

MASS BALANCES MODELLING OVER WASTEWATER TREATMENT PLANTS III

Report to the
Water Research Commission

by

**DS Ikumi, TH Harding, M Vogts, MT Lakay, H Mafungwa, CJ Brouckaert
and GA Ekama**

Water Research Group, Department of Civil Engineering,
University of Cape Town

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Water Research Commission
Private Bag X03
GEZINA, 0031

orders@wrc.org.za or download from www.wrc.org.za

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EXECUTIVE SUMMARY

To aid finding the most cost effective methods for the design and operation of wastewater treatment plants, for minimization of energy consumption and cost while maximizing nutrient recovery and improving effluent quality, the purpose of this project is to develop three phase (aqueous-gas-solid) steady state and dynamic mathematical models for the anaerobic and aerobic digestion of sludge; including waste activated sludge (WAS) produced by enhanced biological phosphorus removal (EBPR) plants, within a plant-wide setting. To accomplish this goal, the following four objectives were achieved:

- 1 Carry out an experimental investigation to generate the data required for both steady state and dynamic model development: The experimental set up was large to mimic three real wastewater treatment plant types at laboratory scale, viz nitrification-denitrification activated sludge treating raw wastewater, a nitrification-denitrification (ND) activated sludge (AS) system treating settled wastewater and a nitrification-denitrification enhanced biological phosphorus removal (NDEBPR) activated sludge system treating settled wastewater with separate anaerobic digestion (AD) of the WAS from each system, the primary sludge (PS) added to the settled wastewater to make up the raw wastewater and a PS-WAS blend.
- 2 Develop a steady state anaerobic digestion model including phosphorus by extending the steady state model of Sötemann et al. (2005a): From the experimental data of five anaerobic digesters, each operated at five different sludge ages, the hydrolysis kinetic rates of primary sludge, ND activated sludge system WAS and NDEBPR activated sludge system WAS were determined and included in the stoichiometric part of the anaerobic digestion model developed by Harding et al. (2009). Since mineral precipitation took place during the anaerobic digestion of NDEBPR WAS containing phosphorus accumulating organisms (PAOs), the steady state mixed weak acid/base chemistry part of the AD model was extended to include three phases (aqueous-gas-solid).
- 3 Develop a dynamic anaerobic digestion model (ADM-3P) that includes phosphorus from NDEBPR WAS by extending the two phase (aqueous-gas) dynamic anaerobic digestion model for PS and ND activated sludge system WAS by Sötemann et al. (2005b), to include multiple organic types and three phase (aqueous-gas-solid) mixed weak acid/base chemistry for multiple mineral precipitation. Due to the significant increase in size and complexity to model the three wastewater treatment plants, as plant-wide configurations, in three phases, the models were coded in WEST®, which is a program capable of simulating many bioprocesses in various unit operations assembled into a wastewater treatment plant.
- 4 Develop a three phase activated sludge dynamic model (ASM2-3P) by adding full element C, H, O, N, P mass balanced stoichiometry to extending the existing NDEBPR activated sludge model ASM2 (Henze et al., 1995) and ensuring (i) its compatibility with the three phase anaerobic digestion dynamic model and (ii) its equivalence to the full element mass balanced stoichiometry ASM dynamic model (without P) of Sötemann et al. (2005c). This three phase activated sludge model with

EBPR was applied to plant-wide simulation of NDEBPR activated sludge with anoxic-aerobic digestion of concentrated phosphorus-rich waste activated sludge with mineral precipitation to produce dewatering liquor with low nitrogen and phosphorus.

The three phase steady state anaerobic digestion model (ADM-3P) developed in this investigation can be used on its own or linked with a steady state NDEBPR model, such as that developed by Wentzel et al. (1990), to construct a steady state plant-wide model, which is useful to make design decisions for the Wastewater Treatment Plant (WWTP)/ Water Resource Recovery Facility (WRRF) unit sizes and layout. Similarly, the ASM2-3P and ADM-3P models, which were linked to form the plant-wide dynamic model, can be used independently for simulating anoxic-aerobic and anaerobic sludge stabilisation systems.

The steady state and dynamic models were developed simultaneously because the steady state models were required to determine kinetic rates and sludge compositions for dynamic model input and calibration. This was possible because the steady state and dynamic activated sludge and anaerobic digestion models are based on the same basic principles, mass balanced stoichiometry, just in simplified form for the steady state model, without significant loss of accuracy. The steady state models allow sizing and optimization of individual wastewater treatment plant unit operations i.e. direct calculation of sludge age, reactor volumes and recycle flows for known wastewater characteristics or wastewater characteristics for existing wastewater treatment plants before performing dynamic simulations and so obviate much of the trial and error use of dynamic models. Once the wastewater treatment plant layout is established with steady state models, dynamic models can be applied to its operation to minimize energy consumption and cost while maximizing nutrient recovery and improving effluent quality.

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LIST OF ABBREVIATIONS and SYMBOLS

Abbreviation	Description
AD	anaerobic digestion
ADM-3P	anaerobic digestion model in 3 phases (developed in this project)
ADM1	IWA anaerobic digestion model No 1
AerD	aerobic digestion
AS	activated sludge
ASM1	IWA activated sludge model No 1
ASM2-3P	activated sludge model No 2 in 3 phases (developed in this project)
AxAerD	anoxic-aerobic digestion
BPO	biodegradable particulate organics
BSM2	benchmark simulation model no 2
BSO	biodegradable soluble organics
C	carbon
Ca	calcium
CBIM	continuity based interface method
COD	chemical oxygen demand
CSTR	continuously stirred tank reactor
DO	dissolved oxygen
DWL	dewatering liquor
EBPR	enhanced biological P removal
FBSO	fermentable biodegradable soluble organics
FSA	free and saline ammonia
GMP	good modelling practice
H	hydrogen
IC	inorganic carbon
ISS	inorganic suspended solids
IWA	International Water Association
K	potassium
MBR	membrane bioreactor
Mg	magnesium
MLE	modified Ludack-Ettinger
N	nitrogen
ND	nitrification denitrification
NDEBPR	nitrification denitrification enhanced biological P removal
O	oxygen
OHO	ordinary heterotrophic organisms
OP	ortho phosphorus
OrgN	organic nitrogen
OrgP	organic phosphorus
OUR	oxygen utilization rate
P	phosphorus
PAO	phosphorus accumulating organisms
PHA	polyhydroxyalkanoates
pK	negative log to base 10 of dissociation constant K
PO	particulate organics (BPO+UPO)

