 gas stripping rates.

From the simulations it was evident that the kinetic model offers considerable advantages over equilibrium based models. Not only can it predict time dependent data, but also it can predict the final equilibrium state (in terms of the duration of the tests) for situations with precipitation of multiple minerals which compete for the same species - equilibrium models are not capable of predicting either situation. Further, the kinetic modelling approach also allows the determination of the specific precipitation rates for a number of minerals simultaneously in an integrated manner from a single batch test. However, it should be noted that the kinetic model developed by Musvoto et al. (2000) is

restricted to the precipitation of minerals and does not consider mineral dissolution; for the tests considered dissolution was not significant compared to the precipitation. For situations where dissolution is significant, the kinetic model will predict neither the time dependent behaviour nor the final equilibrium state correctly. Attempts to include separate processes for dissolution in the model caused instability in model simulations in Aquasim. This aspect requires further investigation.

The three phase kinetic based weak acid/base chemistry model, and the approach on which it is based, proved to be a useful tool for research into and design of wastewater treatment systems in which several weak acid/bases influence the behaviour. For research, the model helps to focus attention on issues not obvious from direct experiment and allows determination of mineral precipitation rates for a particular wastewater from a single batch test. Once calibrated with the precipitation (and gas stripping if included) rates, this kind of model can be used to predict the performance of different treatment systems to identify for investigation those that appear technically and economically viable. In further work, this modelling approach will be extended to include biological processes, such as those of biological nutrient removal activated sludge (Chapter 3) and anaerobic digestion of sewage sludges (Chapter 4). This will allow modelling of biological treatment systems together with the mixed weak acid/base chemical systems within which the biological processes operate or combined biological/chemical systems such as simultaneous chemical/biological P removal.

4.3 APPLICATION OF THE 3 PHASE MIXED WEAK ACID BASE MODEL TO A FULLSCALE WWTP.

At the Cape Flats (CF) Wastewater Treatment Plant (WWTP) (Cape Town, South Africa), waste activated sludge (WAS) and primary sludge (PS) are thickened separately, the WAS by dissolved air flotation and the PS by gravity thickening. The two thickened sludge streams are blended, thickened further with centrifuges and anaerobically digested in a high rate anaerobic digester (sludge age ≈ 10 d). The anaerobically digested sludge is dewatered mechanically and then passes to a collection sump. The sludge is drawn from the sump, dewatered in centrifuges and the dewatered sludge is passed to a thermal drying pelletization plant. In operation of this sludge treatment scheme, problems have been experienced with mineral precipitation in the centrifuges, and in the pipework leading from the centrifuges to the pelletization plant. Precipitation inside the centrifuges reduces the capacity of the centrifuges to lower the moisture content of the digested sludge; precipitation within the pipe network causes pipe blockages and reduced maximum flow rates.

This section summarizes an experimental and theoretical modelling investigation into mineral precipitation in ADL from the CFWWTP, to determine which minerals precipitate, what conditions induce this precipitation, and what operational strategies can minimise the precipitation (for details, see van Rensburg *et al.*, 2001, 2003).

From the investigation, the following conclusions can be drawn with regard to mineral precipitation in the Cape Flats (CF) ADL, some of which apply to ADL in general:

- (1) For the CF ADL, the dominant mineral that precipitates is struvite. For the batch test conducted, struvite was dominant (543 mg/l as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ = 97% of mass of precipitant), followed by ACP (16.1 mg/l as $\text{Ca}_3(\text{PO}_4)_2$ = 3% of the mass of precipitant), and negligible newberyite, calcite and magnesite precipitated. These observations are similar to those of the extended pH change test and Musvoto *et al.* (2000c). With the large volumes of ADL passing to the downstream processes, this is a substantial precipitation potential.

- (2) The precipitation of struvite is stimulated by the increase in pH when CO_2 is lost from the ADL. This increase in pH causes struvite to become supersaturated, and hence it precipitates. Increasing the pH by addition of NaOH also results in struvite precipitation, which confirms that the increase in pH is the primary process driving the struvite precipitation.
- (3) When the ADL exits the CF WWTP digester, it is initially undersaturated with respect to struvite. Depending on the initial conditions in the ADL, significant struvite precipitation starts only when the pH increases above $\text{pH} = 7.3$ to 7.7 . This critical pH for struvite precipitation is reached after 0.67 to 1.0h aeration. However, this time will depend on a number of factors, including aeration rate, initial pH, buffer capacity, initial P and Mg concentrations, etc.
- (4) From the batch tests in which the pH was raised by NaOH addition, the struvite precipitation rate is extremely rapid. The first sample taken immediately after NaOH addition and filtered as soon as possible (~ 1 min) showed closely similar Mg and $\text{PO}_4\text{-P}$ concentrations to those taken after 1h. Therefore with aeration of the CF ADL, struvite was at equilibrium between the precipitant and soluble species at all times. Thus, in this case the rate of struvite precipitation is not limited by the precipitation kinetics, but rather by the rate of increase in pH through aeration. With ADL aeration to increase the pH, the practical upper limit on the aeration (K_{La}) rate therefore generally will limit the struvite precipitation rate.
- (5) The mass of struvite that precipitates is limited by two factors: With aeration to increase pH, the struvite precipitating is limited by the final pH reached and the initial Mg concentration present - if the initial Mg concentration is increased, then more struvite precipitates. With addition of NaOH, the struvite precipitating is limited by the initial Mg concentration present - after precipitation the Mg concentration is very low, while significant concentrations of P and N are still present.
- (6) The initial concentrations of P and Mg in the ADL were variable, with P ranging from 89 to 190 mgP/l , and Mg from 29 to 67 mgMg/l . This is probably indicative of the variable BEPR performance of the activated sludge system with regard to BEPR. The higher P concentrations are in agreement with values measured for other anaerobically digested BEPR sludges, at 150 to 250 mgP/l (Pitman, 1995).
- (7) The increase in pH with aeration also stimulates precipitation of ACP. However, the mass of ACP precipitating is relatively small compared with struvite. The ADL is initially undersaturated with respect to ACP, and ACP precipitation initiates only after the pH increases above 7.7. At $\text{pH} > 7.7$, ACP precipitates because the ionic product of the soluble Ca and $\text{PO}_4\text{-P}$ concentrations exceeds the solubility product after significant struvite precipitation. Because struvite precipitates much faster and at lower pH than ACP, the Ca and $\text{PO}_4\text{-P}$ ionic product remains low as $\text{PO}_4\text{-P}$ is incorporated into struvite with increasing pH.
- (8) Ion pairing plays a significant role in the multiple mineral precipitation dynamics. As soluble ions are incorporated into the precipitating minerals, so ions are "released" from the ion pairs keeping the soluble concentrations higher for longer as pH increases.
- (9) In running experiments on the ADL, the solids concentrations were so high that the ADL could not be effectively filtered. Accordingly, the ADL was settled for 5 days and the supernatant used for the experiments. Thus, the effect of solids concentration on precipitation could not be

evaluated, e.g. factors such as surface area for nucleation of minerals, inhibition or poisoning of crystal growth.

From the simulations it is evident that the kinetic model offers considerable advantages over equilibrium based models. Not only can it predict time dependent data, but also it can predict the final equilibrium state (in terms of the duration of the batch tests) for situations with precipitation of multiple minerals which compete for the same species - equilibrium models are not capable of predicting either situation. Further, the kinetic modelling approach also allows the determination of the specific precipitation rates for a number of minerals simultaneously in an integrated manner from a single batch test. However, the kinetic model is restricted to the precipitation of minerals and does not consider dissolution; for the tests considered dissolution was not significant compared to the precipitation. For situations where dissolution is significant, the kinetic model will predict neither the time dependent behaviour nor the final equilibrium state correctly. Attempts to include separate processes for dissolution in the model caused instability in model simulations in AQUASIM. This aspect requires further investigation.

4.4 FURTHER VALIDATION OF THE MODEL - APPLICATION TO SWINERY WASTEWATER.

4.4.1 Introduction

Recovery of phosphorus (P) by means of struvite (magnesium ammonium phosphate) precipitation requires optimisation of the conditions favouring the precipitation. This in turn requires knowledge of the struvite precipitation chemistry and kinetics, and their interaction with imposed design conditions, e.g. aeration, retention time, pH adjustment. Further, the simultaneous and/or sequential precipitation of competing minerals and formation of competing ion pair complexes are often encountered in the treatment of and/or P recovery from wastes and wastewaters, for example, anaerobic digester liquors (ADL) and swine wastewater (SWW). Such problems are complex interactive multi-phase (aqueous/gas/solid), multi-mineral, mixed weak acid/base ones. The complex nature of these problems requires the development of models to describe the underlying processes, thereby to facilitate design and optimisation. Models based on traditional equilibrium chemistry cannot be applied, because of the inability to correctly predict the changes that take place with time and with competing or sequential mineral precipitations and ion pairing. As an alternative, Musvoto *et al.* (1997, 2000abc) developed a kinetic based model to simulate the three phase chemical and physical reactions that occur on ADL aeration. This model incorporates kinetics for the chemical and physical processes of weak acid/base chemistry, ion pairing, precipitation and gas stripping.

The model was calibrated and validated through application to aeration batch tests on UASB liquors and sewage sludge ADL. For the calibration, values for the constants in the model were obtained from the literature if available, except the mineral precipitation and gas stripping rates, which were obtained by curve fitting theoretical predictions to measured data. From this integrated kinetic approach *inter alia* the dominant precipitating minerals, the conditions that cause these minerals to precipitate and their rates of precipitation could be identified. Similarly, van Rensburg *et al.* (2003) applied the kinetic model to the aeration of ADL from the Cape Flats Wastewater Treatment Plant (CFWWTP) to resolve struvite precipitation problems being experienced at this treatment plant, and were able to successfully simulate batch aeration tests on the ADL. The simulations enabled strategies to be proposed for implementation at the CFWWTP to minimise problems caused by struvite precipitation, which have been successfully implemented, and to possibly implement struvite recovery. From their investigation,

they concluded that the kinetic modelling approach offers major advantages over equilibrium based models. Not only can it predict time dependent data, but also it can predict the final equilibrium state for situations with precipitation of multiple minerals which compete for the same species - equilibrium models are not capable of predicting either situation.

However, in the specific applications above, the precipitation reactions were dominated by the single mineral struvite (up to 97% of the precipitant), so that assessment of the kinetic model for multiple mineral precipitation was limited. In this chapter, multiple mineral precipitation is explored further, through application of the kinetic model to aeration treatment of SWW and ADL.

4.4.2 Model Application

The kinetic model was applied to describe the time dependent three phase reactions that occur when SWW and ADL are aerated, using experimental data in the literature. All simulations were with the computer programme Aquasim (Reichert, 1994).

4.4.2.1 Aeration of swine wastewater (SWW) (Suzuki et al., 2002)

Suzuki *et al.* (2002) experimentally investigated aeration treatment of SWW. Screened (1.5mm mesh) batches (3L) of SWW were aerated (3h) to stimulate CO₂ stripping and hence pH increase. pH, total inorganic carbon (C_T), and total soluble (3000rpm) Mg, Ca and P were monitored with time, as well as initial and final crystallized Mg, Ca and P. The increase in pH caused mineral precipitation, apparently principally struvite and calcium phosphate (accepted by the authors as hydroxyapatite, HAP, but more likely amorphous calcium phosphate, ACP, see below). Both minerals or their equivalents are included in the integrated chemical physical processes model, which facilitated model application.

4.4.2.2 Aeration of anaerobic digester liquor (ADL) (van Rensburg et al., 2003)

Similarly to Suzuki et al. (2002), van Rensburg et al. (2003) experimentally investigated the aeration treatment of ADL from the (CFWWTP, Cape Town, South Africa) to resolve struvite precipitation problems being experienced at this treatment plant, and to aid possible struvite recovery. Batches (10L) of settled ADL were aerated (at 20°C) and conductivity, pH, total soluble (Whatman's No 1 filtrate acidified, then 0.45µm filtered) Mg, Ca, P, Fe, K and Na, total soluble (not acidified 0.45 µm filtrate) H₂CO₃* alkalinity and short-chain fatty acids (together with pH, used to determine C_T), and FSA (Whatman's No1 acidified filtrate) monitored with time. They applied the kinetic model to the experimental data and obtained a good correlation between predicted and measured data. Further, the model was also applied to theoretically examine the effect of changing initial concentrations of Mg and P, and the aeration rate. They found that in the CFWWTP ADL the struvite precipitation was limited by the availability of Mg, and significant ACP precipitation did not occur. This caused residual Ca and P to be present. However, in their simulations values for the ACP precipitation rate constants could not be accurately determined, so this is investigated further in this chapter. The ADL aeration batch test of van Rensburg *et al.* (2003) in which later samples drawn from the test had NaOH added to increase the pH is also simulated.

4.4.3 Model Calibration

In the model, values are required for: (i) weak acid/base equilibrium constants (pK_a), (ii) weak acid/base kinetic rate constants (K_a), (iii) ion pair stability constants (pK_{ST}), (iv) mineral solubility products (pK_{sp}), (v) ion pair kinetic rate constants (K_{ip}), (vi) mineral precipitation rate constants (K_{ppt}) and (vii) gas stripping rate constants (K_{sg} = K_{LaG}). In the calibration, weak acid/base constants (i) and (ii) were regarded as model constants and not changed. Large values for the reverse dissociation rate

constants were applied to ensure rapid equilibrium, and the relative values for the forward and reverse dissociation rate constants were related via the appropriate equilibrium constant (i) obtained from the literature (Musvoto et al., 1997, 2000abc). The ion pair stability constants (iii) were also obtained from the literature and regarded as model constants and not changed (Musvoto et al., 2000c). The mineral solubility product constants (iv) were calibrated within the range of values quoted in the literature and have been used successfully in all subsequent simulations, and hence were retained unmodified from Musvoto et al. (2000a,c). Values for the ion pair kinetic rate constants (v) accepted by Musvoto et al. (1997, 2000bc) were incorrectly calibrated such that formation of the ion pairs were not instantaneous as should be, and is an oversight in their calibration (Wentzel et al., 2001). Accordingly the values of van Rensburg et al. (2003) of $10^7/\text{d}$ were accepted to ensure the ion pair reactions were effectively instantaneous as required. Values for the mineral precipitation rate constants (vi) of van Rensburg et al. (2003) were initially accepted, which are the same as Musvoto et al. (1997, 2000bc) except that the struvite precipitation rate constant was increased from 300/d to 1000/d. The gas stripping rate constants (vii) were calibrated for each specific test; this is expected, as the gas stripping rates are linked to the aeration rate. In calibrating the gas stripping rates for CO_2 , the K_{La} for O_2 was calibrated, and the value for CO_2 determined via the proportionality of the diffusivities of O_2 and CO_2 (Munz and Roberts, 1989). The CO_2 gas dissolution rate was calculated from Henry's Law constant for CO_2 . For the pH values attained in the experiments to be simulated ($\text{pH} < 9$) and the short periods at the higher pH values, NH_3 stripping is not a significant process, and hence the exact value for the NH_3 stripping rates is not of importance.

Except for the gas stripping rates, it was endeavoured to use the same set of "default" constants for all applications and exceptions are mentioned below. Changes to constants were made by visual trial and error fitting of predicted to measured data; previous applications (Musvoto et al., 2000c; van Rensburg et al., 2003; Wentzel et al., 2001) indicated that visually there was little discernable difference between results from this calibration method and the results obtained with the parameter estimation facility in Aquasim (Reichert, 1994).

4.4.4 Results and Discussion

4.4.4.1 Aeration of swine wastewater (Suzuki et al., 2002) Measured and predicted results for the aeration of the SWW batch test of Suzuki et al. are shown in Fig 1. In the simulations, the "default" values for the model constants above were accepted, except for the CO_2 gas stripping rate constant ($K_{\text{La,CO}_2}$) and the ACP precipitation rate constant ($K_{\text{pp,ACP}}$), which were adjusted by trial and error fitting predictions to the measured data. For $K_{\text{La,CO}_2}$, this was calibrated via the $K_{\text{La,O}_2}$ for oxygen (see above) = 800/d; this constant is batch test specific (aeration rate, mixing, solids, etc.). For $K_{\text{pp,ACP}}$, in simulating this test, an inconsistency between predictions and measurements for Ca became apparent; the model could not correctly predict the observed changes in Ca concentration with time. The value for $K_{\text{pp,ACP}}$ accepted (700/d) gave the best match between the measured and predicted initial and final Ca values; with this value the predicted Ca data were consistently less than that measured between the initial and final values (Fig 1d). In examining possible causes for this inconsistency, precipitation of hydroxyapatite (HAP) was included in the model instead of ACP (HAP was the calcium phosphate precipitant accepted by Suzuki et al. Although this improved the pH predictions marginally, it did not resolve the Ca concentration inconsistency. Further, it has been noted that ACP acts as a precursor to HAP, with ACP slowly transforming to HAP over time (months to years), and that the conditions present in ADL (similar to SWW) stabilise ACP and slow its transformation to HAP (Musvoto et al., 2000c); it is unlikely that HAP forms within the time-scale of the test. Accordingly ACP precipitation was accepted as the dominant CaP precipitant. Accepting that the change in Mg species across any

time interval is due to struvite precipitation, then the P in this struvite can be calculated from this mineral's stoichiometric formulation (molar ratio $Mg:N:P = 1:1:1$). Subtracting the struvite precipitated P from the measured change in P, then the non-struvite P precipitated can be determined. Comparing this with the measured decrease in Ca, gives a Ca:P ratio of about 11:1 for the first 0.25h of the test, where-after the ratio decreases to 1.25 then 1:1. No CaP precipitant with such a large Ca:P ratio could be identified from the literature, nor any Ca mineral (with or without P) not included in the model that would precipitate under the conditions present in the test. Hence this inconsistency could not be resolved - either there is an error in the Ca data or an unknown Ca mineral precipitates that is not accounted for in the model. This illustrates the immense value in applying mass balance based models to experimental data, to gain a deeper understanding of the underlying processes and identify possible errors in data.

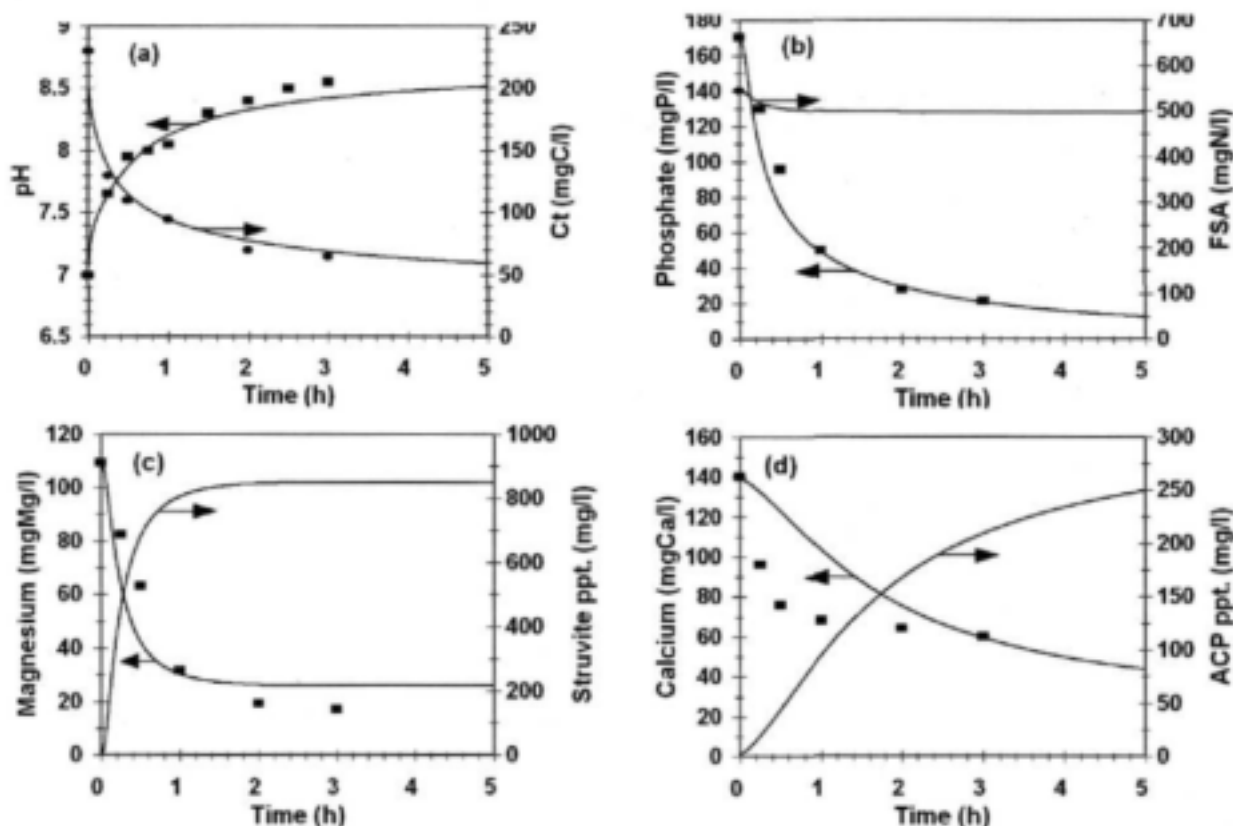


Fig. 1: Predicted (—) and measured (■, ●) concentrations for pH and total inorganic carbon (C_T , Fig 1a, top left), soluble phosphate and free and saline ammonia (FSA, Fig 1b, top right), soluble magnesium and precipitated struvite (Fig 1c, bottom left) and soluble calcium and precipitated amorphous calcium phosphate (ACP, Fig 1d, bottom right) for aerobic batch test on SWW.

Accepting the inconsistency in the Ca values, with the "default" values for the model constants with the exception of the two constants calibrated as above, close correlation was obtained between experimental and measured data (Fig 1). Also, the 3 hour simulated mass precipitations are in close agreement with the measured mass precipitation values; measured Mg, Ca and P precipitated = 86, 84 and 155 mg/L respectively and predicted = 83, 81 and 150 mg/L respectively. From the simulations, as expected aeration strips CO_2 from the wastewater (observed as the decrease in C_T , Fig 1a) causing the pH to increase (Fig 1a). This increase in pH causes struvite to become supersaturated and precipitate (Fig 1c); the initial solution is very close to struvite saturation. Also, with time ACP

precipitates (Fig 1d); the initial solution is slightly supersaturated with respect to ACP, but the precipitation rate is relatively slow. Over the 3 hour test period about 850 mg/L struvite (as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} = 475 \text{ mg/L as MgNH}_4\text{PO}_4$) and 81 mg/L ACP (as $\text{Ca}_3(\text{PO}_4)_2$, the hydration water is unknown) precipitate; negligible newberyite, calcite and magnesite precipitate, in agreement with literature observations. In the precipitation of the minerals, the struvite and ACP essentially compete for P - if ACP precipitation is inhibited by, for example, removing Ca, or if additional P is added (in excess), additional struvite precipitates (about 200 mg/L), and *vice versa*. Hence, it can be concluded that the struvite precipitation with time in the test is controlled by the change in pH, but that the final quantity that precipitates is influenced by the availability of P. The competition between struvite and ACP for P effectively reduces the P available for struvite precipitation. However, due to the rapid rate of struvite precipitation compared with ACP, the majority of P is precipitated in struvite. From the simulations it became evident that for the SWW the molar ratios of Mg, Ca and P are particularly favourable for induced struvite and ACP precipitation, but with P slightly deficient for optimal precipitations.

The close correlation between predicted and measured values (except Ca) enabled theoretical investigation with the model of the precipitation reactions. (1) *Extending aeration*: Aeration was theoretically extended for 1 hour beyond the experiment (Fig 1). Only minor additional ACP precipitation occurred, with minimal additional P and Ca removal. (2) *Aeration rate*: Increasing the aeration rate 2.3 (Suzuki et al., 2002) times ($K_{\text{La},\text{O}_2} = 1600/\text{d}$) causes the pH to increase more rapidly, which causes the precipitation rates to increase (rate constants remain unchanged), and *vice versa*. However, the final condition of the solution and the mass of precipitants remains largely unchanged provided sufficient time is allowed for precipitation at the lower aeration rates, in agreement with experimental observations (Suzuki et al.). Varying the aeration rate, therefore, impacts mainly on reactor retention time and, provided this is appropriately selected, not the removals via precipitation. (3) *Hydroxide dosing*: If instead of aeration, the pH is increased through hydroxide dosing at the start of the test, struvite precipitation is induced to approximately the same extent as with aeration, but the precipitation is much more rapid, virtually immediate. ACP precipitation does not occur immediately, but is a time dependent reaction. Further, depending on the pH attained, calcite and magnesite precipitation may occur reducing the Mg and Ca species available for struvite and ACP respectively. The effect of reduced Mg in struvite precipitation is compensated for by the increased availability of P due to non competition for P by ACP precipitation. However, due to lower P availability, reduced ACP precipitation with time occurs.

If hydroxide is dosed at the end of the aeration (3h), no significant additional minerals precipitate (except for some calcite and magnesite depending on the final pH). Thus, hydroxide dosing, whether instead of or after aeration, offers no significant advantages over aeration, except more rapid struvite precipitation with dosing instead of aeration, reducing reactor retention times.

4.4.4.2 Aeration of anaerobic digester liquor (ADL) (van Rensburg et al., 2003)

Accepting the ACP precipitation rate constant determined from the SWW simulations above, of $K_{\text{p},\text{ACP}} = 700/\text{d}$, and the $K_{\text{La},\text{O}_2} = 130/\text{d}$ of van Rensburg et al., the batch ADL aeration tests of van Rensburg et al. were re-simulated (Fig 2). Close correlation between predicted and measured data were obtained. The increased $K_{\text{p},\text{ACP}}$ value caused an increase in predicted ACP precipitation from 16 (van Rensburg et al.) to 75 mg/L, but did not influence the struvite precipitation; although the ACP and struvite compete for P species, in this test the P is available in excess and Mg is limiting in the struvite precipitation - increasing the initial Mg concentration increased predicted struvite precipitation significantly from 545 (van Rensburg et al.) to 1000 mg/L for increase in initial Mg from 65 to 130

mg/L. Comparing the predicted and measured Ca concentrations, unfortunately the quality of the measurements is inadequate to make a judgement as to whether ACP precipitation (and hence Ca removal) is predicted more correctly than in van Rensburg *et al.* In contrast to the SWW above, in the ADL initially the solution is significantly under saturated with respect to struvite, so that with pH increase saturation is only attained after about 30 minutes aeration, and struvite starts to precipitate. Theoretically, dosing hydroxide instead of aerating has the same effect as for the SWW above; dosing hydroxide at the end of the test to increase the pH to 9 gives minimal additional precipitation (545 to 610 mg/L struvite). Effect of aeration rates on precipitation reported by van Rensburg *et al.* remains unchanged. From the simulations, for this wastewater, the molar ratios of Mg, Ca and P are not as well suited for struvite precipitation as for the SWW - the P is in excess so that after aeration and precipitation significant P remains (about 100 mg/L). Extended aeration (Fig 2) induces only minor additional ACP precipitation and P removal. If the objective is minimising struvite precipitation in subsequent unit operations then the aeration treatment will achieve this. However, if P recovery is the objective, additional P precipitation needs to be induced - this can be best achieved through Mg addition.

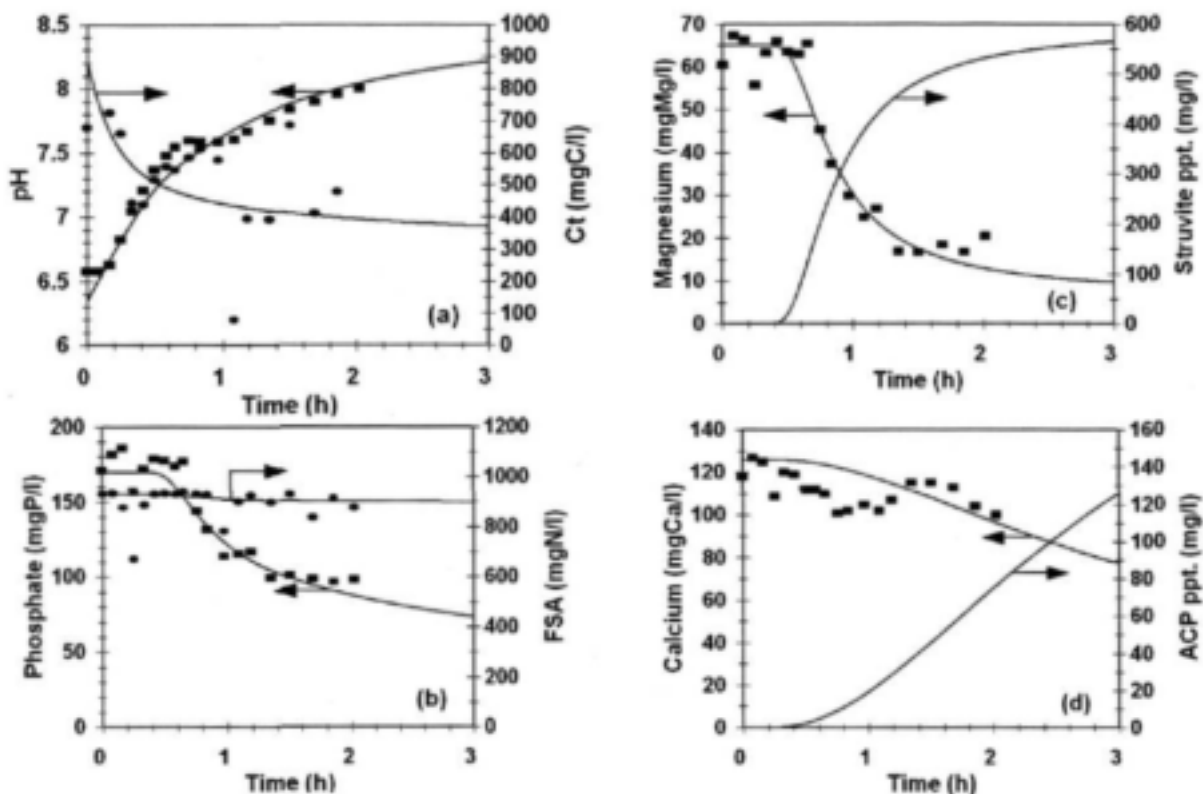


Fig 2: Predicted (—) and measured (■,●) concentrations for pH and total inorganic carbon (C_T , Fig 2a, top left), soluble phosphate and free and saline ammonia (FSA, Fig 2b, top right), soluble magnesium and precipitated struvite (Fig 2c, bottom left) and soluble calcium and precipitated amorphous calcium phosphate (ACP, Fig 2d, bottom right) for aerobic batch test on anaerobic digester liquor from CFWWTP digester treating primary and waste activated sludge.

The additional test on aeration on ADL from the CFWWTP by van Rensburg *et al.* (2001) was also simulated. In this test, additionally to the aeration, NaOH was added to sample numbers 5 to 10 to increase pH further. To accommodate this, in the simulations OH was dosed to the test from sample number 5 (≥ 1.4 h), at quantities to match the measured pHs; the volume of OH dose was kept small so that dilution would not have a significant influence on concentrations. The values for all constants

were as above, except for K_{LaO_2} which was set at 50/d, to match the observed initial pH increase (≤ 1.4 h); as noted above the value for this constant is situation specific. Predicted and measured data are compared in Fig 3; close correlation was obtained. In this test it is evident that despite the increased ACP precipitation rate constant, significant ACP precipitation does not occur (Fig 3d); in this test the initial Ca concentrations were very much reduced (25 mg/L) compared with the test above (125 mg/L), so that ACP is initially under saturated, and only marginally supersaturated as the pH increases. As with the ADL aeration test above, at the end of the aeration significant P remains (90 mgP/L). Dosing Ca to the initial solution does give increased P removal, but Mg dosing is far more efficient due to the relatively rapid struvite precipitation rate compared with ACP.

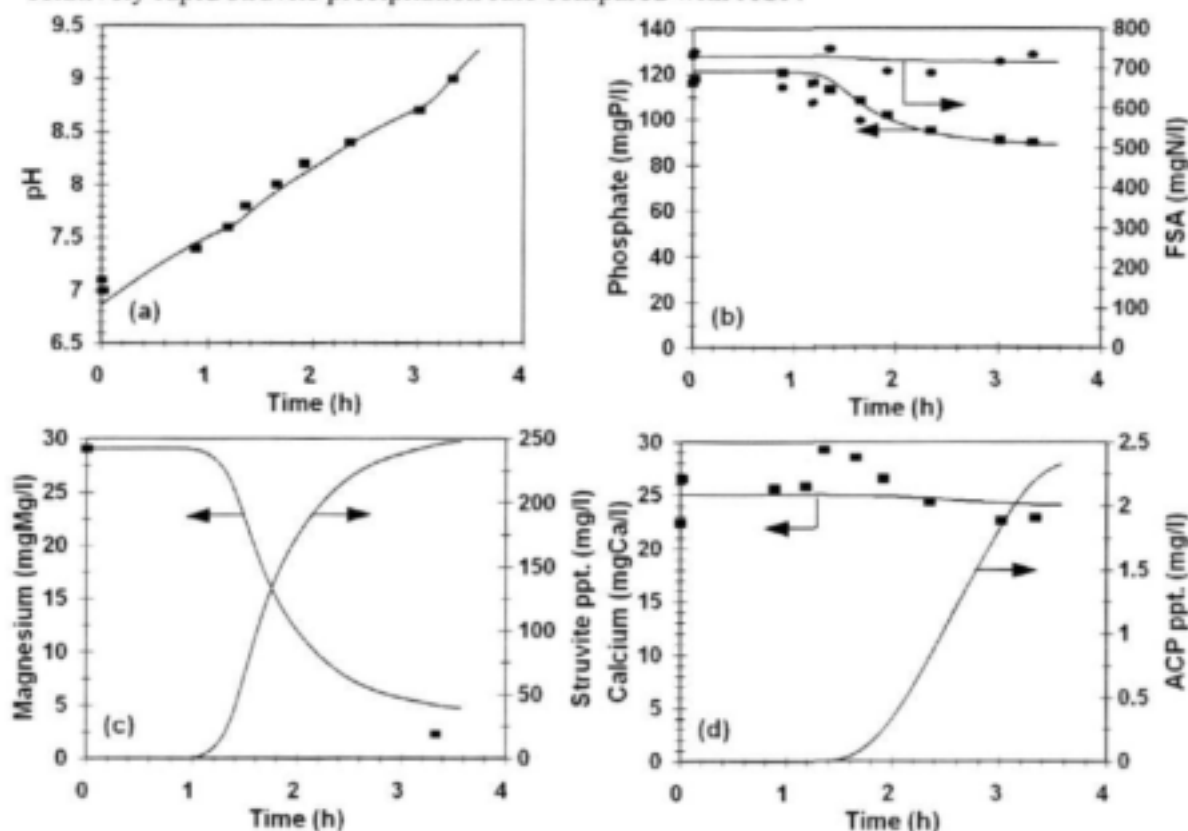


Fig 3: Predicted (—) and measured (■, ●) concentrations for pH (Fig 3a, top left), soluble phosphate and free and saline ammonia (FSA, Fig 3b, top right), soluble magnesium and struvite precipitated (Fig 3c, bottom left) and soluble calcium and precipitated amorphous calcium phosphate (ACP, Fig 3d, bottom right) for aerobic batch test on anaerobic digester liquor from CFWWTP digester treating primary and waste activated sludge; NaOH added from sample 5 (≥ 1.4 h) to raise pH.

The additional test on aeration on ADL from the CFWWTP by van Rensberg *et al.* (2001) was also simulated. In this test, additionally to the aeration, NaOH was added to sample numbers 5 to 10 to increase pH further. To accommodate this, in the simulations OH was dosed to the test from sample number 5 (≥ 1.4 h), at quantities to match the measured pHs; the volume of OH dose was kept small so that dilution would not have a significant influence on concentrations. The values for all constants were as above, except for K_{LaO_2} which was set at 50/d, to match the observed initial pH increase (≤ 1.4 h); as noted above the value for this constant is situation specific. Predicted and measured data are compared in Fig 3; close correlation was obtained. In this test it is evident that despite the increased ACP precipitation rate constant, significant ACP precipitation does not occur (Fig 3d); in this test the initial Ca concentrations were very much reduced (25 mg/L) compared with the test above (125 mg/L),

so that ACP is initially under saturated, and only marginally supersaturated as the pH increases. As with the ADL aeration test above, at the end of the aeration significant P remains (90 mgP/L). Dosing Ca to the initial solution does give increased P removal, but Mg dosing is far more efficient due to the relatively rapid struvite precipitation rate compared with ACP.

4.5 CONCLUSIONS

The considerable value of the integrated chemical physical processes three phase (aqueous-gas - solid) mixed weak acid/base kinetic model as a tool for evaluating experimental data and design options has been demonstrated. In particular, the integrated kinetic model is able to predict the time dependent weak acid/base reactions and the final equilibrium state for situations where multiple minerals competing for the same species (or not) precipitate either simultaneously, sequentially or both (as demonstrated here), a deficiency in equilibrium chemistry based algebraic models such as those incorporated in IWA Anaerobic Digestion Model No. 1 (ADM1).

The three phase kinetic based weak acid/base chemistry model, and the approach on which it is based, has proved to be a very useful framework for research into and design of wastewater treatment systems in which several weak acid/bases influence the behaviour. For research, the model helps to focus attention on issues not obvious from direct experiment and allows determination of mineral precipitation rates for a particular wastewater from a single batch test. Once calibrated with the precipitation (and gas stripping if included) rates, this kind of model can be used to predict the performance of different treatment systems to identify for investigation those that appear technically and economically viable. In the next chapter, this modelling approach will be extended to include biological processes such as those for biological nutrient removal activated sludge (Chapter 3) and anaerobic digestion (Chapter 4). This allows modelling in a seamless way of biological treatment systems together with the mixed weak acid/base chemical systems within which the biological processes operate or combined biological/chemical systems such as simultaneous chemical/biological P removal (de Haas et al., 2001). The objective is to take treatment processes modelling a quantum step further by developing integrated kinetic chemical, physical and biological processes models that can deal with the interaction between the biological processes and the three phase mixed weak acid base chemistry "background" in which these operate.

The integrated kinetic approach to modelling the three phase mixed weak acid/base chemistry is general and can be applied to any combination of mixed weak acid/base systems, mineral precipitations (simultaneous or sequential), ion pairs and physical gas exchange reactions. Further, the model can be readily extended to include kinetics for biological processes, provided that the interaction between these and weak acid/base species is known. The approach has opened the door to modelling in an integrated way systems governed by chemical, physical and biological processes, such as anaerobic digestion, activated sludge treatment of low alkalinity municipal wastewater, simultaneous precipitation in biological nutrient removal activated sludge and biological sulphate removal and sulphur recovery from acid mine drainage. Integrated chemical, physical and biological processes modelling of activated sludge treatment of low alkalinity municipal wastewater and anaerobic digestion of sewage sludge are considered in Chapters 5 and 6.

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CHAPTER 5

INTEGRATED BIOLOGICAL, CHEMICAL AND PHYSICAL PROCESSES KINETIC MODELLING: ANOXIC-AEROBIC C AND N REMOVAL IN THE ACTIVATED SLUDGE SYSTEM

5.1 INTRODUCTION

A number of mathematical models describing the kinetics of the biological processes for carbon (C), nitrogen (N) and phosphorus (P) removal by the activated sludge system have been developed, e.g. the C and N removal models of van Haandel *et al.* (1981) and Activated Sludge Model No.1 (ASM1, Henze *et al.*, 1987), and the C, N and P removal models UCTPHO (Wentzel *et al.*, 1992) and ASM2 and 2d (Henze *et al.*, 1995, 1999). These models are commonly used in research, design, operation and system development and can be coded into computer shell packages such as ASim (Gujer, 1998) and Aquasim (Reichert, 1998) and various versions of them are commercially available.

In all these models, it is assumed that the biological processes operate in an aqueous phase of constant pH, i.e. that there is sufficient buffer capacity in the aqueous phase to absorb or supply the protons (H^+) required or generated directly or indirectly (via e.g. the weak acid base species) by the biological processes without a change in pH. For most applications with municipal wastewater, where the concentrations of C, N and P are low, this is a reasonable assumption. In fact, in some models, the parameter Alkalinity is included to check that this condition remains true (e.g. ASM1, Henze *et al.*, 1987; UCTOLD and IAWPRC, Dold *et al.*, 1991). However, in the treatment of a number of wastewaters this assumption is not valid, e.g. in the nitrification of wastewaters with low buffer capacity and/or high nitrogen (N) concentrations, or in the treatment of wastewaters where the generation or utilisation of short-chain fatty acids (SCFA) is significant.

In this chapter, the biological processes of C and N removal in activated sludge systems are integrated into the three phase mixed weak acid/base chemical-physical kinetic model developed by Musvoto *et al.* (1997, 2000a,b,c). This chemical-physical model includes kinetic descriptions for (i) the ionic equilibrium reactions of the important weak acid/base systems that govern pH in wastewater treatment systems, i.e. the ammonia, carbonate (inorganic carbon), short chain fatty acid (SCFA), phosphate and water systems, (ii) CO_2 and NH_3 gas exchange between aqueous and gas phases, (iii) ion pairing and (iv) precipitation of common minerals associated with Calcium (Ca), Magnesium (Mg), carbonate and phosphate system species. Because in the activated sludge system, mineral precipitation usually is not significant, only parts (i) and (ii) of the model, i.e. the aqueous and gas phase processes, are considered. Furthermore, because of the complex interaction between pH and biological excess P removal (BEPR), only the biological processes of C and N removal are included into the integrated model at this stage. In Chapter 5, the biological processes of anaerobic digestion are incorporated into the model, but initially also only in two (aqueous-gas) phases. In subsequent model extensions, BEPR and the third (solid) phase of mineral precipitation will be incorporated into the models to develop the components required for an integrated chemical, physical and biological process kinetic model for the whole wastewater treatment plant.

5.2 MODEL DEVELOPMENT

Central to the mixed weak acid base chemical-physical model of Musvoto *et al.* (1997, 2000a,b,c) is that the hydrogen ion (H^+) is included explicitly as a compound. Integrating the biological processes of C and N removal of ASM1 into this chemical-physical model requires a number of interactions between the chemical and biological processes to be defined, such as (i) the influence of the biological processes on the weak acid/base systems species and H^+ concentrations, i.e. production and/or utilization of H^+ , CO_2 , ammonia and phosphate in the growth and death (endogenous respiration) processes, and (ii) the effect of pH on the biological process rates where these are expected to be significant, e.g. on the autotrophic nitrifier organism (ANO) maximum specific growth rate. Additionally, interactions with the physical processes require consideration, such as (i) production of N_2 and loss of this species via gas exchange and (ii) input of O_2 via aeration and use of this in biological processes.

The mixed weak acid base kinetic model of Musvoto *et al.* (1997) comprises (see their Table 1):

1. The aqueous phase forward and reverse dissociation chemical processes of the ammonia, carbonate, phosphate, SCFA and water weak acid/base system species, i.e. processes 1-6 and 9-18 involving compounds 1-5 and 7-14.
2. The gas and solid phase physical processes of the carbonate system, i.e. CO_2 gas exchange (dissolution and expulsion) and $CaCO_3$ precipitation, i.e. processes 7, 8 and 19 respectively involving compounds 3, 6 and 15.

Keeping the same numbering of processes and compounds, Musvoto *et al.* (2000a) extended this model to include (see their Tables 1b and 3):

3. Ion pairing of Ca and Mg with hydroxide and the various species of the carbonate and phosphate systems; this added 22 processes, i.e. the aqueous phase forward and reverse dissociation chemical processes of the 11 ion pairs (processes 20-41) and 12 compounds, i.e. Mg and 11 ion pair species (compounds 16-27) respectively (see their Table 1b.)
4. The gas and solid phase physical processes of the ammonia, carbonate and phosphate systems, i.e. ammonia gas stripping and mineral precipitation of four additional minerals associated with Ca and Mg and species of the ammonia, carbonate and phosphate systems, i.e. struvite ($MgNH_4PO_4$), newberyite ($MgHPO_4$), amorphous calcium phosphate [ACP, $Ca_3(PO_4)_2$] and $MgCO_3$; this added 5 additional processes i.e. 42 to 46 but no new compounds as the precipitated minerals were not included explicitly (see their Table 3).

Before incorporating the biological processes of ASM1 into the mixed weak acid/base chemical physical (CP) model of Musvoto *et al.* (1997, 2000a), all the processes and compounds were categorized into chemical (C), physical (P) and biological (B) groups and subgroups (Table 1). This was done for ease of discussion of the assembly of a particular integrated chemical - physical - biological (CPB) processes model, be it aerobic or anaerobic. For easy cross reference to the source chemical physical (CP) and biological (B) models, the numbers of the processes and compounds were not changed from those in the source models. The following general groups and subgroups of processes and compounds were adopted, which are summarized in Table 1:

1. The chemical (C) processes, which comprise those of equilibrium dissociation (CED - forward and reverse weak acid base dissociation) and ion pairing (CIP). These are processes 1-41 in the Musvoto *et al.* (2000a) CP source model, but the physical (P) processes 7, 8 and 19 are excluded.

These processes have the same numbers as in the source model, but the prefix C is added, i.e. C1-C41. The 27 compounds associated with these chemical processes are also numbered identically to the source model, but have the prefix C added, i.e. compounds C1-C5 and C7-C14 involved in the equilibrium dissociation (CED) processes and compounds C4, C5, C8, C10-C12 and C15-C27 involved in the ion pairing (CIP) processes. The only compound that does not belong to this group is the CO₂ gas (C6). CO₂ is included with the compounds associated with the physical (P) processes and so is labelled P1.

2. The physical (P) processes, which comprise those of mineral precipitation (PMP) and gas exchange (PGE). The five mineral precipitation processes 19 and 42 to 45 in the Musvoto et al. (2000a) CP source model are renumbered P1 to P5. Since the precipitants are not explicitly included, these processes involve only existing compounds in the model (viz. C1, C5, C11, C12, C15 and C16) and so add no new compounds. Physical gas exchange (PGE) combines gas dissolution (forward) and expulsion (reverse) processes. The two physical gas exchange processes for CO₂ (dissolution, 7 and expulsion, 8) of Musvoto et al. (1997), are numbered P6 and P7, but from the link with the inter-phase mass transfer developed by Musvoto et al. (1997), the rate formulations are expressed directly in terms of the more conventional mass transfer rate coefficient and the CO₂ partial pressure (p_{CO_2}) (Table 3). Summing these two processes (P6 and P7) is directly equivalent to the conventional inter-phase mass transfer gas exchange. For ammonia, the expulsion ("stripping") process (46) of Musvoto et al. (2000a) is numbered P8 (Table 3). For this gas, the gas phase is accepted to contain zero ammonia (infinite sink) and hence a gaseous ammonia compound is omitted and so also a dissolution process. Added to the PGE processes of the source model to form the integrated CPB activated sludge model are the gas exchange processes for N₂ (dissolution P9 and expulsion P10) formulated in the same manner as for CO₂. Also added is the process for O₂ dissolution by aeration, P11 (Table 3). The new compounds associated with these additional PGE processes are the dissolved and gaseous compounds of oxygen and nitrogen. Dissolved oxygen (A8) and nitrogen (A14) are compounds of the biological processes part of the model (see below) so only 2 physical compounds need to be added for the CPB activated sludge model, i.e. gaseous oxygen (P2) and gaseous nitrogen (P3). No additional physical gas exchange processes would need to be added to incorporate the biological processes of anaerobic digestion, only one gaseous compound methane (CH₄) - it can be assumed that because CH₄ is very insoluble, CH₄ gas is formed directly by the biological processes. Also in anaerobic digestion, dissolved hydrogen is produced and utilized but hydrogen gas production is negligible compared with CO₂ and CH₄ and hence hydrogen need be included only as a dissolved species (Table 1).

In model application, the gas exchange processes can be passive (no gas bubbling) or active (with gas bubbling, e.g. aeration). For both cases, the gas exchange formulations apply, except that of O₂ dissolution (P11), which specifically requires aeration. However, the values of the gas exchange constants (K_{La}) differ significantly for the two situations.

3. The biological (B) processes comprise the biological C and N removal process of activated sludge (ASM1) with prefix A and in Chapter 5 of anaerobic digestion with prefix D (Table 1). Also for the biological processes and compounds of the activated sludge model, the same numbers of ASM1 were retained, except the prefix A was added to each, i.e. processes A1 to A8 and compounds A1 to A13. However, two biological processes are added, viz. aerobic and anoxic growth of heterotrophs (OHOs) with nitrate as N source (Dold and Marais, 1985), because these two processes affect reactor pH and these were numbered A1b and A2b. Of the 13 compounds in ASM1, two become redundant in the integrated CPB model - (i) the free and saline ammonia (FSA, A10) because NH₃ and NH₄⁺ are in the chemical compounds group and (ii) the Alkalinity

(A13), which is now obsolete. Apart from the ammonium (NH_4^+ , C1), three other compounds in the source CP model are also involved with the biological processes, i.e. H_2CO_3^* (C3) through CO_2 generation or uptake, H^+ (i.e. pH, C7) through ammonification, nitrification, denitrification and OHO growth/death and HPO_4^{2-} through uptake for OHO growth and release from OHO death. Details of the biological processes of anaerobic digestion are given in Chapter 5.

Following the grouping and numbering system above (Table 1), the integrated two phase (aqueous-gas) chemical physical biological (CPB) activated sludge model for C and N removal was assembled by including:

1. The chemical equilibrium dissociation (CED) processes for the weak acid/bases (C1-C6 and C9-C18) with associated compounds C1-C5 and C7-C14 (Table 1 of Musvoto et al., 1997, not repeated here). Although the SCFA weak acid/base system is included, in the application here the SCFA are set to zero (see below).
2. The biological activated sludge processes (BA) of C and N removal from ASM1 (A1 to A8), including aerobic and anoxic OHO growth on ammonium (processes A1a and A2a) and nitrate (processes A1b and A2b), with their associated new compounds NH_4^+ (C1), H_2CO_3^* (C3), H^+ (C7), HPO_4^{2-} (C11) and the remaining original 11 activated sludge system compounds (A1-A9, A11-A12) (see Table 2).
3. The physical gas exchange stripping (PGE) processes of ammonia (C46/P8), carbon dioxide (P6 and P7) and nitrogen (P9 and P10) gases and aeration dissolution of oxygen (P11) with their associated compounds dissolved ammonia (C2) and dissolved and gaseous carbon dioxide (C3 and C6), oxygen (A8 and P2) and nitrogen (A14 and P3). A gaseous ammonia compound is not included, because the gas stream is accepted to contain zero ammonia (Table 3).

Not included in the integrated CPB activated sludge model are (i) the chemical ion pairing (CIP) processes (C20-C41), because this was not considered important for activated sludge systems treating municipal wastewater ($\text{TDS} < 1000 \text{ mg/l}$) and (ii) the physical mineral precipitation (PMP) processes (C19, C42-C45 or P1-P5), because only the gas and aqueous phases are considered in this first integrated AS model.

For brevity, only the biological (B) and physical gas exchange (PGE) processes parts of the integrated CPB activated sludge model with their associative compounds are shown in the Petersen matrix of the model (Tables 2 and 3). Because the chemical and physical parts of the model have units mol/l , these were changed to reflect the usual units in biological models, viz. gC/m^3 , gN/m^3 and gP/m^3 . Hence, when the H^+ interacts with C, N or P species, it was divided by the molar mass of C, N and P respectively. Also, the kinetic rate equations for the biological processes were modified to take into account the effect of H^+ where this effect is significant. This was done in two ways: (i) Where there is a direct influence of pH on the biological process rate, pH was included in the kinetic rate formulation, and (ii) the kinetic rates of the biological processes were reformulated to utilize specific species of the weak acid/base systems - stoichiometric coefficients were added and existing ones modified to take this into account.

Table 1: Petersen matrix overview of the integrated chemical-physical-biological processes model for simulating wastewater treatment plant unit operations.

Integrated CPB model matrix structure			COMPOUNDS				
			CHEMICAL (C)		PHYSICAL (P)	BIOLOGICAL (B)	
			Equilibrium Dissociation (CED)	Ion Pairing (CIP)	Gas Exchange	Activated Sludge (BA)	Anaerobic Digest (BD)
P R O C E S S E S	C H E M I C A L	E D	15 compounds of the 6 weak acid base systems: C1-C5 ^a , C7-C14 ^a , C28-C29 ^d	13 compounds associated with 22 ion pairing processes including Ca and Mg: C15-C27 ^b	3 compounds CO ₂ gas P1 (C6) ^a O ₂ and N ₂ gases P2-P3 ^c	13 compounds for activated sludge (A) : A1 - A14; 13 from ASM1 minus A10 (FSA = C1+C2) plus A14 (dissolved N ₂ gas) and	8 compounds for anaerobic digestion (D): D1-D7 and P4. CH ₄ (P4) is produced directly as a gas due to its insolubility and H ₂ (D3) is completely utilized as a dissolved gas
		I P	22 chemical ion pairing processes (CIP) of 11 ion pairs: C20-C41 ^b			replacing in A13 S _{lum} for Alk now obsolete	
	P H Y S I C A L	M P	5 physical mineral precipitation processes (PMP): P1 (C19) ^a , P2-P5 (C42-C45) ^b No additional compounds - all included with CIP				
	B I O L O G I C A L	E G	4 physical gas exchange (PGE) dissolution and expulsion processes; 2 for CO ₂ and 2 for N ₂ , P6-P7c (C7-C8) ^a and P9-P10 ^c .				
		A S	1 physical gas exchange (PGE) expulsion process for NH ₃ ; P8 ^c (C46) ^a 1 physical gas exchange (PGE) dissolution process for O ₂ ; P11 ^c CH ₄ in BD produced directly as a gas (insoluble). H ₂ in BD considered soluble and negligible with respect to CO ₂ and CH ₄ K _{La} rates different with aeration (active) or not (passive).				
	A D I C A L	A S	12 biological (B) activated sludge (BA) processes, i.e. all 8 of ASM1 plus aerobic and anoxic heterotrophic growth with nitrate (A1b and A2b) ^a and anoxic hydrolysis of slowly biodegradable organics (COD, S _{bp}) (A9) ^c and organic N (N _{org} , A10) ^c .				
		A D	10 biological (B) anaerobic digestion (BD) processes. ⁴				

Notes: 1 ^a see Table 1 of Musvoto et al. (1997); b see Tables 1b, 1c and 3 of Musvoto et al. (2000a);

^c see Tables 2 and 3 in this chapter; ^d see Table 2 in Chapter 5;

² Only reactant compounds are specified. Product and inert (unbiodegradable) are omitted but implicit, e.g. mineral precipitates, water, non-reactive sink gases and unbiodegradable COD and OrgN.

Table 2: Matrix representation of the biological processes of ASM1, including anoxic and aerobic growth of OHOs on nitrate (processes A1b and A2b), combined with parts of the mixed weak acid base chemical-physical model of Musvoto et al. (2000a) to yield the two phase (aqueous-gas) integrated chemical-physical-biological (CPB) processes activated sludge system model for C and N removal (see Table 3 for physical processes).

No.	Compounds	C3	C7	C11	A1	A2	A3	A4	A5	A6	A7	A8	A9	C1/A10	A11	A12	A13	A14	Process rate, ρ_i
No.	Processes	H_2CO_3^*	H^+	HPO_4^{2-}	S_i	S_{NH_4}	S_i	S_{NH_4}	Z_{NH_4}	Z_{BA}	Z_i	O dissolved	NO_3^-	NH_4^+	N_{NH_4}	N_{NH_4}	S_{NH_4}	N_i dissolved	Process rate, ρ_i
A1a	Aerobic growth of Z_{NH_4} with NH_4^+	$(1-Y_{\text{NH}_4})/(3Y_{\text{NH}_4})$	$f_{\text{NH}_4}/14 - 2f_{\text{NH}_4}/31$	$-f_{\text{NH}_4}$		$-1/Y_{\text{NH}_4}$			1			$-(1-Y_{\text{NH}_4})/Y_{\text{NH}_4}$		$-f_{\text{NH}_4}$					$\mu_{\text{NH}_4} \left[\frac{\text{S}_{\text{NH}_4}}{K_{\text{NH}_4} + \text{S}_{\text{NH}_4}} \right] \left[\frac{\text{H Air}}{\text{On}} \right] \left[\frac{\text{NH}_4^+}{\text{limit}} \right] \text{Z}_{\text{NH}_4}$
A1b	Aerobic growth of Z_{NH_4} with NO_3^-	F^*	$-f_{\text{NH}_4}/14 - 2f_{\text{NH}_4}/31$	$-f_{\text{NH}_4}$		$-1/Y_{\text{NH}_4}$			1			$-(1-Y_{\text{NH}_4})/Y_{\text{NH}_4}$	$-f_{\text{NH}_4}$				$-64/14 f_{\text{NH}_4}$		$\mu_{\text{NH}_4} \left[\frac{\text{S}_{\text{NH}_4}}{K_{\text{NH}_4} + \text{S}_{\text{NH}_4}} \right] \left[\frac{\text{H Air}}{\text{On}} \right] \left[\frac{1-\text{NH}_4^+}{\text{limit}} \right] \left[\frac{\text{NO}_3^-}{\text{limit}} \right] \text{Z}_{\text{NH}_4}$
A2a	Anoxic growth of Z_{NH_4} with NH_4^+	$(1-Y_{\text{NH}_4})/(3Y_{\text{NH}_4})$	A^*	$-f_{\text{NH}_4}$		$-1/Y_{\text{NH}_4}$			1				$-(1-Y_{\text{NH}_4})/(2.86Y_{\text{NH}_4})$	$-f_{\text{NH}_4}$				D^*	$\mu_{\text{NH}_4} \left[\frac{\text{S}_{\text{NH}_4}}{K_{\text{NH}_4} + \text{S}_{\text{NH}_4}} \right] \left[\frac{\text{H Air}}{\text{Off}} \right] \left[\frac{\text{NH}_4^+}{\text{limit}} \right] \left[\frac{\text{NO}_3^-}{\text{limit}} \right] \text{Z}_{\text{NH}_4} \eta_{\text{O}_2}$
A2b	Anoxic growth of Z_{NH_4} with NO_3^-	F^*	C^*	$-f_{\text{NH}_4}$		$-1/Y_{\text{NH}_4}$			1				B^*				$-64/14 f_{\text{NH}_4}$	D^*	$\mu_{\text{NH}_4} \left[\frac{\text{S}_{\text{NH}_4}}{K_{\text{NH}_4} + \text{S}_{\text{NH}_4}} \right] \left[\frac{\text{H Air}}{\text{Off}} \right] \left[\frac{1-\text{NH}_4^+}{\text{limit}} \right] \left[\frac{\text{NO}_3^-}{\text{limit}} \right] \text{Z}_{\text{NH}_4} \eta_{\text{O}_2}$
A3	Aerobic growth of Z_{BA}	$-3/8$	$f_{\text{NH}_4}/14 + 1/(7Y_{\text{NH}_4})$							1		$-(4.67-Y_{\text{NH}_4})/Y_{\text{NH}_4}$	$1/Y_{\text{NH}_4}$	$-(1/Y_{\text{NH}_4}) - f_{\text{NH}_4}$					$\mu_{\text{BA}} \left[\frac{\text{NH}_4^+}{K_{\text{BA}} + \text{NH}_4^+} \right] \left[\frac{\text{A Air}}{\text{On}} \right] \text{Z}_{\text{BA}}$
A4	Death of Z_{NH_4}		$2(f_{\text{NH}_4})/f_{\text{NH}_4}/31$	$f_{\text{NH}_4} - f_{\text{NH}_4}$				$1-f_{\text{NH}_4}$	-1		f_{NH_4}					$f_{\text{NH}_4}/f_{\text{NH}_4}$			$\rho_{\text{NH}_4} \text{Z}_{\text{NH}_4}$
A5	Death of Z_{BA}							$1-f_{\text{NH}_4}$	-1		f_{NH_4}					$f_{\text{NH}_4}/f_{\text{NH}_4}$			$\rho_{\text{BA}} \text{Z}_{\text{BA}}$
A6	Ammonification of N_{NH_4}		$-1/14$											1	-1				$K_{\text{NH}_4} \text{N}_{\text{NH}_4} \text{Z}_{\text{NH}_4}$
A7	Hydrolysis of S_{NH_4}					1		-1											$E^* ;$
A8	Hydrolysis of N_{NH_4}														1	-1			$E^* (\text{N}_{\text{NH}_4}/\text{S}_{\text{NH}_4})$
	Units	gC/m^3	gH/m^3	gP/m^3	gCOD/m^3	gCOD/m^3	gCOD/m^3	gCOD/m^3	gCOD/m^3	gCOD/m^3	gCOD/m^3	$-\text{gCOD/m}^3$	gN/m^3	gN/m^3	gN/m^3	gN/m^3	$-\text{gCOD/m}^3$	gN/m^3	

$$A^* = -\frac{1-Y_{\text{NH}_4}}{14 \cdot 2.86Y_{\text{NH}_4}} + \frac{f_{\text{NH}_4}}{14} - 2 \cdot \frac{f_{\text{NH}_4}}{31} \quad B^* = -\frac{1-Y_{\text{NH}_4}}{2.86Y_{\text{NH}_4}} + f_{\text{NH}_4} \quad C^* = -\frac{1-Y_{\text{NH}_4}}{14 \cdot 2.86Y_{\text{NH}_4}} - \frac{f_{\text{NH}_4}}{14} - 2 \cdot \frac{f_{\text{NH}_4}}{31} \quad D^* = \frac{1-Y_{\text{NH}_4}}{2.86Y_{\text{NH}_4}} \quad E^* = K_{\text{NH}_4} \left[\frac{\text{S}_{\text{NH}_4}/\text{Z}_{\text{NH}_4}}{K_{\text{NH}_4} + (\text{S}_{\text{NH}_4}/\text{Z}_{\text{NH}_4})} \right] \left[\frac{\text{H Air}}{\text{On}} \right] \left[\frac{\text{H Air}}{\text{Off}} \right] \left[\frac{\text{NO}_3^-}{\text{limit}} \right] \text{Z}_{\text{NH}_4} \quad F^* = \frac{1-Y_{\text{NH}_4}}{3Y_{\text{NH}_4}} + \frac{64}{14 \times 3} f_{\text{NH}_4}$$

Notes: (1) Compound A1-A13 numbered identically to ASM1, except NH_4^+ , which is C1 in Musvoto et al. (1997) and 10 in ASM1. NH_4^+ in ASM1 is actually the free (NH_3) and saline (NH_4^+) ammonia (FSA), where here it is only the saline. H_2CO_3^* alkalinity (compound 13) is no longer required. Ammonium (C1), dissolved CO_2 (C3) and dinitrogen (A14), H^+ (C7) and mono-hydrogen phosphate (C11) are included here because they are involved with the biological activated sludge processes.

Table 3: Matrix representation of the physical gas exchange (PGE) processes incorporated in the integrated two-phase chemical-physical-biological (CPB) model for C and N removal in the activated sludge system (see Table 1 for biological processes).

No	Compound- Process	C2	C3	A8	A14	P1(C6)	P2	P3	
No	Compound- Process	NH ₃ dissolved	H ₂ CO ₃ * CO ₂ diss	O ₂ dissolved	N ₂ dissolved	CO ₂ gas	O ₂ gas	N ₂ gas	Rate
P6	Gas exchange of CO ₂ - dissolution		1			-1			$K_{L,CO_2} P_{CO_2} K_{H,CO_2}$
P7	Gas exchange of CO ₂ - expulsion		-1			1			$K_{L,CO_2} [H_2CO_3^*]$
P8	Gas exchange of NH ₃ - expulsion	-1							$K_{L,NH_3} [NH_{3,aq}]$
P9	Gas exchange of N ₂ - dissolution				1			-1	$K_{L,N_2} P_{N_2} K_{H,N_2}$
P10	Gas exchange of N ₂ - expulsion				-1			1	$K_{L,N_2} [N_{2,aq}]$
P11	Aeration - dissolution of O ₂			1			-1		$K_{L,O_2} ([O_{2,sat}] - [O_{2,aq}])$
	Units	mol/l	mol/l	mgO/l	mol/l	mol/l	mol/l	mol/l	

The modifications outlined above were developed for the two organism groups included in ASM1, i.e. ordinary heterotrophic (OHOs) and autotrophic nitrifier (ANOs) organisms. For both groups, information in the literature on their behaviour was used for the modifications and the derivation of the stoichiometric coefficients of the integrated model are discussed briefly below. A review of bioenergetics and activated sludge model development is not given since these topics are already covered in detail in the literature (e.g. McCarty, 1964, 1972; Dold *et al.*, 1980; van Haandel *et al.*, 1981; Henze *et al.*, 1987; Ohron *et al.*, 1996; Casey *et al.*, 1999; Sperandio *et al.*, 1999). Only aspects relevant to the integration are discussed to clarify the additions and changes to the stoichiometric coefficients and kinetic rates in Tables 2 and 3.

5.3 MODIFICATIONS TO THE ASM1 TO ACCOMPLISH INTEGRATION

5.3.1 Ordinary Heterotrophic Organisms (OHOs)

The processes that involve the OHOs in ASM1 are growth (A1 and A2), death (A4), hydrolysis of enmeshed particulate biodegradable organics (A7) and associated particulate biodegradable organic nitrogen (A8) and ammonification of soluble biodegradable organic nitrogen (A6). The growth of OHOs is described by four processes, two under aerobic conditions using either ammonia (A1a) or nitrate (A1b) as N source, and two under anoxic conditions also using either ammonia (A2a) or nitrate (A2b) as N source. These processes were modified to include (i) production of CO_2 in metabolism, (ii) uptake or release of specific weak acid/base N and P species for growth and death, and (iii) utilization or production of H^+ .

5.3.1.1 OHO metabolism

The bioenergetics of OHO growth are quantified in terms of the lumped electron donating capacity parameter COD, because in wastewater treatment the different organics involved in the growth processes are not known. This is possible because the free energy released per electron (e^-) transferred in the breakdown of different types of organics varies in the narrow range 105 to 121 kJ/ e^- eq. The integrated model requires a carbon balance to be made over the activated sludge system. Thus the mass CO_2 generated in the growth process needs to be known, which requires the COD/TOC ratio of the wastewater organics to be known. For the range of different organics listed in Table 4, the COD/TOC ratio was calculated and varies between 2.67 and 4.0. Because most of the organics in wastewater are of carbohydrate/sugar type with a relatively small proportion of organics with high COD/TOC ratios, an average COD/TOC ratio would seem to be around 3.0. Because CO_2 is generated only in catabolism, the CO_2 generation is proportional to the oxygen utilized, i.e.

$$\text{O}_2 \text{ utilised in producing 1 g OHOs as COD} = (1 - Y_{\text{ZH}})/Y_{\text{ZH}} \quad (1a)$$

where

$$Y_{\text{ZH}} = \text{OHO yield coefficient (mg COD OHOs formed/mg COD organics utilized)}$$

Hence the CO_2 generated in producing 1 gOHOCOD

$$= \text{O}_2 \text{ utilised}/(\text{COD/TOC ratio}) = (1 - Y_{\text{ZH}})/(3.0 Y_{\text{ZH}}) \quad (1b)$$

The CO_2 released during metabolism is in the dissolved form and accepted to add to the H_2CO_3^* concentration in the bulk liquid. Hence, the stoichiometric coefficient $(1 - Y_{\text{ZH}})/(3Y_{\text{ZH}})$ is added to the compound H_2CO_3^* in the integrated model matrix (Table 2).

The COD/TOC ratio accepted will not significantly influence the activated sludge system mixed liquor pH. This is because in the breakdown of the organics listed in Table 4, no direct release of H^+ is envisaged to take place. The CO_2 is generated as $H_2CO_3^*$ but with aeration this is mostly stripped from the bulk liquid which is controlled by gas exchange (higher partial pressure than the atmosphere). Hence, the CO_2 generated is mostly lost to the gaseous phase. Further, if some final dissolved CO_2 state is achieved (e.g. equilibrium with the atmosphere or super-saturation) then any COD/TOC ratio variation is essentially absorbed by the gas phase, not to the bulk liquid and hence does not cause a significant pH change. In contrast, on oxidation the proteins release their N content as NH_3 , which at pH between 6.5 and 8.0, will take up a H^+ to form NH_4^+ , a process called ammonification. This increases the alkalinity of the bulk liquid and at constant CO_2 partial pressure (pCO_2) will produce a pH increase. In contrast to the CO_2 , significant NH_3 loss to the gas phase does not occur (see later). Therefore, in the breakdown of organics, it is not the generation of CO_2 that affects the pH so much as the uptake of a H^+ by the NH_3 released from the breakdown of organic N (proteins). Hence, to predict the pH correctly, the COD/TOC ratio does not need to be known accurately, but the organic N content of the wastewater and its ammonification do need to be known accurately.

Table 4: COD/TOC ratio of some organic compounds.

Organic compound	Formula	COD/TOC Ratio
Carbohydrates	$C_n(H_2O)_n$	2.67 for all n
Sugars	$C_n(H_2O)_{n-2}$	2.67 for all n
¹ Carboxylic acids (SCFA and LCFA)	$CH_3(CH_2)_nCOOH$	$4(3n+2)/[3(n+1)]$ $= 3.33$ for $n=1$; $= 3.94$ for $n=20$
Primary amines	$CH_3(CH_2)_nNH_2$	4 for all n
Amino acids	$H(CH_2)_nC_2H_4O_2N$	$4(n+1)/(n+2) < 4$
Alkanes	$H(CH_2)_nH$	$4(3n+1)/3n \approx 4$
Alcohols	$H(CH_2)_nOH$	4 for all n

¹Unsaturated fats have slightly lower COD/TOC ratio because for every double C bond ($C=C$), there are 2 Hs fewer.

Under anoxic conditions, nitrate (NO_3^-) serves as terminal electron acceptor and the specific yield coefficient is decreased to ~80% of the aerobic value. With nitrate as electron acceptor approximately the same quantity of free energy from the organics is available to the organism as when oxygen is the electron acceptor, but *ideally* only 2 ATP moles are formed per pair of electrons transferred to the nitrate (Payne, 1981) compared with 3 ATP moles per pair of electrons with oxygen. Measurements by Orhon *et al.* (1996), Sperandio *et al.* (1999) and Muller *et al.* (2003) confirm this reduction in yield experimentally with artificial and real domestic wastewaters. This reduction in yield under anoxic conditions is not recognised in early activated sludge models like UCTOLD (Dold *et al.*, 1991), ASM1 (Henze *et al.*, 1987), UCTPHO (Wentzel *et al.*, 1992) and ASM2 (Henze *et al.*, 1995), but is accepted in later models like ASM2d (Henze *et al.*, 1999) and Biowin (Barker and Dold, 1997). This reduction also has been accepted in the model developed here, so that under anoxic conditions, about 20% less OHO biomass and 40% more CO_2 are generated than under aerobic conditions (Table 5). As mentioned earlier, this lower CO_2 generation does not affect the reactor pH but the lower loss of CO_2 to the gas phase (no aeration) does increase the pH above that of the aerobic reactor.

Table 5: Stoichiometric and matrix representation of the aerobic and anoxic growth processes with ammonia and nitrate as N source taking account of the substrate required for the reduction of nitrate to ammonia in the chemical-physical-biological (CPB) processes model for C and N removal in the activated sludge system (see Table 2 for biological processes).

	No	A2 S _{bs}	A13 S _{bl,oxi}	C1 A10	C7	A9	C7	A9	A8	A5	C3	C3	A14	-	-	-
No	Compound- Process I	C ₆ H ₁₂ O ₆ Growth	C ₆ H ₁₂ O ₆ Reductn	NH ₄ ⁺ Growth	H ⁺ Denit	NO ₃ Denit	H ⁺ Growth	NO ₃ Growth	O ₂ Growth	C ₃ H ₇ O ₂ N Biomass	CO ₂ Growth	CO ₂ Reductn	N ₂ Denit	H ₂ O Growth	H ₂ O Reductn	H ₂ O Denit
A1a	Aerobic growth with ammonia	-1	0	-y	0	0	+y	0	-(6-5y)	+y	+(6-5y)	0	0	+(6-2y)	0	0
A1b	Aerobic growth with nitrate	-1	-y/3	0	0	0	-y	-y	-(6-5y)	+y	+(6-5y)	+2y	0	+(6-2y)	+y	0
A2a	Anoxic growth with ammonia	-1	0	-y'	$-\frac{8}{10}(6-5y')$	$-\frac{8}{10}(6-5y')$	+y'	0	0	+y'	+(6-5y')	0	$+\frac{4}{10}(6-5y')$	+(6-2y')	0	$+\frac{4}{10}(6-5y')$
A2b	Anoxic growth with nitrate	-1	-y'/3	0	$-\frac{8}{10}(6-5y')$	$-\frac{8}{10}(6-5y')$	-y'	-y'	0	+y'	+(6-5y')	+2y'	$+\frac{4}{10}(6-5y')$	+(6-2y')	+y'	$+\frac{4}{10}(6-5y')$
	Units	mol	mol	mol	mol	mol	mol	mol	mol	mol	mol	mol	mol	mol	mol	mol
A1a	Aerobic growth with ammonia	$-\frac{1}{Y_{2H}}$	0	$-f_{2H,N}$	0	0	$\frac{f_{2H,N}}{14}$	0	$-\frac{(1-Y_{2H})}{Y_{2H}}$	1	$\frac{(1-Y_{2H})}{3Y_{2H}}$	0	0	-	-	-
A1b	Aerobic growth with nitrate	$-\frac{1}{Y_{2H}}$	$-\frac{64}{14}f_{2H,N}$	0	0	0	$-\frac{f_{2H,N}}{14}$	$-f_{2H,N}$	$-\frac{(1-Y_{2H})}{Y_{2H}}$	1	$\frac{(1-Y_{2H})}{3Y_{2H}}$	$\frac{64}{14 \times 3}f_{2H,N}$	0	-	-	-
A2a	Anoxic growth with ammonia	$-\frac{1}{Y'_{2H}}$	0	$-f'_{2H,N}$	$\frac{(1-Y'_{2H})}{14 \times 2.86 Y'_{2H}}$	$\frac{(1-Y'_{2H})}{2.86 Y'_{2H}}$	$\frac{f'_{2H,N}}{14}$	0	0	1	$-\frac{(1-Y'_{2H})}{3Y'_{2H}}$	0	$\frac{(1-Y'_{2H})}{2.86 Y'_{2H}}$	-	-	-
A2b	Anoxic growth with nitrate	$-\frac{1}{Y'_{2H}}$	$-\frac{64}{14}f'_{2H,N}$	0	$\frac{(1-Y'_{2H})}{14 \times 2.86 Y'_{2H}}$	$\frac{(1-Y'_{2H})}{2.86 Y'_{2H}}$	$-\frac{f'_{2H,N}}{14}$	$-f'_{2H,N}$	0	1	$-\frac{(1-Y'_{2H})}{3Y'_{2H}}$	$\frac{64}{14 \times 3}f'_{2H,N}$	$\frac{(1-Y'_{2H})}{2.86 Y'_{2H}}$	-	-	-
	Units	gCOD	gCOD	gN	gH	gN	gH	gN	gO	gCOD	gC	gC	gN			

Notes:

(1) For an aerobic yield coefficient (Y_{2H}) of 0.67 mgOHOCOD/mgCOD organics $y = Y_{2H} \times 192/160 = 0.67 \times 192/160 = 0.804$ mol OHO/mol organics.

(2) For an anoxic yield coefficient of (Y'_{2H}) 0.54 mgOHOCOD/mgCOD organics $y' = 0.54 \times 192/160 = 0.648$ mol OHO/mol organics.

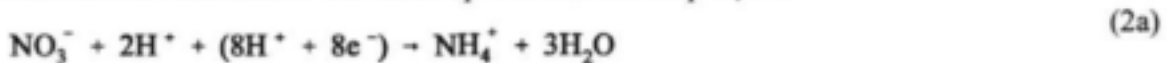
(3) The water production is included in the molar stoichiometric part of the table (upper) to allow element (C, H, O, N) mass balance checks. The COD based stoichiometry in the lower half is calculated from the molar stoichiometry, e.g. y mol biomass (160 gCOD/mol) is synthesized from 1 mole glucose (192 gCOD/mol), so 1 gCOD biomass requires $192/(160y)$ g glucose; substituting $y = Y_{2H} \times 192/160$ from (1) above yields 1 gCOD biomass requires $1/Y_{2H}$ gCOD glucose (-ve for consumption) and y mol biomass (160 gCOD/mol) production yields $(6-5y)$ mol CO₂ in growth process, so 1 gCOD biomass produces $12(6-5Y_{2H} \times 192/160)/(192Y_{2H})$ gCO₂-C = $+72(1-Y_{2H})/(192Y_{2H})$ where $72/192 = \text{TOC/COD ratio of glucose}$; for a COD/TOC ratio of 3 this = $(1-Y_{2H})/(3Y_{2H})$.

5.3.1.2 Use of specific weak acid/base species for OHO growth

The nitrogen required for OHO synthesis is obtained from either ammonia (processes A1a and A2a) or, in the absence of ammonia, nitrate (processes A1b and A2b). Phosphorus is also incorporated in OHO mass. The concentrations of N and P required for synthesis are quantified in ASM1 and similar biological models as N and P content of the active biomass i.e. $f_{ZB,N} = 0.068 \text{ mgN/mgOHOCOD}$ and $f_{ZB,P} = 0.020 \text{ mgP/mgOHOCOD}$ respectively, but it is not specified which of the ammonia and phosphate weak acid/base system species are taken up for synthesis.

From the literature on bioenergetics, it is accepted that the non-ionic ammonia and phosphate system species are taken up for synthesis, i.e. NH_3 and H_2PO_4^- . However, it has been accepted in this model that the most abundant species of the systems in the pH range typical for activated sludge systems of 6.5 to 8.5, NH_4^+ and HPO_4^{2-} , are taken up, releasing one and taking up two protons respectively during cell synthesis. In this operating pH range, the concentrations of NH_3 and H_2PO_4^- are extremely low and their use in kinetic models for synthesis can lead to numerical instability.

When ammonia is depleted, NO_3^- is taken up by the OHOs as the N source for growth. However, the NO_3^- must be first reduced to NH_4^+ by accepting 8H^+ and 8e^- , which are supplied by the biodegradable organics and two additional H^+ are taken up from the bulk liquid, viz.



One of the two H^+ is returned to the bulk liquid when NH_4^+ is taken up for growth, but the other is required in the reduction reaction and therefore increases the bulk liquid pH. Hence, the net change in H^+ concentration with NO_3^- as N source and P uptake as HPO_4^{2-} for OHO growth is

$$= -f_{ZB,N}/14 - 2f_{ZB,P}/31 \quad \text{mgH}^+/\text{l} \quad (2b)$$

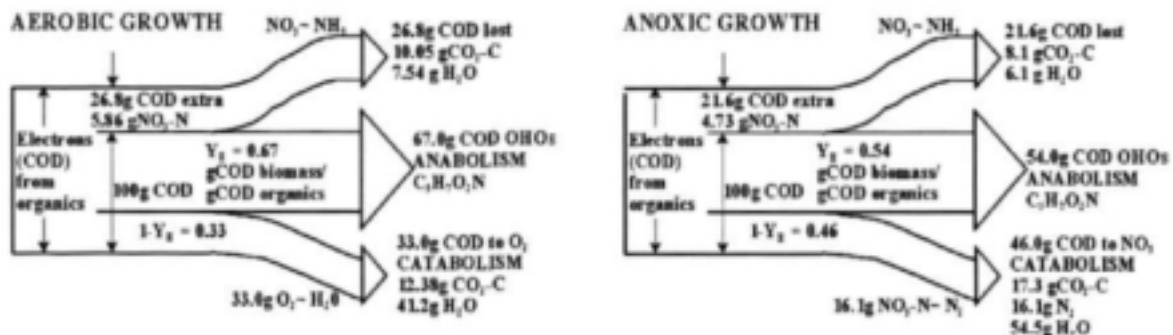


Fig 1: Schematic and quantitative representation of aerobic (left) and anoxic (right) OHO growth using nitrate as nitrogen source (assimilative denitrification) taking account of the organics (electrons) required to reduce nitrate to ammonia.

The biodegradable organics that supply the 8H^+ and 8e^- for the nitrate reduction (Eq 2a) are "lost" from the system, i.e. are no longer available for growth, which is shown quantitatively in Fig 1. Even though nitrate reduction (Eq 2a) thermodynamically is an energy generating reaction, bioenergetically the OHOs get no energy from it. It is, therefore, not correct to change the yield coefficient to account for this additional H^+ and e^- consumption. Accordingly, the yield coefficients under aerobic and anoxic conditions remain $Y_{ZB} = 0.67$ and $Y'_{ZB} = 0.54 \text{ mgOHOCOD formed/mgCOD organics utilized}$. To take account of the COD "lost" by nitrate reduction for growth, the compound $\text{S}_{b\text{Lost}}$ (A13) is added to the model as a compound so that (i) the magnitude of this "lost" COD is tracked and (ii) COD

balances can still be used to verify the model. Integrating the stoichiometry of the reduction of nitrate to ammonia into the growth processes using glucose as an example substrate is shown in Table 5. The Petersen matrix coefficients of the aerobic and anoxic growth processes (1 and 2) in Table 2 were calculated from Table 5. It can be seen that (i) additional CO_2 is generated when nitrate is utilized as N source for growth, but this additional CO_2 generation does not affect the reactor pH, and (ii) H^+ are taken up from the bulk liquid in the reduction of NO_3^- to NH_3 which will cause a pH increase.

In completely mixed single aerobic reactor systems, the ammonia is unlikely to be depleted sufficiently for NO_3^- to be utilized as the N source - this situation is more likely to occur in plug flow type and sequencing batch reactor (SBR) systems. In anoxic reactors, whether completely mixed or plugflow, invariably ammonia is present in excess of synthesis requirements. In completely mixed nitrifying aerobic digestion of waste activated sludge there always should be sufficient ammonia for growth because the ammonia released in OHO death always is greater than that taken up for OHO growth on the slowly biodegradable (SB) COD released in OHO death, but in application of the model nitrate utilization for OHO growth nevertheless can occur. This can also occur with model application to aerobic digestion of primary sludge even when sufficient ammonia is dosed for net OHO biomass production from the primary sludge particulate biodegradable organics. This apparent ammonia deficiency in the model arises because the rate of nitrification is faster than the rate of OHO growth, which is limited by the supply rate of SBCOD from the OHO death process. This leads to uptake of nitrate for OHO growth, but to the release of ammonia in OHO death. This released ammonia is then nitrified with an associated OUR for nitrification. The consequence is an incorrectly predicted high nitrification OUR from the continual supply of ammonia nitrogen from the death process, nitrogen that is taken up as nitrate by the OHOs. This problem is eliminated in the model by reducing the switching function K value which controls the switch from ammonia to nitrate uptake for OHO growth to a very low value (0.0001 mgN/l). This prevents the OHO growth process from slowing down when the ammonia concentration gets low, allowing it to successfully "compete" for ammonia against the nitrification process. This problem therefore has nothing to do with ammonia deficiency but everything to do with the relative rates of processes competing for the same compounds, in this case ammonium (NH_4^+). *K values of switching functions on processes competing for the same compounds therefore require very careful scrutiny in simulation models.*

5.3.1.3 Utilization and generation of H^+ in OHO growth and death (endogenous respiration)

When NH_4^+ (or NO_3^-) and HPO_4^{2-} are taken up for synthesis, a proton is released (or taken up) and two protons taken up respectively to convert these species to their unionised forms NH_3 and H_3PO_4 . This changes the H^+ concentration which has to be taken into account, viz.

$$\text{Concentration } \text{NH}_4^+ \text{ (or } \text{NO}_3^-) \text{ taken up for synthesis} = f_{\text{ZB,N}} \text{ (gN/gOHOCOD)} \quad (3a)$$

$$\text{Concentration } \text{HPO}_4^{2-} \text{ taken up for synthesis} = f_{\text{ZB,P}} \text{ (gP/gOHOCOD)} \quad (3b)$$

$$\text{Hence the change } \text{H}^+ \text{ concentration in synthesis with } \text{NH}_4^+ = f_{\text{ZB,N}}/14 - 2 f_{\text{ZB,P}}/31 \text{ mgH}^+/\text{l} \quad (3c)$$

$$\text{and the change } \text{H}^+ \text{ concentration in synthesis with } \text{NO}_3^- = -f_{\text{ZB,N}}/14 - 2 f_{\text{ZB,P}}/31 \text{ mgH}^+/\text{l} \quad (3d)$$

If the unionized N and P species (NH_3 and H_3PO_4) are used instead for synthesis, virtually the same net effect on H^+ will occur, due to the redistribution of the weak acid/base species via the CED kinetic processes.

In organism death, since the death-regeneration approach is followed, (Dold et al., 1980), the difference in N contents of the active biomass lost and the endogenous residue formed is released as biodegradable particulate N. Hence, this process has no direct influence on the H^+ concentration. In contrast, to reduce complexity in phosphorus compounds, the corresponding P is released as HPO_4^{2-} , with associated H^+ to maintain neutrality. This changes the H^+ concentration which has to be taken into account, viz.

$$\text{Concentration } HPO_4^{2-} \text{ released in OHO death} = f_{ZB,P} - f_E f_{ZE,P} \text{ (gP/gOHOCOD)} \quad (4a)$$

$$\text{Associated change } H^+ \text{ concentration} = +2(f_{ZB,P} - f_E f_{ZE,P})/31 \quad (4b)$$

5.3.1.4 Ammonification of soluble organic nitrogen

Ammonification is the process mediated by OHOs (A6) whereby biodegradable soluble organic nitrogen (N_{obs}), which is in the unionized " NH_3 " form, is converted to saline ammonia (NH_4^+). Associated with ammonification therefore is a decrease in the H^+ concentration of the bulk liquid due to uptake of a H^+ by the NH_3 to form NH_4^+ . The H^+ taken up in ammonification is $1/14 \text{ gH}^+/\text{gN}$ Organic N ammonified.

In ASM2, the ammonification process is omitted. Instead, the conversion of soluble biodegradable organic N (N_{obs}) to ammonia is linked to the utilization of readily biodegradable organics (RBCOD) of which it is part. So if a wastewater has an influent biodegradable soluble organic N to RBCOD ratio (N_{obs}/S_{bbl}) of say 0.03 (i_{NSF} in ASM2), the ammonia (NH_3) released is 0.03 times the rate of RBCOD utilization. The release of ammonia from the particulate biodegradable organic N is modelled in the identical way in ASM1 and ASM2. Two models were developed and compared, one conforming strictly to ASM1 including the ammonification process, and the other linking the release of ammonia from the soluble organic N to the utilization of RBCOD. No significant differences were noted between the predictions of the two model versions, provided the ammonification kinetic rate constants were correctly selected.

5.3.1.5 A note on the utilization of SCFA in OHO growth

Inclusion of the SCFA weak acid/base system in the model arises from the earlier application of the chemical - physical part of the model to aeration treatment of anaerobic digester liquor (ADL) (Musvoto, 2000a,c), where it was required to establish the correct pH. Practically, the SCFA are not explicitly required in this integrated CPB model because the influent SCFA concentration usually is very low and hence is included in the RBCOD. However, if the SCFA concentration is significant, such as with activated sludge treatment of anaerobic digester liquor, then SCFA utilization will influence the pH significantly and will need to be explicitly included in the model. This will require that the SCFA are modelled separately as a subfraction of the RBCOD and that four processes be added to the model, viz. processes A1c and A1d - aerobic growth of OHOs on acetate with ammonia (A1c) and nitrate (A1d) as N source, and processes A2c and A2d which are the anoxic equivalents. These processes will have identical stoichiometry as growth on RBCOD, but the substrate utilization is deducted from the HAc species of the SCFA system. Also, the SCFA concentration would need to be deducted from the RBCOD to correctly reflect the RBCOD as the remaining fermentable RBCOD, as is done in UCTPHO (Wentzel et al., 1992) or ASM2 (Henze et al., 1995), where SCFA is modelled separately from the fermentable RBCOD for biological P removal.

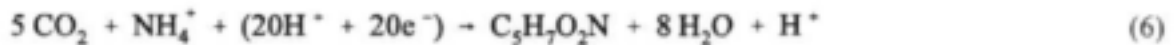
5.3.2 Autotrophic Nitrifier Organisms (ANOs)

5.3.2.1 Autotrophic metabolism

Although mediated by a number of different ammonia oxidizing and nitrite oxidizing organisms in two sequential steps from ammonia to nitrite and nitrite to nitrate, in ASM1 nitrification is modelled as a single step from ammonia to nitrate by a generic group of autotrophic nitrifier organisms (ANOs). The nitrification rate is defined by the slower process rate of the sequence, which under most circumstances is the ammonia oxidation. Stoichiometrically, nitrification of saline ammonia requires 2 mol (64gO) oxygen and produces 1mol nitrate and 2 mol protons, i.e.



The ANOs obtain their anabolic carbon requirements from dissolved CO_2 (H_2CO_3^*) and their catabolic energy (e^-) requirements from oxidizing ammonia to nitrate. Accepting that $\text{C}_5\text{H}_7\text{O}_2\text{N}$ represents the C, H, O and N content of the ANOs and has a COD content of 160g/mol, then five mol CO_2 are required to synthesize one mol ANOs viz.



which includes also the ammonia requirement for cell synthesis.

The catabolic ammonia (e^- and H^+) requirement is determined from the ANO yield coefficient, i.e.

$$\begin{aligned} Y_{\text{ZA}} &= 0.15 \text{ (gANOCOD synthesized/gNH}_4^+\text{-N nitrified)} \\ &= 0.15 \times 14/160 \text{ (mol ANOs/mol NH}_4^+\text{-N nitrified)} \end{aligned}$$

From Eq 6, the mol CO_2 required is 5 times the mol of ANOs formed. Hence

$$\text{CO}_2 \text{ required} = (5 \times 12/160) = 3/8 \text{ (gCO}_2\text{-C/gANOCOD synthesized)} \quad (7)$$

This stoichiometric ratio for CO_2 utilised by the ANOs is added to the model, accepting that the CO_2 taken up is in the dissolved form and represented as H_2CO_3^* (Table 2).

The ANOs are conventionally considered to use the NH_4^+ species because this is the most abundant species in the optimum pH range for nitrification, i.e. 7.2-8.5. However, Suzuki (1974), in studies on *Nitrosomonas europae* concluded that the NH_3 species is used in the oxidation process. Also, Drozd (1976) argued that *Nitrosomonas* uses the NH_3 form because a rapid decrease in pH was noticed in the medium in growing cultures suggesting that a proton remains on the exterior of the cell wall in the medium. In this integrated model, it has been accepted that the unionized NH_3 species is used in oxidation, but that NH_4^+ species is taken up from solution with the release of H^+ . In the operating pH range for nitrification, the NH_3 concentration is extremely low and its use in mathematical models can lead to numerical instability.

5.3.2.2 Production/utilisation of H^+ in ANO growth and death

The change in H^+ during nitrification (NH_4^+ oxidation and uptake for ANO growth) is derived from Eqs 5 and 6 and the stoichiometric coefficient for NH_4^+ in the ASM1 model is;

$$\begin{aligned} \text{Concentration of NH}_4^+\text{-N nitrified to produce 1 gANOCOD/m}^3 &= 1/Y_{\text{ZA}} = 1/0.15 \\ \text{From Eq 5, 14 g of NH}_4^+\text{-N nitrified produce 2g H}^+ & \\ \text{So } 1/Y_{\text{ZA}} \text{ g NH}_4^+\text{-N nitrified produces } 1/(7Y_{\text{ZA}}) \text{ gH}^+ & \end{aligned}$$

Also, from Eq (5), the NH_4^+ incorporated into ANO biomass during synthesis releases a H^+ . The concentration of N incorporated into ANO mass is defined by the N content of the ANOs, which is accepted to be equal to that of the OHO, i.e. $f_{\text{ZB,N}} = 0.068 \text{ mgN/mgANOCOD}$. So from Eq 6,

$$\begin{aligned} 14 \text{ g NH}_4^+\text{-N is incorporated into ANOs releases } 1 \text{ g H}^+ \\ \therefore f_{\text{ZB,N}} \text{ g NH}_4^+\text{-N incorporated into ANOs releases } f_{\text{ZB,N}}/14 \text{ g H}^+ \end{aligned}$$

Thus in total, during nitrification $1/(7Y_{\text{ZA}}) + f_{\text{ZB,N}}/14 \text{ gH}^+$ are released per gANOCOD generated. For ANO death, N transformations are as for OHOs above.

Because the ANO mass constitutes such a small part of the measured reactor COD (or VSS) concentration and the endogenous respiration rate is so low, P uptake and release in ANO growth and death respectively are ignored as negligibly small. However, these can be readily incorporated if required, by following the concepts of the OHOs developed above.

5.3.2.3 Effect of pH on maximum specific growth rate of ANOs

The maximum specific growth rate of nitrifiers μ_A is very sensitive to pH, with nitrification rates declining sharply outside the optimum pH range of 7.0-8.5. In the activated sludge system treating reasonably well buffered wastewaters, quantitative modelling of the effect of pH on nitrification is not critical because pH reduction can be limited or completely obviated by including anoxic zones thereby ensuring alkalinity recovery via denitrification. However, in poorly buffered wastewaters, or wastewaters with high influent N (such as anaerobic digester liquors), the interaction between the biological processes, pH and nitrification is the single most important one for the N removal activated sludge system. Hence, it is essential to include the effect of pH on the nitrification rate in the integrated model to simulate this important interaction.