PP	polyphosphate
PRG	Pollution Research Group (at UKZN)
PS	primary sludge
PST	primary settling tank
PWM_SA	plant wide model – South Africa (developed in this project)
S	sulphur
TKN	total Kjeldahl nitrogen
TOC	total organic carbon
TOD	total oxygen demand
TP	total phosphorus
TSS	total suspended solids
UASB	upflow anaerobic sludge bed
UCT	University of Cape Town
UCTSDM1	UCT (anaerobic) sludge digestion model
UKZN	University of KwaZulu-Natal
UPO	unbiodegradable particulate organics
USO	unbiodegradable soluble organics
VFA	volatile fatty acids
VSS	volatile suspended solids
WAS	waste activated sludge
WDC	WEST development centre
WEST	World-wide engine for simulating treatment plants
WRG	Water Research Group (at UCT)
WRRF	water resource recovery facility
WW	wastewater
WWTP	wastewater treatment plant

Symbol	Description
a	molar nitrogen composition of organics in $C_xH_yO_zN_aP_bS_c^{ch}$ (molN/mol)
b	molar phosphorus composition of organics in $C_xH_yO_zN_aP_bS_c^{ch}$ (molP/mol)
c	molar sulphur composition of organics in $C_xH_yO_zN_aP_bS_c^{ch}$ (molS/mol)
ch	charge composition of organics in $C_xH_yO_zN_aP_bS_c^{ch}$ (charge/mol)
f	ortho-P split between $H_2PO_4^-$ and HPO_4^{2-} species
f_c	mass ratio of carbon (gC/gVSS or gC/g organics)
f_{ch}	charge to mass ratio (charge/gVSS or charge/g organics)
f_{cv}	mass ratio of COD (gCOD/gVSS or gCOD/g organics)
f_h	mass ratio of hydrogen (gH/gVSS or gH/g organics)
f_n	mass ratio of nitrogen (gN/gVSS or gN/g organics)
f_o	mass ratio of oxygen (gO/gVSS or gO/g organics)
f_p	mass ratio of phosphorus (gP/gVSS or gP/g organics)
f_s	mass ratio of sulphur (gS/gVSS or gS/g organics)
$f_{S'up(AD)}$	Unbiodegradable particulate COD in influent wastewater as determined with anaerobic digestion models
$f_{S'up(AS)}$	Unbiodegradable particulate COD in influent wastewater as determined with activated sludge models
K_h	first order hydrolysis rate (/d)

K_H	specific first order hydrolysis rate [$l/(gCOD \cdot d)$]
K_m	maximum specific hydrolysis rate in Monod kinetics ([$gCOD/(gCOD \cdot d)$])
K_M	maximum specific hydrolysis rate in saturation kinetics ([$gCOD/(gCOD \cdot d)$])
K_S	half-saturation concentration in hydrolysis rate in Monod kinetics ($gCOD/l$)
K_S	half-saturation concentration in hydrolysis rate in saturation kinetics ($gCOD/gCOD$)
K_{spm}	mineral solubility product
p_{CO_2}	partial pressure of CO_2 in the gas phase (mol/mol)
pK_{p2}	negative log to base 10 of the 2 nd dissociation constant of the OP system
q_{BPO}	polyphosphate content of BPO (molPP/molBPO)
q_{PO}	polyphosphate content of PO (molPP/molPO)
r_h	volumetric hydrolysis rate [$gCOD/(l \cdot d)$]
$S_{up(AS)}$	Unbiodegradable particulate COD concentration of activated sludge ($mgCOD/l$)
S_{upi}	Influent unbiodegradable particulate COD concentration ($mgCOD/l$)
x	molar carbon composition of organics in $C_xH_yO_zN_aP_bS_c^{ch}$ (molC/mol)
X_{BG}	PAO biomass concentration ($mgCOD/l$ in dynamic models or $mgVSS/l$ in steady state models)
X_{BH}	OHO biomass concentration ($mgCOD/l$ in dynamic models or $mgVSS/l$ in steady state models)
X_{EG}	unbiodegradable endogenous residue from PAO ($mgCOD/l$ in dynamic models or $gVSS/l$ in steady state models)
X_{EH}	unbiodegradable endogenous residue from OHO ($mgCOD/l$ in dynamic models or $gVSS/l$ in steady state models)
X_I	Unbiodegradable particulate COD concentration from the influent accumulating in the activated sludge as VSS ($mgCOD/l$ in dynamic models or $mgVSS/l$ in steady state models)
y	molar hydrogen composition of organics in $C_xH_yO_zN_aP_bS_c^{ch}$ (molH/mol)
z	molar oxygen composition of organics in $C_xH_yO_zN_aP_bS_c^{ch}$ (molO/mol)
μ_{A20}	maximum specific growth rate of nitrifiers at 20°C (/d)

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

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- 650 Ekama GA (2011) Biological nutrient removal, Chapter 4.14 (94) in Treatise on Water Science, Vol 4, 409-528. Ed. Wilderer P. ISBN13:978-0-444-53193-3.
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- 695 Vogts M, Ikumi DS and Ekama GA (2014) Anoxic -aerobic digestion of P rich waste activated sludge. Research Report W139.

Reports obtainable from – Dept of Civil Engineering, Univ of Cape Town, Rondebosch, 7701, Cape, South Africa.

CAPACITY BUILDING

The following BSc (Eng) (equivalently Hons), MSc (Eng) and PhD students completed thesis research projects within this WRC project.