Quantitative modelling of the effect of pH on μ_A has been hampered by a lack of information and the general expected trends have been formulated based on empirical assumptions. Many studies have shown that μ_A can be expressed as a percentage of the highest value at optimum pH. Accepting this approach and that μ_A is highest and remains approximately constant in the pH range for $7.2 < \text{pH} < 8.5$ and decreases as the pH decreases below 7.2 (Downing *et al.*, 1964; Loveless and Painter, 1968), WRC (1984) modelled the μ_A - pH dependency as:

$$\text{For } 7.2 < \text{pH} < 8.5, \quad \mu_{\text{ApH}} = \mu_{\text{A}7.2} \quad (8a)$$

$$\text{For } 5 < \text{pH} < 7.2, \quad \mu_{\text{ApH}} = \mu_{\text{A}7.2} \theta_{\text{ns}}^{(\text{pH}-7.2)} \quad (8b)$$

where

$$\theta_{\text{ns}} = \text{sensitivity coefficient} = 2.35$$

WRC (1984) considered additionally an increase in half saturation concentration (K_n , mgN/l) with decrease in pH, i.e. $K_{\text{npH}} = K_{\text{n}7.2} \theta_{\text{ns}}^{(7.2-\text{pH})}$ with θ_{ns} also = 2.35. They did this because Marais and Ekama (1976) observed an increase in effluent ammonia concentration as the reactor pH decreased with increasing sludge age. It is simple to include this additional effect into the model, but it was omitted because very little data could be found in the literature on the effect of pH on K_n to support the observation of Marais and Ekama (1976), probably because the effect of pH on nitrification was observed as an effect on μ_A , rather than an effect on μ_A and K_n individually.

WRC (1984) did not consider cases where $\text{pH} > 8.5$. Declining μ_A values at $\text{pH} > 8.5$ have been observed and it has been noted that nitrification effectively ceases at a pH of about 9.5 (Malan and

Gouws, 1966; Wild *et al.*, 1971; Antoniou *et al.*, 1990). Accordingly, for $\text{pH} > 7.2$ an additional formulation is proposed to model the decline in the maximum specific growth rate from $\text{pH} > 7.2$ to 9.5 as a function of $\mu_{A7.2}$ using inhibition kinetics as follows:

$$\mu_{ApH} = \mu_{A7.2} K_i \frac{K_{\max} - \text{pH}}{K_{\max} + K_{\Pi} - \text{pH}} \quad (9)$$

where

$$K_i = 1.13, K_{\max} = 9.5, K_{\Pi} \approx 0.3.$$

The overall effect of pH on μ_A is modelled by combining Eqs (8) and (9), giving the maximum specific growth rate at any pH between 5.5 and 9.5 as a fraction of the maximum rate at $\text{pH} = 7.2$, Eq 10, which is shown graphically in Fig 2. It can be seen that in the range $\text{pH} = 7.2$ to 8.3, the change in μ_{ApH} is small, with $\mu_{ApH}/\mu_{A7.2} > 0.9$.

$$\mu_{ApH} = \mu_{A7.2} 2.35^{(\text{pH}-7.2)} K_i \frac{K_{\max} - \text{pH}}{K_{\max} + K_{\Pi} - \text{pH}} \quad (10)$$

where the term $2.35^{(\text{pH}-7.2)}$ is set = 1 for $\text{pH} > 7.2$, the term $K_i \frac{K_{\max} - \text{pH}}{K_{\max} + K_{\Pi} - \text{pH}} = 1$ for $\text{pH} < 7.2$ and $\mu_{ApH} = 0$ for $\text{pH} > 9.5$.

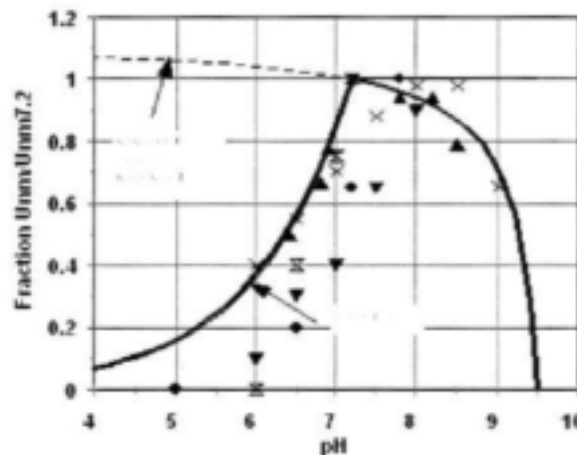


Fig 2: The effect of pH on the maximum specific growth rate of autotrophic nitrifying organisms (ANOs) μ_{nm} .

— Model (Eqs 10-12), • Malan & Gouws (1966)
 • Sawyer *et al.* (1973), ■ Downing *et al.* (1966)
 × Wild *et al.* (1971), ♦ Antoniou *et al.* (1990).

Experimental data from the literature are also shown in Fig 2 to provide some quantitative support for Eq 10. At low pH (<7.2) data from Wild *et al.* (1971) and Antoniou *et al.* (1990) fit the equation reasonably well. Very little data are available for pH>8.5, but the few points from Antoniou *et al.* (1990) show reasonable agreement with Eq 10. Accordingly, Eq 10 was accepted to calculate μ_{ApH} in the integrated model in the pH range 5.5 to 9.5. From Eq 10 the minimum sludge age for nitrification (R_{sm}) at different pH and temperature (T) and unaerated mass fraction (f_{sm}) is given by

$$R_{\text{sm}} = 1 / [\mu_{\text{ApH}}(1 - f_{\text{sm}}) - b_{\text{NT}}] \text{ days} \quad (11)$$

The problem with nitrification in low alkalinity wastewater is that the pH obtained is not known, because it is interactively established between the degree of nitrification, loss of alkalinity, pH and μ_{ApH} (see below).

5.4 MODELLING GAS EXCHANGE IN THE INTEGRATED MODEL

5.4.1 Modelling Approach

In the three phase carbonate system weak acid/base model of Musvoto *et al.* (1997), the physical (P) processes of carbon dioxide gas exchange (passive) with the atmosphere were included. They did this by modelling the expulsion (reverse, K'_{rCO_2}) and dissolution (forward, K'_{fCO_2}) rates of diffusion separately and linking the two rates through the Henry's law constant for CO_2 (K_{HCO_2}), i.e. $K'_{\text{fCO}_2} = K'_{\text{rCO}_2} K'_{\text{HCO}_2} / RT$. They showed this approach yielded identical results to the usual interphase gas mass transfer equation with an overall liquid phase mass transfer rate coefficient K_{LaCO_2} , where $K_{\text{LaCO}_2} = K'_{\text{rCO}_2}$. In their model application, the actual CO_2 expulsion rate constant value (K'_{rCO_2}) was not important, because they considered final steady state conditions only, not the transient dynamic conditions to the final steady state.

Musvoto *et al.* (2000a), van Rensburg *et al.* (2003) and Loewenthal *et al.* (2004) extended this chemical physical (CP) model to include three phase mixed weak acid base systems to simulate multiple mineral precipitation and active gas exchange of CO_2 and NH_3 during aeration of anaerobic digester liquor and swinery wastewater. Because they simulated transient (dynamic) conditions, the gas exchange and mineral precipitation rates were important and these were determined from the experimental batch test results.

In this integrated CPB processes model of the activated sludge system, four gases need to be considered, viz. ammonia, carbon dioxide, nitrogen and oxygen. Because measurements of pH and H_2CO_3^* alkalinity in aerobic reactors of full-scale activated sludge systems showed that equilibrium between the aqueous and gas (atmosphere) CO_2 phases is not reached during aeration in the aerobic reactor, the gas exchange (active) rates of the first three gases and the dissolution rate of oxygen by aeration are important for the simulation results, so that for the K_{La} rate constants for the four gases had to be determined (Table 3).

For active gas exchange (stripping or dissolution), if the dimensionless Henry's law constant of a gas, $H_e [= 1/(K_{\text{H}}RT)]$ is > 0.55, then oxygen can be used as a reference gas and the overall liquid phase mass transfer (expulsion/dissolution) rate coefficient K_{La} ($= K'$) for the other gases can be accepted to be in a fixed relationship to the K_{La} rate for oxygen (K_{LaO_2}) dependent on the relative magnitudes of the diffusivity of the other gases to oxygen (see Eq 12) (Munz and Roberts, 1989). Of the four gases, only ammonia has a $H_e < 0.55$ ($= 0.011$ at 20°C , see Table 6), so the K_{LaNH_3} ($= K'_{\text{rNH}_3}$, Musvoto

et al., 2000a) needs to be determined independently of the K_{La} rate of oxygen. However, because negligibly little ammonia is expelled from the aqueous phase with aeration in the pH range 6.5 to 8 for activated sludge systems, ammonia expulsion could have been omitted from the integrated model without loss of accuracy.

In the CP model of Musvoto et al. (2000a), the concentration of *non-dissolved* CO_2 gas, CO_{2g} , was essentially kept constant; CO_{2g} was included as a compound in the model only for continuity. In this integrated CPB model, CO_{2g} is not constant because dynamic variation in CO_2 production and consumption are considered. In implementation of the integrated CPB model, the CO_{2g} and the other gas compounds can be dealt with as part of the bulk liquid or as in a separate gaseous phase. Since the gas exchanges occur with the atmosphere where the partial pressures of the gases are essentially constant, and the head-space above activated sludge systems usually are not confined, both approaches should lead to near identical simulations, provided the gas exchange rates are independent of the corresponding gas concentration e.g. CO_{2g} . Because the former approach is simpler to implement in the computer programme Aquasim (Reichert, 1998), this approach was followed here. To ensure that the gas exchange rates are independent of the corresponding gas concentration, the original gas exchange dissolution formulation of Musvoto et al. (1997) was changed, with the gas species (e.g. CO_{2g}) concentration substituted for the relevant gas partial pressure and Henry's law constant (e.g. $p_{\text{CO}_2} K_{\text{HCO}_2}$; see Table 3). In effect this allows the gas species concentrations to vary and these are removed from the reactor hydraulically, i.e. with the effluent flow. If a separate gas phase implementation is required in Aquasim, the diffusive link can be used for the gas exchange equations in Table 3. This would be necessary in anaerobic digestion (Batstone et al., 2002).

Therefore, for CO_2 , N_2 and NH_3 gas exchange from the anoxic and aerobic reactors, the following approach was adopted (using CO_2 as example):

Transfer from dissolved form $[\text{H}_2\text{CO}_3^*]$ to non-dissolved form CO_{2g} is the sum of processes P6 and P7 in Table 3.

$$r_{\text{gmeCO}_2} = K_{La\text{CO}_2} \left[[\text{H}_2\text{CO}_3^*] - p_{\text{CO}_2} K_{\text{HCO}_2} \right] \text{ molCO}_2/(\text{m}^3\text{d}) \text{ (see Table 3)} \quad (12a)$$

where

r_{gme} = rate of gas mass transfer (mol gas/(m^3d))

$[\text{H}_2\text{CO}_3^*]$ = concentration of dissolved CO_2 in aqueous phase (mol/l)

p_{CO_2} = partial pressure of CO_2 in the bulk liquid (atm)

K_{HCO_2} = Henry's law constant for CO_2 (Table 6)

$K_{La\text{CO}_2}$ = Overall liquid phase mass transfer rate coefficient for CO_2 (/d)

where

$$K_{La\text{CO}_2} = K_{La\text{O}_2} \left[\frac{D_{L\text{CO}_2}}{D_{L\text{O}_2}} \right]^n \left[1 + \frac{1}{\frac{k_G}{k_L} H_{\text{eCO}_2}} \right]^{-1} \quad (/d) \quad (12b)$$

where

K_{La} = Overall liquid phase mass transfer rate coefficient for CO_2 and O_2 (/d)

D_L = Liquid phase molecular diffusion coefficient for CO_2 and O_2 (cm^2/s) (Table 6)

k_G, k_L = Gas (k_G) and liquid (k_L) phase individual mass transfer coefficients (m/s)

H_{eCO_2} = Dimensionless Henry's constant for CO_2 (Table 6)

n = Diffusivity coefficient = 0.50

Table 6: Dimensionless Henry's Law constants (H_e) at 20°C, liquid phase diffusion coefficient (D_L) at 20°C and liquid phase mass transfer rate coefficient (K_{La}) for oxygen, the reference gas, nitrogen, carbon dioxide and ammonia.

Gas	Diffusivity at 20°C cm ² /s	Dimensionless Henry's law constant H_e	Overall liquid phase mass transfer rate coefficient K_{La}
Oxygen, O ₂	202500	32.54	600/d * ¹
Nitrogen, N ₂	190000	64.2	Based on O ₂ (Eq 12)
Carbon Dioxide CO ₂	175300	1.06	Based on O ₂ (Eq 12)
Ammonia, NH ₃	-	0.011	3.2 /d* ²

Note *1: Model fitted value to obtain 20% CO₂ super-saturation in the aerobic reactor bulk liquid, i.e. partial pressure of CO₂ 20% higher than in the atmosphere (p_{CO_2} atmosphere = 0.00035 atm).

Note *2: Arbitrary low value - actual low value not important because effectively zero ammonia gas strips from the aeration reactor by aeration.

$$K_{HCO_2} = 10^{-\frac{pK_{HCO_2}}{T_K}} \text{ mol}/(\ell \cdot \text{atm}); pK_{HCO_2} = -\frac{2025.3}{T_K} - 0.0104 T_K + 11.365;$$

$$H_{eCO_2} = \frac{1}{K_{HCO_2} R T_K}$$

$$K_{HN_{2T}} = K_{HN_{225}} \exp \left[1300 \left(\frac{1}{T_K} - \frac{1}{289.15} \right) \right] \text{ where } K_{HN_{225}} = 0.000661 \text{ mol}/(\ell \cdot \text{atm})$$

$$r_{dissO_2} = K_{LaO_2} [O_{2sat} - O_{2reactor}] \text{ where } O_{2sat} = 8.9 \text{ mgO}/\ell \text{ (0.000278 mol}/\ell) \text{ at } 20^\circ\text{C and } 1 \text{ atm,}$$

$$O_{2reactor} = \sim 2.0 \text{ mgO}/\ell \text{ (0.000063 mol}/\ell) \text{ and } K_{LaO_2} = 600 /d.$$

In Eq 12, the ratio k_G/k_L represents the relative contribution of the gas and liquid phases mass transfer resistance under turbulent mixing conditions. A value of 30 to 40 is recommended by Munz and Roberts (1989) for the high turbulent mixing conditions created by power inputs (P/V) greater than 70 W/m³ characteristic of aerated activated sludge reactors. In the simulations the k_G/k_L ratio was set to 40. From simulation, it was found that the K_{LaO_2} rate affected the aerobic reactor dissolved oxygen (DO) and CO₂ (H₂CO₃*) concentrations, but not the pH. As the K_{LaO_2} rate was decreased from 600/d to 100/d, the DO decreased from close to saturation (~7 mgO/ℓ) to ~3.0 mgO/ℓ and CO₂ (H₂CO₃*) concentration increased from 1.7 mgCO₂/ℓ (~3x saturated at $p_{CO_2} = 0.00035$) to 6.2 mgCO₂/ℓ (~10 saturated) but the pH remained around 7.0. However, the anoxic reactor pH increased from 7.7 to 8.0 as the K_{LaO_2} rate decreased due to increasing denitrification and greater alkalinity generation resulting from recycling less DO to the anoxic reactor (at a mixed liquor recycle ratio of 1:1). Tests at 2 full-scale activated sludge plants with fine bubble aeration indicated the aerobic reactor effluents were about 20% supersaturated with dissolved CO₂. So to get low dissolved CO₂ concentrations the K_{LaO_2} rate was set at 600/d. Since the H_e for NH₃ is <0.55, the above equations cannot be applied for NH₃. The mass transfer coefficient for ammonia (K_{LaNH_3} , Table 3) was set at a very low value of 3.2/d to

ensure an extremely low loss of ammonia by aeration stripping. The partial pressure of the three gases in Table 3 were set at the standard atmospheric values i.e. $p_{N_2} = 0.79165$, $p_{O_2} = 0.20800$ and $p_{CO_2} = 0.00035$ atmospheres.

5.5 THE INTEGRATED TWO PHASE MIXED WEAK ACID/BASE CHEMICAL, PHYSICAL AND BIOLOGICAL PROCESSES ACTIVATED SLUDGE MODEL

All the changes to the processes of growth for the heterotrophs and autotrophs discussed above were made to ASM1. The amended biological model was combined with the two phase (aqueous-gas) mixed weak acid/base subset model (Musvoto *et al.*, 2000), to give the integrated two phase mixed weak acid/base chemical, physical and biological processes (CPB) activated sludge model shown in matrix form in Tables 2 and 3. This model was incorporated into the Aquasim computer programme (Reichert, 1998).

A number of simulations were done to verify the integrated CPB model, one of which, the aerobic batch test of Still *et al.* (1996), is shown in Fig 3 as illustration. Additional details such as kinetic and stoichiometric constants, are given by Dold *et al.* (1991). Because the total species concentrations of the carbonate, phosphate and SCFA systems were not measured by Still *et al.* (1996), values for these parameters had to be estimated for input to the model - values for the SCFA concentration were accepted to be zero as discussed above. All the remaining input information was taken from Dold *et al.* (1991). The predicted oxygen utilization rate (OUR), nitrate and TKN concentrations by the integrated model are compared with those predicted by the ASM1 (as given by Dold *et al.*, 1991) and the experimental data in Figs 3a, b and c. The predictions of the two models are identical and both compare very well with the experimental data. However, the integrated model predictions for the chemical physical processes could not be compared because ASM1 does not consider these processes, nor were they monitored experimentally in the batch test. Close correlation between predictions of the two models is expected because the simulations are for a municipal wastewater where the pH remained essentially constant so that, despite their inclusion in the integrated model, the weak acid/base systems (pH) have no significant effect on the biological processes. No suitable data on activated sludge treatment of municipal wastewaters where the weak acid/base systems and pH play a significant role could be found in the literature to directly validate the model. Because the chemical-physical and biological processes parts of the integrated model had been validated independently, rigorous validation of the integrated model was not required except where the chemical physical processes affect the biological processes. In this regard, the principal interaction is the effect of pH on nitrification and this interaction was based and calibrated on literature information (Eqs 8 to 10, Fig 2).

5.5.1 A Note on the COD Mass Balance of the Model

Material mass balances (COD, C, N and P) are performed on model outputs and experimental systems to check model and data accuracy. Strictly, COD mass balances cannot be applied to the integrated model because inorganic C (CO_2) is changed to organic nitrifier (ANO) VSS (COD) mass, unless this contribution to the calculated VSS (COD) is specifically excluded. Theoretically, this contribution to the VSS (COD) is large enough (2-4%) to indicate a modelling error (>0.5%), but practically, remains small enough to be considered negligible for normal domestic wastewater where the mass of ANOs is very small compared with the mass of OHOs. However, for wastewaters which have a high TKN/COD ratio, such as sludge treatment liquors, the mass of ANOs will be significant compared with the mass of OHOs and COD mass balances much greater than 100% will be obtained if the ANO VSS (COD) is not excluded from the sludge mass in the COD mass balance. For the C mass balance,

the COD/TOC ratio of the influent organics need to be known and was accepted at 3.0 (see above). Similarly, the COD/TOC ratios of the OHO and ANO active masses and their endogenous mass need to be

known. For these, the active and endogenous masses were accepted to have the same stoichiometric formulation of $C_5H_7O_2N$ (WRC, 1984) which gives a COD/TOC of 2.67 mgCOD/mgC.

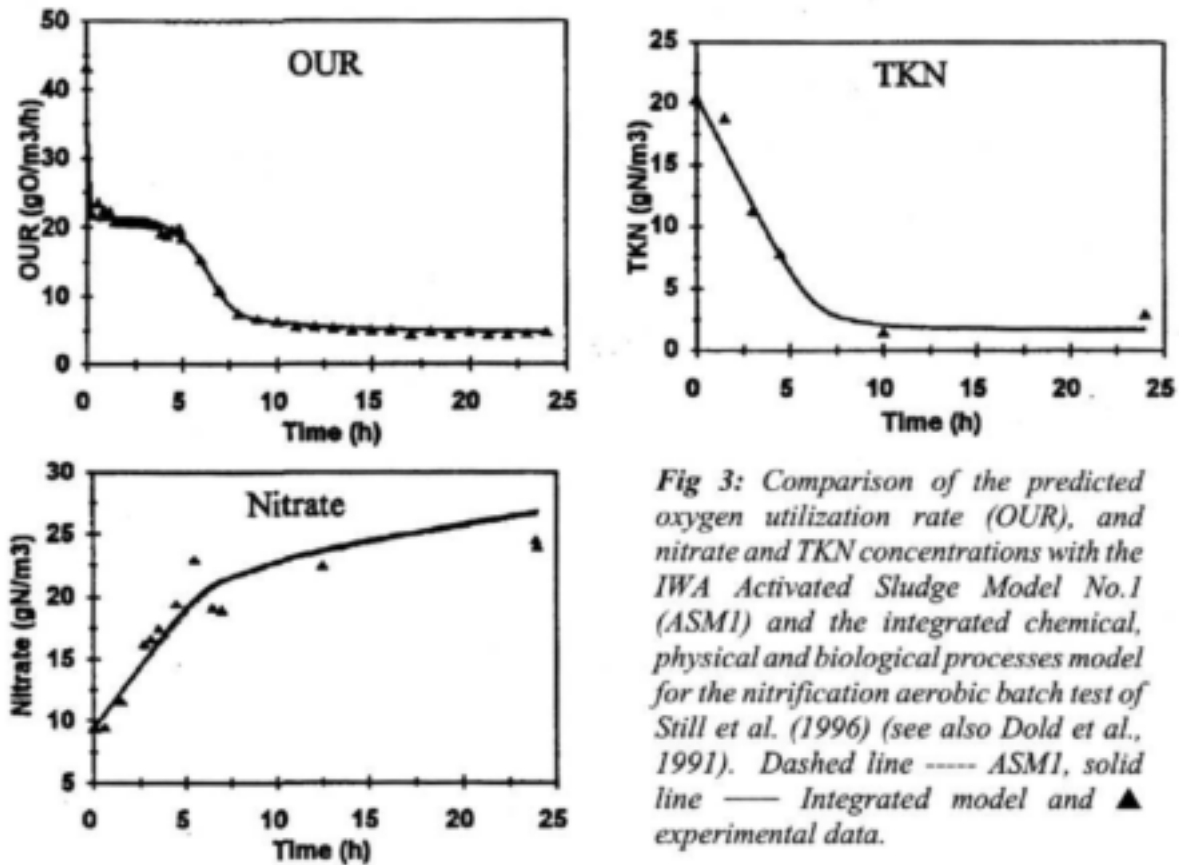


Fig 3: Comparison of the predicted oxygen utilization rate (OUR), and nitrate and TKN concentrations with the IWA Activated Sludge Model No.1 (ASM1) and the integrated chemical, physical and biological processes model for the nitrification aerobic batch test of Still et al. (1996) (see also Dold et al., 1991). Dashed line ---- ASM1, solid line — Integrated model and ▲ experimental data.

5.6 LOW ALKALINITY NITRIFYING / DENITRIFYING (ND) SYSTEM

To evaluate the performance of the integrated CPB model and illustrate the behaviour of ND activated sludge systems with low influent alkalinity, a Modified Ludzack Etttinger (MLE) anoxic -aerobic system was simulated. The influent wastewater characteristics (raw wastewater, COD=750mgCOD/l, TKN=60mgN/l, FSA=45mgN/l, TP=11.27 mgP/l, SCFA=0 mg/l pH = 7.3) and the system design and operating conditions (sludge age 30d, temperature 22°C, anoxic and aerobic mass fractions 0.35 and 0.65 and mixed liquor and sludge return recycles 3:1 and 1:1) were the same for each simulation. Also K_{LaO_2} was set at 600/d to maintain low dissolved CO_2 concentrations (see above). Only the influent $H_2CO_3^*$ alkalinity was varied from 500 down to 15 mg/l as $CaCO_3$. Effluent free and saline ammonia (FSA), nitrate (NO_3), total nitrogen (TN=FSA+ NO_3) and $H_2CO_3^*$ alkalinity (as $CaCO_3$) concentrations and anoxic and aerobic reactor pH versus influent $H_2CO_3^*$ alkalinity are shown in Fig 4.

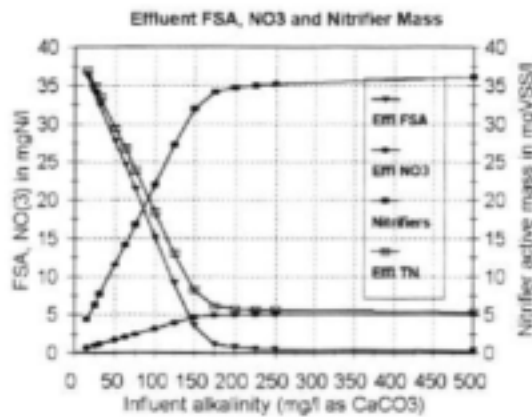


Fig 4a: Effluent free and saline ammonia (FSA), nitrate (NO₃), total nitrogen (TN = FSA + NO₃) and aerobic reactor autotrophic nitrifier organism (ANO) concentration versus influent H₂CO₃* alkalinity.

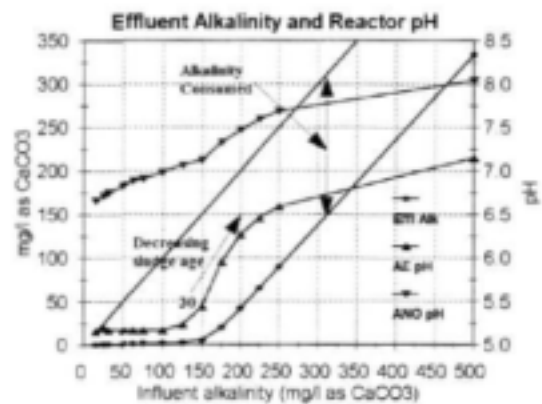


Fig 4b: Influent (diagonal) and effluent H₂CO₃* alkalinity and aerobic and anoxic reactor pH versus influent H₂CO₃* alkalinity.

The ND system delivers < 1 mgFSA-N/l, ~5 mgNO₃-N/l and ~5 mgTN-N/l for influent H₂CO₃* alkalinity > 200 mg/l (all alkalinities as CaCO₃) (Fig 4a). Although the pH in the aerobic reactor (which is about 1 pH unit below that in the anoxic reactor due to the CO₂ stripping by aeration) decreases with decreasing influent H₂CO₃* alkalinity, it remains above 6.3 (Fig 4b), at which pH the growth rate of the nitrifiers is still high enough for the long sludge age (30d) to achieve complete nitrification. The difference between the influent and effluent H₂CO₃* alkalinity is the H₂CO₃* alkalinity consumed by the system and from Fig 4b this is about 150 mg/l when the influent H₂CO₃* alkalinity is >200 mg/l. Once the influent H₂CO₃* alkalinity decreases below 200 mg/l, the effluent H₂CO₃* alkalinity drops below 50 mg/l and the aerobic reactor pH declines rapidly from 6.3 to below 5.5 for an influent H₂CO₃* alkalinity of <150 mg/l. At pH 5.5 (influent H₂CO₃* alkalinity = 150 mg/l), nitrification is at the point of failure and for lower influent alkalinities, the effluent FSA and TN concentrations begin to increase sharply and the effluent nitrate concentration decreases due to the lower concentration of nitrate generated by nitrification. Thus in general, if the effluent H₂CO₃* alkalinity from an activated sludge system, whether fully aerobic or ND, drops below 50 mg/l, the reactor pH will fall below 5.5, which will inhibit nitrification and consequently compromise N removal. This conclusion is not new - WRC (1984) stated the same conclusion and recommended that when the effluent H₂CO₃* alkalinity falls below 50 mg/l, lime dosing should be considered to raise the aerobic reactor pH, or, for fully aerobic systems, denitrification in anoxic zones be introduced to decrease the overall H₂CO₃* alkalinity consumption.

In this example, nitrification fails at the low pH of around 5.5 because the sludge age is very long (30d). At this pH, the maximum specific growth rate of the ANOs (μ_A) is depressed so low that an operating sludge age of 30 days becomes lower than the minimum sludge age for nitrification (R_{sm}) and the nitrifiers are washed out of the system. At shorter operating sludge ages, the pH at which nitrification fails will be higher (as indicated in Fig 4b). So at low influent H₂CO₃* alkalinity (<100 mg/l), the pH declines, μ_A (Eq 10) decreases and R_{sm} increases (Eq 11). Once R_{sm} approaches the operating sludge age of the system (R_A), nitrification becomes unstable and the effluent FSA begins to increase, particularly under cyclic loading conditions.

5.7 CONCLUSION

The biological processes of the nitrification-denitrification (ND) activated sludge model No 1 (ASM1, Henze *et al.*, 1987) were integrated into a two phase (aqueous-gas) subset of the three phase mixed weak acid/base chemical-physical kinetic model of Musvoto *et al.* (2000). In this integration, a number of additions were made to ASM1, such as (1) production and/or utilization of CO_2 , H^+ , NH_3 , and H_3PO_4 in heterotrophic (OHO) and autotrophic (ANO) growth and death (endogenous respiration) and (2) the effect of pH (i.e. H^+) on the biological processes, in particular on the autotrophic nitrifiers (ANOs).

The integrated chemical, physical and biological (CPB) processes activated sludge model simulations were compared with those of ASM1 (Dold *et al.*, 1991) and experimental data in the literature. Identical simulation results were obtained with both models and the correlation of both models with experimental data was good. Strictly, these comparisons serve only as model verification because, although included, the weak acid/bases and pH have no significant effect on the biological processes in the cases considered. However, because the CPB model was developed by integrating previously individually validated models, rigorous independent experimental validation of the integrated model was not deemed necessary, except where the chemical-physical processes interact strongly with the biological processes. The principal interaction is the effect of pH on nitrification and this interaction was based on literature information and so is calibrated as best as possible. It is concluded from this integration that (i) the total organic carbon (TOC) to chemical oxygen demand (COD) ratio of the wastewater does not significantly influence the reactor pH, but (ii) the free and saline ammonia (FSA) to total Kjeldahl nitrogen (TKN) ratio and concentrations, (iii) nitrate uptake for OHO growth once ammonia is depleted (assimilative denitrification) and (iv) extent of denitrification and (v) the extent of CO_2 stripping from the aerobic reactor by aeration do affect reactor pH. Experimental determination of the inorganic carbon concentration (C_T) in effluents from full scale N removal activated sludge plants indicated that the effluents were about 20% supersaturated with CO_2 gas so that CO_2 gas exchange by aeration in the aerobic reactor does not yield CO_2 equilibrium with the atmosphere.

From simulation of long sludge age nitrification-denitrification (ND) activated sludge systems with incrementally decreasing influent H_2CO_3^* alkalinity, when the effluent H_2CO_3^* alkalinity falls below about 50 mg/l as CaCO_3 , the aerobic reactor pH drops below 6.3, which severely retards nitrification and causes the minimum sludge age for nitrification (R_{m}) to increase up to the operating sludge age of the system. Therefore, when treating low H_2CO_3^* alkalinity wastewaters, such as those from the Western and Southern coastal areas of South Africa, the minimum sludge age for nitrification (R_{m}) varies with temperature and reactor pH and for low effluent H_2CO_3^* alkalinity (< 50 mg/l as CaCO_3), nitrification becomes unstable and sensitive to dynamic loading conditions resulting in increases in effluent ammonia concentration and reduced N removal. For effluent H_2CO_3^* alkalinity < 50 mg/l, lime should be dosed raise the aerobic reactor pH and stabilize nitrification.

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CHAPTER 6

INTEGRATED CHEMICAL/PHYSICAL AND BIOLOGICAL PROCESSES MODELLING: ANAEROBIC DIGESTION OF SEWAGE SLUDGES

6.1 INTRODUCTION

Anaerobic digestion (AD) is one of the oldest biological waste treatment processes, dating back more than a century. With the development of digester heating and mixing, AD has established itself as the most common method of sludge stabilization, and has proven to be effective also in reducing the volumes of sludge with the production of energy rich bio-gas. It has been shown that AD is an effective process for the treatment of a number of types of organic sludges, ranging from municipal waste activated (WAS) and primary sludges (Kayhanian and Tchobanoglous, 1992; Cout *et al.* 1994) to industrial organic sludges and agricultural slurries (Hill and Barth, 1977). In particular, the application of AD to the stabilization of sewage sludges (primary, WAS and humus) is widespread, and this chapter focuses on this application.

Despite its widespread application, the design, operation and control of anaerobic digesters treating sewage sludges is still based largely on experience or empirical guidelines. To aid the design, operation and control of (and research into) AD, a mathematical 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 optimize the system performance. Mathematical models provide an integrated framework for the system which can give guidance to design, operation and research.

Recognising the potential usefulness of mathematical models, various researchers have developed such models to describe AD (e.g. McCarty, 1974, Hill and Barth, 1977; Gujer and Zehnder, 1983; Sam-Soon *et al.*, 1991; Kiely *et al.*, 1997, Batstone *et al.*, 2002). The early models focussed primarily on the biological processes operating in an anaerobic digester. Although the importance of the interaction between the biological processes and the weak acid/base chemistry environment in which they operate was recognised early on, because of the effect of pH on the biological processes, modelling this interaction proved to be a far more complex problem than delineating the biological processes themselves. Initially the impact of the biological processes on pH was assessed graphically based on equilibrium chemistry principles of the carbonate weak acid/base system (e.g. Capri and Marais, 1975). The advent of computers and development of numerical algorithms made it easier to model the interaction based on single or two phase (aqueous-gas) weak acid/base chemistry equilibrium equations to estimate the pH in anaerobic digesters. The approach of Loewenthal *et al.* (1989, 1991) made it possible to include multiple mixed weak acid/base systems, both for estimating the digester pH and in the determination and interpretation of the commonly measured digester control parameters, short chain (volatile) fatty acids (SCFA) and alkalinity (Moosbrugger *et al.*, 1992; Lahav and Loewenthal, 2000). The latest AD model (IWAADM1, Batstone *et al.*, 2002) includes algebraic algorithms, based on equilibrium weak acid/base chemistry and continuity of charge balances, that seek to model the environment in which the biological processes operate, to predict the pH. These algebraic algorithms and calculation of pH operate externally to the kinetic model structure. As alternative, dynamic equilibria equations for the weak acid/base systems are described (similar to the approach of Musvoto *et al.*, 1997, 2000a). However, the weak acid/base water is not included so that pH is again

algebraically calculated externally to the kinetic model, via the charge balance. Calculation of pH externally via the charge balance cannot deal simply with multiple weak acid/base systems in three phases (aqueous/gas/solid), where several minerals competing for the same species may precipitate simultaneously or sequentially (Musvoto *et al.*, 2000a,c): In some anaerobic digestion systems precipitation of minerals is significant, either within the digester itself or in pipework leading from the digester so that the relevant chemical precipitation processes would require inclusion. For such situations, the biological processes and multiple weak acid/base systems in three phases should be modelled in an integrated way within the same kinetic model structure.

In Chapter 4, an integrated chemical (C), physical (P) and biological (B) processes model for the N removal activated sludge system was presented. This model was developed by integrating the biological processes of the International Water Association (IWA) Activated Sludge Model No 1 (ASM1, Henze *et al.*, 1987) into a two phase (aqueous-gas) subset of the three phase mixed weak acid/base C-P model of Musvoto *et al.* (1997, 2000a,b,c), and included additionally gas exchange of N_2 . This chapter describes the development of an integrated two phase (aqueous-gas) chemical (C), physical (P) and biological (B) processes AD model for sewage sludges, by integrating the biological processes for AD with the same two phase subset of the three phase CP model of Musvoto *et al.* (1997, 2000a,b,c). In a subsequent project, this AD model will be extended to include the third (solid) phase of mineral precipitation. In fact, the N removal activated sludge and AD models are two parts of a single larger model being developed for simulating the entire wastewater treatment plant (WWTP) on materials mass balance and continuity principles. It is planned to include also biological excess P removal (BEPR) and AD of P rich waste activated sludges in the WWTP model.

The AD model is built up in stages. First, the biological processes are defined and then these are integrated into the mixed weak acid/base model of Musvoto *et al.* (1997, 2000a,b,c). For ease of cross-referencing to the source chapters, the same process and compound numbering system described in Chapter 4 will be used in this Chapter (see Table 1, Chapter 4).

6.2 BIOLOGICAL PROCESSES OF ANAEROBIC DIGESTION

6.2.1 Conceptual Model

In the literature there is considerable variation in conceptual schemes for describing the biological processes of AD with sewage sludge as influent, from simple two stage reaction schemes including only hydrolysis/acidogenesis and methanogenesis (Kiely *et al.*, 1997) to the most commonly used six step reaction scheme as proposed by Gujer and Zehnder (1983).

In the reaction scheme of Gujer and Zehnder (1983) (Fig 1), the hydrolysis process acts separately on three main groups of complex organics, viz (i) proteins, (ii) carbohydrates and (iii) lipids. These complex polymeric materials are hydrolysed by extracellular enzymes to soluble products that are small enough to allow their transport across the cell membrane. The products of the separate hydrolysis processes are amino acids, sugars and fatty acids respectively. These relatively simple, soluble compounds are fermented (acidogenesis) or anaerobically oxidised to short chain fatty acids (SCFAs) (acetate), alcohols, CO_2 , hydrogen and ammonia. A portion of the hydrolysis products are also converted to intermediate products (propionate, butyrate, etc.), which are then converted to acetate, hydrogen gas and CO_2 through a process called acetogenesis. Lastly, methanogenesis occurs by hydrogen reduction with CO_2 (hydrogenotrophic methanogenesis) and from acetate cleavage (acetoclastic methanogenesis).

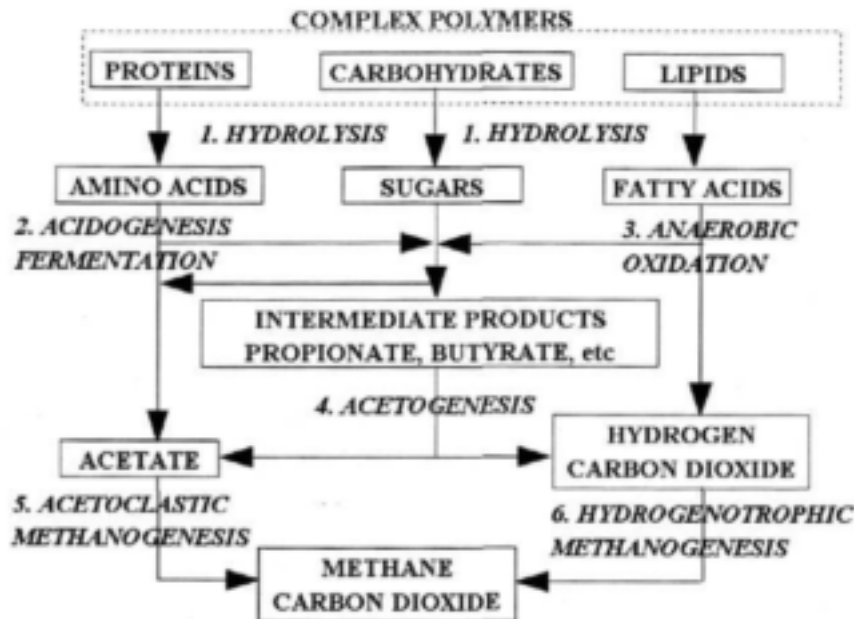


Fig 1: Anaerobic digestion processes scheme of Gujer and Zehnder (1983)

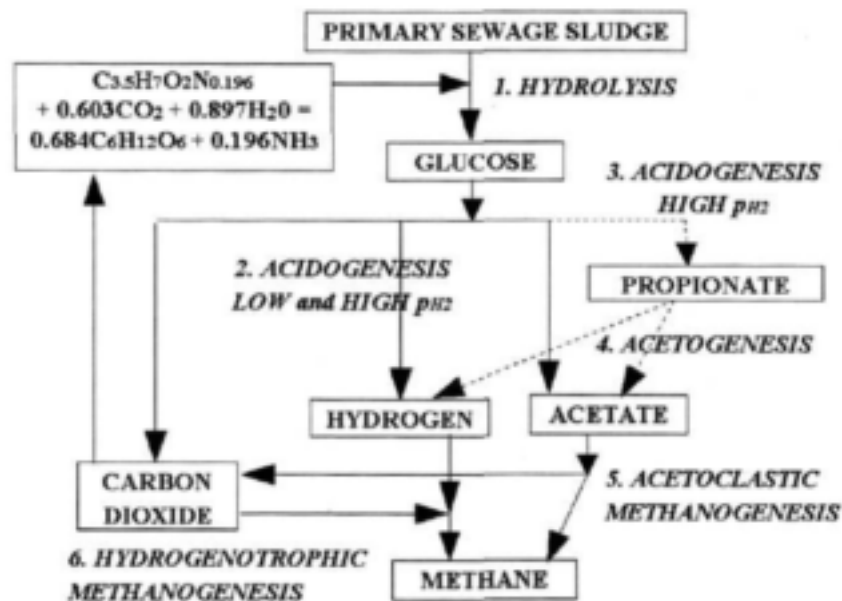


Fig 2: Anaerobic digestion processes scheme of University of Cape Town Anaerobic Digestion Model No 1 (UCTADM1) including (i) the effect of high hydrogen partial pressure on acidogenesis and (ii) COD, carbon and nitrogen mass balances with a generic CHON sludge composition.

The Gujer and Zehnder (1983) reaction scheme formed the basis for the AD model developed here, but with four main modifications (Fig 2), viz.

- (1) Recognising that carbohydrate, protein and lipid measurements on sewage sludges are unlikely to be routinely available and indeed are difficult to do, the hydrolysis of the three separate organic materials was modified to a single hydrolysis process acting on a generic organic material representing sewage sludge ($C_XH_YO_ZN_A$, McCarty, 1974). This simplification is not unreasonable since the end products of hydrolysis and subsequent acidogenesis of the three organic groups are essentially the same, namely SCFAs. In this approach, the C, H, O and N contents of sewage sludges are needed to determine the X, Y, Z and A values in $C_XH_YO_ZN_A$; These were determined by simulation of measured data and direct measurement, see below. In follow-up work to extend the model to AD of waste activated sludges (including biological excess P removal sludges) in 3 phases (liquid-gas-solid), i.e. including mineral precipitation, the P content of sewage sludges will be added to this formulation (i.e. $C_XH_YO_ZN_AP_B$).
- (2) With the proposed single hydrolysis process, recognition of three separate hydrolysis products was no longer necessary. Accordingly, a single hydrolysis process and end product were included. This end product was chosen to be the idealised carbohydrate "glucose" for a number of reasons: The subsequent biological processes on "glucose" are well established and the acidogenic/fermentation process acting on "glucose" to convert it to SCFAs is unlikely ever to be rate limiting. Accordingly, in model application accumulation of 'glucose' will not occur, even under digester failure conditions. This implies that the "glucose" acts merely as an *intermediate* compound, which is acidified to SCFAs as soon as it is produced. In any event, because the end products of hydrolysis and acidogenesis in the scheme of Gujer and Zehnder (1983) (Fig 1) are the same as in the revised scheme (Fig 2), the net result is the same in both schemes. In order to maintain the COD, C, H, O and N balances, water and carbon dioxide are taken up from the bulk liquid to generate the glucose from the sewage sludge (Fig 2), and ammonia is released.
- (3) As a consequence of accepting a single hydrolysis process, separate anaerobic oxidation of fatty acids does not need to be included.
- (4) In the reaction scheme of Gujer and Zehnder (1983), a fixed proportion of hydrolysis end products are converted to intermediate SCFA (propionate, butyrate, etc.) and the balance directly to acetate. As an alternative, the influence of the hydrogen partial pressure (p_{H_2}) on acidogenesis of glucose to acetate and propionate as proposed by Sam - Soon *et al.* (1991) was included in the revised scheme. This provides a better description of AD behaviour under failure conditions. To include the proposals of Sam - Soon *et al.* (1991), the acidogenesis was divided into two processes - (i) under high p_{H_2} conditions, acetic and propionic acids are generated together with H_2 and CO_2 and (ii) under low p_{H_2} conditions, acetic acid only is generated together with H_2 and CO_2 . In this revised scheme, generation of butyrate and higher SCFAs was not considered, because with sewage sludge as influent these usually are only found in minor concentrations, even under digester failure conditions.

6.2.2 Mathematical Model - UCTADM1

Accepting the revised reaction scheme (Fig 2), the biological processes mediated by the four recognized AD organism groups were included in the two phase (aqueous-gas) chemical (C), physical (P) and biological (B) anaerobic digestion model (UCTADM1, see Table 1). Following ASM1 for activated sludge systems (Henze *et al.*, 1987), the processes were formulated either as hydrolysis or organism group growth processes. All four organism groups were accepted to be subject to endogenous respiration and so an endogenous mass loss process was included in the model for each group. It is recognised that the organism groups are not representative of a single organism species, but rather are 'surrogates' representing all organism species performing a particular function of interest; this is similar to the approach followed for modelling of activated sludge systems (e.g. Dold *et al.*, 1980, Henze *et*

al., 1987). In formulating the model, since weak acid/base chemistry is included directly, all biological processes that act on weak acid/base species needed to be formulated in terms of the relevant dissociated or undissociated species (see below). This included both the stoichiometric consumption or production of weak acid/base species by the processes, and the formulation of the kinetic rate expressions. Whichever species is selected, in the production or consumption of weak acid/base species, because the weak acid/base chemistry is included directly, the model will automatically redistribute the weak acid/base species including the hydrogen ion (H^+) and establish a new pH.

Table 1: Biological processes included in the two phase anaerobic digestion model.

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_{H_2}	Acidogens, Z_{AD}
	D3. Acidogens on 'glucose' under high p_{H_2}	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 1 act on 14 compounds and cause changes in their concentrations. The changes in some compound concentrations may be directly measurable, but the changes in the non-measurable compound concentrations are inferred from the conceptual model of the processes (Fig 2) and mass balance requirements. The compounds and processes of AD based on the reaction scheme of Fig 2 are shown in the Petersen matrix format in Table 2, in which each row represents a biological process and each column a compound, and the stoichiometric relationships between the compounds and processes are listed at their intersection blocks, the process kinetic rates on the right hand side and the units of the compounds along the bottom. Note that all the compounds in Table 2 are specified as mol/l, including the sewage sludge. The mol/l of the sewage sludge is calculated from its measured COD concentration and its gCOD/mol, which is calculated from its known composition, i.e. known X, Y, Z and A in $C_xH_yO_zN_A$ (see below). The AD organism concentrations for all four organism groups are also specified as mol/l based on a formulation of $C_5H_7O_2N$, which has a molar mass of 113g/mol and a COD/VSS ratio of 1.42 mgCOD/mgVSS (McCarty, 1964). The gCOD, gN or $gH_2CO_3^*$ Alk per mol of the compounds as appropriate are also given along the bottom of the matrix. If the gCOD/mol ratios are multiplied by the corresponding stoichiometric value in the matrix and summed across a process, it will be found that these sums are zero, i.e. the COD mass balance applies across each process. The requirement to express the model compounds in mole units arises from the requirement to model CO_2 production/utilisation (zero COD), which is essential for the weak acid/base chemistry part of the model.

6.2.3 Stoichiometry of the Biological Processes

The stoichiometry in the model was deduced directly from the biochemical stoichiometric equations of the processes. The metabolic pathways used by fermentative organisms for the degradation of carbohydrates to SCFAs are well defined. As noted above, for this reason amongst others, the biodegradable particulate COD entering the system was directly hydrolysed to the intermediate

Table 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 is calculated from the measured COD concentration of the sludge and the sludge composition formula $C_3H_1O_2N_4$ with measured values of X , Y , Z and A .

	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	$C_3H_1O_2N_4$	$C_3H_1O_2N_4$	H_2	Z_{ac}	Z_{ac}	Z_{am}	Z_{am}	
No	Processes		Dslvd	Dslvd					Gas	Gas	S_{O_2}	S_{red}	Dslvd	Acidogens	Acetogens	AMs	HM	Process rates
C46	Forward dissociation of HPr				1		-1	1										$K_{HPr}[HPr]$
C47	Reverse dissociation of HPr				-1		1	-1										$K_{HPr}[Pr][H^+]$
P6†	Dissolution of CO_2 gas			1					-1									$K_{HCO_3}(pCO_2)(K_{HCO_3})$
P7†	Expulsion of CO_2 gas			-1					1									$K_{HCO_3}[H_2CO_3^*]$
P8†	Expulsion of NH_3 gas		-1															$K_{NH_3}[NH_3]$
D1	Hydrolysis		S1	S2							-1	S3						Eq 8d
D2	Acidogenesis (low pH _i)	-1		S4	1	S5						-1/Y _{ap}	S6	1				Eq 9
D3	Acidogenesis (high pH _i)	-1		S7	1	S8	S9					-1/Y _{ap}	S10	1				Eq 10
D4	Acidogen endogenous decay		S11	S12							S13			-1				$b_{ap}[Z_{ap}]$
D5	Acetogenesis	-1		S14	1	S15	-1/Y _{ac}						S16		1			Eq 11
D6	Acetogen endogenous decay		S11	S12							S13				-1			$b_{ac}[Z_{ac}]$
D7	Acetoclastic methanogenesis	-1		S17	1	-1/Y _{am}				S18						1		Eq 12
D8	Acetoclastic methanogen endogenous decay		S11	S12							S13					-1		$b_{am}[Z_{am}]$
D9	Hydrogenotrophic methanogenesis	-1		S19	1					S20			-1/Y _{hc}				1	Eq 13
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	-	-	-	-	-	-	-	-	-	-	-	-	

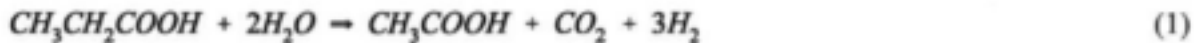
† These processes and compound were included in the models of Musvoto *et al.* (1997, 2000a) as follows: Processes P6 was C7, P7 was C8, and P8 was C46 and compound P1 was C6.

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.

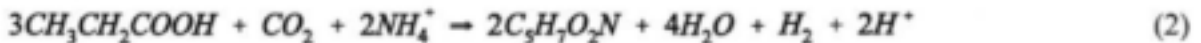
‡ This is the g COD/mol for the primary sludge CHON content measured and predicted in this investigation, i.e. $C_{13}H_1O_2N_4$.

"glucose", from which the remainder of the products were formed. As an example for calculating the stoichiometry, consider the process of acetogenesis:

Acetogenesis (Process D5, Table 2) is the process whereby under low hydrogen partial pressure (p_{H_2}) the acetogens convert propionic acid (HPr) (generated by acidogenesis under high p_{H_2}) to acetic acid (HAc). The stoichiometric equation for the acetogenesis reaction is:

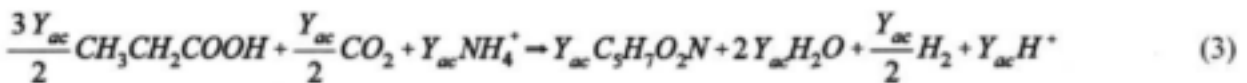


During acetogenesis, growth of acetogenic organisms (Z_{AC}) takes place which can be stoichiometrically represented by:

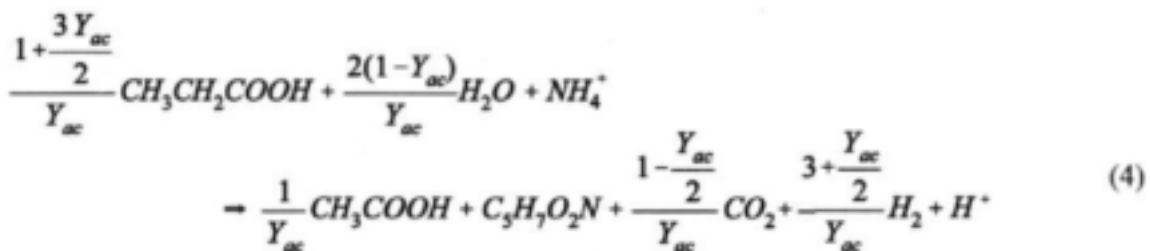


Note that in Eqs 1 and 2 (i) CO_2 is utilised as an additional carbon source - in all CO_2 consumption/production the undissociated carbonate species $H_2CO_3^*$ acts as source/sink respectively, (ii) ammonium is the nitrogen source for organism growth - under normal operating conditions and pH ($6.5 < pH < 7.5$) of an anaerobic digester, the ammonium species (NH_4^+) dominates over the ammonia species (NH_3) so that using ammonia as the N species for organism growth can cause numerical instability in solution procedures for the model, (iii) the undissociated propionic acid species is used as substrate source, in agreement with observations in the literature, and (iv) the chemical formulation for organisms is assumed to be $C_5H_7O_2N$, which is the formulation generally accepted to represent organism active mass in activated sludge (WRC, 1984).

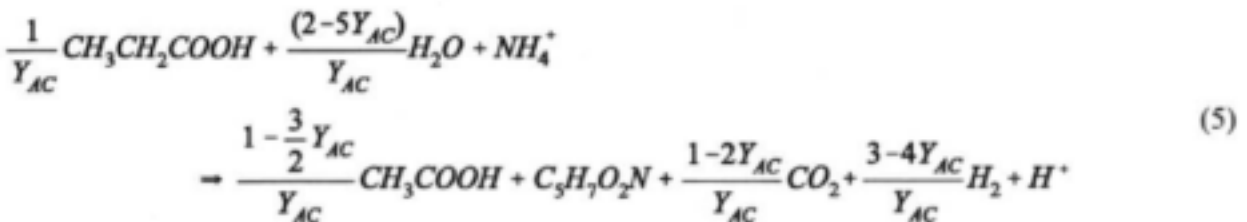
Accepting that Y_{ac} mol of acetogen organisms are formed (i.e. the anabolic yield of acetogens), Eq 2 can be rewritten as:



Adding Eqs 1 and 3 and dividing by Y_{ac} yields:



Recognising that in Eq 4 the "true" acetogen yield (Y_{AC} , mole organism/mole propionate) is $Y_{ac}/(1 + 3/2Y_{ac})$, and substituting Y_{AC} into Eq 4 and solving gives:



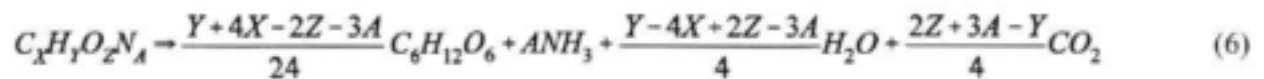
The stoichiometry for acetogenesis and acetogen growth was extracted from Eq 5 directly, and is summarised in Table 3. Note that compounds that are utilised (reactants, left hand side of Eq 5) are

negative (reduction), while compounds produced (products, right hand side of Eq 5) are positive (production), that H_2O has been included in Eq 5 for an element balance, but is not included directly in Table 3, and that there is a net production of CO_2 expressed as $H_2CO_3^*$ in the kinetic model ($1/Y_{AC} > 2$). Following this procedure, the stoichiometries for the remaining processes were derived and are summarised in Table 4.

Table 3: Stoichiometry for acetogenesis and acetogen growth (Process D5 in Table 2). The *S* numbers in brackets cross reference to the model Petersen matrix (Table 2).

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

In the hydrolysis process, the biodegradable particulate organics measured as COD (S_{bp}) in the sewage sludge are first changed to mole units "outside" of the kinetic model, i.e. matrix, by dividing by the COD/mol ratio = $\{(Y + 4X - 2Z - 3A) \cdot MW_{O_2}/4\}$, with MW_{O_2} being the molecular weight of $O_2 = 32$ g/mol. Thereafter, the sewage sludge biodegradable particulate organics measured as moles (S_{bp}) are transformed to the intermediate organic "glucose" also as moles (S_b). This process is crucial in anaerobic digestion modelling, as the amount of "glucose" formed will determine the amount of the end products (CH_4 , CO_2 and biomass) in a stable digester. To develop the stoichiometry for the hydrolysis process, the stoichiometric reaction was separated into two half reactions, effectively the redox half reactions, which were added based on an electron (COD) balance. In setting up the conversion of the primary sludge COD to mole units and the two subsequent half reactions in the transformation to the intermediate "glucose", the chemical formulation for the sewage sludge was kept as a variable, i.e. $C_xH_yO_zN_A$, to allow the composition of the influent sewage sludge to the AD to be easily changed (McCarty, 1974). The formulation for the sewage sludge was assumed to be the same for all sewage sludge fractions (i.e. biodegradable and unbiodegradable), and to remain constant with degradation. This gives the stoichiometric reaction for sewage sludge hydrolysis as:



In the death / endogenous decay processes for the four organism groups (Table 4), it was accepted that the organisms die releasing biodegradable particulate organics (S_{bp}), which are assumed to have the same formulation as the sewage sludge, i.e. $C_xH_yO_zN_A$ with CO_2 , H_2O and NH_3 released or taken up from the bulk liquid as required to maintain the C, H, O and N mass balances. Due to the low organism yields and relatively low death rates, and the relatively large fraction of unbiodegradable particulate organics in the influent, generation of endogenous residue (Dold *et al.*, 1980) was not included, but this can be done relatively simply if required. Hence, the stoichiometric reaction for organism death is (Table 4):

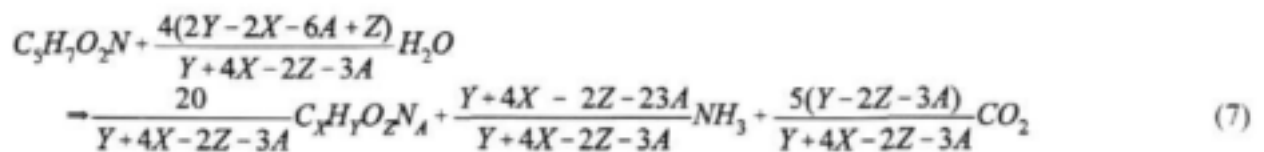


Table 4: Stoichiometry for of the AD processes hydrolysis (D1), acidogenesis (D2, D3), acetoclastic methanogenesis (D7), hydrogenotrophic methanogenesis (D9) and endogenous respiration of the four organism species (D4, D6, D8 and D10). The S1 to S13 numbers cross-reference to the stoichiometry in the Petersen matrix (Table 2). Stoichiometry of process D5 is given in Table 3.

Hydrolysis (Process D1)			
C2 - NH ₃ (S1)	C3 - H ₂ CO 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 ₂ CO 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 ₂ CO 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 ₂ CO 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 ₂ CO 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 ₂ CO ₃ * (S12)	D1 S _{bp} (S13)	D4, D6, D8, D10 Z _{AC} , Z _{AD} , Z _{AM} , Z _{HM}
moles	moles	moles	moles
$\frac{Y + 4X - 2Z - 23A}{Y + 4X - 2Z - 3A}$	$\frac{5(Y - 2Z - 3A)}{Y + 4X - 2Z - 3A}$	$\frac{20}{Y + 4X - 2Z - 3A}$	-1

The position of the stoichiometric formulae of Tables 3 and 4 are shown in the Petersen matrix in Table 2. By tracking through with defined organism yield values (Table 5) the stoichiometric sequence of AD processes (ignoring high p_{H_2} conditions, which has no effect under stable steady state conditions, and endogenous respiration processes, which have a very small effect, <3%), degradation of 100 gCOD biodegradable particulate sewage sludge of composition $C_{3.5}H_7O_2N_{0.196}$ (see below) produces 88.3 g COD methane and 11.7 gCOD biomass (Fig 3). Also the 100 gCOD contains 2.67 mol carbon (32.0 gC). Stoichiometrically 88.3 gCOD methane contains 1.38 molC (16.5 gC) and the 11.7 gCOD biomass of composition $C_5H_7O_2N$ contains 0.37 molC (4.4 gC). The difference between the input and output molC is the molC CO₂ produced, viz. $2.67 - (1.38 + 0.37) = 0.92$ molC (11.0 gC), which is equal to the model predicted net CO₂ production. This CO₂ production exits the digester as CO₂ gas and dissolved CO₂ in the effluent flow. The split between the gaseous and dissolved CO₂, or equivalently the partial pressure of CO₂ in the gas phase, is governed by the sludge feed COD concentration, i.e. the influent (and effluent) flow with which the 100 gCOD enters the digester, and the digester pH through the mixed weak acid/base chemistry of the system. This calculation is complex because the digester pH is unknown. The pH is affected by the mol N released as ammonia in the breakdown of the sludge organics (0.15 molN from the 100gCOD $C_{3.5}H_7O_2N_{0.196}$ sewage sludge) and the partial pressure of CO₂ in the gas phase (p_{CO_2}). While estimates of the p_{CO_2} and digester pH can be obtained iteratively manually (see Chapter 6), the usefulness of the integrated two phase weak acid/base chemistry and biological processes kinetic model is that this calculation of the effluent gas p_{CO_2} and digester pH is done seamlessly within the model structure including all the weak acid/bases in the digester influencing pH (not only the inorganic C system) and the measured (or estimated) dissolved constituents in the sludge feed as a result of prior acidogenesis. Also, while not validated for this yet, the integrated AD model can deal with cyclic flow and load conditions.

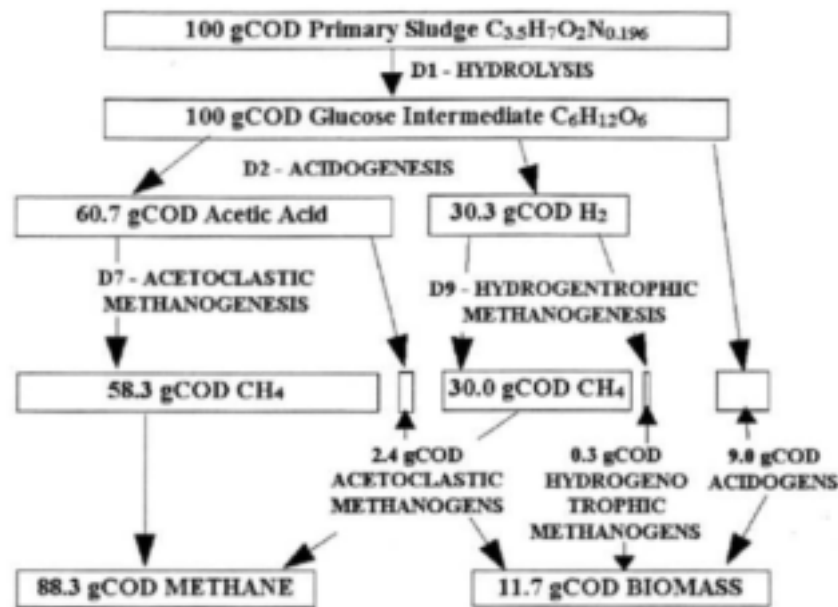


Fig 3: Stoichiometry of anaerobic digestion 100 gCOD primary sludge ignoring high partial pressure of hydrogen and endogenous respiration.

Table 5: Kinetic and stoichiometric constants at 37 °C for the four anaerobic digestion organism groups. The Y , μ_{max} , K_s and b values were obtained from Sam-soon et al. (1991); the $K_{max,HYD}$ and $K_{SS,HYD}$ values by calibration in this application.

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_{H_2}	$K_{H_2} = 6.25 \times 10^{-4} \text{ molH}_2/\ell$			
Acidogenic hydrolysis of biodeg 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})

6.2.4 Kinetic Equations of the Biological Processes

The rate equations for the 10 biological processes (Table 2) were obtained from various literature sources, where possible, and modified to describe the reactions as realistically and accurately as possible. The rate equations chosen for each of the biological processes included in the two phase CPB processes AD model are briefly described below.

1. Hydrolysis process (D1)

A number of different kinetic formulations for the hydrolysis process were investigated:

(i) First order kinetics

The most common way of modelling the rate of hydrolysis of particulate organic material (process D1) has been to use first order kinetics. A number of researchers (e.g. Eastman and Ferguson, 1981; Gujer and Zehnder, 1983; Pavlostathis and Giraldo-Gomez, 1991) used simple first order equations, dependent only on the biodegradable substrate (as COD) concentration:

$$r_{HYD} = K_h [S_{bp}] \quad [8a]$$

where:

r_{HYD} = hydrolysis rate (mol S_{bp} /l.d)

K_h = first order hydrolysis kinetic rate constant (/d)

$[S_{bp}]$ = biodegradable particulate organics concentration (mol/l).

Application of the first order kinetics has been found to result in values for the first order rate constant (K_h) that are situation specific, varying with, for example, sludge age or equivalently hydraulic retention time (e.g. Henze and Harremoës, 1983; Bryers, 1985; Pavlostathis and Giraldo-Gomez, 1991; Chapter 6). Because the objective is to develop a kinetic model for anaerobic digestion that would be applicable over a range of sludge ages, alternative more general approaches were investigated. It is well known that the rate of hydrolysis is affected by temperature, pH, acidogen organism concentration, and type, particle size and concentration of organics. Among these, intuitively at least the acidogen organism concentration plays a major role in regulating the rate of hydrolysis and should be included in the kinetic rate expression in some way. Eliosov and Argaman (1995) included the acidogen active biomass directly into the first order kinetics:

$$r_{HYD} = K_H [S_{bp}][Z_{AD}] \quad (8b)$$

where:

K_H = first order specific hydrolysis kinetic rate constant (l/mol Z_{AD} .d)

$[Z_{AD}]$ = acidogen active biomass concentration (mol/l)

(ii) Monod kinetics

Monod kinetics are commonly used in modelling biological wastewater treatment processes (e.g. McCarty, 1974; Dold *et al.*, 1980, Henze *et al.*, 1987):

$$r_{HYD} = \left[\frac{\mu_{max,HYD} [S_{bp}]}{K_{SM,HYD} + [S_{bp}]} \right] [Z_{AD}] \quad (8c)$$

where:

$\mu_{max,HYD}$ = maximum specific hydrolysis rate constant (mol S_{bp} /(mol Z_{AD} .d))

$K_{SM,HYD}$ = Monod half saturation constant for hydrolysis (mol S_{bp} /l)

(iii) Surface mediated reaction (or Contois) kinetics

To model the hydrolysis of particulate slowly biodegradable COD in activated sludge systems, Dold *et al.* (1980) used Levenspiel (1972) planar surface mediated reaction kinetics (also known as Contois kinetics, Vavilin *et al.*, 1996). With a single set of constant values, these kinetics gave reasonable predictions over a wide range of activated sludge system conditions including sludge age. Since the hydrolysis processes in activated sludge and anaerobic digestion could be regarded as similar and operate on the same organics (present in raw sewage), this approach also was investigated for the AD model:

$$r_{HYD} = \frac{k_{max, HYD} \frac{[S_{bp}]}{[Z_{AD}]}}{K_{SS, HYD} + \frac{[S_{bp}]}{[Z_{AD}]}} [Z_{AD}] \quad (8d)$$

where

$$\begin{aligned} k_{max, HYD} &= \text{Maximum specific hydrolysis rate constant [mol } S_{bp}/(\text{mol } Z_{AD} \cdot \text{d})] \\ K_{SS, HYD} &= \text{Half saturation constant for hydrolysis (mol } S_{bp}/\text{mol } Z_{AD}) \end{aligned}$$

Selection of the most suitable hydrolysis kinetic formulation is investigated later in this chapter. Irrespective of the hydrolysis formulation used, no acidogen biomass growth takes place in this hydrolysis process, and 1 gCOD sewage sludge forms 1 gCOD "glucose" intermediate (Fig 3, Eq 6). Growth of acidogens arises from the acidogenic conversion of the glucose intermediate to SCFA and hydrogen, which, relative to the rate of hydrolysis, is immediate resulting in zero accumulation of glucose in the AD system.

2 Acidogenesis process (D2 and D3)

As noted above, acidogenesis refers to the utilization of the model intermediate "glucose" (S_{bg}) by the acidogenic organisms, producing propionic acid, acetic acid, hydrogen, carbon dioxide and protons. Under conditions of low hydrogen partial pressure (p_{H_2}), the acidogenic reaction (process D2) produces only acetic acid, hydrogen and CO_2 . The process is formulated in terms of the growth rate of acidogens (r_{ZAD}), which is modelled with a Monod equation (Gujer and Zehnder, 1983; Pavlostathis and Giraldo-Gomez, 1991), as follows:

$$r_{ZAD} = \frac{\mu_{max, AD} [S_{bg}]}{K_{S, AD} + [S_{bg}]} \left\{ 1 - \frac{[H_2]}{k_{H_2} + [H_2]} \right\} [Z_{AD}] \quad (9)$$

where:

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

The second part of the term in { } brackets in Eq 9, called a non-competitive inhibition function, takes account of the reduction in rate when the p_{H_2} is high. At high p_{H_2} , in addition to acetic acid, hydrogen and CO_2 , propionic acid also is produced (process D3). For the production of propionic acid under high p_{H_2} , the growth rate of the acidogens (r_{ZAD}) is based on the same Monod kinetic equation (Eq 9) as for low p_{H_2} , viz.:

$$r_{ZAD} = \frac{\mu_{max, AD} [S_{bg}]}{K_{S, AD} + [S_{bg}]} \left\{ \frac{[H_2]}{k_{H_2} + [H_2]} \right\} [Z_{AD}] \quad (10)$$

To ensure that this process only operates when the p_{H_2} is high, the non-competitive inhibition function in { } switches the process "on" under conditions of high p_{H_2} and "off" under conditions of low p_{H_2} , controlled by switching constant k_{H_2} . Additionally, to ensure that the rate of glucose (S_{glf}) utilisation is the same under both conditions and in the intermediate condition, the rate of acetate production (Eq 9) is reduced by subtracting the inhibition function value from 1 in Eq 9.

3 Acetogenesis process (D5)

In the process of acetogenesis, the propionic acid produced under high p_{H_2} conditions is degraded under low p_{H_2} by acetogenic organisms to produce acetate (Eq 1). This rate was modelled in terms of the acetogen growth rate (r_{ZAC}), also with a Monod equation for the specific growth rate:

$$r_{ZAC} = \frac{\mu_{max,AC} [HPr]}{K_{S,AC} + [HPr]} \left\{ 1 - \frac{[H_2]}{k_{H_2} + [H_2]} \right\} [Z_{AC}] \quad [11]$$

where:

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

Since the weak acid/base chemistry is being modelled, both the undissociated and dissociated species of propionic acid are included as compounds, and the growth rate needs to be formulated in terms of the appropriate species. In Eq 11, the specific growth rate is a Monod function in terms of the undissociated propionic acid species, and not the more abundant dissociated species, in agreement with observations. Also, in the stoichiometry (Table 2) the undissociated propionic acid species (HPr) is used as substrate source. Should this approach lead to numerical instability in solution procedures (due to the low concentrations of HPr), the dissociated species (Pr⁻) can be used instead without undue difficulty, but taking due cognisance of the concentration effects in the Monod expression and the requirement of the charge balance in the stoichiometric equations.

The same non-competitive inhibition function in the { } brackets of Eq 9 appears in Eq 11, because the acetogenesis process is sensitive to p_{H_2} , decreasing as p_{H_2} increases. This means that as p_{H_2} increases, not only do acidogens begin to produce propionic acid (process D3), but also the rate of propionic acid utilization by acetogens (process D5) decreases. This causes a progressive build up of propionic acid as p_{H_2} increases and contributes to the decrease in pH when the hydrogen consuming hydrogenotrophic methanogen growth rate (D9) decreases for some reason (see below).

4 Acetoclastic methanogenesis process (D7)

Acetoclastic methanogenesis (or acetate cleavage) is the process whereby acetic acid is converted to methane and CO_2 ($CH_3COOH \rightarrow CO_2 + CH_4$), and growth of acetoclastic methanogens takes place. As for processes D2 and D3, the rate is modelled in terms of the rate of growth of the acetoclastic methanogens (r_{ZAM}) with a Monod equation, viz.:

$$r_{ZAM} = \frac{\mu_{max,AM} [HAc]}{K_{S,AM} + [HAc]} [Z_{AM}] \quad (12)$$

where:

$\mu_{max,AM}$	= Acetoclastic methanogens maximum specific growth rate constant (/d)
$K_{S,AM}$	= Half saturation concentration of acetoclastic methanogens growth on acetic acid

	(mol/l)
[HAc]	= Undissociated acetic acid concentration (mol/l)
[Z _{AM}]	= Acetoclastic methanogen organism concentration (mol/l)

As for the acetogens, the specific growth rate of the acetoclastic methanogens is a function of the undissociated acetic acid species (HAc). Also, in the stoichiometry acetic acid uptake is via the undissociated species, and CO₂ production via H₂CO₃*.

5 Hydrogenotrophic methanogenesis process (D9)

Hydrogenotrophic methanogenic organisms use H₂ and CO₂ to form methane and water (CO₂ + 4H₂ → CH₄ + 2H₂O). This process (D9) is also modelled in terms of the rate of growth of the hydrogenotrophic methanogens (r_{ZHM}), with a Monod equation:

$$r_{ZHM} = \frac{\mu_{max,HM} [H_2]}{K_{S,HM} + [H_2]} [Z_{HM}] \quad (13)$$

where:

$\mu_{max,HM}$	= Maximum specific growth rate of hydrogenotrophic methanogens (/d)
$K_{S,HM}$	= Half saturation concentration of hydrogenotrophic methanogens growth on hydrogen (mol/l)
[H ₂]	= Molecular hydrogen concentration (mol/l)
[Z _{HM}]	= Hydrogenotrophic methanogen organism concentration (mol/l)

In agreement with the other processes, CO₂ uptake for hydrogenotrophic methanogenesis is via the H₂CO₃* species.

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

Organism death in AD consists of endogenous respiration/death only, since predation apparently does not occur under anaerobic conditions. Hence, for each organism group the organism death rate is modelled with first order kinetics, viz.:

$$-r_Z = b_Z [Z] \quad (14)$$

where:

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

The organism mass that dies adds to the slowly biodegradable organics (S_{sp}) of the influent (Table 4, Eq 7), which passes through the same hydrolysis, acidogenesis and subsequent processes as the influent biodegradable organics. Because the organism yields and endogenous respiration rates of the AD organisms are relatively very low, it was accepted that no endogenous residue (particulate unbiodegradable organics) forms and no COD (electrons) is utilized by the AD organisms for maintenance.

The stoichiometric and kinetic constants for the four organism groups (yield coefficients, maximum specific growth rates, half saturation concentrations, endogenous mass loss rates) were obtained from the literature and are listed in Table 5.

6.3 AQUEOUS CHEMICAL PROCESSES

The reaction scheme for the weak acid/base part of this two phase AD model was taken unchanged from Musvoto *et al.* (1997, 2000a,b,c). The 16 chemical equilibrium dissociation (CED) processes (C1-C6 and C9- C18) of the ammonia, carbonate, phosphate, short chain (volatile) fatty acid (SCFA, acetate) and water weak acid/base systems and their 13 associated compounds (C1-C5 and C7-C14) were included in the AD model (Tables 1 of Musvoto *et al.*, 1997 and Chapter 4). Only the five chemical (C) and one physical (P) compounds directly associated with the 10 biological (B) and 3 physical (P) processes of AD (D1-D10 and P6-P8) are shown in the Petersen matrix in Table 2, i.e. NH_4^+ (C1/B10), NH_3 (C2), H_2CO_3^* (C3), H^+ (C7), HAc (C13) and CO_2 gas (P1/C6). Two additional CED processes had to be added, viz. the reverse and forward dissociation processes for the propionate weak acid/base system (C46 and C47), together with its two associated compounds propionic acid (HPr, C28) and propionate (Pr⁻, C29). The 22 chemical ion pairing processes (CIP, C20-C41) with their 13 associated chemical compounds (C15-C27) were not included in this two phase AD model, because mineral precipitation (3rd phase) is not yet included (Table 1, Chapter 4).

6.4 PHYSICAL PROCESSES - GAS EXCHANGE

In the three phase carbonate system weak acid/base model of Musvoto *et al.* (1997), the physical (P) processes for carbon dioxide gas exchange (PGE) with the atmosphere were included, by modelling the expulsion (reverse, K'_{rCO_2}) and dissolution (forward, K'_{fCO_2}) processes separately and linking the rates for these two processes through the Henry's law constant for CO_2 (K_{HCO_2}), i.e. $K'_{\text{fCO}_2} = K'_{\text{rCO}_2} K_{\text{HCO}_2} \cdot \text{RT}$. Musvoto *et al.* showed that this approach yielded identical results to the usual interphase gas mass transfer equation with an overall liquid phase mass transfer rate coefficient K_{LaCO_2} , where $K_{\text{LaCO}_2} = K'_{\text{rCO}_2}$. In their model application, the actual CO_2 expulsion rate constant value (K'_{rCO_2}) was not important because they considered initial and final steady state conditions only, not the transient dynamic conditions to the final steady state. Also, the CO_2 gas concentration ($\text{CO}_2(\text{g})$) was kept constant as calculated from a selected partial pressure of CO_2 ($\text{CO}_2(\text{g}) = p_{\text{CO}_2}/\text{RT}$), since gain or loss of $\text{CO}_2(\text{g})$ did not need to be determined.

Musvoto *et al.* (2000a), van Rensburg *et al.* (2003) and Loewenthal *et al.* (2004) extended this model to include three phase mixed weak acid/base systems to simulate multiple mineral precipitation and active gas exchange of CO_2 and NH_3 during aeration of anaerobic digester liquor and swine wastewater. For CO_2 , they followed the approach of Musvoto *et al.* (1997) above. For the NH_3 , they noted that the atmospheric concentration of NH_3 is negligible (i.e. acts as an infinite sink), so that only NH_3 expulsion need be included, and dissolution could be neglected. Because they simulated transient (dynamic) conditions, the CO_2 gas exchange (as above) and NH_3 gas expulsion (stripping) (and mineral precipitation) rates were important and these were determined from the experimental results. In determining the rates for the gas exchanges, Musvoto *et al.* (2000a) noted that, if the dimensionless Henry's law constant of a gas, $H_e [= \{1/(K_H \text{ R T})\}]$ is > 0.55 , then O_2 can be used as a reference gas and the expulsion rate constant K' , ($= K_{\text{La}}$) for the individual gases will be in the same proportion to the rate for O_2 ($K'_{\text{rO}_2} = K_{\text{LaO}_2}$) as their diffusivity is to the diffusivity of O_2 . Of the two gases they considered, only NH_3 has a $H_e < 0.55$ ($= 0.011$ at 20°C), so the value for K'_{rNH_3} had to be determined independently of the values for K'_{rO_2} , by calibration. For CO_2 $H_e = 0.95$ at 20°C (Katehis *et al.*, 1998) and accordingly they defined K_{LaCO_2} in terms of K_{LaO_2} . However, since the compound oxygen was not included in their model, in effect only K_{LaCO_2} was determined by calibration against measured data.

In Chapter 4 the biological processes of IWA Activated Sludge Model No 1 were integrated into the two phase (aqueous-gas) mixed weak acid/base chemistry model of Musvoto *et al.* (2000a) allowing

the reactor pH to become a model predicted parameter. Four gases were considered, viz. O_2 , N_2 , CO_2 and NH_3 . For CO_2 and NH_3 , the formulations of Musvoto *et al.* and van Rensburg *et al.* above were accepted. However, since gas production was of interest, for CO_2 they substituted $K'_{rCO_2} \cdot K'_{HCO_2} \cdot p_{CO_2}$ for $K'_{rCO_2} \cdot [CO_2(g)]$ (Table 3, Chapter 4). This allows the $CO_2(g)$ concentration to vary without influencing the rate of CO_2 gas exchange, of importance in their implementation of the model in Aquasim (Reichert, 1998), where for simplicity the gas compounds were considered part of the bulk liquid. This approach for CO_2 was adopted for N_2 gas also. For O_2 , the more conventional approach for aeration transfer to the bulk liquid was followed (Process P11 in Table 3, Chapter 4). In their application, because equilibrium between the aqueous and gas (atmosphere) phases is not reached during aeration in the aerobic reactor, the expulsion rates of the four gases were important for the simulation results and so values for K' , ($= K_{La}$) for the four gases had to be determined. For the K_{La} values for the gases, they followed the approach of Musvoto *et al.* (2000a) above. The K_{La} for CO_2 and N_2 were linked to the K_{La} for O_2 through the diffusivities. The K_{LaO_2} was calibrated to reflect the CO_2 supersaturation observed on samples from the aerobic reactor of full-scale plants (~20%), and cross-checked against the model determined dissolved O_2 concentration. For K'_{rNH_3} ($= K_{LaNH_3}$), this was calibrated independently. However, because negligibly little NH_3 actually strips out of the aqueous phase with aeration in the usual pH range of 6.5 to 8 for activated sludge systems, the actual NH_3 stripping rate, and hence the value for K'_{rNH_3} , was of little consequence (provided it is not excessively large) and in fact the process itself could have been omitted from the integrated model without loss in accuracy.

In the application here of integrating the biological processes of AD into the two phase (aqueous-gas) mixed weak acid/base chemistry model of Musvoto *et al.* (2000a), four gases also need to be considered, i.e. CO_2 , CH_4 , H_2 and NH_3 . Of these four, only CO_2 needs to be modelled with both expulsion and dissolution processes, because this gas is significantly soluble. Hence, both dissolved and gaseous CO_2 compounds are included (compounds C3 and P1, Table 2) and the process scheme of Chapter 4 above was followed. CH_4 is (i) very insoluble and (ii) not utilized in the biological or chemical processes, so its dissolved (aqueous) phase is bypassed and only a gas phase CH_4 compound is included (compound P4, Table 2). It is therefore assumed that the acetoclastic and hydrogenotrophic methanogenesis processes (D7 and D9) produce CH_4 gas directly and no CH_4 expulsion and dissolution processes need to be included in the model. Although H_2 also is very insoluble, it is utilized at an interspecies level in the hydrogenotrophic methanogenesis process (D9) and so it cannot be transferred instantaneously to the gas phase. H_2 is therefore modelled as a dissolved compound (D3, Table 2), but because it is utilized so rapidly and at an inter-organism species level, its residual concentration is extremely small; from a gas production perspective, it can be ignored. Hence, expulsion and dissolution processes for H_2 are not included in the model. 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 diffuse from the dissolved (aqueous) to the gas phases and so a process for expulsion of NH_3 is included in the 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 digester pH range 6.8 to 8, the gas phase is assumed to maintain a negligible NH_3 partial pressure. An NH_3 dissolution process is therefore not included in the model, only an expulsion process (in agreement with Musvoto *et al.*, 2000a, van Rensburg *et al.*, 2003 and Chapter 4). 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). Thus, only the K' ($= K_{La}$) values for these two gases need to be considered. However, because transient conditions are not being modelled in this particular application, but only the final steady state, the expulsion rates of the gases are not important provided the simulation run times are long enough to reach steady state. From the above it is clear that the gas phase partial pressure required in the rate formulations for CO_2 gas exchange need be calculated only from the CO_2 and CH_4 gas concentrations.

6.5 INFLUENT SEWAGE SLUDGE CHARACTERISATION

In terms of the structure of the UCTADM1 above, in addition to requiring as input the influent concentrations of the various inorganic compounds (e.g. total inorganic carbon, C_T , speciated into $H_2CO_3^*$, HCO_3^- and CO_3^{2-} for the relevant pH), various sewage sludge organic compounds need to be specified. For UCTADM1, the sewage sludge characterisation into its constituent fractions is shown in Fig 4; the characterisation structure adopted is near identical to that for sewage in activated sludge modelling (ASM2, Henze *et al.*, 1995). For undigested pristine sewage sludges, the two particulate fractions (biodegradable and unbiodegradable) can be expected to dominate to the extent that the other fractions can be neglected (this is evident from a mass balance around the primary settling tank for primary sludges, and simulation of activated sludge systems for waste activated sludges). However, primary sewage sludges are seldom in the pristine state, having undergone hydrolysis and acidogenesis within the primary settling tank (e.g. Barnard, 1984 measured SCFA concentrations in primary settling tank underflows in the range 1 700 to 2 700 mg/l at various treatment plants in South Africa), and in transport and storage for laboratory investigations. The SCFA thus produced (and equal concentrations of non-SCFA soluble COD, Lilley *et al.*, 1990) have a significant influence on the predicted pH in simulating anaerobic digesters, since uptake and utilisation of dissociated SCFA generates significant alkalinity (see Chapter 6). Furthermore, the SCFAs influence the hydrolysis rate constants in model calibration Ristow *et al.* (2004a,b). Thus, quantifying and specifying the influent sludge organic fractions are essential both in model calibration and simulation. Of the sewage sludge fractions (Fig 4), the unbiodegradable and biodegradable particulate (S_{upl} and S_{bpl}) and the two readily biodegradable fractions (S_{bsol} and S_{bfi}) are of importance - the unbiodegradable soluble organics (S_{usi}) usually are present in such low concentrations that they can be neglected. For S_{bsol} , two SCFA types are recognised in the model, acetic and propionic, and hence these form two subfractions of the S_{bsol} .

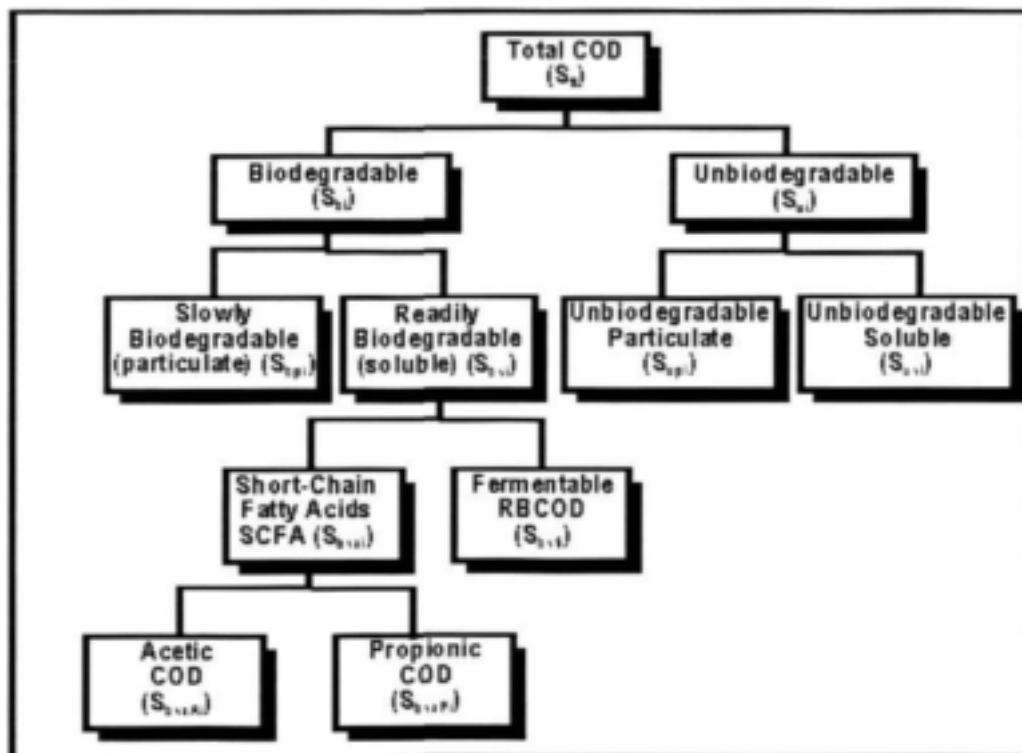


Fig 4: Schematic showing characterization of the influent sewage sludge organics, required as input to the model; the acetic and propionic require speciation for the influent pH.

The characterisation structure is based on COD units, which are widely applied to quantify wastes. Since the kinetic model is based on mole units, conversion between the COD and mole units would be needed to generate the input for the model. For the two readily biodegradable fractions, the S_{bnd} usually are measured directly, while in terms of the model presented here the S_{bnd} is "idealised" glucose so that conversion of these to mole units is relatively simple. For the particulate fractions, the conversion to mole units requires that the stoichiometric formulation for these sewage sludge fractions be specified, i.e. X, Y, Z and A in $C_XH_YO_ZN_A$. This is discussed in more detail below.

6.6 MODEL CALIBRATION

From the above model development, the integrated two phase (aqueous-gas) chemical (C), physical (P) biological (B) processes AD model comprises (Table 2): (1) the 16 forward and reverse chemical equilibrium dissociation (CED) processes (C1-C6, C9-C18) and their 13 associated compounds (C1-C2, C4-C14) - Table 1 in Musvoto *et al.* (1997); (2) the two forward and reverse CED processes for propionic acid (C47-C48) and their two associated compounds (C28-C29), (3) the three physical gas exchange processes of dissolution of CO_2 (P6) and its associated compound CO_2 gas (P1) and expulsion of CO_2 (P7) and NH_3 (P8) and, (4) the 10 biological processes for AD (D1-D10) and their 8 associated compounds (P4 and D1-D7). The model was implemented in the computer programme Aquasim (Reichert, 1998).

Omitted from this AD model are the five mineral precipitation processes (P1/C19 - Musvoto *et al.*, 1997 and P2/C42-P5/C45 - Musvoto *et al.*, 2000a), because mineral precipitation is not included in this two phase AD model. Also omitted are the 22 chemical iron pairing (CIP) processes (C20-C41) and their 13 associated compounds (C15-C27), because these processes are important mainly for multiple mineral precipitation modelling, which will be included in the next phase of the AD and wastewater treatment plant model development.

In implementation of the model in Aquasim, since initial simulations were 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 is possible because at steady state the gas composition does not change. For dynamic simulations, the gas composition may change significantly 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, see later.

6.6.1 Kinetics and Stoichiometric Constants

The kinetic constants required for the C and P 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,CO_2}), and the apparent reverse dissociation and expulsion rate constants (K'_r) respectively for these processes. The equilibrium constants (pK) and Henry's law constant for CO_2 (K'_{H,CO_2}), and their temperature sensitivity equations were obtained from the literature (see Table 2c of Musvoto *et al.*, 1997 - 1940s database). The pK value for propionic acid (pK_{Pr}) was accepted to be the same as for acetic acid, and is given by $pK_{Pr} = 1170.5/T_k - 3.165 + 0.0134T_k$, where T_k = temperature in Kelvin. The weak acid/base apparent reverse dissociation rate constants (K'_r) were 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 $K'_{rN} = 10^{12}/d$, see Table 2a in Musvoto *et al.* (1997). 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. $K'_{rCl} = K'_{rCl} 10^{-pK_{Cl}/f_m^2}$, where f_m is the mono-valent 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 the K'_{La,CO_2} was assumed to have a high value (1000/d) since only the steady state was

initially simulated, while for NH_3 the K'_{NH_3} was accepted to have a low value (1/d). As noted above, the value for K'_{NH_3} does not influence the simulations provided it is not too high, since little NH_3 is lost at the $\text{pH} < 7.5$.

In the BD processes part of the model, required are the kinetic and stoichiometric constants (Y , μ_{max} , K_s and b) for the four AD organism groups (Table 5). In the literature there is considerable variation and hence uncertainty in these values. Accepting this uncertainty, values for these constants were taken 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), the rate constants (e.g. Monod half saturation coefficients) had to be appropriately adjusted 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 ($\mu_{\text{max,AM}}$ in Eq 12) was increased 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; due to the low HAc/Ac^- concentrations, decreasing the intuitively more satisfying half saturation constant ($K_{s,AM}$ in Eq 12) as alternative caused instability in solution procedures. This aspect requires further investigation.

This left two parts of the AD model that required calibration against experimental data, viz, (i) the kinetic constants for the various hydrolysis rate expressions, e.g. maximum specific hydrolysis rate ($k_{\text{max,HYD}}$) and half saturation coefficient ($K_{s,HYD}$) in Eq 8d, and selection of the most appropriate kinetic formulation, and (ii) the sewage sludge CHON composition, i.e. the X , Y , Z and A values in $\text{C}_x\text{H}_y\text{O}_z\text{N}_a$. Additionally, in model application the sewage sludge constituent fractions and the input concentrations of the various compounds would need to be quantified. Values for all these parameters were obtained interactively through analysis of and model application to the experimental data set of Izzett *et al.* (1992), as described below.

6.6.2 Experimental Anaerobic Digester Systems

In any calibration and validation exercise, the measured parameters must conform to the same mass balance and continuity principles as in the model, and hence (i) must be sufficient to be able to calculate the material mass balances and (ii) the mass balances must be as close as possible to 100%. The data of Izzett *et al.* (1992) appeared to conform reasonably well to these criteria. They conducted a series of experiments aimed at identifying the effects of thermophilic heat pre-treatment on the anaerobic digestibility of a mixture of primary and humus sewage sludges. In this investigation four laboratory scale anaerobic digesters were operated at a controlled temperature of 37 °C, two of which were fed heat pre-treated (70°C for 24h) sludge while the other two were fed untreated sludge. The digesters were run in parallel, and the retention times were progressively reduced to observe possible differences in digestibility (fraction unbiodegradable and rate of hydrolysis) between the heat pre-treated and untreated sludges. The digester fed untreated sludge was operated for a period of 211 days, during which time the retention time was reduced from 20 to 15, then 12, 10 and finally 7 days after the system had run at steady state for two to three retention times at each retention time. The data collected from this AD system (influent and effluent COD, VSS, TSS, TKN, FSA, SCFA, pH , H_2CO_3^* alkalinity and gas production and CO_2 composition) at a particular retention time were averaged over the final two to three steady state retention times (Table 6). The averages were used to check the N and COD mass balances. The N and COD balances obtained at the 20, 15, 12, 10 and 7 day retention times were 91 to 99% and 107 to 109% respectively (Table 6), indicating that the measured parameters conformed closely to the mass balance requirement. The measured averages therefore could be accepted to represent the behavioural characteristics of the digester under stable operating conditions at the different retention times.

Table 6: Experimental results for Izzett *et al.* (1992) 14l flow though mesophilic (37°C) anaerobic digesters operated from 20 to 7 days retention time on primary sewage sludge.