BSc (Eng) – 14

- 2007 Lancaster, Luke; Vogts, Michelle
- 2008 Motsumi, Gracious
- 2010 Robertson, Jennifer; Robertson, Struan; Biccari, Danillo; Hargey, Yusaf; Nefale, Mashau; Scurr, Edwin.
- 2012 Rudi Botha, Simon Woolf ; Matthew Gruter; Fasil Haile; Natsai Verenga,

MSc (Eng) – 2

- 2009 Harding Theo
- 2013 Vogts, Michelle

PhD – 1

- 2009 Ikumi, David

CHAPTER ONE

INTRODUCTION

1.1 STEADY STATE AND DYNAMIC MODELS OF WRRFs

1.1.1 Plant wide models

Recently research attention has been devoted to linking dynamic models for activated sludge (AS) and anaerobic digestion (AD) to develop plant-wide water resource recovery facility (WRRF) /wastewater treatment plant (WWTP) models (Jeppsson et al., 2006). In such models, the outputs of one unit operation become inputs to the next downstream one. However, the output compounds (components) of the source model, e.g. Activated Sludge Model No1 (ASM1, Henze et al., 1987), are not compatible with the input compounds of the destination model, e.g. Anaerobic Digestion Model No1 (ADM1, Batstone et al., 2002) (Volcke et al., 2006). Two basic approaches have been proposed to resolve this – (i) develop mass balance based compound transformation interfaces which map one set of compounds (outputs) onto another set of compounds (inputs) – the continuity based interface method or CBIM approach (Volcke et al., 2006), (ii) define all the compounds required in the entire WRRF and model the changes in these through each unit operation – the “super-model approach” of Jones and Tákaacs (2004) and Seco et al. (2004), both cited in Grau et al. (2007), and (iii) the approach of Grau et al. (2007), which is a combination of the CBIM and super-model approaches. All three approaches require the definition of the composition of the state-variables (compounds) in either relative molar composition x, y, z, a and b values in $C_xH_yO_zN_aP_b$ as per Sötemann et al. (2005b) or as elemental mass fractions (g C, H, O, N and P/g compound) as per Volcke et al. (2006) because AD influent carbon fluxes are required to predict its gas production and composition. The organics composition in these forms require elemental data, in particular carbon data, which are not commonly measured at WRRFs, with the result that case studies used to describe the modelling approaches (e.g. Zaher et al. 2007; Volcke, et al., 2006; Jeppsson et al., 2006) have used assumed compositions for the different organics.

1.1.2 Complementing dynamic models with steady state models

Irrespective of the approach, plant-wide dynamic models are large, complex and require significant modelling skills, experience and understanding to master and use effectively. Dynamic models comprise differential equations of many bioprocesses that require numerical integration for solution and so demand much input information because each of the bioprocesses has several kinetic constants that need to be defined (Figure 1.1). In contrast, in steady-state models, many of the bioprocesses are assumed to reach completion, e.g. utilization of influent biodegradable organics, which reduce these bioprocesses to ones of stoichiometry only, while other bioprocesses which do not reach completion, are either simplified, such as ordinary heterotrophic organism (OHO) death regeneration to endogenous respiration, or retained because they are the slowest and so govern the sizing of the system, such as nitrification for the activated sludge system. The steady-state models therefore have the advantage that they demand much less input information. Also, their equations, which link system design parameters (such as sludge age) to system performance (such as effluent quality), are algebraic and so give direct explicit solutions. This makes steady state models

very useful for determining WRRF size for specified capacity (design) or WRRF capacity for specified size (operation).

Dynamic models are not compatible with design and operation because they require all the influent characteristics, reactor sizes, inter-connecting flows and the initial reactor concentrations to be quantitatively defined before simulation. In contrast, the explicit equations linking influent characteristics to unit operation performance of steady-state models allow (i) reactor sizes and interconnecting flows to be directly calculated from influent characteristics (design) or (ii) reactor concentrations and influent characteristics to be calculated from known reactor volumes and system performance (operation). Because steady state models use the same bio-processes as dynamic models, but in much simpler ways, their solutions closely match dynamic model outputs (Sötemann et al., 2005a, 2006). Steady state models therefore can enhance, simplify and increase the reliable use of dynamic models if they are incorporated as pre-processors to generate the required input information for the dynamic models. Steady-state models of WRRF unit operations are therefore a very useful complement to the dynamic simulation ones (Figure 1.1).