Retention time (d)	20	15	12	10	7
Feed rate (l/d)	0.7	0.93	1.17	1.4	2
Feed COD (mgCOD/l)	42595	42367	39222	40721	43286
Feed VFA (mgCOD/l as HAc)	2249	1824	2872	1961	1871
Feed TKN (mgN/l)	1171	1075	1028	1100	1105
Feed FSA (mgN/l)	244	221	235	203	196
Feed VSS (mgVSS/l)	25690	25863	24727	25768	25971
Feed H ₂ CO ₃ * Alk (mg/l as CaCO ₃)	56	82	90	81	80
Feed pH	5.28	5.42	5.2	5.34	5.34
Effluent COD (mgCOD/l)	19005	19969	18678	20521	23637
Effluent VFA (mgCOD/l as HAc)	23	27	28	28	50
Effluent TKN (mgN/l)	1157	976	992	1039	1041
Effluent FSA (mgN/l)	511	404	430	404	511
Effluent H ₂ CO ₃ * Alk (mg/l as CaCO ₃)	2066	1994	2072	1951	1882
Effluent pH	7.15	7.14	7.2	7.11	7.12
Gas production (l/d at 20°C)	11.053	13.958	16.696	20.07	27.932
Gas composition (% methane)	63.3	63.6	63.3	62.1	63.2
COD balance (%)	107.3	106.9	109.1	108.6	108.4
N balances (%)	98.8	90.8	96.5	94.5	94.2

Model COD and N balances at all retention times 100.0053% and 99.999% respectively.

As input to the various simulations and calculations below, the influent inorganic and organic constituent fractions need to be specified. A number of these were available from direct measurements, or could be derived directly. For the inorganic concentrations, the inorganic carbon and nitrogen weak acid/base species are required. The total inorganic nitrogen (free and saline ammonia, FSA, Table 6) was measured directly and the total inorganic carbon (C_T) could be calculated from the measured influent H₂CO₃* alkalinity and pH (Loewenthal *et al.*, 1986). From the influent total species concentrations, pH, temperature and relevant pK values adjusted for ionic strength effects, the influent inorganic carbon and nitrogen weak acid/base species concentrations could be calculated, as required for the simulations.

For the organic concentrations (Fig 4), the total COD (S_0) and SCFA ($S_{b,scf}$) concentrations were available from direct measurement (Table 6). For the simulations, all $S_{b,scf}$ were accepted to be HAc/Ac⁻ and this weak acid/base was speciated from the influent total species concentration, pH, temperature and relevant pK value adjusted for ionic strength effects (see Chapter 6). Further, from the experimental work of Lilley *et al.* (1990) and Ristow *et al.* (2004a), the non-SCFA fermentable biodegradable soluble COD concentration ($S_{b,fd}$) was accepted to be equal to the $S_{b,scf}$ concentration. The unbiodegradable soluble COD ($S_{u,scf}$) was accepted to be so low as to be negligible. This left two COD fractions to be quantified, the unbiodegradable and biodegradable particulates ($S_{u,pi}$ and $S_{b,pi}$). In the calculations and simulation below, the $S_{u,pi}$ was determined, and hence $S_{b,pi}$ was calculated by difference.

Thus, the Izzett *et al.* (1992) data set was used to calibrate three parts of the model; (i) hydrolysis process kinetic formulation and associated rate constants, (ii) sewage sludge CHON composition, and (iii) the unbiodegradable particulate fraction of the sewage sludge. The three parts were determined interactively and iteratively through calculation and simulation of the experimental systems.

6.6.3 Sewage Sludge Stoichiometric Formula

In the model, the biodegradable sewage sludge is hydrolysed to the intermediary compound "glucose" (Fig 2). Since the stoichiometry of the subsequent products for complete anaerobic oxidation of the intermediate "glucose" is well established and essentially fixed (see above), the stoichiometric transformation of the sewage sludge to the intermediate "glucose" is crucial to predict the observed digester effluent and gas compositions. This is directly influenced by the CHON stoichiometric composition for the sewage sludge, Eq 7. Furthermore, the carbonate weak acid/base species play an important role in fixing digester pH, H_2CO_3^* alkalinity, CO_2 and CH_4 gas produced, and it is therefore necessary to establish the correct C content of the influent sewage sludge to correctly predict these parameters also.

As a starting point, the sewage sludge composition was assumed to be the same as the generally accepted stoichiometric formula for activated sludge: $\text{C}_5\text{H}_7\text{O}_2\text{N}$ (WRC, 1984). However, $\text{C}_5\text{H}_7\text{O}_2\text{N}$ could not correctly predict the digester output (pH, gas flow and composition) as measured by Izzett *et al.* (1992) and therefore needed to be changed. Accordingly an improved estimate was derived from the measurements made on the influent.

Since influent TKN and FSA measurements were available (Table 6), the organic nitrogen (OrgN) in the feed was calculated for the different retention times. The result was expressed as a ratio of the measured COD and remained fairly constant during the investigation, ranging between 0.0201 and 0.0220 gN/gCOD for the different retention times. VSS measurements on the influent were also available (Table 6). Recognising that the VSS represents particulate organics, the equivalent particulate COD was determined as (total COD - 2·SCFA COD, i.e. $S_{\text{ti}} - 2 \cdot S_{\text{bssu}}$). The particulate COD/VSS ratio at each retention time was calculated, and ranged from 1.36 to 1.52 gCOD/gVSS. Additionally the organic N/VSS ratios were calculated and ranged from 0.032 to 0.036 gN/gVSS. From these ratios and accepting the H:O ratio in $\text{C}_x\text{H}_y\text{O}_z\text{N}_a$ as 7:2 (from $\text{C}_5\text{H}_7\text{O}_2\text{N}$ above), X and A could be calculated for each retention time, from:

$$\frac{\text{COD}}{\text{orgN}} = \frac{(Y + 4X - 2Z - 3A) \cdot \text{MW}_{\text{O}_2}}{4 \cdot A \cdot \text{MW}_\text{N}} \quad (15)$$

$$\frac{\text{COD}}{\text{VSS}} = \frac{(Y + 4X - 2Z - 3A) \cdot \text{MW}_{\text{O}_2}}{4(\text{MW}_\text{C} \cdot X + \text{MW}_\text{H} \cdot Y + \text{MW}_\text{O} \cdot Z + \text{MW}_\text{N} \cdot A)} \quad (16)$$

$$\frac{\text{orgN}}{\text{VSS}} = \frac{A \cdot \text{MW}_\text{N}}{(\text{MW}_\text{C} \cdot X + \text{MW}_\text{H} \cdot Y + \text{MW}_\text{O} \cdot Z + \text{MW}_\text{N} \cdot A)} \quad (17)$$

where:

MW_X = molecular weight of compound X

In Eqs 15 to 17 above, accepting $Y = 7$ and $Z = 2$, from the different pairings of equations (Eqs 15 and 17, and Eqs 15 and 16) two sets of (X; A) data pairs could be calculated for each retention time. The (X; A) pairs at the different retention times were all averaged, to give $X = 3.4$ and $A = 0.192$, giving a stoichiometric formulation for the sewage sludge of $\text{C}_{3.4}\text{H}_7\text{O}_{2.192}\text{N}_{0.192}$. These calculations did not require *a priori* information on the hydrolysis kinetics and S_{api} and hence this formulation formed the starting point for the simulations, which were used to refine the stoichiometry (in conjunction with the hydrolysis kinetics and S_{api}).

In the simulations the parameters that were targeted for improved estimation of the sewage sludge formulation were the gas flow and composition, which requires a carbon (C) balance over the digester. Izzett *et al.* (1992) did not measure the C content of the sewage sludge, so the influent C was calculated from an assumed 100% C balance over the digester (Fig 3), through combined use of measured and predicted C output values. This was reasonable because the COD balances were good (107-109%). Essentially, the C content of the influent sewage sludge appears in the outputs, as gaseous CO₂ and CH₄, dissolved inorganic carbon weak acid/base species and effluent soluble and particulate organic C, the particulate organic C being made up of biomass, S_{up} and undegraded S_{bp}.

By tracking all the measured C in CO₂ (gaseous and dissolved) and CH₄ and the simulated organic C exiting the digester at different retention times and ensuring that the predicted and measured effluent CODs corresponded, the C content of the influent could be equated to the C exiting the digester. Subtracting the influent inorganic C (calculated from the measured influent H₂CO₃* and pH) gave the influent organic C. This was expressed as an influent organic C/COD ratio for the different retention times. Like the OrgN/COD ratio, the organic C/COD ratios also varied in a narrow band for the different retention times. The average organic C/COD ratio was therefore used to calculate the C content (X) in the sewage sludge feed. Taking due consideration that the influent OrgN/COD ratio must also remain at the measured value, a sewage sludge composition formula of C_{3.5}H₇O₂N_{0.196} was determined, very close to the stoichiometry calculated above from the available influent measurements. This formulation was accepted for all subsequent calculations on and simulations of the Izzett *et al.* (1992) data. In the simulations, to derive the organic C/COD ratio the hydrolysis kinetics and S_{upi} needed to be correctly specified, and hence the requirement for interactive calculations and simulations.

To check how the model sewage sludge composition compares with real sludges, primary sludge from two different full-scale wastewater treatment plants (WWTP) around Cape Town (South Africa) were analysed for VSS, TSS, COD and their organic C, H, N and phosphorus (P) contents (see Appendix A). From the measured data, the CHON composition of the primary sludge was calculated (P was omitted because it was not measured by Izzett *et al.*, 1992). The average measured composition was C_{3.65}H₇O_{1.97}N_{0.19}. The model C, H, O, N content and molar mass of primary sludge are 95.9%, 100%, 98.5%, 94.5% and 98.7% of the measured values. This provides powerful validation of the UCTADM1 model.

6.6.4 Estimating the Unbiodegradable Fraction of Sewage Sludge and Hydrolysis Kinetics and Constants

Before an even remotely reasonable correspondence could be obtained between model predicted and measured effluent parameters and gas composition and production, the fraction of unbiodegradable particulate COD of the sewage sludge ($f_{psup} = S_{up}/S_u$) and the hydrolysis rate kinetics and constants needed to be determined. These were determined interactively between mass balance based calculations and simulations on the Izzett *et al.* data set. Initially, a value for the f_{psup} was estimated and then the various kinetic formulations evaluated, and thereafter the estimate for f_{psup} improved. In the mass balance based calculations below, COD units are used. The calculated values for the various parameters can be readily converted to the mole units required in the model, see below.

For the Izzett *et al.* data set, the influent sewage sludge is characterised by (Fig 4):

$$S_{it} = S_{bpi} + S_{bfi} + S_{basi} + S_{usi} + S_{upi} \quad (\text{mgCOD/l}) \quad (18)$$

In Eq 18 as noted above, S_{it} and S_{basi} were directly available from measurement (Table 6); S_{usi} could be accepted to be negligible, and S_{bfi} could be accepted to be equal to S_{basi}. This left two unknowns, S_{bpi} and S_{upi}. Letting $S_{upi} = f_{psup} \cdot S_u$, then S_{bpi} could be found by difference and hence f_{psup} was the only

unknown.

For the effluent:

$$S_{te} = S_{bpe} + S_{bfe} + S_{bsae} + S_{use} + S_{upe} + \text{biomass} \quad (\text{mgCOD/l}) \quad (19)$$

In Eq 19, S_{te} and S_{bsae} were available from direct measurement and it could be accepted that $S_{bfe} = S_{bsae}$ (the values are very low due to stable digester operation and hence do not influence the analysis significantly). Accepting negligible generation of unbiodegradable material in the anaerobic digester, then $S_{use} = S_{ue} = 0$ and $S_{upe} = S_{upi}$. With regard to the biomass, under stable digester operation three organism groups are generated, acidogens (Z_{AD}), acetoclastic methanogens (Z_{AM}) and hydrogenotrophic methanogens (Z_{HM}). Of these, the mass of Z_{HM} developed is very much smaller than that of Z_{AD} and Z_{AM} , and accordingly can be neglected in an initial steady state analysis. Thus Eq 19 reduces to:

$$S_{te} = S_{bpe} + S_{bfe} + S_{bsae} + S_{use} + S_{upe} + Z_{AD} + Z_{AM} \quad (\text{mgCOD/l}) \quad (20)$$

Developing mass balances around the digester (Ristow *et al.*, 2004a,b) and recognising from Table 2 that in the death of biomass the released organics add to the sewage sludge, for biodegradable particulate COD (S_{bp}):

$$V \cdot S_{bp} = Q_i \cdot S_{bpi} \cdot dt - Q_e \cdot S_{bpe} \cdot dt - r_{HYD}^* \cdot V \cdot dt + (b_{AD} \cdot Z_{AD} + b_{AM} \cdot Z_{AM}) \cdot V \cdot dt \quad (\text{mgCOD/l}) \quad (21)$$

where:

r_{HYD}^* = volumetric hydrolysis rate, COD units (mgCOD/l.d)

V_d = digester volume (l)

$Q_i = Q_e$ = influent and effluent flow rate respectively (l/d)

At steady state, solving for r_{HYD}^* :

$$r_{HYD}^* = \frac{1}{R_h} (S_{bpi} - S_{bpe}) + b_{AD} \cdot Z_{AD} + b_{AM} \cdot Z_{AM} \quad (\text{mgCOD/l.d}) \quad (22)$$

where:

$R_h = V_d / Q_i$ = hydraulic retention time (d)

Similarly for S_{bsf} and S_{bsa} with r_{AD}^* and r_{AM}^* as the volumetric rates in COD units of acidogenesis and acetoclastic methanogenesis respectively:

$$r_{AD}^* = \frac{1}{R_h} (S_{bsf} - S_{bfe}) + r_{HYD}^* \quad (\text{mgCOD/l.d}) \quad (23)$$

$$r_{AM}^* = \frac{1}{R_h} (S_{bsai} - S_{bsae}) + f_{Sbsai/Sbsf} \cdot r_{AD}^* \quad (\text{mgCOD/l.d}) \quad (24)$$

where:

$f_{Sbsai/Sbsf}$ = fraction of S_{bsf} appearing as S_{bsa} in the acidogenesis reaction (Table 4)
= 0.607 (mgCOD/mgCOD)

Developing similar mass balances for the biomass concentrations:

$$Z_{AD} = \frac{r_{AD}^* \cdot Y_{AD}^* \cdot R_h}{(1 + b_{AD} \cdot R_h)} \quad (\text{mgCOD/l}) \quad (25)$$

$$Z_{AM} = \frac{r_{AM}^* Y_{AM}^* R_h}{(1 + b_{AM} R_h)} \quad (\text{mg COD/l}) \quad (26)$$

where:

$$\begin{aligned} Y_{AD}^* &= \text{acidogen yield (mg COD/mg COD)} \\ Y_{AM}^* &= \text{acetoclastic methanogen yield (mg COD/mg COD)} \end{aligned}$$

Recognising that from Eq 20:

$$S_{bpe} = S_{te} - S_{bqf} - S_{base} - f_{PSup} \cdot S_{fl} - Z_{AD} - Z_{AM} \quad (\text{mg COD/l}) \quad (27)$$

In the set of equations above, f_{PSup} , S_{bpe} , Z_{AD} and Z_{AM} are the principal unknowns. If an estimate for f_{PSup} is available, then S_{bpe} , Z_{AD} and Z_{AM} can be calculated through iteration. However, f_{PSup} is not known for the Izzett *et al.* data set, and would need to be determined via some other technique, see later.

6.6.5 Determining Hydrolysis Rate Constants

In the section above, for any selected f_{PSup} , the volumetric rate of hydrolysis (r_{HYD}^*) can be calculated, as well as Z_{AD} , Z_{AM} and S_{bpe} , all in COD units. Converting these values to mole units:

$$r_{HYD} = r_{HYD}^* \left(\frac{\text{COD}}{\text{mol}} \right)_{S_{bp}} \quad (\text{mol } S_{bp}/\text{l.d}) \quad (28)$$

$$[S_{bpe}] = S_{bpe} \left(\frac{\text{COD}}{\text{mol}} \right)_{S_{bp}} \quad (\text{mol } S_{bp}/\text{l}) \quad (29)$$

$$[Z] = Z \left(\frac{\text{COD}}{\text{mol}} \right)_Z \quad (\text{mol } Z/\text{l}) \quad (30)$$

where:

$$\left(\frac{\text{COD}}{\text{mol}} \right)_{S_{bp}} = \text{COD/mol ratio for } S_{bp} \quad 131.3 \text{ gCOD/mol for } C_{3.5}H_7O_2N_{0.196}$$

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

$$[] = \text{mole concentration}$$

Equating this r_{HYD} with the first order and first order specific kinetic expressions for the hydrolysis (Eqs 8a and 8b respectively), and solving for K_H and K_{Hspec} yields:

$$K_H = r_{HYD}/[S_{bpe}] \quad (/d) \quad (31)$$

$$K_{Hspec} = r_{HYD}/([S_{bpe}][Z_{AD}]) \quad (\text{l/mol } Z_{AD} \cdot d) \quad (32)$$

Thus, from Eqs 31 and 32 above, values for K_H and K_{Hspec} could be determined, provided f_{PSup} was known.

Similarly, for the Monod (Eq 8c) and surface mediated reaction (Contois, Eq 8d) kinetics:

$$r_{HYD} = \frac{\mu_{max,HYD} [S_{bp}]}{K_{SM,HYD} + [S_{bp}]} [Z_{AD}] \quad (33)$$

$$r_{HYD} = \left[\frac{k_{max,HYD} \frac{[S_{bp}]}{[Z_{AD}]}}{K_{SS,HYD} + \frac{[S_{bp}]}{[Z_{AD}]}} \right] [Z_{AD}] \quad (34)$$

In each of Eqs 33 and 34 above, the values for the two constants needed to be determined, namely $\mu_{max,HYD}$ and $K_{SM,HYD}$ and $k_{max,HYD}$ and $K_{S,HYD}$ respectively. To determine these constants, the equations were linearized by three different methods, i.e. (i) Lineweaver-Burke, (ii) inversion and (iii) Eadie-Hofstee (Lehninger, 1977). For the Monod kinetics for example, these yielded respectively:

$$(i) \frac{[Z_{AD}]}{r_{HYD}} = \frac{K_{SM,HYD}}{\mu_{max,HYD}} \cdot \frac{1}{[S_{bpe}]} + \frac{1}{\mu_{max,HYD}} \quad (35a)$$

$$(ii) \frac{[S_{bpe}]}{r_{HYD}} = \frac{K_{SM,HYD}}{\mu_{max,HYD}} + [S_{bpe}] \cdot \frac{1}{\mu_{max,HYD}} \quad (35b)$$

$$(iii) \frac{r_{HYD}}{[Z_{AD}]} = -K_{SM,HYD} \cdot \frac{r_{HYD}}{[S_{bpe}] \cdot [Z_{AD}]} + \mu_{max,HYD} \quad (35c)$$

Linear regression was fitted to the Izzett *et al.* experimental data plotted according to the three linearization methods, for example see Figs 5a, b and c respectively for Monod kinetics. From the slopes and y-intercepts of the fitted lines, the appropriate pair of kinetic constants was determined. Again these calculations required that the value for f_{PSup} was known.

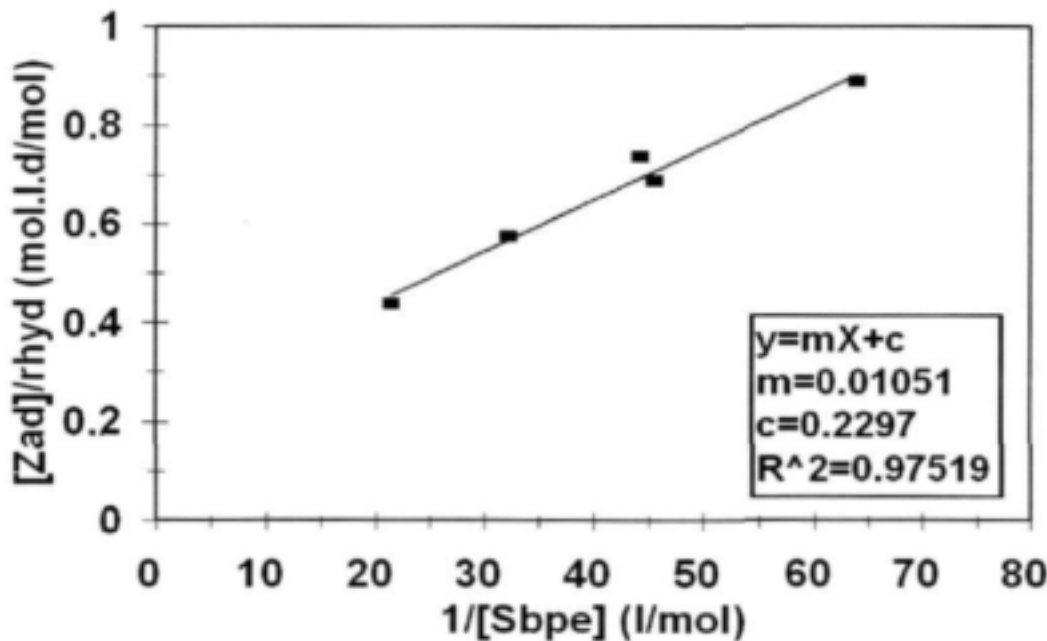


Fig 5a: Linearisation by Lineweaver-Burke of Monod kinetics for hydrolysis of sewage sludge for the data of Izzet *et al* (1992) at retention times of 7, 10, 12, 15 and 20d, with linear regression fit of straight line to data.

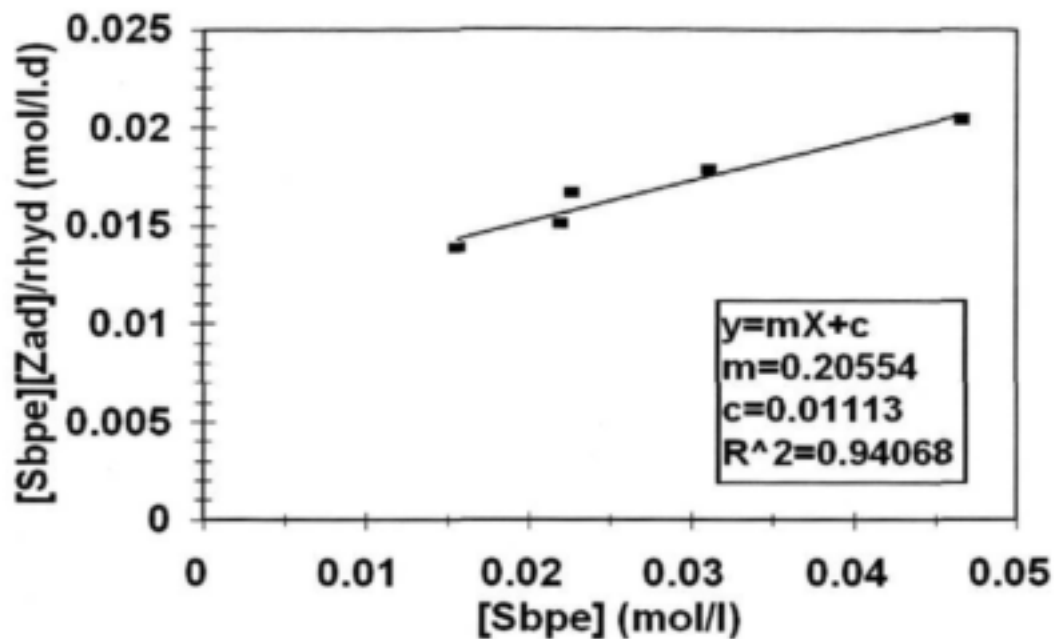


Fig 5b: Linearisation by inversion of Monod kinetics for hydrolysis of sewage sludge for the data of Izzet et al (1992) at retention times of 7, 10, 12, 15 and 20d, with linear regression fit of straight line to data.

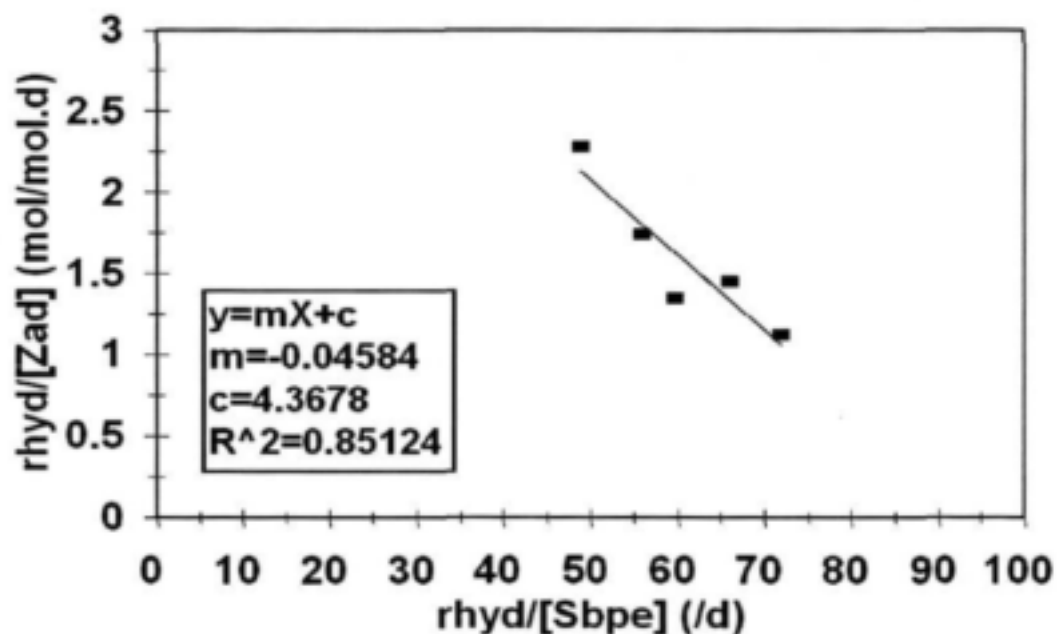


Fig 5c: Linearisation by Eadie-Hofstee of Monod kinetics for hydrolysis of sewage sludge for the data of Izzet et al (1992) at retention times of 7, 10, 12, 15 and 20d, with linear regression fit of straight line to data.

6.6.6 Determining the Sewage Sludge Unbiodegradable Particulate Fraction (f_{psup})

In all the calculations above, a value for f_{psup} needed to be known. However, this value was not directly available from the Izzett *et al.* data set. In the calculations, for each value of f_{psup} selected, a different set of kinetic constants was obtained for the different kinetic formulations.

Working on the principle that the most appropriate set of kinetic constants would be the one that provides the greatest consistency between predicted and measured values for all retention times of the Izzett *et al.* data set, techniques were devised to identify these constants and the corresponding f_{psup} value. For the first order and first order specific kinetic formulations, the value for f_{psup} was varied and the coefficient of variation (standard deviation/average) calculated for the relevant K values for the four retention times, for each f_{psup} value. The coefficients of variations were then plotted against f_{psup} , see Fig 6. From Fig 6, the coefficients of variations for first order and first order specific kinetics both exhibit minima; for the first order kinetics this is at $f_{psup} = 0.34$, and for the first order specific kinetics at $f_{psup} = 0.32$. In effect these values of f_{psup} are the ones that give the least variation in the relevant kinetic rate constants across the four retention times. Since the Izzett *et al.* systems were operated on the same source sewage sludge, these values would provide the most suitable estimate for f_{psup} and the kinetic constants. Furthermore, these values for f_{psup} are very similar to that determined by O'Rourke (1968) of 0.36, and that expected (0.32 or 0.36) from a mass balance around the primary settling tank with typical South African raw and settled wastewater characteristics, i.e. raw (f_{supR}) and settled (f_{supS}) wastewater unbiodegradable particulate COD fractions of 0.15 and 0.04 and a COD removal (f_{PSR}) of 40% or 35% respectively in primary sedimentation (WRC, 1984), where (see Chapter 4):

$$f_{PSup} = f_{supS} + (f_{supR} - f_{supS})/f_{PSR} \quad (36)$$

Thus, accepting that for the first order kinetics $f_{psup} = 0.34$, then $K_h = 0.381 \text{ /d} \pm 0.0066$, and for first order specific kinetics that $f_{psup} = 0.32$, then $K_H = 40 \text{ l/mol } Z_{AD}/\text{d} \pm 2.0$.

For the Monod and surface mediated reaction kinetics, in the three linearization techniques, linear regression was used to fit a straight line to the data, and the correlation coefficients (R^2) of these lines calculated, for example see Figs 5a, b and c for linearization of the Monod kinetics. Thus, for each selected value of f_{psup} three correlation coefficients were obtained for each of Monod and surface mediated reaction kinetics. These correlation coefficients were plotted against f_{psup} , see Figs 7 and 8 for Monod and surface mediated reaction kinetics respectively. Both sets of R^2 values exhibit maximum values at $f_{psup} = 0.36$, and hence this value was selected for these kinetics. Averaging the values for the three linearizations gives $\mu_{max,HYD} = 4.529 \text{ mol } S_{bp}/(\text{mol } Z_{AD} \cdot \text{d})$ and $K_{SM,HYD} = 0.0486 \text{ mol } S_{bp}/\text{l}$ for Monod kinetics and $k_{max,HYD} = 6.797 \text{ mol } S_{bp}/(\text{mol } Z_{AD} \cdot \text{d})$ and $K_{SS,HYD} = 10.829 \text{ mol } S_{bp}/\text{mol } Z_{AD}$ for surface mediated reaction kinetics. To confirm the values determined with this method, the experimental data and predicted lines were plotted on the Monod type plot for both Monod kinetics (Fig 9) and surface saturation kinetics (Fig 10); in both cases a close fit to the data is obtained.

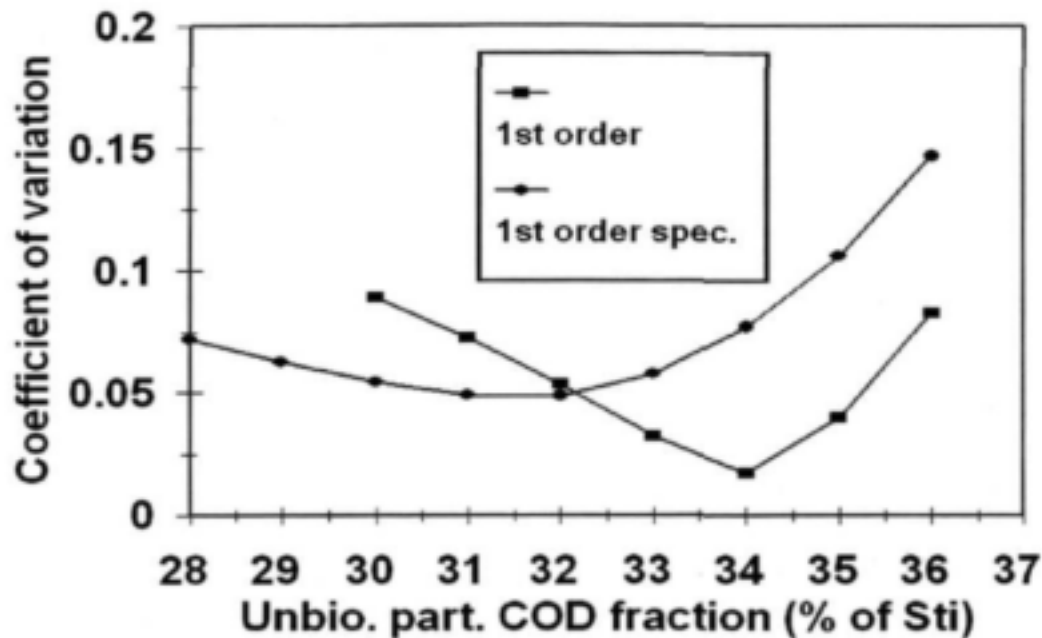


Fig 6: Coefficient of variation in the kinetic constants for 1st order and 1st order specific kinetics for sewage sludge hydrolysis, for the data of Izzet et al. (1992) at retention times of 7, 10, 12, 15 and 20d.

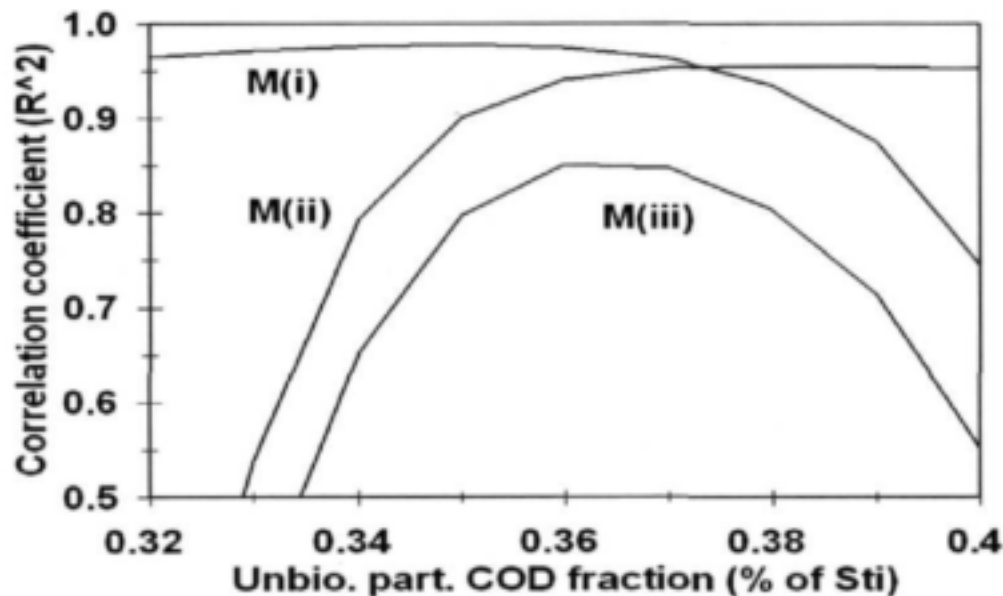


Fig 7: Correlation coefficients versus unbiodegradable particulate COD fraction for linear fits to Monod hydrolysis kinetics, for the data of Izzet et al. (1992) at retention times of 7, 10, 12, 15 and 20d: M(i) Lineweaver-Burke, M(ii) inversion, M(iii) Eadie-Hofstee linearisations (see Fig 5a to c).

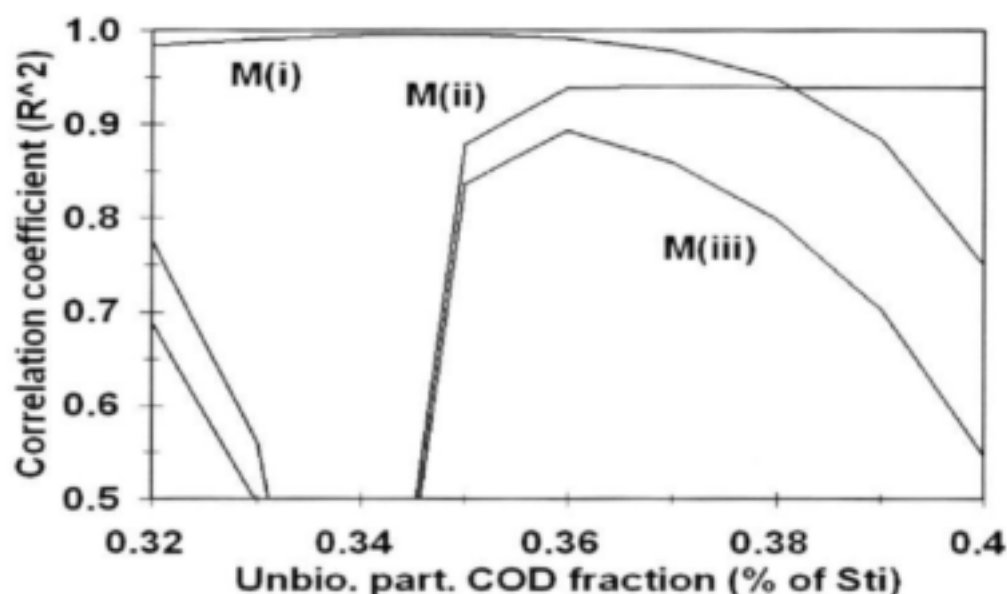


Fig 8. Correlation coefficients versus unbiodegradable particulate COD fraction for linear fits to surface mediated reaction hydrolysis kinetics, for the data of Izzet et al. (1992) at retention times of 7, 10, 12, 15 and 20d: M(i) Lineweaver-Burke, M(ii) inversion, M(iii) Eadie-Hofstee linearisations.

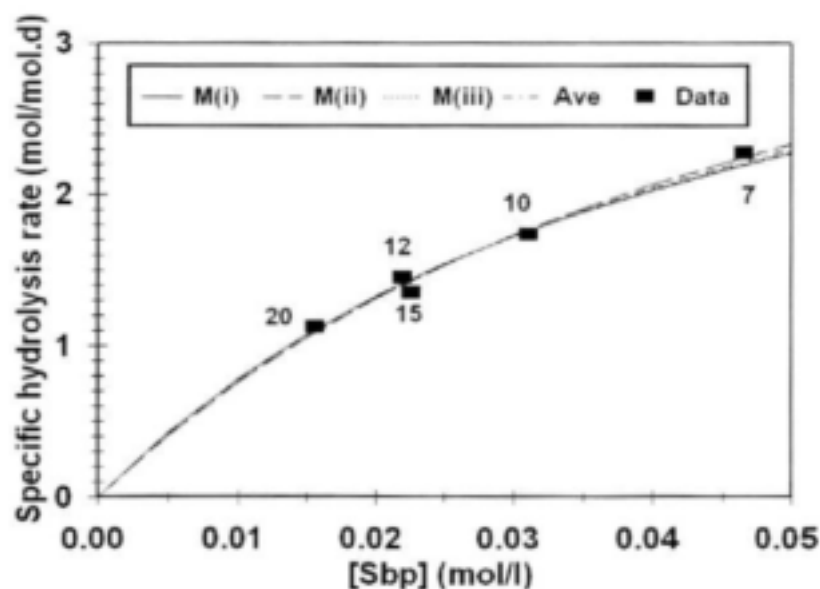


Fig 9. Monod specific hydrolysis rate versus biodegradable particulate organics (S_{bp} mole/l) for the Izzet et al. (1992) data at 7, 10, 12, 15 and 20d retention time: M(i) Lineweaver-Burke, M(ii) inversion, M(iii) Eadie-Hofstee linearisations, see Fig 5.

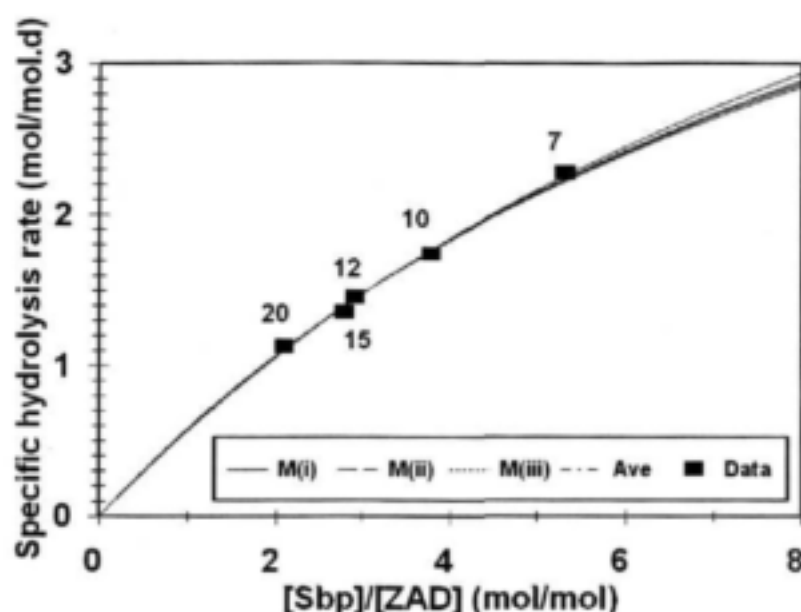


Fig 10. Surface mediated reaction specific hydrolysis rate versus biodegradable particulate organics (S_{bp} mole/t) to acidogen biomass (Z_{AD} mole/t) ratio for the Izzett *et al.* (1992) data at 7, 10, 12, 15 and 20d retention time: M(i) Lineweaver-Burke, M(ii) inversion, M(iii) Eadie-Hofstee linearisations, see Fig 5.

6.6.7 Selection of Hydrolysis Kinetics

In the section above, the data set of Izzett *et al.* was used to calibrate the constants for the four variations in hydrolysis kinetics, first order (Eq 8a), first order specific (Eq 8b), Monod (Eq 8c) and surface mediated reaction or Contois (Eq 8d). In this exercise, measures of variability were derived for the various kinetic expressions, namely coefficient of variation for the first two formulations and correlation coefficients (R^2) for the second two. Comparing the coefficients of variation (Fig 6), the minimum value for the first order kinetics is smaller than that for the first order specific, which would suggest that the former describes this data set marginally better. Comparing the R^2 values (Figs 7 and 8), the values for surface mediated reaction kinetics are higher than those for Monod kinetics, also suggesting that the former kinetics describes the data set marginally better. With regard to first order versus surface mediated reaction kinetics, the data set cannot provide guidance as to which is superior, i.e. both kinetic formulations with the appropriate constants provide equally acceptable descriptions of the hydrolysis process for the Izzett *et al.* data set. However, since this process is mediated by the acidogens, the surface mediated reaction kinetics which includes this organism group intuitively would appear more reasonable. Furthermore, this kinetic formulation has been applied with considerable success in activated sludge system models (e.g. ASM1, Henze *et al.*, 1987), in which the organisms act on the same biodegradable particulate substrate. Accordingly, the surface mediated reaction kinetics were accepted for incorporation in UCTADM1.

6.6.8 Refinement of Values for Sewage Sludge Composition, and Model Validation

Accepting the surface mediated reaction kinetics for hydrolysis and the estimates for the various constants (f_{PSup} , $k_{\text{max,HYD}}$ and $K_{\text{SS,HYD}}$) as determined above, the averages of the Izzett *et al.* measured influent parameters were set as input to AD model, with the influent weak acid/bases ($\text{NH}_3/\text{NH}_4^+$; HAc/Ac^- ; $\text{H}_2\text{CO}_3^*/\text{HCO}_3^-/\text{CO}_3^{2-}$; phosphorus not included as measurements not available). The model predictions for the effluent parameters and gas streams compositions and flows were compared with the corresponding measured averages at the different retention times. Only one part of the model required refinement (sewage sludge CHON composition) and this was then adjusted iteratively until the best correspondence between predicted and measured results at all retention times was obtained, to give $\text{C}_{3.5}\text{H}_7\text{O}_2\text{N}_{0.196}$; because the model is internally consistent and fixed by the kinetic and stoichiometric equations and determined constants, the only way a different effluent pH or gas composition can be predicted by the model is by changing the influent composition of the feed sludge. as noted above, independent validation was obtained by comparing the determined primary sludge composition with measured values. The model predicted parameters are compared with the corresponding measured values for all retention times in Fig 11 a to f. The predicted COD removal (Fig 11a) and gas composition (Fig 11c) correspond very well to those measured. The gas production (Fig 11b) is under predicted, because the model is based on 100% COD balance and the experimental data COD balances range from 107 to 109% (Table 6) - model calibration was on COD removal and hence the COD over recovery manifests in the gas production. The predicted effluent free and saline ammonia (FSA) concentration is generally higher than that measured, because the model is based on 100% N mass balance and the experimental mass balances were 91 to 99% (Table 6). By decreasing the N content of the influent organics (A in $\text{C}_x\text{H}_y\text{O}_z\text{N}_A$) by a small amount (5% to 0.186), the predicted effluent FSA could be made to closely match the measured values, but this would cause the influent organic N concentration to be in error. The effluent H_2CO_3^* alkalinity is over predicted, and this prediction can be improved by decreasing the N content of the organics or including some of the influent SCFA as propionic. However, both these would cause the predicted pH to decrease causing it to deviate from the measured value. Since insufficient experimental data are available to resolve this, these changes were not implemented. The experimentally measured pH, H_2CO_3^* alkalinity and p_{CO_2} show inconsistency in that these are not in equilibrium. Accepting the gas composition and H_2CO_3^* alkalinity as the most reliable measurements (CO_2 loss on sampling would influence pH but not H_2CO_3^* alkalinity, Loewenthal *et al.*, 1991), the equilibrium "corrected" pH was calculated. Both experimentally measured and "corrected" pH are shown in Fig 11f together with the predicted pH values; the predicted and "corrected" pH values correspond closely. Overall, accepting the margin for error in the experimental measurements, good correlation between measured and predicted parameters was obtained. More extensive simulations with the model of a wider range of experimental systems is required for further model validation.

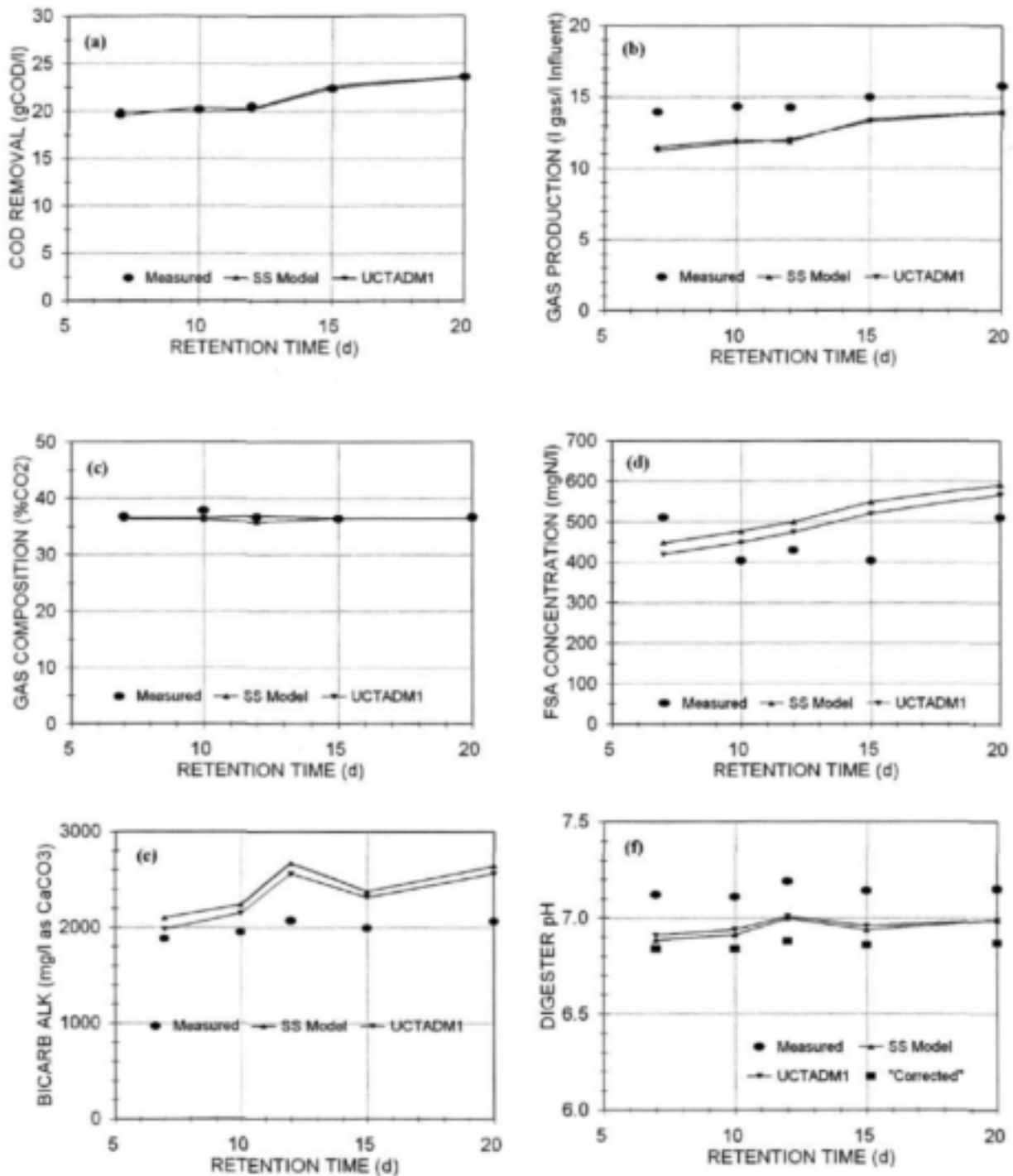


Fig 11: Comparison between kinetic simulation model (UCTADM1) predicted (lines) and measured (points) (a) COD removal, (b) gas production, (c) gas composition, (d) free and saline ammonia, (e) H_2CO_3^* alkalinity and (f) digester pH versus retention time for the Izzett et al. (1992) data set; also shown are the predictions of the steady state AD model presented in Chapter 7.

6.7 MODELLING DIGESTER FAILURE

The model applications above are all to stable anaerobic digesters operating at steady state. Under such conditions the rate limiting process is the hydrolysis, so that the other processes are essentially stoichiometric. This precluded assessment of the ability of the model to predict dynamic variations (except for hydrolysis). Very little quantitative information is available in the literature on the dynamics of anaerobic digestion. Accordingly, a theoretical simulation exercise was undertaken to evaluate dynamics, namely anaerobic digester failure. Acetoclastic methanogens are probably the most sensitive organisms in anaerobic digesters (Gujer and Zehnder, 1983) and so are strongly influenced by their surrounding environment. It is commonly accepted that failure of anaerobic digesters usually starts with the inhibition of acetoclastic methanogens. This can happen by an inhibitor or toxin in the influent, a shock load on the digester and/or a sudden drop in temperature because the acetoclastic methanogens (e.g. *Methanothrix soehngenii*) have been reported to show extreme temperature sensitivity (Zehnder *et al.*, 1980). Any of these factors will slow down or inhibit the growth rate of the acetoclastic methanogens, resulting in an increase in acetic acid concentration in the digester. This increase causes a decrease in pH. Both acetoclastic methanogens and hydrogenotrophic methanogens (e.g. *Methanobrevibacter arboriphilus*) are pH sensitive, the latter also showing some sensitivity to temperature changes. Thus, the drop in pH will slow down their rates of growth, resulting in a further increase in acetic acid and an increase in hydrogen partial pressure p_{H_2} . The increase in p_{H_2} affects the acidogenesis process as described above (Eqs 9 and 10) and instead of producing only acetic acid, propionic acid also is produced. The increase in p_{H_2} also slows the acetogenesis process (Eq 11) so that the propionic acid concentration increases, causing a further decrease in pH. Clearly, anaerobic digestion is a poised system and even a small disturbance in one of the methanogenic processes causes irreversible system collapse. Such a collapse, called digester souring, is characterized by increases in acetic and propionic acid concentrations and hydrogen partial pressure and decreases in pH and gas production. The digester pH should not drop below 6.6 to maintain methanogenesis processes uninhibited by pH (Moosbrugger *et al.*, 1993). The AD kinetic model was extended to include the above failure condition.

Inhibition of acetoclastic methanogens (process 7)

These organisms are inhibited by the hydrogen ion concentration (pH). To include this, the inhibition term commonly used with Monod kinetics of $(1 + I/K_i)$, where I is the aqueous inhibitor compound concentration and K_i the concentration at which the growth rate is half the normal rate (Batstone *et al.*, 2002), was introduced into the growth rate equation (Eq 12) i.e.:

$$r_{Z_{AM}} = \frac{\mu_{max,AM} [HAc]}{(K_{S,AM} + [HAc]) \left(1 + \frac{[H^+]}{K_{IAM}} \right)} [Z_{AM}] \quad (37)$$

where:

- K_{IAM} = Inhibition constant i.e. the hydrogen ion concentration at which the growth of acetoclastic methanogens is half the normal rate (mol/l)
- $[H^+]$ = Hydrogen ion concentration (mol/l) from which $pH = -\log (H^+)$

Inhibition of hydrogenotrophic methanogens (process 9)

Hydrogenotrophic methanogens function to keep the hydrogen partial pressure p_{H_2} low, and like the acetoclastic methanogens, they are also neutrophiles and are inhibited at pH values below 6.6 (Gujer and Zehnder, 1983, Zehnder and Wuhrmann, 1977). Hence, an inhibition term was also introduced into the growth rate equation for this organism group (Eq 13) i.e.:

$$r_{Z_{HM}} = \frac{\mu_{max, HM} [H_2]}{(K_{S, HM} + [H_2]) \left(1 + \frac{[H^+]}{K_{I, HM}} \right)} [Z_{HM}] \quad (38)$$

Inhibition of acetogens (process 5)

Due to the thermodynamics of the acetogenic process, the growth of acetogens decreases when the hydrogen partial pressure p_{H_2} increases. This reduces the rate of propionic acid conversion to acetic acid and hydrogen. This reduction in growth rate at elevated p_{H_2} has already been included in the acetogen growth process (Eq 11).

The inhibition constants for the above are listed in Table 7.

Table 7: Inhibition constants for the different organism groups in anaerobic digestion.

Organism group	Process	Compound	Symbol	Value	Units
Acetoclastic methanogens	D7	Hydrogen ion	$K_{I, AM}$	1.15×10^{-6}	mol/l
Hydrogenotrophic methanogens	D9	Hydrogen ion	$K_{I, HM}$	530×10^{-6}	mol/l
Acetogens	D5	Hydrogen gas	$K_{I, AC}$	0.45×10^{-6}	mol/l

Gas expulsion from aqueous to head space gas phases

In the implementation above of the kinetic model in Aquasim, the exchange of gases between the aqueous and gas (head-space) phases was not specifically modelled; the dissolved and non-dissolved gases were accepted to be part of the bulk liquid and hence flow out of the digester with the effluent, which is equivalent to a zero volume head-space. For steady state conditions this is acceptable, because the molar gas composition remains constant with time. Under digester failure conditions, the molar composition of the gas phase may not remain constant with time and hence have an influence on the dissolved gas concentrations. To ensure a more realistic AD system under failure conditions, a head-space compartment was added to the model in Aquasim, with a diffusive link to the reactor aqueous phase. The dissolved gaseous compounds CO_2 (as $H_2CO_3^*$), CH_4 and H_2 diffuse from the aqueous phase to the gas phase in the head-space, in accordance with the usual diffusion gas exchange equations (Batstone *et al.*, 2002), i.e. the gas exchange equations are applied across the diffusive link. In such an implementation, due cognizance must be taken of the different forms of the Henry's law constant and its dimensions. In Aquasim, the diffusive link is modelled as:

$$r_{gas} = K_{LA, gas} (K_{c, gas} C_{h, gas} - C_{d, gas}) \quad \text{mol gas/d} \quad (39)$$

where:

- r_{gas} = Rate of gas diffusion across head-space - bioreactor link
- $K_{LA, gas}$ = Specific gas mass transfer rate (/d)
- $K_{c, gas}$ = Constant for the phase change from liquid to gas
- = $K_{H, gas}$ or $1/K_{H, gas}$ depending on the form of the Henry's law constant
- $K_{H, gas}$ = **Dimensionless** Henry's law constant for the gas
- $C_{d, gas}$ = Dissolved (aqueous) gas concentration in reactor liquid (mol/l)
- $C_{h, gas}$ = Concentration of gas in the headspace (mol/l)
- p_{gas} = Partial pressure of the gas
- = $C_{h, gas} \times RT_k$
- R = Universal gas constant = 8.206×10^{-2} (l.atm)/(mol.K)

T_k = Temperature in Kelvin = (T in °C + 273).

In modelling this gas exchange ammonia was omitted, because with its high pK value (9.1), negligibly little diffuses into the gas phase for pH < 8. The partial pressure of the three gases were calculated from the head-space gas concentrations (C_{hgas}) using Dalton's law of partial pressures ($p_{\text{gas}} = [C_{\text{hgas}}] RT$) and the total gas pressure in head-space (P_{tot}) is sum of the partial pressures. The vent gas flow rate from the head-space (q_{gas}) was calculated from a proportional control loop with respect to atmospheric pressure (P_{atm}), which was accepted to be 101.3 kPa, viz.

$$q_{\text{gas}} = K_p \frac{(P_{\text{tot}} - P_{\text{atm}})}{P_{\text{atm}}} V_h \quad \text{l/d} \quad (40)$$

where:

K_p = Gas vent rate constant (/d)

V_h = Volume of head space (1ℓ for Izzett *et al.* digesters)

One constant in Eq 39 has an important influence on the dynamics of the head-space gas concentrations, i.e. the specific gas mass transfer rate ($K_{\text{La gas}}$). If this rate is very rapid, then the head-space concentrations respond very quickly to the dissolved gas concentrations. The actual rate would be situation specific, depending on the mixing regime in the anaerobic digester, and would be faster with gas recirculation mixing than with mechanical mixing. Since no guidance in the literature could be found for this value, a fast rate of 1000 /d was selected for all $K_{\text{La gas}}$ so that the head-space gas concentrations rapidly respond to the dissolved gas concentrations. To provide a sense of the magnitude of this value, Musvoto *et al.* (2000a) observed K_{La} values between 200 and 600 /d for CO₂ stripping in their anaerobic digester liquor aeration batch tests. The values for this constant requires further investigation.

Simulating digester failure

With the model set up as described, digester failure was simulated by halving the maximum specific growth rate of the acetoclastic methanogens ($\mu_{\text{max,AM}}$) for three days (72h) in the middle of a 60 day simulation. The anaerobic digester at 15d retention time in Table 6 was simulated for sufficient time to ensure steady state - very low effluent SCFA concentrations and hydrogen partial pressure were obtained and the pH was about 6.9. Failure was then artificially induced by temporarily halving the $\mu_{\text{max,AM}}$ value for the period of 3 days, and thereafter restoring it to its original value.

Immediately after halving $\mu_{\text{max,AM}}$, the acetic acid concentration increased sharply to reach a maximum of 0.14 mol/ℓ (8 400 mgHAc/ℓ) after 15h. This increase caused the pH to decrease from 6.9 to 4.5 in 4h. The reduction in pH caused (i) the acetoclastic methanogen growth rate to reduce further, contributing to the sharp increase in acetic acid concentration and (ii) the hydrogenotrophic methanogen growth rate to reduce causing the hydrogen concentration to increase to a maximum of 0.00012 mol/ℓ (0.24 mgH₂/ℓ) after 22h. The increased H₂ concentration raised the p_{H_2} which caused the acidogens to produce also propionic acid, which increased from a very low concentration at around 5h to a maximum concentration of 0.15 mol/ℓ (11 100 mgHPr/ℓ) at 55h. Immediately after halving $\mu_{\text{max,AM}}$ of the acetoclastic methanogens, their concentration decreased sharply to reach 10% of its initial value after 15h. The hydrogenotrophic methanogen organism concentration also decreased rapidly after about 4h to less than 10% of its initial value after 40h. Concomitantly with the decrease in methanogen biomass concentrations, the CO₂ and CH₄ gas production rates decreased rapidly, reaching 10% of their original rates at 20 and 28h respectively. Restoring the $\mu_{\text{max,AM}}$ of the acetoclastic methanogens to its original rate after 72h had no affect on the results indicating that the failure was irreversible. Also, simulating this digester failure situation with and without the head-space gas

dynamics made negligibly little difference to the results.

This simulation of AD failure by halving temporarily the acetoclastic methanogen growth rate indicates that (i) the AD model correctly reflects the qualitatively observed digester failure behaviour and (ii) even a short (3 days) inhibition of these species causes irreversible failure ($\text{pH} < 5.5$) within 4h. The % decrease in acetoclastic methanogen growth rate from which the digester can recover without intervention was not determined. Because the conceptual AD model (Fig 2) is similar to that developed for UASB digesters (Sam-Soon *et al.*, 1991), the simulation model shows the same progression to failure as the lower bed volume of an upflow anaerobic sludge bed (UASB) digester, except that in the UASB system, collapse of the methanogens does not take place because the pH is maintained above 6.6 in the high SCFA concentration region (Moosbrugger *et al.*, 1993). From the UASB digester behaviour and practical experience, anaerobic digestion failure due to a reduction in methanogen activity can be averted if the pH can be maintained above 6.6. This may require dosing lime which needs to be carefully controlled to avoid calcium carbonate precipitation (Capri and Marais, 1974). Digester failure and recovery is a dynamic modelling problem and will be examined in further research.

6.8 CONCLUSIONS

An integrated two phase (aqueous-gas) mixed weak acid/base chemistry and biological processes anaerobic digester kinetic model for sewage sludge is presented. The salient features of this model are:

- (1) As an alternative to characterizing the sewage sludge feed into carbohydrates, proteins and lipids, as is done in IWA ADM1 (Batstone *et al.*, 2002), it is characterized in terms of total COD, its particulate unbiodegradable COD fraction (f_{psup}), the short chain fatty acid (SCFA) COD and the CHON content of the particulate organics, i.e. X, Y, Z and A in $\text{C}_x\text{H}_y\text{O}_z\text{N}_a$. This approach characterizes the sludge in terms of measurable parameters and allows COD, C and N mass balances to be set up over the anaerobic digestion system. With this approach, the interactions between the biological processes and weak acid/base chemistry could be correctly predicted for stable steady state operation of anaerobic digesters. While not validated for dynamic flow and load conditions, the model has the capability of being applied to such conditions.
- The COD, C and N mass balances 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 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. All the kinetic and stoichiometric constants in the model, except those for hydrolysis, were obtained from the literature so that model calibration 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 $\text{C}_x\text{H}_y\text{O}_z\text{N}_a$.
- Interactively with determining the hydrolysis kinetics ((4) below), the unbiodegradable particulate fraction of the sewage sludge was estimated at 0.32 - 0.36 for the sewage sludge fed to the mesophilic anaerobic digesters of Izzett *et al.* (1992) ranging over 7 - 20 days retention time, depending on the type of hydrolysis kinetics selected. These values are very close to the value of 0.36 determined by O'Rourke (1968) and the values estimated from a COD mass balance around the primary settling tank from typical raw and settled wastewater characteristics (0.32 - 0.36 for COD removals of 40 - 35%).
- (4) Various formulations for the hydrolysis rate of sewage sludge particulate biodegradable organics were evaluated, see below. Surface mediated reaction (Contois) kinetics similar to that used by Dold *et al.* (1980) and IWA Activated Sludge Model 1 (Henze *et al.*, 1987) for slowly

biodegradable organics in activated sludge systems, were selected. Once calibrated against the Izzett *et al.* (1992) data, this formulation showed the required sensitivity of gas production and unfiltered effluent COD concentration to variation in retention time, without changing the constants in the hydrolysis rate equation.

- (5) From the influent COD, organic N and VSS measurements of Izzett *et al.*, the stoichiometric formulation of the influent sewage sludge was estimated to be $C_{3.4}H_7O_2N_{0.192}$. With the sludge biodegradability and hydrolysis process rate defined, to match the anaerobic digester performance data of Izzett *et al.* (1992) ranging over 7 - 20 days retention time, (i.e. effluent COD, TKN, FSA, SCFA, $H_2CO_3^*$ Alk, pH, gaseous CO_2 and CH_4 production and partial pressures), the sewage sludge composition was refined to $C_{3.5}H_7O_2N_{0.196}$ to conform to the COD, C and N mass balances of the model. This formulation was confirmed with primary sludge CHON composition tests, the average of which was $C_{3.65}H_7O_{1.97}N_{0.19}$. The model predicted CHON content and molar mass of the PS was therefore 95.9%, 100%, 98.5%, 94.5% and 98.7% of the measured values. This provides persuasive validation of the UCTADM1 model.
- (6) Validation of the AD model under steady state conditions validates only its stoichiometry and the system rate limiting process, which is hydrolysis. However, the model, which includes the influence of high hydrogen partial pressure on the acidogenesis and acetogenesis processes, showed the expected sensitivity to a digester upset initiated by temporary inhibition of the acetoclastic methanogens, which is the usual cause in practise. The model demonstrated that even a brief inhibition of this organism group causes an irreversible failure of the digester (pH < 6.6).

The proposed surface mediated reaction (or Contois kinetic) hydrolysis rate equation reproduced the observed change in biodegradable particulate COD acidified versus retention time with the same kinetic constants. Based on the Izzett *et al.* anaerobic digester data, a Monod type hydrolysis rate equation also showed consistency of constants over 7 to 20 d retention time, but simple first order and first order specific hydrolysis rate equations yielded different rate constants at different retention times. However, by changing the unbiodegradable particulate COD fraction of the sewage sludge (f_{psup}) the fit of both the first order and first order specific hydrolysis rate equations to the experimental data of Izzett *et al.* (1992) could be significantly improved (with concomitant deterioration in the fit with Contois and Monod kinetics). Hence, the Izzett *et al.* anaerobic digester data set is too limited to make a definitive conclusion as to which is the best equation to model the hydrolysis process, and what the best value for f_{psup} is. Intuitively and based on its widespread application in activated sludge systems acting on the same biodegradable particulates, the surface mediated reaction (Contois) kinetics has been selected for hydrolysis. Experimental work to *inter alia* refine the modelling of the hydrolysis process is currently being conducted on mesophilic methanogenic and sulphidogenic anaerobic digester systems (Ristow *et al.*, 2004a,b,c).

The characterisation of sewage sludge in terms of its CHON(P) contents appears a sound approach. While testing primary sludges for the UCTADM1 model validation, a range of other sewage sludges were also tested, such as waste activated, anaerobic digested and mixtures of primary and waste activated. From the tests done to date, it seems that the CHON contents of sludges are consistent and grouped approximately in conformity with type. It appears likely, therefore, that typical CHON(P) contents of the different sludges may be selected, and that the standard characterisation tests such as COD, TKN and VSS, are sufficiently discerning and accurate for modelling AD of sewage sludges. Measurement of sewage sludge composition is continuing and its effect on digester pH and gas composition will be evaluated when more information has been collected.

The successful integration in a kinetic way of the two phase mixed weak acid/base chemistry and biological processes of AD has provided a sound basis for further model development. Still to be included in the AD model 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 quantitative link between feed sludge composition and mineral precipitation problems in digesters.

The integrated physical, chemical and biological processes kinetic modelling approach, applied in this series of report to biological N removal activated sludge systems and anaerobic digesters, has opened the way to develop a kinetic simulation model for the entire wastewater treatment plant on a materials mass balance and continuity basis. The plant would comprise selected unit operations such as primary settling, biological N and/or P removal activated sludge and anaerobic or aerobic digestion of waste sludges. With such a model, the impact of wastewater characteristics and type and upstream unit operations performance on downstream unit operations, and the recycling of liquors from downstream unit operations to upstream unit operations, can be assessed for improved and more economical design and operation.

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CHAPTER 7

A STEADY STATE MODEL FOR ANAEROBIC DIGESTION OF SEWAGE SLUDGES

7.1 INTRODUCTION

In Chapter 5 an integrated two phase (aqueous-gas) mixed weak acid base chemical, physical and biological processes kinetic model for anaerobic digestion (AD) of sewage sludge was developed. The COD, C and N mass balances and continuity basis of this model fixes quantitatively, via the interrelated chemical, physical and biological processes, the relationship between all the compounds of the system. Thus for a given sewage sludge COD removal 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 solids (and dissolved) constituents. In this steady state model, the sewage sludge feed is characterized in terms of total COD, its particulate unbiodegradable COD fraction ($f_{\text{ps-up}}$), the short chain fatty acid (SCFA) COD and the CHON content, i.e. X, Y, Z and A in $\text{C}_x\text{H}_y\text{O}_z\text{N}_a$ of the particulate organics. This approach characterizes the sludge in terms of measurable parameters in conformity with the COD, C and N mass balances approach. With this approach, the interactions between the biological processes and weak acid/base chemistry could be correctly predicted for stable steady state operation of anaerobic digesters. While not validated for dynamic flow and load conditions, the model has the capability of being applied to such conditions. In this chapter this complex dynamic simulation model is simplified to a steady state one for integration into a steady state mass balance model of the whole wastewater treatment plant (see Chapter 4).

Steady state models are based on the slowest process kinetic rate that governs the overall behaviour of the system and relates this process rate to the system design and operating parameters. Therefore, steady state models allow the system design and operating parameters, such as reactor volume and recycle ratios, to be estimated reasonably simply and quickly from system performance criteria specified for the design, such as effluent quality. Once approximate design and operating parameters are known, these can serve as input to the more complex simulation models to investigate dynamic behaviour of the system and refine the design and operating parameters. A steady state AD model is therefore useful to (i) estimate retention time, reactor volume, gas production and composition for a required system performance like COD (or VSS) removal, (ii) investigate the sensitivity of the system performance to the design and operation parameters, (iii) provide a basis for cross-checking simulation model results, and (iv) estimate product stream concentrations for design of down- (or up-) stream unit operations of the wastewater treatment plant.

Anaerobic digestion of organics require a consortium of four organism groups (see Chapter 5) viz. (i) acidogens, which convert complex organics to SCFA acetic and propionic (HAc, HPr), carbon dioxide (CO_2) and hydrogen (H_2), (ii) acetogens, which convert HPr to HAc and H_2 , (ii) acetoclastic methanogens, which convert HAc to CO_2 and methane (CH_4) and (iv) hydrogenotrophic methanogens, which convert H_2 and CO_2 to CH_4 and water. The two methanogenic groups are very sensitive to pH and so the acetogens and acetoclastic methanogens must utilize the HAc and HPr respectively as soon as they are produced to maintain a near neutral pH for optimal operation. Because the hydrolysis/acidogenesis process mediated by the acidogens ((i) above), is the slowest process in the system, high SCFA concentrations and therefore low pH, arise only under unstable and digester upset operating conditions caused by a shock load in organics, a rapid decrease in temperature or a methanogen inhibitor in the influent. A steady state model, therefore, need only consider the kinetics

of this process. The processes following hydrolysis/acidogenesis, being much more rapid (usually), can be accepted to reach completion. This implies that in stable AD systems the intermediate products of the processes following after hydrolysis/acidogenesis such as SCFAs and H_2 , do not build up in the system and their concentrations are sufficiently low to be considered negligible. Consequently, in the steady state AD model, the products of hydrolysis/acidogenesis can be dealt with stoichiometrically and converted to digester end products. In effect, it can be assumed that the hydrolysis/ acidogenesis process generates directly the digester end-products biomass, CH_4 , CO_2 and water. Thus the steady state anaerobic digester model developed below considers two aspects, (i) the kinetics of the hydrolysis/acidogenesis process and (ii) stoichiometric conversion of the products from (i) to digester end-products.

7.2 HYDROLYSIS/ACIDOGENESIS KINETICS

7.2.1 Hydrolysis Rate Equations

Since the hydrolysis/acidogenesis process is the slowest one in the sewage sludge anaerobic digester and does not reach completion within the normal range of the principal digester design parameter of hydraulic retention time, a kinetic expression describing this process rate is required for the steady state model. In Chapter 5 four kinetic equations for this process were considered, viz. (1) first order with respect to the residual biodegradable particulate organic (COD) concentration S_{bp} , (2) first order with respect to S_{bp} and the acidogen biomass concentration (Z_{AD}) which mediates this process, (3) Monod kinetics and (4) saturation (or Contois) kinetics (see Eqs 1 to 4 in Table 1). All these equations have been used to model various biological processes for many years; the first to describe the hydrolysis/acidogenesis of sewage sludge solids in AD (e.g. Henze and Harremoës, 1983, Bryers, 1985), the second for modelling the conversion of readily biodegradable organics to short chain fatty acids in the anaerobic reactor of biological P removal systems (e.g. Wentzel et al., 1985), and the last two for the utilization of soluble readily and particulate slowly biodegradable organics respectively in activated sludge models (Dold et al., 1980; Henze et al., 1987). From Chapter 5 it can be seen that it cannot be determined which equation was superior for modelling hydrolysis/acidogenesis process in AD because for the experimental data evaluated, the unbiodegradable particulate COD fraction (f_{PS-up}) of the sewage sludge (primary+humus) organics was not sufficiently well known - by changing f_{PS-up} in a fairly narrow range from 0.32 to 0.36, each of the equations gave a better correlation coefficient than the other equations at different specific f_{PS-up} values. It was accepted that the saturation kinetics for the integrated model (UCTADM1) because this equation (i) gave a similar f_{PS-up} value (0.36) to O'Rourke (1967) (0.34) working with AD of "pure" primary sludge (no trickling filter humus or waste activated sludge) and (ii) has been successfully used to model hydrolysis/utilization of the same particulate biodegradable organics in activated sludge kinetic models. In the evaluation of the four hydrolysis/acidogenesis equations in Chapter 5, the effect of the acidogen (Z_{AD}) and acetoclastic methanogen (Z_{AM}) biomass formation was included, because these two organism groups have the highest yield coefficients and so contribute significantly to the effluent organics (COD) concentration and decrease the gas production.

Table 1: Steady state anaerobic digester kinetic equations for the residual biodegradable particulate organics concentration (S_{bp}), acidogen biomass concentration (Z_{AD}), unbiodegradable organics concentration (S_{up}) and methane production in gCOD/l influent (S_m) for four different hydrolysis kinetic rate

Hydrolysis kinetic equation	1 st order with respect to (wrt) S_{bp}	1 st order specific (wrt to S_{bp} & Z_{AD})	Monod kinetics	Saturation kinetics
Hydrolysis rate r_h gCOD/(l.d)	$r_h = K_h S_{bp} \dots\dots\dots 1$	$r_h = K_H S_{bp} Z_{AD} \dots\dots 2$	$r_h = \frac{K_m S_{bp}}{(K_s + S_{bp})} Z_{AD} \dots\dots 3$	$r_h = \frac{K_M (S_{bp}/Z_{AD})}{[K_S + (S_{bp}/Z_{AD})]} Z_{AD} \dots\dots 4$
Residual biodegradable organics concentration gCOD/l S_{bp}	$S_{bp} = \frac{S_{bp0}}{\left[1 + K_h R \frac{[1 + b_{AD} R (1 - Y_{AD})]}{(1 + b_{AD} R)}\right]}$	$S_{bp} = \frac{1/R + b_{AD}}{Y_{AD} K_H}$	$S_{bp} = \frac{K_s (1/R + b_{AD})}{Y_{AD} K_m - (1/R + b_{AD})}$	$S_{bp} = \frac{S_{bp0}}{\left[1 + \frac{[Y_{AD} K_M - (1/R + b_{AD})] [1 + b_{AD} R (1 - Y_{AD})]}{Y_{AD} K_S (1/R + b_{AD})}\right]}$
Acidogen biomass concentration Z_{AD} gCOD/l	$Z_{AD} = \frac{Y_{AD} (S_{bp0} - S_{bp})}{[1 + b_{AD} R (1 - Y_{AD})]}$			
Unbiodegradable organics concentration S_{up} gCOD/l	$S_{up} = S_{up0}$			
Methane production concentration S_m gCOD/l	$S_m = (1 - Y_{AD}) R r_h$			
Kinetic constants (Izzett et al., 1992 data)	$K_h = 0.515 \pm 0.041$ /d $*K_h = 0.481 \pm 0.040$ /d	$K_H = 0.322 \pm 0.047$ $*K_H = 0.379 \pm 0.056$ l/(gCOD biomass.d)	$K_m = 3.34$ (*3.72) gCOD organics/(gCOD biomass.d) $K_s = 6.76$ (*6.38) gCOD/l	$K_M = 5.27$ (*5.58) gCOD organics/(gCOD biomass.d); $K_S = 7.98$ (*8.89) gCOD/l
COD balance	$S_{in} = S_m + S_{up} + S_{bp} + Z_{AD} + S_{up} + S_m$; $S_{in} = \text{COD in}; S_m = S_{bp} + Z_{AD} + S_{up} = \text{COD out as sludge solids}; S_m = \text{COD out as methane gas}$			

equations. Kinetic constants of the four hydrolysis equations for unbiodegradable particulate COD fraction ($f_{PS,up}$) = 0.36.

*Determined with the more complex hydrolysis model of Sötemann et al. (2005a) at $f_{PS,up}$ = 0.36.

In steady state models, detail is not required - in fact, it is undesirable. From the simulation model, sufficient accuracy for a steady state model is obtained by selecting any of the four hydrolysis/acidogenesis equations and increasing the acidogen biomass yield to include the acetoclastic methanogens. The acidogens have the highest yield coefficient ($Y_{AC}=0.089$ gCOD biomass/gCOD substrate hydrolysed) and make up more than 77% of the total biomass formed. Increasing Y_{AD} from 0.089 to 0.113 would very closely take into account the biomass formation of the other organism groups (see Fig 4, Chapter 5). A consequence of accepting this approach is that in kinetic rate formulations that include the acidogen biomass concentration (first order specific, Monod and saturation), the specific rate constants in the steady state model here will be lower compared with the corresponding values in the dynamic model discussed in Chapter 5 but the predicted performances (e.g. %COD removal) will be the same.

The steady state model will be derived using the COD to quantify the organics and biomass concentrations and the Monod equation for the hydrolysis/acidogenesis rate. However, the model equations for all four hydrolysis kinetics rate expressions have been derived and are summarized in Table 1.

7.3 STEADY STATE MODEL DEVELOPMENT - HYDROLYSIS KINETICS

Consider a flow through digester of volume V and influent flow Q giving a hydraulic retention time or sludge age of $R = V/Q$ days (Fig 1).

Defining the unbiodegradable fraction of the influent total particulate sewage sludge COD (S_{ti}) as $f_{PS'up}$, then the particulate biodegradable (S_{bpi}) and unbiodegradable (S_{upi}) COD concentrations in the influent are (see Fig 2)

$$S_{bpi} = (1 - f_{PS'up}) S_{ti} - S_{bsai} \quad (5)$$

$$S_{upi} = f_{PS'up} S_{ti} \quad (6)$$

where

S_{bsai} = Influent volatile fatty acid (VFA) concentration (mgCOD/l)

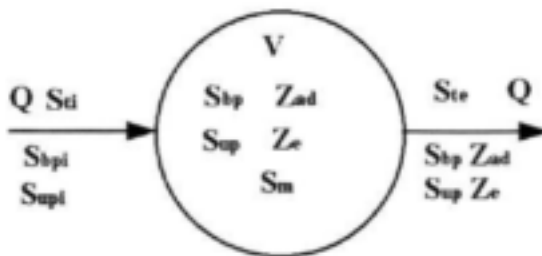


Fig 1: Schematic diagram of the flow through anaerobic digester of retention time $R = V/Q$ showing symbols used in the steady state AD model.

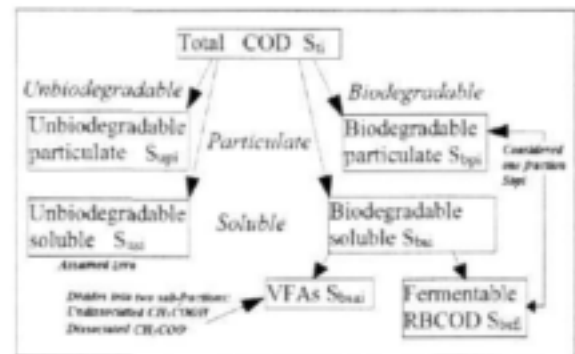


Fig 2: Influent primary sludge COD fractionation for the steady state anaerobic digestion model.

Sewage sludge comprises two additional dissolved COD fractions, i.e. the unbiodegradable soluble COD (S_{usi}) and the fermentable (non-VFA) readily biodegradable soluble COD (S_{bsfi}) (Fig 2). The S_{usi} is very low in relation to the S_{upi} and so can be assumed zero for the purposes of this steady state model. The S_{bsfi} goes through the same hydrolysis/acidogenesis processes as the particulate

biodegradable COD (S_{bpi}) and so is included with the S_{bpi} . Because the steady state model is based on the hydrolysis process as stated in Eq 5, the S_{bmi} is not included with the COD passing through this process. However, the S_{bmi} does generate methane and CO_2 (but negligible sludge mass) mediated by the two methanogenic species. Hence S_{bmi} can be excluded in the hydrolysis part of the model but needs to be included in the stoichiometry part of the model due to its effect on gas composition and digester pH. Hence S_d is given by $S_{api} + S_{bpi} + S_{bmi}$ (Fig 2).

The net acidogen growth rate from the hydrolysis/acidogenesis and endogenous processes is given by

$$\frac{dZ_{AD}}{dt} = Y_{AD} r_h - b_{AD} Z_{AD}$$

where r_h = volumetric hydrolysis/acidogenesis rate in gCOD/(l.d) (Eqs 1 to 4 in Table 1)

Y_{AD} = pseudo acidogen yield coefficient (gCOD biomass/ gCOD organics hydrolysed)

b_{AD} = acidogen endogenous respiration rate (/d).

The steady state model is derived by applying the general mass balance equation (Eq 7) over the system (Fig 1) to the four system variable compound concentrations (all gCOD/l), i.e. S_{bpi} , S_{api} , Z_{AD} and methane (S_m) concentrations. For the flow through system, the effluent compound concentrations are equal to the reactor concentrations. For example, the mass balance for S_{bpi} over a time interval dt is

$$\left[\begin{array}{c} \text{Mass} \\ \text{change} \\ \text{in system} \end{array} \right] = \left[\begin{array}{c} \text{Mass flow} \\ \text{into} \\ \text{system} \end{array} \right] - \left[\begin{array}{c} \text{Mass flow} \\ \text{out of} \\ \text{system} \end{array} \right] - \left[\begin{array}{c} \text{Mass loss} \\ \text{by bio-} \\ \text{process} \end{array} \right] + \left[\begin{array}{c} \text{Mass gain} \\ \text{by bio-} \\ \text{process} \end{array} \right] \quad (7)$$

$$dS_{bpi} V = +Q S_{bpi} dt - Q S_{bpi} dt - r_h V dt + b_{AD} Z_{AD} V dt \quad (8)$$

In Eq 8, the first and second terms on the right hand side are the biodegradable organics flowing in and out of the digester, and the third and fourth terms the decrease in biodegradable organics due to hydrolysis and the increase from the biodegradable part of the acidogen biomass that dies. Dividing Eq 8 through by $V dt$ yields,

$$\frac{dS_{bpi}}{dt} = +\frac{S_{bpi} - S_{bpi}}{R} - r_h + b_{AD} Z_{AD} \text{ gCOD/(l.d)} \quad (9)$$

Similarly the mass balance on acidogen biomass concentration (Z_{AD}) yields

$$dZ_{AD} V = +0 - Q Z_{AD} dt + Y_{AD} r_h V dt - b_{AD} Z_{AD} V dt$$

Again dividing through by $V dt$ yields

$$\frac{dZ_{AD}}{dt} = -\frac{Z_{AD}}{R} + Y_{AD} r_h - b_{AD} Z_{AD} \quad (10)$$

At steady state the transient dZ_{AD}/dt in Eq 10 = 0 and solving for the hydrolysis rate r_h yields,

$$r_h = \frac{Z_{AD}}{Y_{AD}} \left(\frac{1}{R} + b_{AD} \right) \text{ gCOD/(l.d)} \quad (11)$$

Setting Eq 9 = 0 for steady state and solving for r_h yields,

$$r_h = \frac{S_{bpt} - S_{bp}}{R} + b_{AD} Z_{AD} \quad \text{gCOD}/(\ell \cdot \text{d}) \quad (12)$$

Then substituting Eq 11 for r_h into Eq 12 and solving for Z_{AD} yields,

$$Z_{AD} = \frac{Y_{AD}(S_{bpt} - S_{bp})}{[1 + b_{AD}R(1 - Y_{AD})]} \quad \text{gCOD}/\ell \quad (13)$$

Equation 13 seems to indicate that the acidogen biomass concentration (Z_{AD}) is independent of the hydrolysis kinetic rate (and hence its formulation) because r_h does not appear in it. However, it is implicitly dependent on r_h because S_{bp} appears in the equation and S_{bp} is dependent on the hydrolysis kinetic rate. Equation 13 does show that once S_{bp} is known, then Z_{AD} can be calculated for any hydrolysis rate equation.

Substituting the Monod equation (Eq 3 in Table 1) for r_h into Eq 11 and solving for S_{bp} yields

$$S_{bp} = \frac{K_s(1/R + b_{AD})}{Y_{AD}K_m - (1/R + b_{AD})} \quad \text{gCOD}/\ell \quad (14)$$

Ignoring as negligible the formation of unbiodegradable organics from the acidogens that die (i.e. endogenous residue is zero), the total unbiodegradable organics concentration in the effluent (S_{up}) is equal to the influent, i.e.

$$S_{up} = S_{upl} \quad \text{gCOD}/\ell \quad (15)$$

The methane production in COD units is directly related to the rate of hydrolysis of biodegradable organics. If the methane concentration in the effluent in COD units is S_m , a mass balance on S_m yields

$$dS_m V = 0 - Q S_m dt + (1 - Y_{AD}) r_h V dt \quad (16)$$

where S_m = methane concentration in the effluent in gCOD/ ℓ (if it were dissolved)

Dividing Eq 16 through by $V dt$ and setting $dS_m/dt = 0$ and solving for S_m yields

$$S_m = (1 - Y_{AD}) R r_h \quad \text{gCOD}/\ell \quad (17)$$

Because methane has a COD 64 gCOD/mol and a gas volume at ambient temperature 20°C of 22.4 (293/273) = 24.0 ℓ /mole, the methane gas production Q_m is

$$Q_m = (1 - Y_{AD}) R r_h 24.0/64 \quad (\ell \text{ methane}/\text{d}) / (\ell \text{ influent flow}/\text{d}) \quad (18)$$

The partial pressure of CO_2 in the gas (p_{CO_2}) and the CO_2 composition of the gas are numerically equal. Hence, if the partial pressure of CO_2 or the CO_2 gas composition are known (in atmospheres, or volume or mole fractions), then the total gas production at 20°C (Q_{gas}) is

$$Q_{\text{gas}} = \frac{Q_m}{(1 - p_{\text{CO}_2})} = \frac{(1 - Y_{AD}) R r_h 24.0}{(1 - p_{\text{CO}_2}) 64} \quad (\ell \text{ gas}/\text{d}) / (\ell \text{ influent flow}/\text{d}) \quad (19)$$

A COD mass balance over the digester system (Fig 1) yields

$$S_{ti} = S_{te} + S_m = S_{bpi} + Z_{AD} + S_{up} + S_m \quad (20)$$

Equation 20 shows that COD exits the digester only as sludge mass in the effluent (S_{te}) and as methane gas (S_m). Substituting Eq 13 with S_{bp} as its subject for S_{bpi} , Eq 15 for S_{up} , Eq 17 for S_m and Eq 3 for r_h into Eq 20 yields,

$$S_{ti} = S_{bpi} - \frac{Z_{AD}}{Y_{AD}}[1 + b_{AD}R(1 - Y_{AD})] + Z_{AD} + S_{up} + (1 - Y_{AD})R \frac{K_m S_{bp}}{K_s + S_{bp}} Z_{AD}$$

which on simplifying gives Eq 14 for S_{bp} , and therefore proves the input and output COD masses balance exactly.

The total (S_{tr}) and biodegradable (S_{bpr}) COD removals and methane production (S_m) are given by

$$S_{tr} = S_{ti} - S_{te} = S_m \quad (21)$$

$$S_{bpr} = S_{bpi} - S_{bp} \quad (22)$$

The equations for the biodegradable organics (S_{bp}), acidogen (Z_{AD}), unbiodegradable (S_{up}) and methane (S_m) concentrations for all four hydrolysis rate formulations are given in Table 1.

7.4 CALIBRATION OF HYDROLYSIS KINETICS

The equations developed above were evaluated and calibrated against data from steady state anaerobic digesters.

7.4.1 Calculating the Effluent COD Concentration (S_{te})

From the steady state COD mass balance equation (Eq 20), the effluent total particulate COD concentration, S_{te} is given by

$$S_{te} = S_{up} + S_{bp} + Z_{AD} \quad \text{gCOD/l} \quad (23)$$

Substituting Eq 15 for S_{up} , Eq 6 for S_{bpi} and Eq 13 for Z_{AD} in Eq 23 yields,

$$S_{te} = f_{PS'up} S_{ti} + S_{bp} + \frac{Y_{AD}[(1 - f_{PS'up})S_{ti} - S_{bp}]}{[1 + b_{AD}R(1 - Y_{AD})]} \quad \text{gCOD/l} \quad (24)$$

Solving Eq 24 for S_{bp} yields,

$$S_{bp} = \frac{S_{ti}[f_{PS'up} + E(1 - f_{PS'up})] - S_{te}}{[E - 1]} \quad \text{gCOD/l} \quad (25a)$$

$$\text{where } E = \frac{Y_{AD}}{1 + b_{AD}R(1 - Y_{AD})} \quad (25b)$$

With S_{ic} and S_{ii} known from measurement, Eq 25 defines S_{bp} in terms of the unbiodegradable fraction of the primary sludge ($f_{ps,up}$), the retention time of the digester (R) and the acidogen constants (Y_{AD} , b_{AD}). By estimating an unbiodegradable fraction of the primary sludge ($f_{ps,up}$) and selecting acidogen biomass constants (i.e. $Y_{AD} = 0.113$ gCOD biomass/ gCOD organics, $b_{AD} = 0.041$ /d), S_{bp} can be calculated with Eq 25 from experimental data. The yield coefficient of the acidogens (Y_{AD}) has been increased from 0.089 to 0.113 to take account of the acetoclastic methanogen biomass that grows in the system. Because acidogenesis produces 61% acetic acid (and 39% hydrogen), 61% of the acetoclastic methanogen yield coefficient ($Y_{AM} = 0.040$) was added to Y_{AD} . This simplification is acceptable because the endogenous respiration rate is closely the same for these two organism groups ($b_{AD} = 0.041$ /d and $b_{AM} = 0.037$ /d). However, as noted above this simplification does influence the values of the constants in the hydrolysis rate equations. The hydrogenotrophic methanogen yield (Y_{HM}) is low enough (0.01 gCODbiomass/gCOD H_2) to be ignored.

7.4.2 Estimating the Unbiodegradable COD Fraction of Primary Sludge

For wastewater treatment plant design, the primary sludge (PS) unbiodegradable COD fraction ($f_{ps,up}$) is entirely dependent on the unbiodegradable particulate COD fractions ($f_{s,up}$) selected for the raw and settled wastewaters and the fraction of COD removed by primary sedimentation (f_{pr}). From a COD mass balance around the primary settling tank (PST), the $f_{ps,up}$ in terms of the raw and settled wastewater $f_{s,up}$ values and the PST f_{pr} is

$$f_{ps,up} = f_{s,up,Set} + \frac{1}{f_{pr}} (f_{s,up,Raw} - f_{s,up,Set}) \quad (26)$$

where

- $f_{ps,up}$ = unbiodegradable COD fraction of primary sludge (PS)
- $f_{s,up,Set}$ = Settled wastewater unbiodegradable particulate COD fraction
- $f_{s,up,Raw}$ = Raw wastewater unbiodegradable particulate COD fraction
- f_{pr} = fraction of COD removed in the primary settling tank (PST)

Equation 26 has been simplified and is not strictly in conformity with a water flow balance over the PST. In Eq 26, it has been assumed that the raw and settled wastewater flows entering and exiting the PST are equal. In practice, this is not true due to the low PST underflow, typically between 0.5 and 2% of average dry weather flow (ADWF). The error is very small on $f_{ps,up}$, but large enough to cause an error of ~1% on the COD mass balance around the whole WWTP. Mass balances are used wherever possible to verify the mathematical equations in models and errors > 1% are signals of possible errors in logic and formulae.

A graphical representation of Eq 26 is given in Fig 3. For the typical South African raw and settled municipal wastewaters, $f_{s,up}$ fractions of 0.15 and 0.04 respectively (WRC, 1984) and 35% COD removal ($f_{pr} = 0.35$), the $f_{ps,up}$ is 0.36. Literature on full-scale AD of primary sludge (PS) give maximum VS removals at long retention times at around 0.60 (Eckenfelder, 1980), suggesting an unbiodegradable fraction of around 0.35. O'Rourke (1967) determined a $f_{ps,up}$ of 0.36 in their investigation into AD of PS.

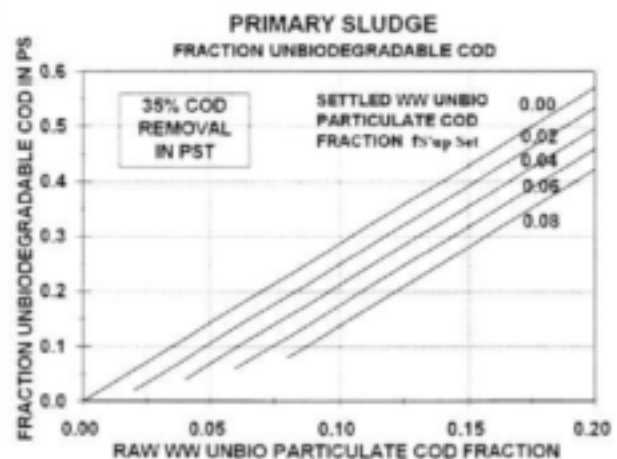


Fig 3: Fraction of unbiodegradable COD in primary sludge versus raw wastewater unbiodegradable particulate COD fraction for different settled wastewater unbiodegradable particulate COD fraction.

Incidentally, Eq 26 shows that (1) the $f_{s,up}$ values selected for the raw and settled wastewaters must be consistent with observed PS characteristics and (2) the % removal of unbiodegradable organics (COD) in PSTs is apparently much higher (83% for the selected $f_{s,up}$ values above) than that of biodegradable organics (38%). The latter is of significant economic benefit for the activated sludge system because a large mass of burdensome unbiodegradable organics from the influent do not accumulate in the reactor. In some wastewater treatment plant simulation models, equal proportions of biodegradable and unbiodegradable particulate organics are removed in the PST. This leads to settled wastewater and PS characteristics that deviate significantly from observed values, e.g. if equal proportions of the raw wastewater biodegradable and unbiodegradable particulate COD are removed and the %COD removal remains at 35%, then the settled wastewater $f_{s,up}$ would have to be 0.12 and $f_{ps,up} = 0.20$. Both these values are considerably different than those observed.

7.4.3 Calculating the Constants in the Hydrolysis Kinetic Equations - Izzett et al. (1992) Results

Izzett et al. (1992) operated two laboratory-scale mesophilic (37°C) anaerobic digesters fed a mixture of primary and humus (trickling filter) sludge from the Potsdam wastewater treatment plant (Milnerton, Cape, South Africa) at 7, 10, 12, 15 and 20 days retention time. The steady state experimental results measured on the systems are listed in Table 2.

Table 2: Experimental data measured by Izzett et al. (1992) on 14l completely mixed mesophilic (37°C) anaerobic digesters at 7 to 20 days retention time fed a mixture of primary and humus (trickling filter) sludge from the Potsdam wastewater treatment plant (Milnerton, Cape, South Africa).