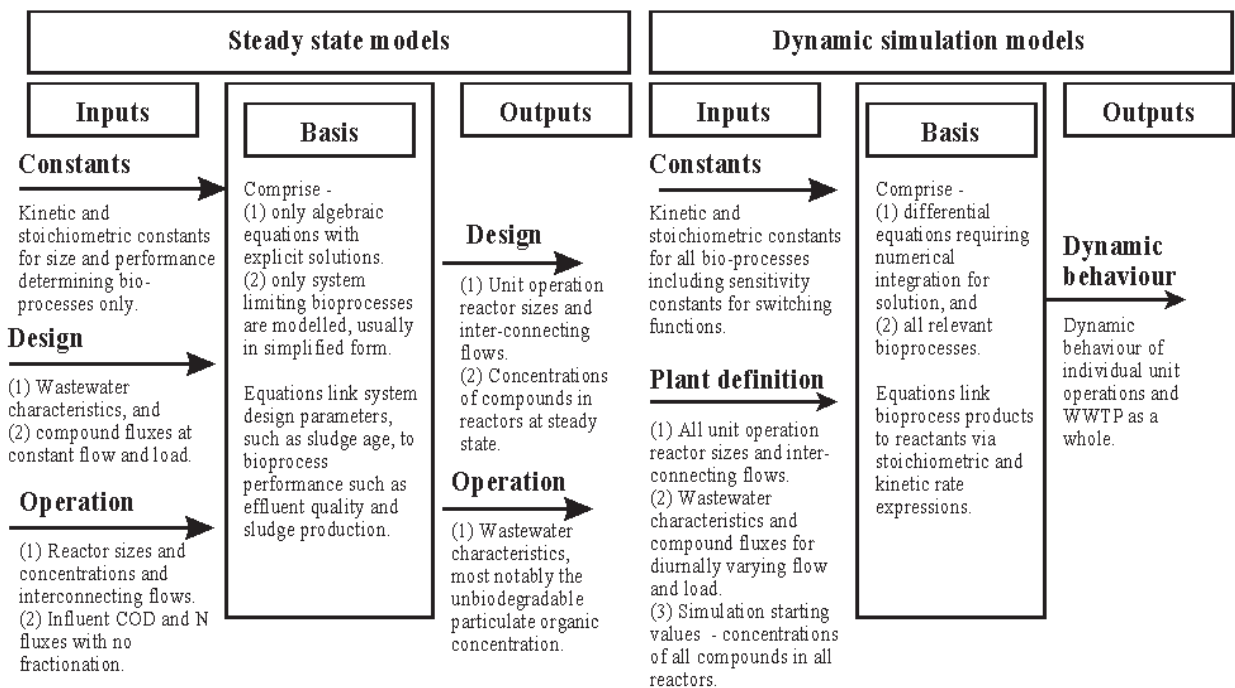


Figure 1.1: Inputs, basis and outputs of steady state (left) and dynamic models (right) showing that steady state models can conveniently and accurately generate the input for dynamic simulation software.

With steady-state models one can (i) estimate reasonably simply and quickly the principal system design and operating parameters, such as sludge age, reactor volume, un-aerated (anaerobic and/or anoxic) mass fractions, recycle ratios and oxygen requirement, aerobic or anaerobic digester retention time and gas production from system performance criteria specified for the design, such as effluent and sludge quality, (ii) estimate reactor concentrations and influent characteristics from existing plant data, (iii) investigate the sensitivity of the system performance to parameters that most affect the system, i.e. the

influent characteristics unbiodegradable particulate organic (UPO) fraction, maximum specific growth rate of nitrifiers (μ_{A20}) and readily biodegradable soluble organics (BSO) fraction and design and operation parameters, i.e. sludge age, (iv) estimate product stream concentrations for design of down- (or up-) stream unit operations of the WRRF and (v) very importantly, provide a basis for cross-checking dynamic model output results. In fact, all the preparatory work recommended by the IWA Good Modelling Practice Task Group (Gilliot et al., 2008; Rieger et al., 2012) for applying dynamic models to existing WRRFs does not require dynamic models and can be done with steady-state models such as checking water (flow), COD, N and total phosphorus (TP) balances and estimating the influent wastewater characteristics, in particular the influent unbiodegradable particulate organic (UPO) fraction, to match sludge production and oxygen demand. For design, once the overall WRRF scheme is established and the main system defining parameters of the individual unit operations are estimated, and for operation, once the major sources of plant data error have been eliminated, dynamic models can be applied to the connected unit operations to refine their design and evaluate their performance under dynamic flow and load conditions. Accordingly, not only dynamic simulation but also steady-state WRRF models need to be developed.

While steady state models require similar process knowledge as dynamic models, the level of detail required is significantly different. Being more accessible (can be programmed into spreadsheets), steady state models make explicit the calculation steps, and hence knowledge gaps. In fact, if the basics cannot be managed with the "hand" calculation steady state models, it is best not to use dynamic models. If dynamic models are used to cover gaps in knowledge and understanding (which they often are), a range of knobs, switches and buttons (like kinetic constants) will be twiddled that can lead to serious error (like me with flight simulator, where I have at least 10 times as many take-offs as landings!). Dynamic models always demand more information than available and prompt more questions than can be answered. So they drive users too quickly to try and answer questions at too a low level of detail and supply information that is often irrelevant when determining size for design or capacity for operation. The main problem of using dynamic models in WRRF simulation is to keep the main problem the main problem. Inexperienced users of dynamic models too quickly get their attention diverted away from the main problem. Steady state models help keep in focus the high level decisions and the main drivers for WRRF size in design or capacity in operation (Ekama, 2010).

1.1.3 Plant wide modelling approach of the project

For both steady-state and dynamic plant-wide models, Wentzel et al. (2006), Ekama et al. (2006 a,b), Sötemann et al. (2006) and Ekama (2009) took the view that if one is going to add carbon fluxes at the AD influent to model it within a WRRF (as is done in the BSM2 plant-wide model and the CBIM approach to link ASM1 and ADM1), one may as well add the carbon fluxes in the WRRF influent and track the carbon (and H, O, N, P, S, COD and charge) through all the unit operations of the WRRF including the AD. However, to do this requires element (C, H, O, N, P, S), COD and charge mass balanced stoichiometry for all the bioprocesses in the WRRF, not only the AD.