Retention time (d)	7	10	12	15	20
Influent flow l/d	2	1.4	1.17	0.93	0.7
Influent COD gCOD/l	43.286	40.721	39.222	42.367	42.595
Influent VFA gCOD/l	1871	1961	2872	1824	2249
Influent TKN mgN/l	1105	1100	1028	1075	1171
Influent FSA mgN/l	196	203	235	221	244
Influent Alk mg/l as CaCO ₃	80	81	90	82	56
Influent pH	5.34	5.34	5.2	5.42	5.28
Effluent COD gCOD/l	23.637	20.521	18.678	19.969	19.005
Effluent VFA mgCOD/l	50	28	28	27	23
Effluent TKN mgN/l	1041	1039	992	976	1157
Effluent FSA mgN/l	511	404	430	404	511
Effluent Alk mg/l as CaCO ₃	1882	1951	2072	1994	2066
Gas Composition %CH ₄	63.2	62.1	63.3	63.6	63.3
COD removal	19.649	20.2	20.544	22.398	23.59
Gas prod l gas/l influent	13.97	14.33	14.27	15.01	15.79
Gas Composition %CO ₂	36.8	37.9	36.7	36.4	36.7
FSA released	315	201	195	183	267
Measured digester pH	7.12	7.11	7.19	7.14	7.15
"Corrected" digester pH	6.84	6.84	6.88	6.86	6.87
COD balance (%)	108.4	108.6	109.1	106.9	107.3
Nitrogen Balance (%)	94.2	94.5	96.5	90.8	98.8
Carbon Balance (%)*	99	100	99.5	101.3	101.4

*Based on a sludge composition of C_{3.5}H₇O₂N_{0.196} calculated from the influent COD and N masses and effluent C mass in the gas and liquid streams.

Accepting $f_{PS,up} = 0.36$ from Chapter 5 for the Izzett data, the calculated S_{bp} concentrations from Eq 25 are listed in Table 3. With S_{bp} known, Z_{AD} and ΔS_{bp} ($= S_{bpi} - S_{bp}$) can be calculated from the measured results (Table 3). Because the hydrolysis process does not reach completion in the digester, the observed hydrolysis rate r_h is given by Eq 12 and the calculated values are listed in Table 3. With the hydrolysis rate known, the kinetic constants in the various hydrolysis rate equations can be calculated, i.e. for the first order rate with respect to S_{bp} only (Eq 1), $K_h = r_h / S_{bp}$ (/d) and for the first order specific rate with respect to S_{bp} and Z_{AD} (Eq 2), $K_H = r_h / (S_{bp} Z_{AD})$ [$t/(gCOD \text{ biomass.d})$]. The calculated K_h and K_H rates for the different retention times are listed in Table 3 and plotted versus R in Fig 4. For a hydrolysis rate equation to be reasonably general, it should take into account the major factors that influence the rate. If it achieves this, then the K constants in the rate equation will not change with the principal design parameters, in this case, hydraulic retention time (or sludge age). For the first order and the first order specific hydrolysis rate equations (Eqs 1 and 2 in Table 1), it can be seen that this would not appear to be the case (Fig 4) - both K_h and K_H increase with increasing retention time. The average K_h and K_H rates over the five retention times are 0.515 /d and 0.322 $t/(gCOD \text{ biomass.d})$ respectively (Table 3, see also Table 1). Although these rate equations do not appear to be sufficiently general to describe the change in hydrolysis rate with retention time, the difference in predicted %COD removal based on the average K_h and K_H rates compared with experimental results is very small.

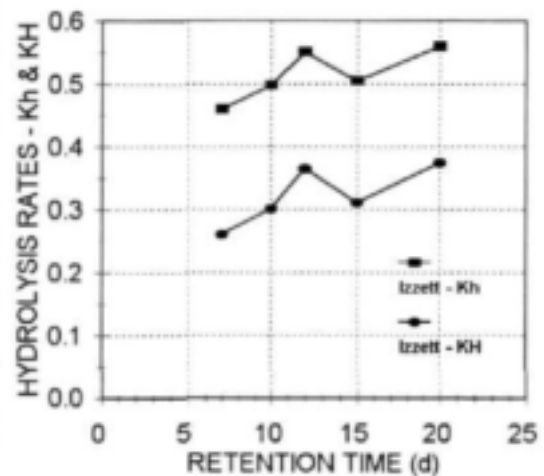


Fig 4: Hydrolysis rate constants for the 1st order (K_h /d) and 1st order specific [K_H , $t/(gCOD \text{ biomass.d})$] hydrolysis kinetic rate equations versus retention time for the Izzett *et al.* (1992) anaerobic digester data set.

Determination of the K constants in the Monod and saturation kinetic rate equations require linearization of these rate equations and linear regression over the retention time range of the experimental results, as described in Chapter 5. For the Monod equation, the hydrolysis rate r_h is given by Eq 3 in Table 1, where r_h , S_{bp} and Z_{AD} are calculated from experimental data (Table 3). The linearization can be done by three methods, viz. (i) Lineweaver-Burke, (ii) inversion and (iii) Eadie-Hofstee, each giving different K values, because each method emphasizes different aspects of the Monod equation.

The specific hydrolysis rate (r_h / Z_{AD}) versus S_{bp} graphs obtained for the Monod rate equation with constants derived from the three linearization methods (listed in Table 4) are shown in Fig 5, together with the Izzett experimental data. Although method (i) gives the best fit with the data (highest correlation coefficient $R^2 = 0.948$), method (ii) gives marginally the best fit at the short retention time (7d). Linearization method (iii) showed that the 15d retention time data is an outlier and is the reason for the low R^2 value (0.688) for all five retention time data. Excluding the 15d data significantly improved the R^2 value for method (iii) (0.888). The average K_m and K_s values obtained from the three methods, with the 15d retention time data excluded for method (iii), are given in Table 4 (see also Table 1). Figure 5 shows that even though different K values are obtained with the three different methods, the specific hydrolysis rate (r_h / Z_{AD}) versus biodegradable COD concentration (S_{bp}) curves obtained from each and the average are virtually the same and plot very closely to one another.

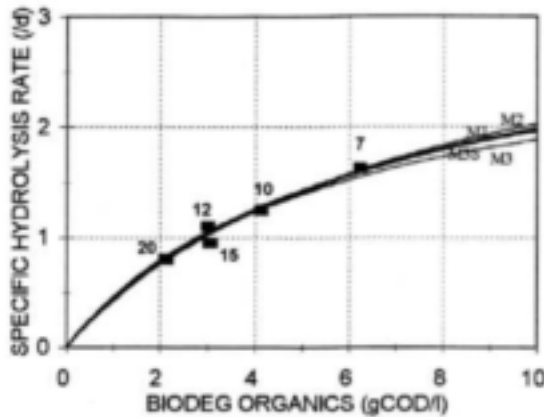


Fig 5: Specific hydrolysis rate $[r_h / Z_{ad}, \text{gCOD organics}/(\text{g COD biomass} \cdot \text{d})]$ versus residual biodegradable organics concentration (S_{bp} , gCOD/l) calculated for Monod hydrolysis kinetic rate equation with constants determined from the Lineweaver-Burke (M1), inversion (M2) and Eadie-Hofstee (M3) linearization and regression methods for the Izzett et al (1992) anaerobic digester data from 7 to 20 days retention time; experimental data (■) also shown.

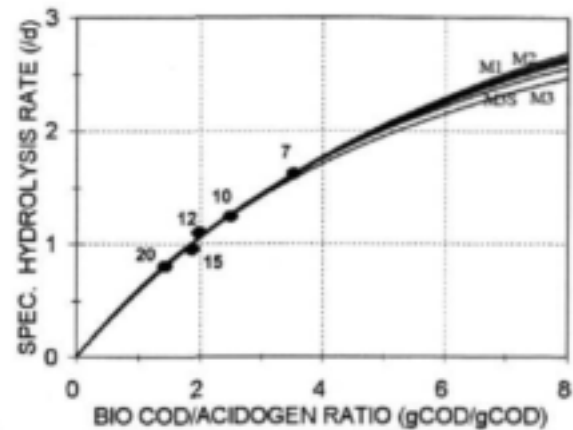


Fig 6: Specific hydrolysis rate $[r_h / Z_{ad}, \text{gCOD organics}/(\text{g COD biomass} \cdot \text{d})]$ versus residual biodegradable organics to acidogen biomass concentration ratio (S_{bp} / Z_{ad} , gCOD/gCOD) calculated for saturation hydrolysis kinetic rate equation with constants determined from the Lineweaver-Burke (M1), inversion (M2) and Eadie-Hofstee (M3) linearization and regression methods for the Izzett et al (1992) anaerobic digester data from 7 to 20 days retention time; experimental data (●) also shown.

The K_M and K_S values for the saturation hydrolysis rate equation (Eq 4 in Table 1) are found by the same linearization methods, the only difference being that for saturation kinetics, the concentration variable is S_{bp}/Z_{AD} instead of S_{bp} . The K_M and K_S values so obtained are listed in Table 4. The specific hydrolysis rate, r_h/Z_{AD} (gCOD organics/ gCOD biomass.d) versus the saturation ratio S_{bp}/Z_{AD} (gCOD organics/ gCOD biomass) graphs obtained for the saturation rate equation from the three linearization methods are shown in Fig 6 with the Izzett experimental data. As with the Monod kinetics, although method (i) gives the highest R^2 (0.979), method (ii) fits the experimental data marginally best at the shortest retention time (7d). For saturation kinetics also, linearization method (iii) showed that the 15d retention time data is an outlier and is the reason for the low R^2 value (0.699) for all five retention time data. Excluding the 15d data significantly improved the R^2 value for method (iii) (0.897). The average K_M and K_S values obtained from the three methods, with the 15d retention time data excluded for method (iii), are given in Table 4. As with the Monod equations, Fig 6 shows that even though different K values are obtained with the three different methods, the specific hydrolysis rate (r_h/Z_{AD}) versus saturation ratio (S_{bp}/Z_{AD}) curves obtained from each and the average are virtually the same and plot very closely to one another. Moreover, each of the four different hydrolysis kinetics equations yield near identical specific hydrolysis rate (r_h/Z_{AD}) versus biodegradable COD acidogen biomass concentration ratio (S_{bp}/Z_{AD}) curves.

The unbiodegradable fraction of sludge ($f_{PS'up}$) influences the calibration results of the different hydrolysis/acidogenesis rate equations. For the more complex approach in Chapter 5, it was found that the lowest coefficient of variation (C_{var} , standard deviation/mean) for the first order ($C_{var} = 0.017$) and first order specific ($C_{var} = 0.049$) hydrolysis equations at $f_{PS'up} = 0.34$ and 0.32 respectively and the highest correlation coefficient (R^2) for the Monod ($R^2=0.98$) and saturation ($R^2=0.99$) equations at $f_{PS'up} = 0.36$. For this simpler steady state model the results are virtually the same. For the first order and first order specific hydrolysis equations, the lowest coefficient of variation (C_{var}) is at $f_{PS'up} = 0.34$ ($C_{var} = 0.040$) and 0.32 ($C_{var} = 0.074$) respectively (Fig 7a) and the highest correlation coefficient (R^2) for

Table 3: Izzett et al. (1992) 7 to 20 d retention time (R) anaerobic digester measured influent* (S_u) and effluent* (S_e) COD concentrations, influent unbiodegradable (S_{upi}) and biodegradable COD (S_{bpi}) concentrations for an unbiodegradable COD fraction (f_{PS-up}) of 0.36, calculated residual biodegradable COD concentration (S_{bp}) (Eq 25), change in biodegradable concentration across digester (ΔS_{bp}), observed hydrolysis rate ($r_h = dS_{bp}/R + b_{AD}Z_{AD}$, Eq12), acidogen biomass concentration (Z_{AD}), specific hydrolysis rate [r_h/Z_{AD}] and the 1st order and 1st order specific hydrolysis rate constants (K_h and K_H). All mass units in gCOD.

R	* S_u	* S_e	S_{upi}	S_{bpi}	S_{bp}	ΔS_{bp}	r_h	Z_{AD}	r_h/Z_{AD}	K_h	K_H
d	g/l	g/l	g/l	g/l	g/l	g/l	g/(l.d)	g/l	gCOD S_{bp} / (gCOD Z_{AD} .d)	/d	l/ (gCOD Z_{AD} .d)
7	43.3	23.637	15.583	25.832	6.24	19.59	2.871	1.765	1.586	0.46	0.261
10	40.7	20.521	14.66	24.1	4.142	19.96	2.064	1.654	1.207	0.498	0.301
12	39.2	18.678	14.12	22.23	3.018	19.21	1.663	1.511	1.059	0.551	0.365
15	42.4	19.969	15.252	25.291	3.065	22.23	1.548	1.625	0.912	0.505	0.311
20	42.6	19.005	15.334	25.012	2.151	22.86	1.204	1.495	0.764	0.56	0.374
									Mean**	0.515	0.322

* Measured total unfiltered COD. The VFA concentration was subtracted from this in conformity with Eq 5 when calculating the Z_{AD} because this concentration is already hydrolysed and produces negligible biomass in the digester. The unbiodegradable soluble COD concentration was assumed zero. The fermentable (non-VFA) soluble COD (Fig 2) was included in the S_{bpi} (in conformity with Eq 5) because these organics pass through the hydrolysis process like the S_{bpi} . The unbiodegradable COD concentration (S_{upi}) of the sludge was calculated from the influent total unfiltered COD as listed and therefore included the soluble COD. This was done to approximate the unbiodegradable COD concentration of the "pristine" sewage sludge before any acidogenesis commenced. This is approximate because hydrogen is generated and lost in the acidogenesis that takes place in the sludge before feeding to the digester. ** Mean of all five retention time values.

Table 4: Monod and saturation kinetics K constants and correlation coefficients (R^2) for the anaerobic digester data of Izzett et al. (1992) obtained from Lineweaver-Burke (M1), inversion (M2) and Eadie-Hofstee (M3) linearization and regression methods, for the Eadie-Hofstee (M3) method without the 15 day retention time data (M3S), and the averages of the M1, M2 and M3 and the M1, M2, and M3S methods for unbiodegradable fraction ($f_{S_{un-up}}$) of 0.36.

Kinetic rate	Monod kinetics			Saturation kinetics		
Linearization Method	K_m	K_s	R^2	K_M	K_S	R^2
Units	g organics/ (g biomass.d)	g organics/l	-	g organics/ (g biomass.d)	g organics/ g biomass	-
Method 1 (M1)	3.33	6.81	0.948	5.44	8.35	0.979
Method 2 (M2)	3.55	7.49	0.876	5.61	8.69	0.823
Method 3 (M3)	2.94	5.55	0.688	4.46	6.44	0.699
Method 3S (M3S)	3.14	5.98	0.888	4.77	6.91	0.897
Average M1, M2, M3	3.27	6.62	-	5.17	7.82	-
Average M1, M2, M3S	3.34	6.76	-	5.27	7.98	-

the Monod ($R^2=0.945$) and saturation ($R^2=0.972$) equations at $f_{PS'wp} = 0.37$ (Fig 7b). It is clear that the steady state model gives almost the same results as the more complex hydrolysis model derived for UCTADM1. Even though this simpler steady state model yields different K values to the more complex model for reasons describe above, the specific hydrolysis rate (r_h/Z_{AD}) versus biodegradable COD concentration (S_{bp}) curves obtained from the model are virtually the same as for the more complex model, and similarly for the saturation kinetics.

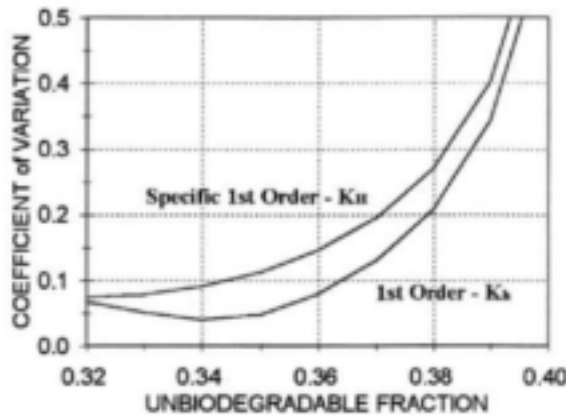


Fig 7a: Coefficient of variation versus unbiodegradable COD fraction of the primary sludge ($f_{PS'wp}$) for the 1st order and 1st order specific hydrolysis equations for the Izzett et al. digester data set.

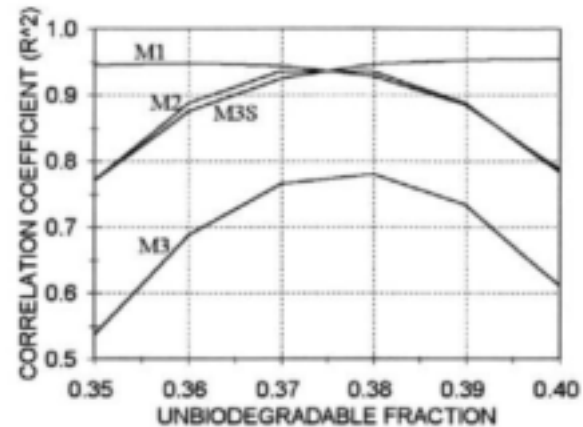


Fig 7b: Regression correlation coefficient (R^2) versus unbiodegradable COD fraction of the primary sludge ($f_{PS'wp}$) for the Lineweaver-Burke (M1), inversion (M2) and Eadie-Hofstee linearization methods, with (M3) and without (M3S) the 15 day retention time data, with the Monod hydrolysis rate equation for the Izzett et al. digester data set.

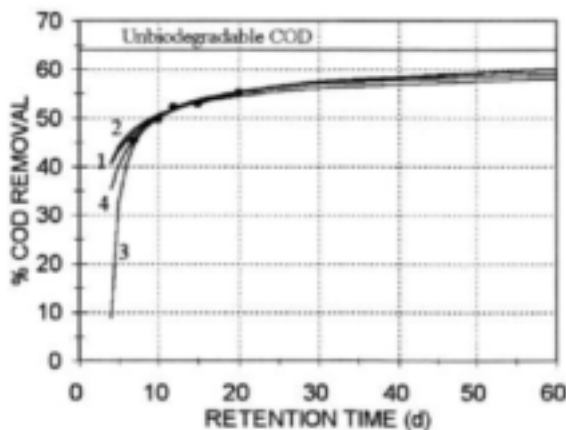


Fig 8: Percentage COD removal versus retention time for the 1st order (1), 1st order specific (2), Monod (3) and saturation (4) hydrolysis rate equations showing also the Izzett et al experimental data at 7, 10, 12, 15 and 20 days.

high volatile fatty acid (VFA) concentration reduces the hydrolysis rate but does not cause it to stop (O'Rourke, 1967, Ristow et al., 2004).

With the hydrolysis rate kinetic constants determined from the Izzett et al. experimental results for the four different kinetic hydrolysis rate equations, plots of the %COD removal (i.e. %COD converted to methane, Eq 21) versus retention time (R) calculated from the four hydrolysis rate equations are shown in Fig 8. It is clear that the different rate equations give virtually identical results at long retention times ($>10d$), but that critical differences between them arise at short retention times ($<10d$). It seems, therefore, that different digester failure retention times are predicted by different hydrolysis rate equations. However, this is not so because the hydrolysis process is not the one that causes digester failure - it is loss of methanogen species activity, usually the acetoclastic methanogens, that causes the digester pH to decrease that leads to failure. The low pH and

From the above evaluation and Fig 8, it can be concluded that the mixture of primary and humus sludge tested by Izzett et al. (1992) conforms very closely to both the Monod and saturation kinetics, because the % COD removal increases gradually with increasing retention time. From the Fig 8 it can be seen that digesters at very long retention times (>60d) are required to determine the $f_{ps,up}$ and at short retention times (<15d) to calibrate and determine the best hydrolysis rate equation.

7.4.4 Calculating the Constants in the Hydrolysis Kinetic Equations - O'Rourke (1967) Results

O'Rourke (1967) studied the kinetics of anaerobic sludge treatment at ambient temperatures, since at the time, most AD systems were operated at 35°C, and little was known about the performance of the systems at ambient temperatures. To determine the kinetics of AD at the ambient temperatures and the influence of temperature, digesters were fed a primary sludge concentration of 28.4 gCOD/l and operated at 35, 25, 20 and 15°C and hydraulic retention times from 60 days to as low as 2.75 days, in which methanogenesis had failed. For this evaluation, only the methanogenic systems operated at 35°C are considered, of which there were five, i.e. 7.5, 10, 15, 30 and 60d systems. The experimental results of these five systems are listed in Table 5.

Initially, all five retention time data were analysed in the identical way as the five retention time data of Izzett et al. From this analysis it was found that the validity of the hydrolysis kinetic constants obtained was very sensitive to the unbiodegradable COD fraction ($f_{ps,up}$). Values higher than 0.338 yielded negative effluent biodegradable COD concentrations (S_{bp}). This set an upper limit of 0.338 on the $f_{ps,up}$ value. A lower $f_{ps,up}$ for primary sludge seems reasonable in comparison with the 0.36 value obtained for the mixture of primary and humus sludge. Furthermore, the R^2 values for the Monod and saturation models were very low (<0.60) for all reasonable $f_{ps,up}$ from 0.32 to 0.34 and $f_{ps,up} > 0.336$ yielded negative K_s values with linearization method (iii) (because $S_{bp} < 0$). The best $f_{ps,up}$ value was 0.334 - it yielded the lowest C_{var} for the first order and first order specific hydrolysis equations and the highest R^2 values (0.54 - 0.60) for the Monod and saturation equations. The calculated K_s and K_H rates and the Monod and saturation kinetics constants for all five retention times for $f_{ps,up} = 0.334$ are listed in Tables 6 and 7 respectively. The average K_s and K_H rates over the five retention times are 1.591 /d and 1.538 l/(gCOD biomass.d) respectively. The K_s and K_H rates are plotted versus R in Fig 9 together with the Izzett et al. data K_s and K_H rates. The O'Rourke K rates are significantly higher and vary widely over 7.5 to 60 days retention time. Higher K rates are expected from the O'Rourke data, because "pure" primary sludge would be expected to hydrolyse faster than a mixture of primary and humus sludge. The large variation of the K values is due to the sensitivity of the hydrolysis equations to the measured effluent total COD concentration (see Table 6), which do not decrease consistently with retention time (as anticipated by the hydrolysis equations). This is also the reason for the low correlation coefficients (R^2) obtained from the three linearization methods for the Monod and saturation equations (Table 7).

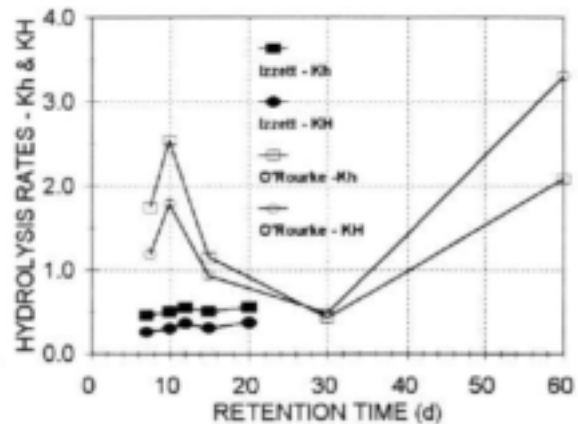


Fig 9: Hydrolysis rate constants for the 1st order (K_s /d) and 1st order specific [K_H l/(gCOD biomass.d)] hydrolysis kinetic rate equations versus retention time for the Izzett et al. and O'Rourke anaerobic digester data sets.

Table 5: Experimental data measured by O'Rourke (1967) on completely mixed mesophilic (37°C) anaerobic digesters at 7 to 60 days retention time fed primary sludge.

Retention time (d)	7.5	10	15	30	60
Influent COD gCOD/l	28.4	28.4	28.4	28.4	28.4
Influent VFA gCOD/l	1020	1020	1020	1020	1020
Influent Lipids g/l	12.6	12.6	12.6	12.6	12.6
Influent Cellulose g/l	4.47	4.47	4.47	4.47	4.47
Influent Proteins g/l	6.4	6.4	6.4	6.4	6.4
Influent VSS g/l	18.4	18.4	18.4	18.4	18.4
Effluent COD gCOD/l	12.4	11.7	11.8	11.8	10.3
Effluent VFA gCOD/l	0.14	0.09	0.06	0.06	0.03
Effluent Lipids g/l	5.05	4.66	40.7	4.45	3.52
Effluent Cellulose g/l	0.41	0.34	0.44	0.36	0.33
Effluent Proteins g/l	4.32	4.33	4.35	3.78	3.67
Effluent VSS g/l	8.3	8.1	7.2	7.1	6.6
Gas Composition %CH ₄	?	?	?	?	?
Gas prod ml CH ₄ /gCOD	308	328	330	350	347
COD balance (%)	99.7	100.9	101.6	105.3	99.4
FSA released	315	201	195	183	267
Effluent Alk mg/l as CaCO ₃	1800	1600	1800	2000	2300
Digester pH	6.9-7.3	6.8-7.3	6.9-7.3	7.0-7.4	7.0-7.4

To try and bring some consistency to the K rates obtained from the O'Rourke data, the 60 day retention time system was used to determine the $f_{PS,up}$ and the three shortest retention time systems (7.5, 10 and 15d) to determine the K rates, i.e. the 30d system was omitted from the analysis, which seems reasonable from Fig 9. For the 60d system, a $f_{PS,up} = 0.338$ yielded a very low effluent biodegradable COD, i.e. $S_{up} = 0.041$ gCOD/l (0.340 makes it -ve). For this $f_{PS,up}$, determining the hydrolysis rate r_h and K rates with the 7.5, 10 and 15d retention time systems yielded (i) the same r_h rates determined previously for these retention times with $f_{PS,up} = 0.334$ (see Table 6 and 8), (ii) the K_h and K_M rates still varied considerably, from 1.296 to 3.034 /d and 1.050 to 2.129 l/(gCOD.d) at 15 and 10 days retention time respectively (Table 8) with little improvement in the coefficient of variation (C_{var}), and (iii) lower R^2 values for the Monod and saturation kinetics (Table 9). The reason for (ii) and (iii) for the three retention time systems compared with the five retention time systems is because the measured effluent COD concentration from the 15d system is higher than that from the 10d system, which is contrary to the functional form of the hydrolysis equations. Furthermore, while the K_h and K_M rates increased, the increase was not large enough to indicate that primary sludge hydrolysed faster than a mixture of primary and humus sludges. Accordingly, the 15 day system data was also removed from the data set and the K rates calculated with only the 7.5 and 10d system data (see Tables 8 and 10). The calculated K_h and K_M rates at 7.5 and 10d retention time do not change, only the average changes because it is based on only the 7.5 and 10d system K rates (Table 8). The average 1st order K_h rate and 1st order specific K_M rate constants obtained are 2.474 /d and 1.714 l/(mgCOD.d) respectively (Table 8). Because there are only two systems and 2 degrees of freedom (i.e. 2 unknowns), the R^2 values for the Monod and saturation equations are 1.00 (i.e. perfect fit, Table 10). The percentage COD removal versus retention time calculated from the four calibrated hydrolysis equations for the 7.5 and 10d system data only is shown in Fig 10.

Table 6: O'Rourke (1967) 7.5 to 60 d retention time (R) anaerobic digester measured influent* (S_0) and effluent* (S_e) COD concentrations, influent unbiodegradable (S_{up}) and biodegradable COD (S_{bp}) concentrations for an unbiodegradable COD fraction ($f_{PS_{up}}$) of 0.334, calculated biodegradable COD concentration (S_{bp}) (Eq 25), change in biodegradable concentration across digester (ΔS_{bp}), observed hydrolysis rate ($r_h = dS_{bp}/R + b_{AD}Z_{AD}$, Eq 12), acidogen biomass concentration (Z_{AD}), specific hydrolysis rate [r_h/Z_{AD}] and the 1st order and 1st order specific hydrolysis rate constants (K_h and K_H). All mass units in gCOD.

R	* S_0	* S_e	S_{up}	S_{bp}	S_{bp}	ΔS_{bp}	r_h	Z_{AD}	r_h/Z_{AD}	K_h	K_H
d	g/l	g/l	g/l	g/l	g/l	g/l	g/(l.d)	g/l	gCOD S_{bp} / (gCOD Z_{AD} .d)	/d	l/ (gCOD Z_{AD} .d)
7.5	28.4	12.4	9.486	17.894	1.301	16.593	2.273	1.473	1.543	1.746	1.186
10	28.4	11.7	9.486	17.894	0.7	17.195	1.778	1.425	1.248	2.541	1.784
15	28.4	11.8	9.486	17.894	1.021	16.874	1.175	1.234	0.953	1.152	0.934
30	28.4	11.8	9.486	17.894	1.361	16.533	0.588	0.893	0.658	0.432	0.483
60	28.4	10.3	9.486	17.894	0.154	17.74	0.321	0.63	0.51	2.082	3.305
									Mean**	1.591	1.538

* See note on Table 3 . **Mean of all five retention time values.

Table 7: Monod and saturation kinetics K constants and correlation coefficients (R^2) for the 7.5 to 60d anaerobic digester data of O'Rourke (1967) obtained from Lineweaver-Burke (M1), inversion (M2) and Eadie-Hofstee (M3) linearization and regression methods and the mean values of the three methods for unbiodegradable fraction ($f_{PS_{up}}$) of 0.334.

Kinetic rate	Monod kinetics			Saturation kinetics		
Linearization Method	K_m	K_s	R^2	K_M	K_S	R^2
Units	g organics/ (g biomass.d)	g organics/l	-	g organics/ (g biomass.d)	g organics/ g biomass	-
Method 1 (M1)	1.174	0.195	0.577	1.303	0.306	0.349
Method 2 (M2)	0.939	0.003	0.604	0.674	-0.17	0.809
Method 3 (M3)	1.177	0.127	0.108	0.69	-0.184	0.128
Average M1, M2, M3	1.097	0.108	-	0.889	-0.016	-

Table 8: O'Rourke (1967) 7.5 to 60d retention time (R) anaerobic digester measured influent* (S_u) and effluent* (S_{ue}) COD concentrations, influent unbiodegradable (S_{up}) and biodegradable COD (S_{bp}) concentrations for an unbiodegradable COD fraction ($f_{PS_{up}}$) of 0.338, calculated residual biodegradable COD concentration (S_{bp}) (Eq 25), change in biodegradable concentration across digester (ΔS_{bp}), observed hydrolysis rate ($r_h = dS_{bp}/R + b_{AD}Z_{AD}$, Eq 12), acidogen biomass concentration (Z_{AD}), specific hydrolysis rate [r_h/Z_{AD}] and the 1st order and 1st order specific hydrolysis rate constants (K_h and K_H). All mass units in gCOD. Note that r_h , Z_{AD} and r_h/Z_{AD} are identical to the values calculated in Table 4 for $f_{PS_{up}}$ of 0.334.

R	* S_u	* S_{ue}	S_{up}	S_{bp}	S_{bp}	ΔS_{bp}	r_h	Z_{AD}	r_h/Z_{AD}	K_h	K_H
d	g/l	g/l	g/l	g/l	g/l	g/l	g/(l.d)	g/l	gCOD S_{bp} / (gCOD Z_{AD} .d)	/d	l/ (gCOD Z_{AD} .d)
7.5	28.4	12.4	9.599	17.781	1.188	16.593	2.273	1.473	1.543	1.914	1.299
10	28.4	11.7	9.599	17.781	0.586	17.195	1.778	1.425	1.248	3.034	2.129
15	28.4	11.8	9.599	17.781	0.907	16.874	1.175	1.234	0.953	1.296	1.05
30	28.4	11.8	9.599	17.781	1.247	16.553	0.588	0.893	0.658	0.471	0.527
60	28.4	10.3	9.599	17.781	0.04	17.74	0.321	0.63	0.51	7.876	12.503
									Mean**	2.081	1.493
									Mean***	2.474	1.714

* See note on Table 3. **Mean of 7.5, 10 and 15d retention time values.

***Mean of 7.5 and 10d retention time values only.

Table 9: Monod and saturation kinetics K constants and correlation coefficients (R^2) for the O'Rourke 7.5, 10 and 15 d retention time data obtained from Lineweaver-Burke (M1), inversion (M2) and Eadie-Hofstee (M3) linearization and regression methods for unbiodegradable fraction ($f_{PS_{up}}$) of 0.338.

Kinetic rate	Monod kinetics			Saturation kinetics		
Linearization Method	K_m	K_s	R^2	K_M	K_S	R^2
Units	g organics/ (g biomass.d)	g organics/l	-	g organics/ (g biomass.d)	g organics/ g biomass	-
Method 1 (M1)	1.35	0.1	0.026	1.17	-0.016	0
Method 2 (M2)	1.91	0.5	0.418	1.32	0.063	0.519
Method 3 (M3)	1.08	-0.12	0.048	1	-0.117	0.123

Table 10: Monod and saturation kinetics K constants and correlation coefficients (R^2) for the O'Rourke 7.5 and 10d retention time data for unbiodegradable fraction ($f_{PS_{up}}$) of 0.338. Note that all three linearization and regression methods give the same results and perfect correlation for a pair of results.

Kinetic rate	Monod kinetics			Saturation kinetics		
Linearization Method	K_m	K_s	R^2	K_M	K_S	R^2
Units	g organics/ (g biomass.d)	g organics/l	-	g organics/ (g biomass.d)	g organics/ g biomass	-
Methods 1, 2 & 3	2.004	0.355	1	2.047	0.263	1

It can be seen that with primary sludge only, a high %COD removal (> 60%) is obtained even at short retention times (<10d). In contrast, because humus sludge in the primary and humus sludge mixture hydrolyses more slowly than primary sludge, the %COD removal is only 55% at significantly longer retention times (>20d) (Figs 6 and 8). A comparison between the Monod curves obtained for the primary sludge (O'Rourke data) and the primary and humus sludge mixture (Izzett et al. data) calculated from the respective Monod K_m and K_s values is shown in Fig 11 together with the experimental data. Figure 11 reinforces the conclusion above, because with its low K_s value, higher rates of hydrolysis are maintained with "pure" primary sludge for much lower biodegradable COD concentrations, S_{bp} (and therefore shorter retention times) than for the primary and humus sludge mixture.

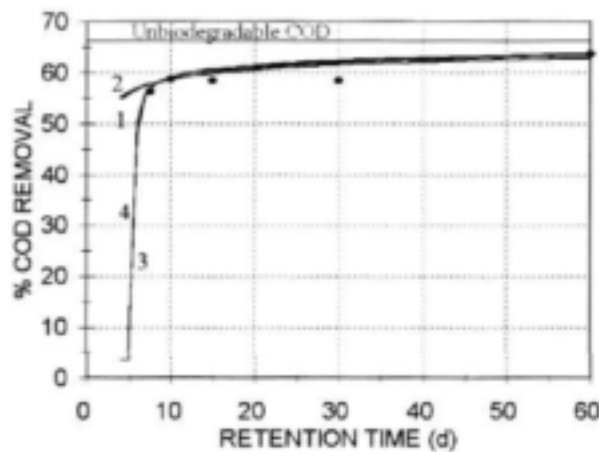


Fig 10: Percentage COD removal versus retention time for the 1st order (1), 1st order specific (2), Monod (3) and saturation (4) hydrolysis rate equations calibrated on the 7.5 and 10 day retention time systems of O'Rourke showing also the experimental data at 7.5, 10, 15, 30 and 60 days.

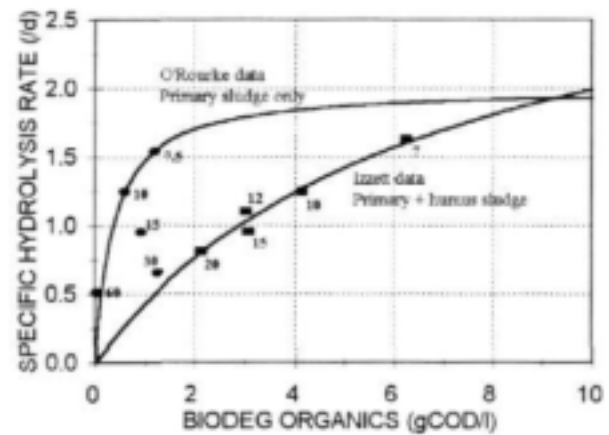
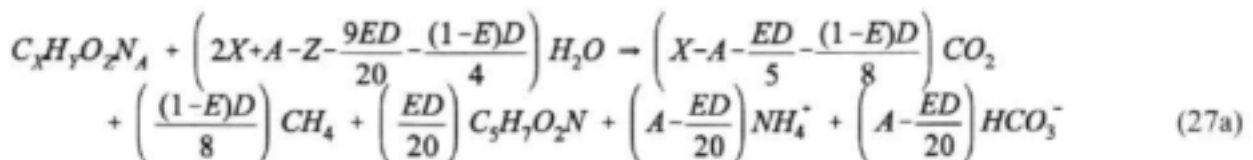


Fig 11: Specific hydrolysis rate [r_h / Z_{ad} gCOD organics/(g COD biomass .d)] versus biodegradable organics concentration (S_{bp} gCOD/l) calculated for Monod hydrolysis kinetic rate equation for the Izzett et al. (1992) (all 5 retention times) and O'Rourke (1967) (7.5 and 10d retention times) anaerobic digester data showing also their experimental data (■, Izzett) and (●, O'Rourke) with retention time indicated.

7.5 STEADY STATE MODEL DEVELOPMENT - STOICHIOMETRY

Once the concentration of hydrolysable organics utilized in the anaerobic digester is known from the hydrolysis kinetics, the sludge composition and stoichiometry of the biological processes following the hydrolysis process and the utilization of the influent VFA concentration (S_{bui}) define the digester gas composition and pH.

McCarty (1974) gives the following general stoichiometric reaction for the overall AD system fed an organic waste of empirical composition $C_xH_yO_zN_A$ to methane, carbon dioxide and biomass (of composition $C_5H_7O_2N$) as final end products:



where $D = 4X + Y - 2Z - 3A$

In Eq 27a, E is the fraction of hydrolysed COD utilized (ΔS_{bp}) that is converted to biomass (Z_{AD}), which from Eqs 13 or 25 is

$$E = \frac{Z_{AD}}{S_{bpl} - S_{bp}} = \frac{Y_{AD}}{[1 + b_{AD}R(1 - Y_{AD})]} \quad (27b)$$

The gCOD/mol and molar mass (MM) of the influent organics $C_XH_YO_ZN_A$ are given by:

$$COD = 8[Y + 2(2X - Z) - 3A] \quad \text{gCOD/mol} \quad (28a)$$

$$MM = 12X + Y + 16Z + 14A \quad \text{g drymass/mol or gVSS/mol} \quad (28b)$$

where VSS = volatile suspended solids

The influent VFA concentration are assumed to be acetate species with a MM = 60 g/mol and COD=64 gCOD/mol. The stoichiometry of utilization of the undissociated and dissociated acetate species by the methanogens, assuming zero sludge production ($E=0$ in Eq 27a), is



The total CH_4 , CO_2 and HCO_3^- species produced is the sum of Eqs 27 and 29. The split between the undissociated and dissociated acetate species is governed by the influent pH (Eq 30). This split is shown versus pH in Fig 12 for a pK'_a value for acetate of 4.68 obtained for an influent TDS concentration of 2500 mg/l and a temperature of 37°C (Loewenthal et al., 1989). Figure 12 shows that the higher influent pH, the higher the fraction of dissociated acetate species, the higher the alkalinity generation (Eq 29b) and therefore the higher the digester pH.

$$S_{baHAcI} = \frac{S_{baI}}{(1 + 10^{pH_i - pK'_a})} \quad \text{and} \quad S_{baAcI} = \frac{S_{baI}}{(1 + 10^{pK'_a - pH_i})} \quad \text{mgCOD/l} \quad (30)$$

where pH_i is the influent pH and S_{baHAcI} and S_{baAcI} the undissociated and dissociated acetate species concentration in the influent respectively.

For acidogen organism constants $Y_{AD} = 0.113$ mgCOD biomass/mg COD organics degraded and $b_{AD} = 0.041$ /d, the fraction of COD hydrolysed converted to sludge mass (E , Eq 27b) and methane ($1-E$) are shown as % in Fig 13. One of the major advantages of anaerobic treatment is evident in Fig 13, i.e. sludge production is extremely low compared with aerobic treatment - only 9 and 5% of COD degraded from 5 to 40 days retention time with practically all (91 to 95%) converted to useful methane gas.

7.6 STEADY STATE MODEL DEVELOPMENT - WEAK ACID BASE CHEMISTRY

In Eqs 27 and 29, the total CO_2 produced is the sum of the gaseous CO_2 and the dissolved CO_2 , which, at the near neutral pH of AD (6.5 to 7.5), is mostly in the bicarbonate (HCO_3^-) form. The proportion of the total CO_2 that is in the bicarbonate form is governed by (i) the ammonia released in the breakdown of the hydrolysable organics (Eq27a), which at neutral pH, picks up a proton from the dissolved CO_2 ($H_2CO_3^*$) to form saline ammonia (NH_4^+) and bicarbonate (HCO_3^-) according to $NH_3 + H_2CO_3^* \rightarrow NH_4^+ + HCO_3^-$ and (ii) the concentration of influent dissociated acetate species utilized in the digester (Eq 29b), which is governed by the degree of hydrolysis of the sludge prior to entry to the digester and the influent pH. The gaseous CO_2 and CH_4 produced define the gas composition,

which sets the partial pressure of CO_2 (p_{CO_2}). The pH of the digester is defined by the p_{CO_2} and the bicarbonate concentration (HCO_3^-) generated, which is equal to the alkalinity generated. Clearly, the N content of the influent organics and the influent VFA concentration and pH are very important because these (i) define the HCO_3^- alkalinity concentration generated and p_{CO_2} of the gas, both of which (ii) set the digester pH. If the N content of the influent organics is too low, lime may need to be dosed to augment the uptake of H^+ by the NH_3 released from the organics and establish the appropriate HCO_3^- concentration and p_{CO_2} for the required digester pH (>6.5) (Capri and Marais, 1975). Accepting that (i) the pH is established predominantly by the carbonate weak acid base system and (ii) the bicarbonate concentration ($[\text{HCO}_3^-]$, mol/l) is generated principally from the ammonia released from the breakdown of the influent hydrolysable organics and the utilization of influent dissociated acetate species, (i.e. low influent alkalinity with respect to that generated, see Table 2) and (iii) equilibrium exists between the dissolved and gaseous inorganic carbon species (reasonable at long retention times), the relationship between the bicarbonate concentration, p_{CO_2} and pH is given by,

$$p_{\text{CO}_2} = \frac{[\text{HCO}_3^-] (1 + 10^{pK'_{a1} - \text{pH}} + 10^{\text{pH} - pK'_{a2}})}{10^{-pK'_{\text{HCO}_2}} (1 + 10^{\text{pH} - pK'_{a1}} + 10^{2\text{pH} - pK'_{a1} - pK'_{a2}})} \quad \text{atm or mole fraction} \quad (31)$$

where

$[\text{HCO}_3^-]$ = bicarbonate concentration $\sim \text{H}_2\text{CO}_3^*$ alkalinity (mol/l) $\sim$ Total alkalinity (mol/l)

p_{CO_2} = partial pressure of CO_2 in the gas phase

pH = $-\text{ve } \log_{10}$ of the (H^+) activity

pK'_{HCO_2} = $-\text{ve } \log_{10}$ of the apparent Henry's law constant for CO_2

pK'_{a1}, pK'_{a2} = $-\text{ve } \log_{10}$ of 1st and 2nd carbonate system apparent dissociation constants

where apparent means corrected for ionic strength effects (see Loewenthal et al., 1989).

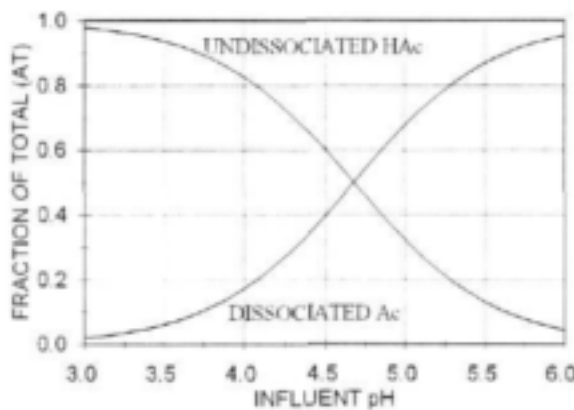


Fig 12: Fraction of undissociated and dissociated acetate species versus influent pH for a pK'_a value of 4.68 for a TDS of 2500 mg/l and temperature of 37°C .

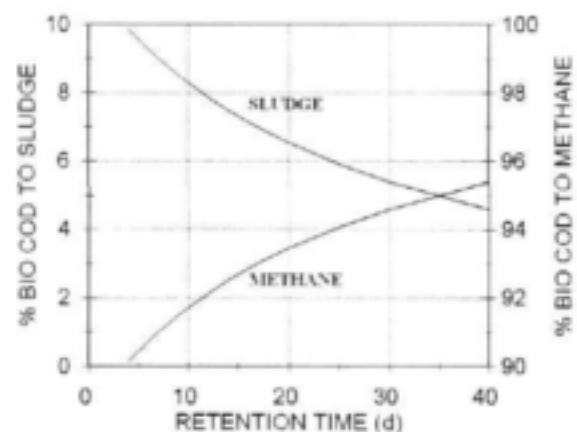


Fig 13: Percentage of biodegradable COD removed [$\Delta S_{bp}/S_{bpi} = (S_{bpi} - S_{bp})/S_{bpi}$] converted to sludge mass (E factor in Eq 27) and methane versus retention time. Although very slow, the endogenous process results in lower sludge and higher methane production at longer retention time.

Equation 31 is plotted in Fig 14 for a temperature of 37°C and a TDS of 2500 mg/l at which $pK'_{c1} = 6.211$, $pK'_{c2} = 9.960$ and $pK'_{HCO_2} = +1.609$ (Loewenthal et al., 1989), together with the range of normal anaerobic digester operation.

7.7 DESIGN EXAMPLE

The steady state model with the Monod hydrolysis rate equation and its associated kinetic constants (Table 1) are applied to the 20d retention time system of Izzett et al. (1992) (Table 2).

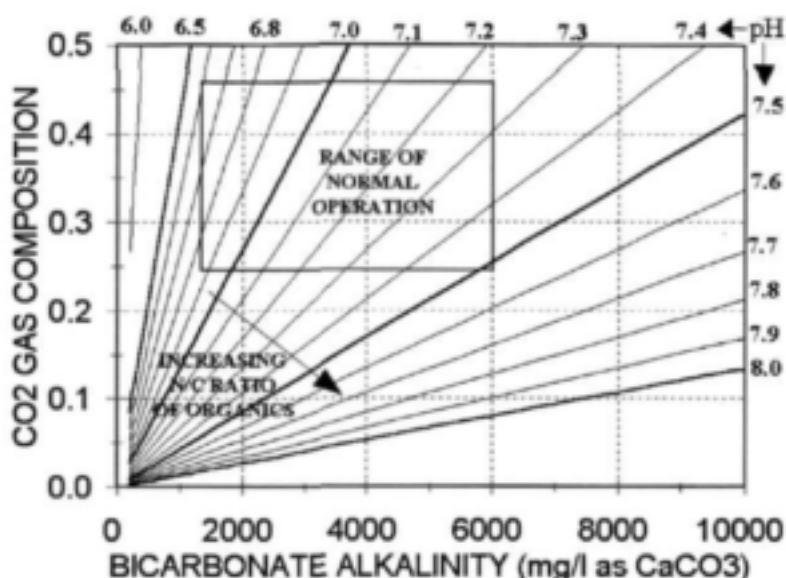


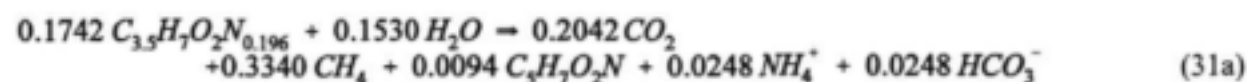
Fig 14: Fraction CO_2 gas composition versus reactor bicarbonate concentration (= alkalinity) for pH ranging from 6.5 to 8.0. Also shown is the range of normal anaerobic digester operation.