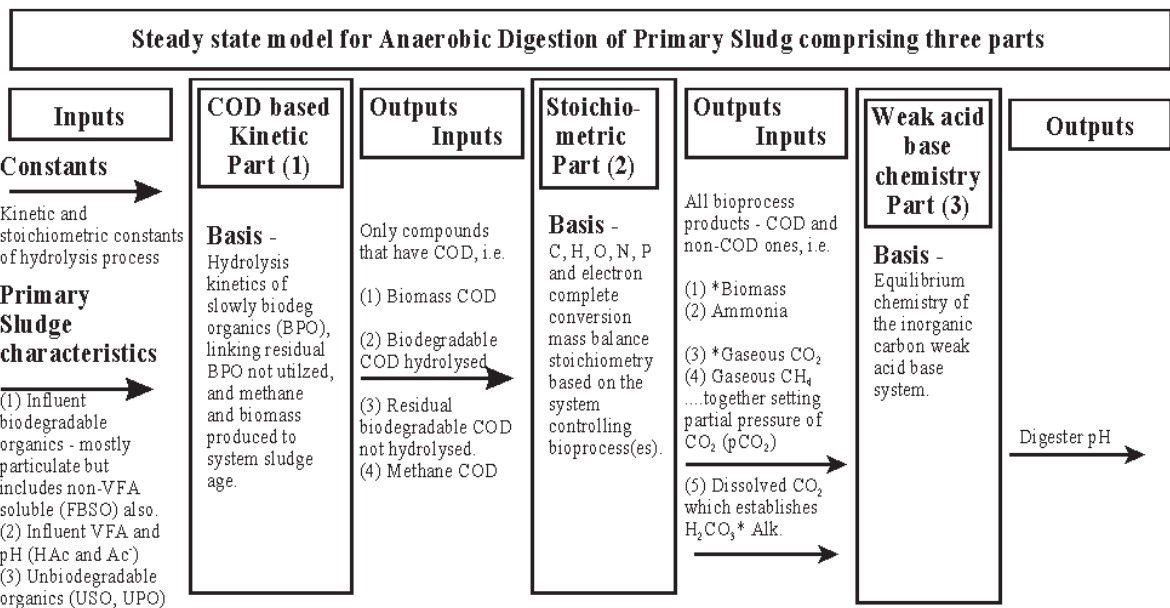


Figure 1.2: Steady state model for anaerobic digestion of primary sludge showing its three constituent parts: A COD mass balanced kinetic part (Part 1), from which is calculated the biodegradable COD hydrolyzed and utilized, an element and electron mass balance stoichiometric part (Part 2), from which all the bioprocess products are calculated, including the non (zero)-COD ones from the biodegradable COD utilized, and a weak acid based chemistry part (Part 3), from which the digester pH is calculated from the products of the stoichiometric part.

Current steady state models of WRRF unit operations (except AD) are based on COD, N and P mass balances and exclude C, H, O (and S) mass and charge balances. In this project, to complement the dynamic plant-wide modelling software, the existing COD and N mass balanced kinetic steady-state AS and aerobic (AerD) ND models (WRC, 1984; Henze et al. 2008) are extended with element mass balanced stoichiometry like the steady state AD model. The steady state AD model comprises three parts (Figure 1.2): (i) A COD based kinetic part which links the biodegradable organics (COD) concentration removed and methane (COD) production to the digester sludge age, (ii) a stoichiometry part which transforms the biodegradable COD removed and its C, H, O and N composition (reactant) to AD biomass, gaseous CO₂, ammonia, methane and dissolved CO₂ (HCO₃⁻ ≈ alkalinity) (products) and (iii) an inorganic carbon weak acid/base chemistry part from which the digester pH is calculated from the partial pressure of CO₂ and alkalinity generated (Sötemann et al., 2005a). To develop the stoichiometric parts for the other WRRF unit operations, the same approach, which is essentially a C, H, O, N, P, S and charge balance, will be applied to activated sludge (AS) and aerobic digestion (AerD) of waste activated sludge (WAS), both with nitrification and denitrification (ND). For the aerobic and anoxic-aerobic systems, the weak acid base chemistry part (Part 3) cannot be used to calculate the reactor pH because the partial pressure of CO₂ in the liquid phase is not in equilibrium with the head-space (atmosphere) – it is usually supersaturated by an unknown amount (Sötemann et al., 2005c). However, it can be used to calculate the alkalinity change and so establish whether or not

chemical dosing is required to keep the alkalinity above 40 mg/l as CaCO₃ which usually keeps the pH above 7 (WRC, 1984).

By assigning a stoichiometric composition, either with x, y, z, a, b and c values in C_xH_yO_zN_aP_bS_c^{ch} or with f_C, f_H, f_O, f_N, f_P, f_S, f_{cv} mass fractions (g element/g compound) to each of the five main influent wastewater organic fractions, i.e. (i) influent volatile fatty acids (VFA, assumed to be acetic acid), (ii) fermentable readily biodegradable soluble organics (FBSO), (iii) unbiodegradable soluble organics (USO), (iv) slowly biodegradable particulate organics (BPO) and (v) unbiodegradable particulate organics (UPO), the influent free and saline ammonia (FSA) and the activated sludge (AS) and anaerobic digester (AD) biomass (organics that have zero N, P, S or charge (ch), have zeros assigned to these mass fractions), these, and the products generated from them via the biological processes, are tracked through the WRRF. This approach is feasible because Ekama et al. (2006b) showed that the influent and endogenously generated unbiodegradable particulate organics, as defined by aerobic (AS) conditions are also unbiodegradable under anaerobic (AD) conditions. This was validated more rigorously in this project (Chapter 3). This simplifies the steady-state and dynamic models (and has been assumed to be true in the plant-wide models developed to date, Volcke, et al., 2006; Jeppsson et al., 2006), because it allows calculation of the unbiodegradable particulate fraction of (i) the primary sludge (PS) from the wastewater characteristics of the raw and settled wastewater and compound mass balances around the primary settling tank (PST) and (ii) of the waste activated sludge (WAS) from the ordinary heterotrophic organism (OHO) and phosphorus accumulating organism (PAO) active fractions.

1.1.4 Some background to the project

The previous project (K5/1620) made significant advances towards developing steady state mass balances based integrated WRRF models which link primary sedimentation, nitrification denitrification activated sludge and aerobic or anaerobic digestion of primary and waste activated sludges. The most significant of these developments is the finding that particulate organics that are unbiodegradable in the activated sludge reactor, i.e. those from the influent wastewater and from the endogenous process generated in the reactor, are also unbiodegradable under anaerobic digestion conditions. Activated sludge and anaerobic digestion models can therefore be linked with common compounds at the link to form plant wide WRRF models. Development of a mass balances based steady state model for the entire WRRF comprising primary settling, ND activated sludge and aerobic or anaerobic digestion of primary and waste activated sludge was completed in the project. Mass balance carbon (C), nitrogen (N), oxygen (O), hydrogen (H) and total oxygen demand (TOD) stoichiometry was also developed to complement the steady state models so that the different products exiting the WRRF via the solid, liquid and gas streams could be calculated, such N loads in recycle streams, methane production for energy recovery and greenhouse gas (CO₂, CH₄) generation.

Not considered in the K5/1620 project were the behaviour of the phosphorus accumulating organisms (PAO) from enhanced biological P removal (EBPR) activated sludge systems under anaerobic digestion conditions. The release rates of N and P from the cell bound phase to the dissolved phase under (anoxic) aerobic and anaerobic digestion conditions needed to be investigated to include anaerobic digestion and anoxic -aerobic digestion of EBPR WAS into

plant wide WRRF models to determine potential N and P concentrations in digester dewatering liquor. Also, it is not clear whether anaerobic digestion of WAS together with primary sludge (PS) has a beneficial effect on the hydrolysis rate of WAS compared with anaerobically digesting the WAS by itself. Hence the main objectives of this research project are:

- (1) Determine the P release processes and kinetics of EBPR WAS under AD and anoxic aerobic digestion conditions.
- (2) Determine the hydrolysis rates of WAS from nitrification denitrification (ND) and NDEBPR activated sludge systems when anaerobically digested by itself and when co-digested with PS.
- (3) Build complete element mass balanced plant wide steady state and dynamic simulation models capable of simulating primary settling, ND with or without EBPR activated sludge, PS and WAS thickening, anaerobic digestion of PS with or without WAS, and anoxic-aerobic digestion of WAS.

These objectives were all achieved by this project. The results are summarized in this report. Detailed results can be found in the Water Research Group (WRG) reports and/or the higher degree theses awarded on the research completed in this project, viz.

Harding TH, Ikumi DS, and Ekama GA (2009) A steady state stoichiometric model describing the anaerobic digestion of biological excess phosphorus removal waste activated sludge. Research Report No W132.

Ikumi DS, Harding TH, Brouckaert CJ and Ekama GA (2013) Development of a three phase plant wide mathematical model for sewage treatment. Research Report W138.

Vogts M, Ikumi DS and Ekama GA (2014) Anoxic -aerobic digestion of P rich waste activated sludge. Research Report W139.

These detailed reports can be obtained from the Department of Civil Engineering, University of Cape Town, Rondebosch, 7701, Cape, South Africa.

1.2 PROJECT METHODOLOGY

1.2.1 Experimental research work

To achieve the above objectives the following experimental programme was undertaken:

- 1 Operate three continuous flow activated sludge (AS) systems – one membrane UCT NDEBPR system and two Modified Ludzack-Ettinger (MLE) ND systems – and five flow-through ADs, three of which were fed waste activated sludge (WAS) from the three AS systems.
- 2 Collect settled wastewater and PS from Mitchells Plain WRRF and make the raw wastewater by adding a defined mass of PS. Feed the PS to the fourth AD.
- 3 Feed raw wastewater to one MLE system and settled wastewater to the other MLE and membrane UCT systems. Feed a PS-Settled WW MLE WAS blend to the fifth AD.
- 4 Operate the five ADs at five sludge ages (10, 18, 25 and 40d) to determine the sludge hydrolysis rate and at a very long sludge age (60d) to determine the sludge unbiodegradable fraction.

- 5 Conduct anaerobic batch tests on mixtures of sludge harvested from the ADs and AS reactors to measure the P and N release rates.
- 6 Extend steady state plant wide model developed for K5/1620 to include P and ISS.
- 7 Calibrate the ASM1 (for ND) and ASM2 (for NDEBPR), modified to include the ISS model developed in the previous project (K5/1620) with the two MLE and one UCT system data such that these models simulate the performance of these systems accurately. The predicted mixed liquor concentrations reflected the initial concentration and WAS sludge characteristics fed to the ADs. Measure influent and effluent Mg, K and Ca concentrations to track these cations – they are the main cations associated with polyphosphate in the phosphate accumulating organisms (PAOs).
- 8 With the measured AD performance data, calibrate and simulate the flow through ADs with the steady state and simulation AD models in WEST. Does the predicted performance match that observed? If yes then the AS and AD models are a good representation of the processes in the systems. If not, find reasons for the differences and appropriately modify the models to accurately simulate the observed data.
- 9 Operate two continuously fed anoxic-aerobic (AxAerD) sludge digesters fed WAS from the UCT system, one fed a high TSS concentration (20gTSS/l) the other fed a low high TSS concentration (3gTSS/l).
- 10 Run long term (20d) aerobic batch tests on dilute and concentrated WAS from the UCT systems and the continuous anoxic-aerobic digesters to observe VSS and TSS changes and nitrate and ortho-P increases with time.

The above experimental programme will provide information to address the following important issues for plant wide modelling:

- 1 Determine the kinetics of P release from enhanced biological P removal (EBPR) waste activated sludge (WAS) under anaerobic (AD) conditions.
- 2 Establish to what extent mineral precipitation takes place in EBPR WAS ADs?
- 3 Compare the P release in AD with that observed in batch aerobic digestion of the previous investigation (K5/1620).
- 4 Confirm mineral precipitation in anoxic aerobic digestion with parallel aerobic digestion tests in this investigation.
- 5 Confirm unbiodegradable fraction of primary sludge with two sources – mass balance round primary settling (PST) and primary sludge (PS) AD.
- 6 Confirm unbiodegradable fraction of nitrification-denitrification (ND) system WAS from the modified Ludzack-Ettinger (MLE) system performance data and AD of MLE system WAS for both raw and settled wastewater.
- 7 Measure the hydrolysis rate of WAS co-digested with PS – does the much larger acidogen biomass generated with PS digestion assist in the hydrolysis of WAS leading to a faster hydrolysis rate of WAS compared with digesting it by itself.