7.7.1 Calculating the COD Removal and Methane Production - Hydrolysis Kinetics

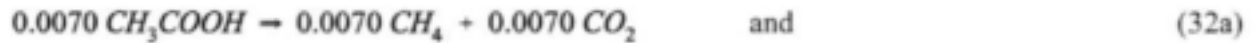
Total influent COD concentration (S_{ti}) = 42.59 gCOD/l (measured)
 Influent VFA concentration (S_{bmi}) = 2.24 gCOD/l (measured)
 Unbiodegradable fraction of the primary sludge ($f_{ps,up}$) = 0.36 (determined above)
 Influent hydrolysable COD concentration (S_{bpi}) = $(1-0.36)42.59 - 2.24 = 25.02$ gCOD/l (Eq 5)
 Influent unbiodegradable COD concentration (S_{upi}) = $0.36 \times 42.59 = 15.33$ gCOD/l (Eq 6)
 Residual biodegradable COD concentration (S_{bp}) = 2.15 gCOD/l (Eq 14)
 Biodegradable COD concentration removed ($\Delta S_{bp} = S_{bpi} - S_{bp}$) = 22.87 gCOD/l (Eq 22)
 Acidogen biomass concentration (Z_{AD}) = 1.50 gCOD/l (Eq 13)
 Unbiodegradable COD concentration (S_{up}) = 15.33 gCOD/l (Eq 15)
 Total effluent COD concentration (S_{te}) = $15.33 + 2.15 + 1.50 = 18.98$ gCOD/l (Eq 23)
 Methane production concentration (S_m) = 21.38 gCOD/l influent (Eq 17)
 Methane production from VFA = 2.24 gCOD/l influent (Equal to VFA COD, Eq 29)
 Total methane production concentration = $21.38 + 2.24 = 23.62$ gCOD/l influent
 Total COD concentration out ($S_{te} + S_m$) = $18.98 + 23.82 = 42.60$ gCOD/l (Eq 20)
 Hence COD balance $100(S_{te} + S_m)/S_{ti} = 100.0\%$
 Methane production gas volume (Q_m) = 8.87 (l methane/d)/(l influent flow/d) (Eq 18).
 Fraction of biodegradable COD removed converted to sludge mass (E) = 0.0654 (Eq 27b).
 Fraction of biodegradable COD removed converted to methane ($1-E$) = 0.9346.

7.7.2 Calculating the Partial Pressure of CO_2 , and the Ammonia and Alkalinity Concentrations Generated - Stoichiometry

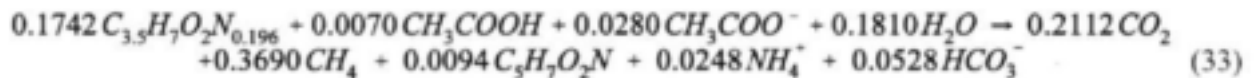
The primary sludge composition was estimated as $C_{3.5}H_7O_2N_{0.196}$ (see Chapter 5). Hence the COD content of the sludge is 131.3 gCOD/mol (Eq 28a) and the hydrolysable COD concentration removed $22.87/131.3 = 0.1742$ mol/l. From Eq 27, with $E=0.0654$, the stoichiometric equation for the overall digestion process therefore is



The influent VFA concentration was 2.240 gCOD/l, which at an influent pH of 5.28 (Table 2) comprises 20% (0.4480 gCOD/l = 0.4480/64 = 0.0070 mol/l) undissociated (Eq 30a) and 80% (1.792 gCOD/l = 1.792/64 = 0.0280 mol/l) dissociated acetate species (Eq 30b). From Eq 29, this yields



Adding Eqs 31a, 32a and 32b yields for the total biodegradable COD utilized,



Equation 33 shows that 0.0094 mol/l biomass ($\text{C}_5\text{H}_7\text{O}_2\text{N}$) is formed, which is 0.0094 x 160 gCOD/mol = 1.50 gCOD/l and corresponds exactly with Eq 13. It also shows that 0.2112 and 0.3690 mols gaseous CO_2 and CH_4 are produced yielding a total gas volume 0.5802 mol/l influent. At 24.0 l gas/mol at 20°C and 1 atm pressure (Eq 19), this is 5.08, 8.87 and 13.95 l CO_2 , CH_4 and total gas volume per l influent flow. It can be seen that the volume of methane production calculated from the kinetic part of the AD model is the same as that calculated from the stoichiometric part of the model, i.e. 8.87 l methane/l influent flow. This because the E value calculated from the kinetic model (fraction of COD removed converted to sludge mass = 0.0654, Eq 27b) was applied to the stoichiometric model. From the CO_2 and CH_4 gas production, the CO_2 gas composition (in mol fraction or partial pressure, p_{CO_2}) is 5.08/13.95 = 0.364. From Eq 33, 0.0248 mol/l ammonia and 0.0528 mol/l bicarbonate alkalinity are generated. This is 0.0248 x 14000 = 347 mgN/l and 0.0528 x 50000 = 2640 mg/l as CaCO_3 respectively. Adding these generated ammonia and alkalinity concentrations to the influent concentrations (Table 2) yields the predicted effluent concentrations, i.e. 244 + 347 = 591 mgFSA-N/l and 56 + 2640 = 2696 mg CaCO_3 /l.

7.7.3 Calculating the Digester pH - Weak Acid Base Chemistry

With the p_{CO_2} = 0.364 and HCO_3^- concentration = 2696 mg/l as CaCO_3 , the digester pH is 6.99 (Eq 31, Fig 14). Following the above procedure, a comparison between theoretically predicted and experimentally observed (a) COD removal (gCOD/l) (b) gas production (l gas/d per l influent/d), (c) gas composition (% CO_2), (d) effluent FSA concentration (mgN/l), (e) alkalinity (mg/l as CaCO_3) and (f) digester pH are given in Chapter 6, Figs 11a to f (page 6.33) respectively for the Izzett et al. 7, 10, 12, 15 and 20 day retention time digesters.

7.7.4 Comparison Between Theoretically Predicted and Experimentally Observed Results

The predicted COD removal (Fig 11a) corresponds very well to those measured. The gas production (Fig 11b) is under predicted because the model is based on 100% COD balance and experimental data COD balances ranged between 107 and 109% (Table 2) and also due to uncertainty in the gas temperature (20°C was assumed but if it was 37°C to would be 6% higher). Because the steady state model was calibrated on COD removal (rather than on gas production, which can also be done depending on whether effluent COD or gas production data show the best consistency, i.e. sequentially decreasing or increasing respectively with retention time), the predicted COD removal conforms almost exactly to that measured (Fig 11a) and so the error in the experimental COD balance manifests in the gas production (Fig 11b). The gas composition (Fig 11c) corresponds very well to that measured. The predicted effluent FSA concentration (Fig 11d) is higher than that measured, because the model is based on 100% N balance and the N balance of experimental data range between 90 and 99% (Table 2). By decreasing the N content of the hydrolysable organics (A in $\text{C}_x\text{H}_y\text{O}_z\text{N}_x$) by a small amount (5% to 0.186), the predicted effluent FSA can be made to closely fit the measured effluent FSA

of the 10 to 20d retention time systems. This also will result in an improved correlation between predicted and measured alkalinity (Fig 11e), because with a lower N content in the sludge, less alkalinity is generated. The lower alkalinity will decrease the predicted digester pH causing it to deviate further (~ 0.3 pH units) from the actual measured pH but closer to the "corrected" measured pH (Fig 11f). The actual measured pH data (7.11 to 7.19) show an inconsistency in that these pH values and the measured alkalinity and gas composition do not conform to Eq 31 - accepting the data that are most reliably measured, i.e. gas composition (Fig 11c) and alkalinity (Fig 11e) with the five point titration method of Moosbrugger et al. (1992), the digester pH must be lower than that measured to conform to Eq 31 (see Table 2 and Fig 11f). A digester pH lower than that actually measured is quite likely because CO_2 loss during sampling and testing will increase the pH. Despite the improvement between predicted and measured results that reducing the A value to 0.186 will yield to conform to the measured effluent N mass, the $A=0.196$ value in $\text{C}_x\text{H}_y\text{O}_z\text{N}_A$ was retained because it is based in the influent N mass. Further, Chapter 6 shows that the $\text{C}_{3.5}\text{H}_7\text{O}_2\text{N}_{0.196}$ stoichiometry accepted for the primary and humus sludge composition, which was obtained from the COD, C and N mass balances over the Izzett et al. AD systems (Table 2), conforms very closely to independently measured CHON composition measurements on "pure" primary sludge, i.e. within 96%, 100%, 95% and 99% respectively. Considering the complexity of the system and the margin of error in the experimental data, overall the steady state model predicts the anaerobic digester performance over the 7 to 20 d retention time satisfactorily for steady state design. The predictions of the more detailed two phase (aqueous-gas) integrated chemical, physical and biological processes anaerobic digester model (UCTADM1) presented in Chapter 6 are also shown in Figs 11a to f and the steady state AD model can be seen to correlate very closely also with UCTADM1. Hence, the steady state AD model provides a reliable basis for cross-checking simulation model results.

7.8 CONCLUSION

A steady state AD model for the treatment of sewage sludge has been developed. It comprises three sequential parts, (i) a kinetic part with which the influent COD hydrolysed/ utilized, gas and biomass production and effluent COD concentration are calculated for a given retention time, (ii) a stoichiometry part with which the gas composition (or partial pressure of CO_2), ammonia released and alkalinity generated are calculated from the COD utilized and the CHON composition of the hydrolysed COD and (iii) a carbonate system weak acid base chemistry part with which the digester pH is calculated from the partial pressure of CO_2 and alkalinity generated. This model shows that for a given %COD removal, the partial pressure of CO_2 and alkalinity generated, and hence the digester pH, are governed entirely by the influent sludge composition, i.e. X, Y, Z and A in $\text{C}_x\text{H}_y\text{O}_z\text{N}_A$ and the undissociated volatile fatty acids (VFA) species concentration of the influent.

The hydrolysis kinetic part of the model was calibrated against AD data for two types of sewage sludge, (i) a primary and humus sludge mixture extending over a retention time range of 7 to 20 days and (ii) a "pure" primary sludge extending over a retention time range of 7.5 to 60 days. Also, four hydrolysis kinetic rate (r_h) equations were calibrated against both sludge types, viz. (i) first order ($r_h = K_h S_{bp}$), (ii) first order specific ($r_h = K_H S_{bp} Z_{AD}$), (iii) Monod [$r_h = K_m S_{bp} / (K_s + S_{bp}) Z_{AD}$] and (iv) saturation [$r_h = K_M (S_{bp}/Z_{AD}) / (K_s + S_{bp}/Z_{AD}) Z_{AD}$]. Once calibrated against the particular sludge type and taking due account of experimental error, the %COD removals predicted by the four hydrolysis kinetic equations were closely similar, which made it difficult to select the best kinetic equation. Also, by varying the unbiodegradable COD fraction ($f_{ps,up}$) of the sewage sludges within a narrow range ($\sim 2\%$) changed the coefficient of variation (C_{var}) for the first order and first order specific kinetic equations, and the correlation coefficient (R^2) for the Monod and saturation kinetic equations. Within the 2% range in unbiodegradable COD fraction, the different hydrolysis kinetic equations yielded best statistical fits between theoretically predicted and experimentally measured COD removals (or gas production) at different $f_{ps,up}$ values. It is concluded that for both types of sewage sludge, taking due

account of experimental error (i.e. COD mass balance errors) each calibrated kinetic equation is equally good for calculating the %COD removal and gas production versus retention time. For each sewage sludge type, different hydrolysis kinetic rates and unbiodegradable COD fractions were obtained which showed that the pure primary sludge hydrolysed significantly faster and had a lower unbiodegradable particulate COD fraction ($f_{ps,up} = 0.33$) than the primary and humus sludge mixture ($f_{ps,up} = 0.36$). Anaerobic digesters treating pure primary sludge therefore will achieve higher COD or VSS removals at shorter retention times than digesters treating a primary and humus sludge mixture.

Once the COD removal is known from the hydrolysis kinetics part of the model, the CHON composition of the COD removed and the dissociated acetate species concentration in the influent (all utilised in the digester) fixes the gas composition (or partial pressure of CO_2), the ammonia released and the bicarbonate generated (equal to alkalinity generated) through the C, H, O and N mass balances based stoichiometry part of the model. From the influent COD, C and N masses of the primary and humus sludge digesters, a sludge composition of $C_{3.5}H_7O_2N_{0.196}$ has been determined (see Chapter 5). With this sludge composition and measured influent VFA concentration and pH, from which the dissociated acetate species concentration was calculated, the stoichiometry part of the model predicted the experimentally observed gas composition (or CO_2 partial pressure), ammonia released and alkalinity generated well, taking due account of experimental error. With the CO_2 partial pressure and alkalinity generated, the digester pH was calculated from the carbonate system weak acid base chemistry part of the model. The model predicted pH was significantly lower (by ~ 0.30 pH units) than that experimentally measured. From the observed CO_2 partial pressure and alkalinity, which can be measured reliably, there is an error in the measured digester pH, probably due to CO_2 gas loss in sampling and measurement. The "corrected" measured pH should be between 6.84 and 6.88 for the 7, 10, 12, 15 and 20 day retention time systems and the predicted pH is 0.08 to 0.12 pH units higher than these corrected values. A significantly closer correlation between theoretically calculated and experimentally measured digester effluent FSA, alkalinity and pH can be obtained if the N content of the feed sludge is decreased from 0.196 to 0.186 based on the measured N mass exiting the digesters rather than on that entering the digesters. Taking into consideration experimental error (C and N mass balances errors) it is concluded that the steady state model predicts very well the observed 7 to 20 day retention time primary and humus sludge digester performance. The stoichiometry and carbonate system weak acid base chemistry part of the model could not be checked against the "pure" primary sludge digester data set of O'Rourke (1967) because the N concentrations in the effluent were not measured for this data set. The steady state AD model also correlated very closely with the predictions of the two phase (aqueous-gas) integrated chemical, physical and biological processes dynamic simulation anaerobic digester model (UCTADM1) presented in Chapter 5. Provided the hydrolysis rate of the particulate biodegradable organics is known for a particular sewage sludge, the steady state model is useful to (i) estimate retention time, reactor volume, gas production and composition for a required system performance like COD (or VSS) removal, (ii) investigate the sensitivity of the system performance to the design and operation parameters, (iii) provide a basis for cross-checking simulation model results, and (iv) estimate product stream concentrations for design of down- (or up-) stream unit operations of the wastewater treatment plant

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CHAPTER 8

COMPARISON OF A SBR SYSTEM AND A MLE SYSTEM MODELLED IN AQUASIM USING THE UCTOLD MATHEMATICAL MODEL

8.1 INTRODUCTION

Sequencing batch reactor (SBR) technology is widely and successfully applied in many countries the world over (e.g. Australia), however it has not found much application in South Africa. SBRs are essentially batch reactors that combine various treatment process (aerobic, anoxic and anaerobic processes) as well as the solid-liquid separation (sludge settling) into one reactor. This is achieved by alternating cycles of subsequent:

- (i) Batch feeding
- (ii) aerobic conditions,
- (iii) unaerated conditions (anoxic conditions),
- (iv) not aerating and not mixing (for sludge settling)
- (v) supernatant draw off after settling has occurred (effluent)
- (vi) re-filling with a batch of feed.

These cycles are carefully engineered to achieve either full or partial nutrient removal as required (i.e. COD, nitrogen (N), phosphorus (P) removal). This approach has obvious cost savings (in terms of initial capital costs) associated with it, as multiple separate reactors and settling tanks are combined into one single reactor. However, it requires skilled staff to operate as well as a strict operating schedule to achieve the anticipated biological nutrient removal.

The biological processes coupled with the complexity of the SBR hydraulics and operation make it difficult to apply steady state models to SBRs and hence, in order to predict SBR behaviour, a kinetic mathematical model needs to be applied. In order to obtain some insight into SBR system performance it was decided to model SBR systems in AQUASIM using the dynamic model of van Haandel, Ekama and Marais (1981) and comparing the simulated results with those of a similar MLE system also modelled in AQUASIM using the same dynamic model.

The dynamic activated sludge system model used for the simulations is the same as the one incorporated in the UCTOLD program. It evolved out of the steady state aerobic model of Marais and Ekama (1976). This steady state model incorporates carbonaceous energy removal, nitrification and denitrification. Progressively three dynamic models were produced from the Marais and Ekama (1976) steady state model and of those three the van Haandel et al. (1981) dynamic model was incorporated into UCTOLD. Appendix 1 shows this model in matrix format, presenting the processes in the model, its kinetics and the stoichiometric interaction with the compounds. The van Haandel et al. (1981) dynamic model was coded into Aquasim to simulate a MLE system and subsequently a SBR system and compare the simulated results.

8.2 MLE SYSTEM

Figure 1 shows a typical MLE system. As a MLE system only has two reactors (one anoxic and one aerobic reactor), COD and N removal (nitrification, denitrification) only can be achieved in a MLE system, and hence is a suitable system to be modelled by the van Haandel et al. (1981) dynamic model.

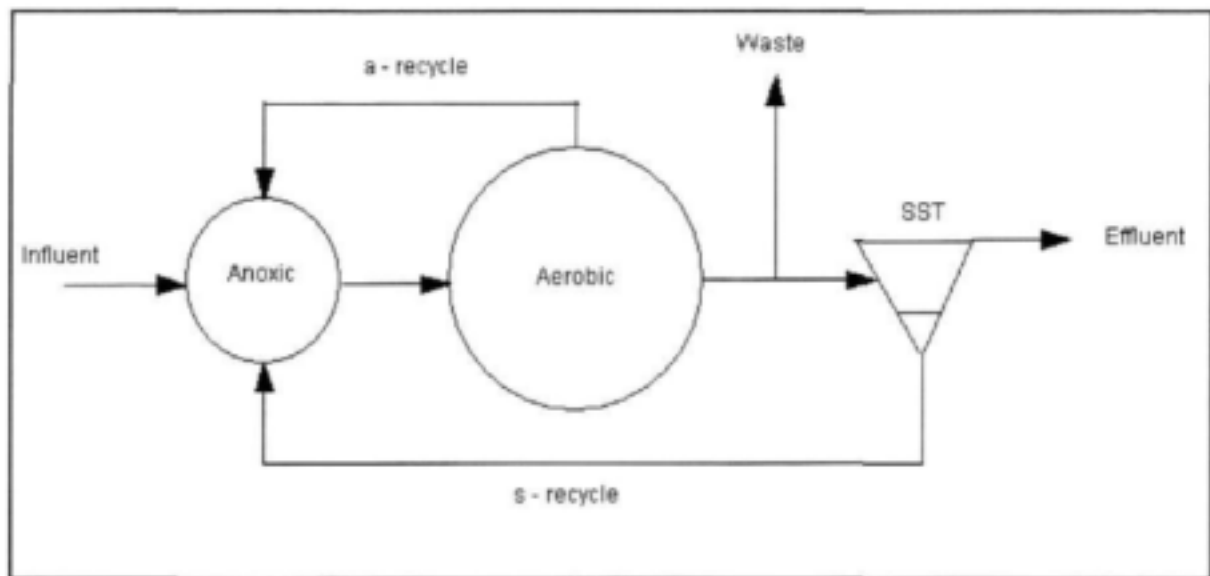


Fig 1: General layout of a MLE system.

The design and operating parameters of the MLE system used in the simulation are as follows:

- (i) Influent flow 20 Ml/d
- (ii) System volume 20 Ml, anoxic mass fraction 0.46 and aerobic mass fraction 0.54
- (iii) Sludge age 30 days
- (iv) Ambient temperature 20°C

The characteristics of the influent wastewater used for the simulations are summarised below:

COD (mg/l): $S_a = 750$; $S_{bpl} = 439$; $S_{btl} = 146$; $S_{upl} = 112.5$; $S_{ustl} = 52.5$.

TKN (mgN/l): $N_e = 60.0$; $N_{obpl} = 3.8$; $N_{obtl} = 1.7$; $N_{cupl} = 7.6$; $N_{oustl} = 1.9$; $N_{al} = 45.0$.

The MLE system described above was set up in AQUASIM, together with the van Haandel et al. (1981) dynamic model. Mass balances (COD and N) were calculated to ensure that no errors occurred in setting up the model in AQUASIM: The COD and N mass balances were 100.73% and 100.00% respectively, indicating that the AQUASIM MLE model was complete and inputted correctly.

8.3 SBR SYSTEM

The design and operating parameters of the SBR were chosen to reflect those of the MLE system as closely as possible:

- (i) Influent flow 20 Ml/d
- (ii) Reactor volume 20 Ml
- (iii) Sludge age 30 days
- (iv) Ambient temperature 20°C

The cycles of the SBR system were modelled in AQUASIM using square wave real list variables, i.e. the required parameters were switched on and off at certain time intervals to create the necessary conditions. For example, for the aerobic period, the K_{la} for oxygen is set to 1000, to create fully

aerobic conditions. For the subsequent anoxic period, the K_{La} for oxygen is set to zero, resulting in zero dissolved oxygen being present in the reactor. Figure 2 shows a graphical example of a K_{La} square wave, with a cycle time of 6 hours, 3 hours of the cycle being aerobic with the subsequent 3 hours being anoxic (un-aerated).

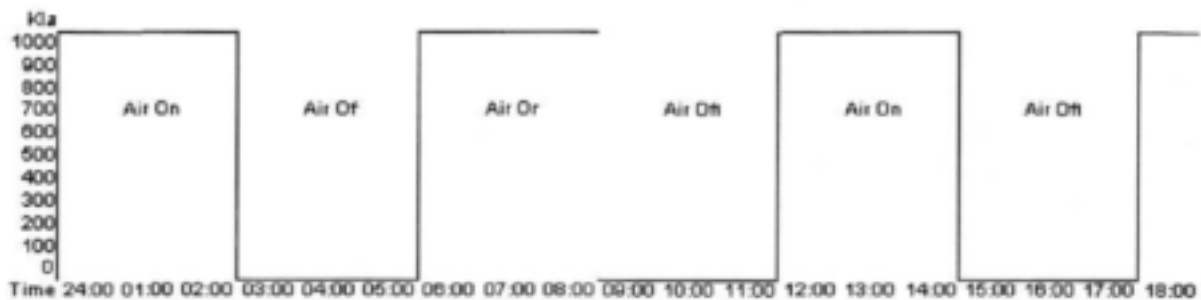


Fig 2: Example of a square wave for the control of aeration: A K_{La} of 1000 represents aerobic conditions (air on), and a K_{La} of zero represents un-aerated conditions (air off).

In the SBR model, three parameters were modelled as square waves, (i) the oxygen supply to switch between aerobic and anoxic conditions and vice versa, (ii) the influent flow to control the batch feeding of the influent and (iii) the effluent flow to simulate SBR decanting.

For the SBR system modelled in AQUASIM, a cycle time of 6 hours was chosen, each cycle consisting of 3.25 hours fully aerobic conditions and a subsequent anoxic period of 2.75 hours. This corresponds to an aerobic mass fraction of 0.54 and an anoxic mass fraction of 0.46 over 24 hours, the same aerobic and anoxic mass fractions used for the MLE system described above. At the beginning of each cycle the influent flow is switched on for 3 hours, batch feeding a quarter of the daily flow to the reactor over a 3 hour period (this corresponds to an influent flow of 40 Mt/d for three hours). After three hours the influent flow is switched off completely. 5 hours into each cycle time the effluent flow is switched on, simulating the decanting of the effluent, and the required effluent volume is abstracted over a period of one hour (corresponding to an effluent flow of 116 Mt/d for one hour). At the end of each cycle the effluent flow is switched off completely and the next cycle begins by switching the influent back on to batch feed the next influent, thereby filling the reactor, which will reach maximum volume after three hours, when the influent is switched off again. The aerobic and anoxic periods include the respective batch feeding and decanting periods, i.e. for hours 1 to 3 the influent flow and aeration is switched on, for hours 3 to 3.25 the influent flow is off and the aeration is on, for hours 3.25 to 5 the influent flow is off and aeration is off and for hours 5 to 6 the influent flow is off, aeration is off and effluent flow is switched on.

The waste flow is abstracted only when the reactor is full (i.e. after the influent has been switched off, but before the effluent flow is switched on) so that the concentration of mixed liquor wasted does not vary significantly. The daily waste volume is wasted in batches of a quarter of the daily volume required during each cycle.

The decanting period (hours 5 to 6 for each cycle) includes the time that the sludge would require to settle to the bottom of the reactor once the mixing has been switched off in a full scale SBR system. The actual settling of the sludge is of no consequence in the model, as ideal solids separation is assumed, i.e. the effluent decanted contains zero solids and therefore all solids remain in the reactor when the effluent is abstracted.

The SBR system described above was set up in AQUASIM, together with the van Haandel, Ekama and Marais (1981) dynamic model, receiving the identical influent wastewater as the MLE system.

Mass balances (COD and N) were calculated to ensure that no errors occurred in setting up the model in AQUASIM: The COD and N mass balances were 99.97% and 100% respectively, indicating that the AQUASIM SBR model was complete and inputted co Biodeg. particulate rectly.

8.4 SIMULATION RESULTS

Table 1 lists the results obtained from the simulation of the MLE and SBR systems.

Comparing the effluent of the MLE and SBR systems, it can be seen that with the exception of the free and saline ammonia (FSA) and nitrate effluent values, the results are very similar. The SBR system effluent FSA and nitrate is 0.6 mgN/l and 7.9 mgN/l respectively higher than that in the effluent of the MLE system, which indicates that while the two systems nitrify effectively equally well (FSA difference <1 mgN/l) the MLE system denitrifies better than the SBR system does. This result is most likely due to the cycle times and cycle compositions chosen. It was found that the performance of the SBR system is very sensitive to the cycle times and inner-cycle setups and it may therefore be possible to optimise the cycles to achieve the best performance for the SBR system. Further, it should be noted that in full scale SBR plants, the plant operators deliberately throttle the aeration during the aerobic periods to effect simultaneous nitrification / denitrification during the aerobic periods. This practice enhances the N removal in full scale operations and was not considered for the simulations discussed here.

Comparing the simulated results for the mixed liquor, it can again be seen that overall the results for the MLE and SBR systems are similar. It can be seen that the effluent FSA concentration for the MLE (aerobic reactor) and SBR systems are effectively equal, suggesting that the difference seen in the effluent results may be due to the fact that the mixed liquor results were averaged over a complete 24 hour period, while the effluent results in effect only represent 6 hours, the six hours when the effluent was abstracted. The difference in nitrate concentrations is more pronounced in the mixed liquor, the SBR mixed liquor containing on average 11.7 mgN/l more nitrate than the MLE mixed liquor.

The biodegradable and unbiodegradable soluble compounds for both the MLE and SBR systems are effectively equal. The particulate concentrations (biodegradable as well as unbiodegradable) are similar, however the SBR system shows consistent marginally lower values for all particulate compounds (including the organism masses and endogenous residue). This can more than likely be attributed to the average values used for the SBR system as well as the constantly changing concentrations in the SBR reactor rather than being an indication that the system response of the two systems is different.

8.5 CONCLUSION

This investigation has shown that it is possible to successfully simulate SBR type systems in AQUASIM, and the comparison to a MLE system with similar design and operating parameters has further shown that the two systems produce mixed liquors and effluents of similar quality. The main differences seem to be the denitrification performance of the MLE and SBR systems in so far as that in the simulations described here, the MLE system effluent nitrate concentration was considerably lower than that of the SBR system. While this may in part be due to the fact that the SBR concentrations are averaged from a data set in which the concentrations vary widely (because of the way that a SBR system operates) it has also been found that the SBR system is extremely sensitive to the cycle durations and cycle compositions chosen. Further, the N removal in full scale SBR systems is increased by throttling the aeration during the aerobic periods, thereby creating simultaneous nitrification / denitrification during the aerobic periods and increasing the overall N removal of the

system. This was however not included in the simulations discussed above.

This shows that in future simulation runs the cycle lengths and compositions as well as the effect they have on the overall SBR system performance must be investigated more closely. It may be possible that when the optimum cycle time and composition combination is found, the denitrification performance of the SBR system may be closer to that of the MLE system in this investigation. A further area of interest would be to repeat the above exercise with a phosphorus removal kinetic model, e.g. UCTPHO, to investigate if it is possible to have P removal in a SBR system and if so, how this SBR P removal compares with that of a conventional P removal system (e.g. a UCT configuration).

Table 1: Results from the simulations on the MLE and SBR systems.

Compound	Type	MLE Mixed Liquor	MLE Effluent	SBR Mixed Liquor ^{*1}	SBR Effluent ^{*2}
NH ₄ ⁺ - mgN/l	Free & Saline Ammonia	7.9 / 0.7 ³	0.7	0.6	1.3
NO ₃ - mgN/l	Nitrate	0 / 0.9	0.9	12.6	8.8
N _{obs} - mgN/l	Biodeg. soluble	1.6 / 0.5	0.5	1.3	0.7
N _{ous} - mgN/l	Unbiodeg. soluble	1.8 / 1.8	1.8	1.8	1.8
N _{obp} - mgN/l	Biodeg. particulate	50.7 / 47.8	0	44	0
N _{oup} - mgN/l	Unbiodeg. particulate	226 / 228	0	212.2	0
S _{bs} - mgCOD/l	Biodeg. soluble	15.4 / 0.2	0.2	0.1	0
S _{us} - mgCOD/l	Unbiodeg. soluble	52 / 52	52	52	52
S _{bep} - mgCOD/l	Unbiodeg. particulate	3375 / 3375	0	3105	0
S _{bep} - mgCOD/l	Biodeg. particulate	85 / 75	0	65	0
Z _{bh} - mgCOD/l	Heterotroph biomass	1345 / 1389	0	1377	0
Z _{ba} - mgCOD/l	Autotroph biomass	86 / 81	0	82	0
Z _e - mgCOD/l	Endogenous residue	1800 / 1800	0	1770	0

^{*1} Because the volume of the SBR fluctuates constantly, these values represent 24hr averages.

^{*2} Because the effluent of the SBR is produced in 6 batches over 24 hours, these values represent the batch averages, averaged over 24hrs.

³ First value (before slash) is anoxic reactor, second value (after slash) is aerobic reactor.

8.6 REFERENCES

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- Van Haandel AC, Ekama GA and Marais GvR(1981). The activated sludge process Part 3 - single sludge denitrification. *Water Research* 15 1135-1152.

APPENDIX A

PRELIMINARY EVALUATION OF PRIMARY AND WASTE ACTIVATED SLUDGE CHARACTERISATION RESULTS

A.1 INTRODUCTION

During the development of the model for anaerobic digestion of sewage sludges (see Appendix 3), initially the primary sewage sludge composition was assumed to be the same as the generally accepted stoichiometric formulation for activated sludge: $C_5H_7O_2N$ (WRC, 1984). However, since the output (pH, gas volume and composition) from the digester is a direct consequence of the input and its composition, $C_5H_7O_2N$ could not reflect the output of the system that was used to calibrate the anaerobic model (the anaerobic model was calibrated using data from Izzet *et al.*, 1992), and had to be changed accordingly. Through a series of calculations (see Appendix 3) the general formulation for the primary sewage sludge used by Izzet *et al.* (1992) experiments was found to be $C_{3.5}H_7O_2N_{0.196}$. This stoichiometric formulation for primary sewage sludge was accepted for all subsequent simulations of the Izzet *et al.* (1992) experiments.

It is not certain whether this composition applies to primary sewage sludges in general or not, and this prompted further investigations into characterising primary and waste activated sludges (WAS). Different sewage sludges (primary sludge, waste activated sludge and anaerobic digester sludge) were sampled and analysed for C, H and N (by an external laboratory) and COD, N, P and settleable solids (in the water research laboratory at the University of Cape Town). With this measured data the CHON composition can be calculated for each of the sludges and the primary sewage sludge compared with that estimated from the anaerobic digester model, and the WAS with the 'standard' value of $C_5H_7O_2N$.

A.2 RESULTS

The following sewage sludges were analysed:

- WAS from a laboratory scale MLE system (10 day sludge age, N removal only).
- WAS from a laboratory scale UCT system (15 day sludge age, N and P removal).
- WAS from a second laboratory scale MLE system (10 day sludge age, N removal only).
- WAS from a laboratory scale UCT system (12 day sludge age, N and P removal).
- Primary sewage sludge from the Mitchell's Plain treatment plant in Cape Town.
- Anaerobic digester sludge from a laboratory scale anaerobic digester (10 day retention time).
- Primary sewage sludge from the Athlone treatment plant in Cape Town.
- Anaerobic digester sludge from a laboratory scale anaerobic digester (10 day retention time)

One litre of each sludge was drawn, and the following analysis was done on the sludge in the water research laboratory at the University of Cape Town:

1. Mixed liquor volatile (VSS) and total (TSS) suspended solids.
2. Chemical oxygen demand (COD).
3. Total Kjeldahl nitrogen (TKN) and free and saline ammonia (FSA).
4. Total phosphorus and orthophosphates.

A.2

The laboratory analysis above was done according to the respective methods contained in 'Standard Methods for the Examination of Water and Wastewater', American Public Health Association, 13th Edition, 1971.

The remainder of the sludge was dried in a drying oven at 100°C. After drying, the solids were pulverised using a mortar and pestle and sent to the ESCOM laboratories for CHN testing. ESCOM uses the Leco CHN 1000 Instrument for CHN testing. The dry samples are homogenised by micronising the nominal top size down to at least 212 micron and ideally 150 micron, after which the samples are analysed for CHN by the Leco CHN 1000 instrument. The results are returned as %C, %H and %N.

With the above analysis results available, the general CHON(P) composition can be calculated as follows:

From the carbon (C), hydrogen (H), nitrogen (N) and phosphorus (P) (% or mg) analyses, the respective compound masses are calculated from the TSS (or VSS). Since the masses of C, H, N, P and oxygen (O) must add up to the total TSS mass, once the masses of C, H, N and P are known, it is assumed that the remaining TSS mass is O. This assumption is not true in reality, because there may be minerals and other compounds present in the sample, however the O value is revised later on in the calculations to take account of this.

Once the TSS is apportioned into its respective masses of C, H, O, N and P, the values are converted into proportions of 1 gram of TSS. This is then converted to the molar scale and the moles of each of the compounds is divided by the molar mass of the compound with the smallest molar mass, which is usually P. This yields a general formulation in terms of C, H, O, N and P (e.g. $C_{86.1}H_{150.58}O_{83.41}N_{15.58}P_1$ for (a) in Table 1 below). This general formulation has to be simplified further to resemble the generally accepted formulations, e.g. $C_5H_7O_2N$. It was decided to simplify the general formulation by bringing it to a H_7 basis, and in case of (a) below in Table 1, this simplification yields $C_4H_7O_{2.295}N_{0.72}P_{0.05}$.

Table 1: COD/VSS, TKN/VSS and calculated stoichiometric formulation for the sludges tested.

Sample	COD/VSS Ratio	TKN/VSS Ratio	Measured formulation	Literature formulation
(a) 10d MLE WAS	1.387	0.087	$C_{4.91}H_7O_{2.295}N_{0.72}P_{0.05}$	$C_5H_7O_2N$
(b) 15d UCT WAS	1.222	0.073	$C_{3.91}H_7O_{2.87}N_{0.54}P_{0.09}$	$C_5H_7O_2N$
(c) 10d MLE 2 WAS	1.147	0.086	$C_{4.32}H_7O_{3.44}N_{0.65}P_{0.07}$	$C_5H_7O_2N$
(d) 12d UCT WAS	1.181	0.081	$C_{4.31}H_7O_{3.39}N_{0.61}P_{0.11}$	$C_5H_7O_2N$
(e) Mitchell's Plain PS	2.029	0.054	$C_{3.91}H_7O_{2.04}N_{0.16}P_{0.01}$	* $C_{3.5}H_7O_{2.1}N_{0.196}$
(f) Anaerobic Digested Sludge	1.720	0.054	$C_{3.92}H_7O_{2.64}N_{0.35}P_{0.1}$	$C_5H_7O_2N$
(g) Athlone Primary Sludge	2.124	0.037	$C_{3.38}H_7O_{1.5}N_{0.21}P_{0.01}$	* $C_{3.5}H_7O_{2.1}N_{0.196}$
(h) Anaerobic Digested Sludge	1.687	0.038	$C_{4.08}H_7O_{1.63}N_{0.22}P_{0.04}$	$C_5H_7O_2N$

* Determined by Sotemann et al. (2005) with a anaerobic digestion mass balances model.

This simplified general formulation is then used to calculate the theoretical COD, which is compared to the actual measured COD. If the theoretical and measured COD differ substantially, the COD is recalculated with the O as a variable and substituting the measured TSS and COD values, yielding a revised O, which in the case of (a) in Table 1 worked out to $O_{2.295}$. The corrected general formulation for sludge (a) is $C_4H_7O_{2.295}N_{0.72}P_{0.05}$, as can be seen from Table 1.

The calculations were done on a TSS basis as well as a VSS basis, but it was found that the differences in the resulting general formulations were negligible. Table 1 summarises the results for all the sludges analysed.

A.3 CONCLUSIONS

From Table 1 it can be seen that the general formulations calculated for the WAS (a, b, c and d) deviate considerably from the generally accepted $C_5H_7O_2N$ formulation. The WAS tested here have a lower carbon content (~4 as opposed to 5), higher oxygen content (~3 as opposed to 2) and lower nitrogen content (~0.5-0.7 as opposed to 1) than the generally accepted formulation. The lower oxygen and nitrogen values can also be seen from the measured COD/VSS and TKN/VSS ratios: The theoretical values are 1.48 and 0.1 respectively and it can be seen that all the values for the WAS samples are considerably lower than the theoretical ratios.

This does not have an effect on the anaerobic sludge digestion model of primary sludge only, however it will have an effect when the model is used to simulate the digestion of WAS only, or a blend of WAS and primary sludge. If the WAS has a lower carbon content than the generally accepted formulation suggests, this will impact on the methane production and the carbonate weak acid/base system (which will in turn impact on the CO_2 produced and the pH of the system). Similarly, if the WAS has a lower nitrogen content than the generally accepted formulation suggests, this will have an impact on the effluent free and saline ammonia concentrations.

The general formulations for the Mitchell's Plain (e) and Athlone (g) primary sludges (see Table 1) are very close to the formulation that was found for the anaerobic model ($C_{3.5}H_7O_2N_{0.196}$). This indicates that the formulation used in the anaerobic model is in fact the correct one to use, and that the formulation for primary sewage sludge may be general and is not the same as that generally accepted for activated sludge ($C_5H_7O_2N$).

The anaerobic digester sludges (f and h, Table 1) seem to lie between the calculated formulations for waste activated sludge and primary sewage sludge, which is not unexpected. Anaerobic digester sludge is a blend of residual primary sludge and the active organism population that grow in the digester and effect anaerobic digestion, hence the general formulation for anaerobic digester sludge would be a combination of the general formulations for primary sewage sludge and that of the organisms (which may be similar to that of WAS).

The results from this investigation are encouraging and warrant a more in depth investigation into the general formulations of primary sewage sludges, waste activated sludges and anaerobic digester sludges. More sampling on a wider range of samples would be required to ascertain whether:

1. Primary sewage sludges from other sources (treatment plants) than those tested in this investigation will have a similar calculated formulation.
2. The formulation of a blend of primary sewage sludge and WAS is in fact the sum of the general formulations of the separate primary sewage and WAS sludges.
3. The general formulation of anaerobic digester sludge is the sum of the general formulation for the organisms and the residual primary sewage sludge.

A more in depth investigation into the general formulation of primary sewage, waste activated and anaerobic digester sludges will help with the understanding of the sludges and have a valuable input to the anaerobic digestion model, the integrated mixed weak acid/base chemical, physical and biological processes activated sludge model (Appendix 2) and the mass balances project as a whole.

A.4 REFERENCES

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- Izzet HB, Wentzel MC, Ekama GA (1992). The effect of thermophilic heat treatment on the anaerobic digestibility of primary sludges. Research Report W76, University of Cape Town, Department of Civil Engineering, Rondebosch 7701, Cape, South Africa.
- Sötemann SW, Ristow NE, Wentzel MC and Ekama GA (2005b) A steady state model for anaerobic digestion of sewage sludges. *Water SA* (submitted).
- WRC (1984). Theory, design and operation of nutrient removal activated sludge processes. Published by the WRC, P O Box 824, Pretoria 0001, South Africa.

APPENDIX B

**PRODUCTS DURING CONTRACT PERIOD
(APRIL 2002 TO MARCH 2005)**

1. Books and chapters in books

- 416 Wentzel MC, Ekama GA and Loewenthal RE (2003) Fundamentals of biological behaviour and wastewater strength measurement; Chapter 9 in Handbook of water and wastewater microbiology. Elsevier Science Ltd., 131-157.

2. Referred international journal papers.

- 411 van Rensburg P, Musvoto EV, Wentzel MC and Ekama GA (2003) Modelling multiple mineral precipitation in anaerobic digester liquor. *Water Research* 37(13) 3087-3097.
- 498 van Rensburg P, Musvoto EV, Wentzel MC and Ekama GA (2003) Mineral precipitation from anaerobic digester liquor at the Cape Flats Sewage Treatment Plant. *Water SA*, WISA 2002 Edn 92-99.
- 501 Ekama GA and Wentzel MC (2004) Modelling inorganic material in activated sludge systems. *Water SA* 30(2) 153-174.
- 516 Ekama GA and Wentzel MC (2004) A predictive model for the reactor inorganic suspended solids concentration in activated sludge systems. *Water Research* 38(19) 4093-4106.

3. International conference papers

- 480 van Rensburg P, Ekama GA and Wentzel MC (2003) Mineral precipitation from anaerobic digester liquor at the Cape Flats Treatment plant. Procs 9th IWA Design, operation and economics of large wastewater treatment plants, Prague, 1-4 Sept.
- 503 Wentzel MC and Ekama GA (2003) Strengths and weaknesses of biological nutrient removal activated sludge simulation models. Procs. World Wide Engine for Simulation and Training (WEST) of wastewater treatment plants Scientific Support Centres conference, Gent, 14-16 Apr.
- 521 Sotemann SW, Ristow NE, van Rensburg P, Wentzel MC, Loewenthal RE and Ekama GA (2004) Integrated biological, chemical and physical processes kinetic model for anaerobic digestion of sewage sludge. Procs. Anaerobic digestion 2004 - 10th World Congress - Anaerobic Bioconversion for Sustainability, Montreal, 29 Aug - 2 Sep. Vol 3, 1416-1420.
- 522 Loewenthal RE, Sotemann SW, Wentzel MC and Ekama GA (2004) Three phase mixed weak acid/base chemistry kinetic modelling of multiple mineral precipitation problems. Procs. CEFIC-CEEP International conference on Struvite: Its role in phosphorus recovery and reuse. Cranfield, UK, 17-18 June.

4. Local (SA) conference papers

- 412 van Rensburg P, Musvoto EV, Wentzel MC and Ekama GA (2002) Mineral precipitation from anaerobic digester liquor at the Cape Flats Treatment plant. Procs 7th WISA Biennial conference 19-23 May Durban, ISBN 1-86845-844-X, Paper 038.
- 507 Ekama GA and Wentzel MC (2004) Estimating the reactor inorganic suspended solids concentration in activated sludge systems. Procs. 8th biennial WISA conference and exhibition, Cape Town, 2-6 May, 1459-1473, CD-ROM ISBN 1-920-01728-3.
- 514 Sotemann SW, Musvoto EV, Wentzel MC and Ekama GA (2004) Integrated biological, chemical and physical processes kinetic modelling Part 1 - Anoxic and aerobic processes of carbon and nitrogen removal in the activated sludge system. Procs. 8th biennial WISA conference and exhibition, Cape Town, 2-6 May, 1044-1062, CD-ROM ISBN 1-920-01728-3.

B.2

- 515 Sotemann SW, van Rensburg P, Ristow NE, Wentzel MC, Loewenthal RE and Ekama GA (2004) Integrated biological, chemical and physical processes kinetic modelling Part 2 - Anaerobic digestion of sewage sludges. Procs. 8th biennial WISA conference and exhibition, Cape Town, 2-6 May, 1327-1344, CD-ROM ISBN 1-920-01728-3.

APPENDIX C

CAPACITY BUILDING REPORT

Undergraduate and postgraduate students who did undergraduate final year (4th year equivalent to Honours) and postgraduate thesis projects within the ambit of this project.

- 1) Wilma Legodi (Bachelor of Science in Engineering graduated Dec 2002)
- 2) Dumisani Nxumalo (Bachelor of Science in Engineering graduated Dec 2003)
- 3) Brian Enslin (Bachelor of Science in Engineering graduated Dec 2003)
- 4) Sandile Gqoboka (Bachelor of Science in Engineering graduated Dec 2004)
- 5) Sven Sotemann (Doctor of Philosophy- graduated Dec 2005)

Other related WRC reports available:

A technical and financial review of sludge treatment technologies

Marx CJ; Alexander WV; Johannes WG; Steinbach-Kane S

In this project an authoritative reference document was developed, which reviews and evaluates the applicability and cost implications under South African conditions of sludge management technologies that are available both locally and internationally. It therefore fills a gap experienced by local sludge handling agencies which previously did not have access to a reference standard that could guide them in making decisions regarding technical performance and relative costs of alternative sludge treatment and management options. As background to the presentation of available sludge management technologies, the report gives an overview of current sludge management practices in South Africa, an estimate of sludge quantities and qualities and a brief description of commonly used sludge treatment and disposal methods. The report also describes the status quo of South African legislation regarding sludge management and describes the possible utilisation and disposal routes available within the South African legal framework. The sludge treatment requirements and available technologies for each of the utilisation or disposal routes are listed in matrix form for easy reference and use. The processes are classified in different categories (embryonic, innovative and established) according to their South African application. Established processes are described in technology sheets that can be easily updated. These sheets provide a brief description of each process; assess its applicability under South African conditions list advantages and disadvantages as well as references to existing installations and typical literature references. First order cost estimates are given for the established processes considered most applicable to South African circumstances. Cost estimates are presented in cost sheets and include estimates of capital costs, annual costs of the capital expenditure operating costs. Typical case studies are presented to illustrate the use of the Sludge Management Decision Matrix and the cost sheets.

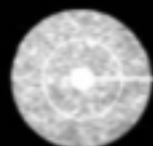
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