1.2.2 Model development work

An overview of the status of development of steady state and dynamic simulation activated sludge and aerobic and anaerobic digestion models in the Aquasim and WEST computer platforms is given in Table 1.1. In a former WRC project (K5/1338), full mass balanced

stoichiometry versions of ASM1 and UCTSDM11 were programmed into a two phase (aqueous-gas) mixed weak acid base framework in Aquasim (www.eawag.ch/forschung/siam/software/aquasim/index_EN), to form two phase integrated mixed weak acid base chemical, physical and biological process models for these systems. Adding full mass balanced stoichiometry needs to be done also for (1) ASM2, which includes the enhanced biological P removal. Then the biological processes of (2) ASM2 and (3) UCTSDM1 need to be modelled in a three phase (aqueous-gas-solid) mixed weak acid base chemical-physical framework to form three phase integrated chemical, physical and biological process models. With these models, mineral precipitation in aerobic (as happened in the aerobic batch tests of project K5/1620 and in this project) and anaerobic digestion of EBPR WAS (as happened in this project) can be investigated in greater depth by simulation. This model development work is a major undertaking and cannot be done in this project without an ionic speciation model specialist so Chris Brouckaert of the PRG at UKZN was contracted to this project to undertake this part of the project and assist with WEST modelling.

The UCTSDM1 deviates from the IWA ADM1 in several respects: (1) Acidogens are affected by hydrogen partial pressure (p_{H_2}) to produce acetate only under low p_{H_2} and acetate and propionate under high p_{H_2} (Sam-soon et al., 1987), (2) the influent organics are defined with a more general stoichiometry which can be measured by the usual tests (COD, TOC, TKN, FSA, TP, OP, VSS, ISS) and elemental (C, H, N, S) analysis rather than force fitting the influent organics into carbohydrates, lipids and proteins which are not measured on sewage sludge and when they are, they do not account for all the influent COD, and (3) implementation of the ionic equilibrium using the dissociation of water and activity coefficients to calculate pH because it is recognized that pH is hydrogen ion activity not concentration. The last is required when modelling simultaneous multiple mineral precipitation kinetics in 3 phase (gas-liquid-solid) mixed weak acid base solutions where minerals compete for the same species – in real solutions a trivalent ion may have an activity of only 20% of its molar mass as measured. This approach has been successfully applied to the multiple mineral precipitation in aeration of sewage sludge AD, winery UASB liquors and piggery wastewater Musvoto et al. 1997, 2000; van Rensburg et al., 2003). This approach, which solves the very fast aqueous equilibrium reactions as differential equations together with the slow bioprocesses, precipitation and gas equilibrium processes leading to stiff matrices, has been criticized by modellers, and rightly so, because it is computationally intensive (long run times) and can lead to numerical instability in the solvers due to the stiff matrices. Solving the very fast aqueous equilibrium reactions with algebraic equations based on the charge balance is preferred because it obviates these problems. However, the charge balance approach also has problems, e.g. it requires all the ions in the aqueous phase to be quantified, which is analytically not possible. The problem was resolved in this project by developing a generalized aqueous phase ion speciation routine, which is combination of both approaches – mixed weak acid/base chemistry, activity considerations, ion pairing and hypothetical (NaCl) addition to obtain the measured ionic strength for initial conditions specification and charge balance and algebraic expressions for aqueous phase speciation in simulation algorithms.

¹Sötemann et al. (2005b) called this model UCTADM1. However, since it is not a variant of IWA ADM1 and tailored for sewage sludge digestion, it has been renamed UCT sludge digestion model to distinguish it as different to IWA ADM1.

1.2.3 International co-operation

Other research groups are also building plant-wide WRRF models and these groups are either following the “transformer” or “supermodel” approaches. The “transformer” groups link existing well known (IWA) models like ASM1 (or ASM2) with ADM1 and address the research questions and problems that arise from this. Some of these questions are more artificial than real and arise out of incompatibilities between the ASM and ADM model structures rather than experimental observation and measurement. Where experimental data are required, some groups gather this from the literature, including ours (UCT/UKZN). The “supermodel” groups tailor existing models to create a single integrated plant -wide model with seamlessly connected unit operations. The UCT/UKZN group have adopted the “supermodel” approach as will be evident from this report.

Although pursuing different approaches, there is significant international co-operation between the groups in the plant wide modelling drive. The WRG at UCT and PRG at UKZN groups have been (and still are) involved in the following international task groups –

- 1 IWA Task Group on Physico-Chemical Modelling (PCM) – to develop a generalized framework for physico-chemical modelling of bioprocess systems.
- 2 IWA Task Group on Benchmark Simulation Model BSM2P – to including P into the BSM2.
- 3 WRG/PRG are one of 5 international WEST Development Centres (WDC) working with MikebyDHI who own the WEST WRRF modelling software. There are monthly Webex meetings and 2 or 3 face to face meetings of WDC members per year at international conferences. The dynamic plant wide model developed in this project (PWM_SA) was released with the latest WEST version (WEST2014) late last year.

Table 1.1a: Status of development of biological and chemical-physical models and their integration to build plant wide WRRF models (June 2007).

	Unit process model	(A) Steady State Models - Bio-processes only plus experimental data.	(B) Dynamic Simulation Models - Bio-processes only	(C) Chemical physical processes only	Integrated chemical physical biological model with complete element mass balances	
					(D) In 2 phases (gas-liquid)	(E) In 3 phases (gas-liquid- solid)
0	Kinetic weak acid/base chemistry model for inorganic carbon (IC) only in three phases (solid-liquid-gas). Mixed fast and slow processes.	Not applicable	Not applicable	Mixed fast and slow processes - in Aquasim Musvoto et al. (1997)	Not Applicable	Not Applicable
1b	Kinetic mixed weak acid/base chemistry model for IC, PO ₄ , VFA and FSA in 3 phases (solid-liquid-gas). Mixed fast and slow processes.	Not applicable	Not applicable	Mixed fast and slow processes - in Aquasim Musvoto et al. (2000)	Not Applicable	Not Applicable
0	Activated Sludge for organics and N removal including ISS.	COD and N balances only WRC (1984), Henze et al. (2008)	COD, N and P balances Wentzel et al (1992), ASM1 Henze et al. (1987)	Not applicable	Complete element balances - In Aquasim Söttemann et al. (2005b).	Done in WEST in this project
2b	Activated Sludge for organics and N and P removal - >90% Aerobic P uptake EBPR including ISS.	COD, N and P mass balances only Wentzel et al. (1990).	COD, N and P balances UCTPHO - Wentzel et al. (1992), ASM2 - Henze et al. (1997).	Not applicable	See column E	Done in WEST in this project
2c	Activated Sludge for organics and N and P removal - Anoxic/Aerobic P uptake EBPR	COD, N and P mass balances only -partly developed - no active projects	Done in Aquasim - UCTPHO+ Hu et al. (2006), ASM2d - Henze et al. (2001).	Not applicable	No active projects in this area.	No active projects in this area
0.1	Aerobic digestion of primary (PS) and waste activated (WAS) sludges from ND systems including ISS	COD and N mass balances only, Ekama et al. (2006a,b).	Complete element balances In Aquasim - Söttemann et al. (2006).	Not applicable	See column E	Done in WEST in this project
3b	Aerobic digestion of PS and waste activated (WAS) sludges from NDEBPR systems including ISS	Done in this project.	See Column E	Not applicable	Done in WEST in this project	Done in WEST in this project

Table 1.1b: Status of development of biological and chemical-physical models and their integration to build plant wide WRRF models (June 2007).

Unit process model	(A) Steady State Models- Bio-processes only plus experimental data	(B) Dynamic Simulation Models - Bio-processes only	(C) Chemical physical processes only	Integrated chemical physical complete element mass balances	
				(D) In 2 phases (gas-liquid) (E) In 3 phases (gas-liquid-solid)	
0	Anaerobic digestion of primary sludge (PS) with methanogenesis only	Not applicable	Not applicable	UCTSDM1 in Aquasim - Sotemann et al (2005b) PRG done in WEST	Done in WEST in this project
4b	Anaerobic digestion of primary sludge (PS) with methanogenesis and sulphidogenesis for BSR	Not applicable	Not applicable	Active under UCT K5/1637 for UASB systems (Aquasim) PRG done in WEST	
4c	Anaerobic digestion of waste activated sludge (WAS) from ND systems	Not applicable	Not applicable	Done in WEST in this project	Done in WEST in this project
4d	Anaerobic digestion of waste activated sludge (WAS) from NDEBPR systems (include P)	Not applicable	Not applicable	Done in WEST in this project	Done in WEST in this project
4	Anaerobic digestion of PS and WAS blends from ND systems	Not applicable	Not applicable	Done in WEST in this project	Done in WEST in this project
4f	Anaerobic digestion of PS and WAS blends from NDEBPR systems (include P)	Not applicable	Not applicable	Done in WEST in this project	Done in WEST in this project
5	WRRF model linking 2a & 3a or 2a, 3a and 4a	Not applicable	Not applicable	To be attempted in WEST	To be attempted in WEST
6	WRRF model linking 2b, 3b and 4b.	Not done in this project	Not applicable	To be attempted in WEST	Possibly too complex to succeed in this project

Note 1: Developed = Kinetics and stoichiometry of all biological processes quantified in a mathematical model and coded into a computer program (Aquasim).
 Verified = Mathematical model debugged and generates internally consistent results conforming to mass balance and continuity principles.
 Validation = Mathematical model calibrated against experimental data and predicts results resembling reality.

* Carbon still to be integrated fully – Carbon is included in 2a and 3a and 3b as a C/COD ratio, not formally as in the steady state stoichiometric (spreadsheet) model developed in K5/1620. To integrate C fully requires the inclusion of at least seven (instead of one) influent organic compounds each with its own COD/VSS (or molar mass), TKN/VSS and C/VSS from which x, y, z, and a in C_xH_yO_zN_a are calculated. To establish continuity for a plant wide WRRF model, the anaerobic digestion models** also have to be modified to include the same seven influent organic compounds.

CHAPTER TWO

A STEADY STATE STOICHIOMETRIC MODEL DESCRIBING THE ANAEROBIC DIGESTION OF ENHANCED BIOLOGICAL PHOSPHORUS REMOVAL WASTE ACTIVATED SLUDGE

2.1 BACKGROUND, PRINCIPLE OBJECTIVES AND SCOPE

Until the mid-1990's model-based studies on water resource recovery facilities (WRRFs) focussed on the development of models describing a single unit operation within the WRRF i.e. an activated sludge system, an anaerobic digester or some other WRRF unit operation. The focus of these model-based studies changed in the late 1990's due to limitations in linking different models in applications for multi-unit operation or full scales plant-wide designs or process evaluations. The boundaries related to the focus of these model-based studies within the WRRF, was widened to develop models that describe more than one unit operation and ultimately the whole WRRF.

In line with these plant-wide model-based studies, the Water Research Group (WRG), at the University of Cape Town, published in 2006 a four part (Wentzel *et al.*, 2006; Ekama *et al.*, 2006a,b; Söttemann *et al.*, 2006) mass balance-based plant-wide WRRF model that describes the coupling of different unit operations within the WRRF. These studies conducted in the WRG focused on a primary settling tank (PST) unit coupled to an anaerobic digester (AD) (Söttemann *et al.*, 2005a,b) and a UCT enhanced biological phosphorus removal (EBPR) activated sludge (AS) system coupled to an aerobic digester (Söttemann *et al.*, 2005c). Furthermore, the Söttemann *et al.* (2005c) model can also be used to couple the nitrification-denitrification (ND) AS system to an anaerobic digester (i.e. excluding P). In continuity with these studies, this study focuses on the development of a steady state model that couples an NDEBPR AS system to an anaerobic digester (i.e. includes P).

This study, with the support of a parallel study by Ikumi *et al.* (2014) (Chapter 3), aims at developing a steady state AD model that describes the anaerobic digestion of waste activated sludge (WAS) from a NDEBPR AS system and, secondly, comparing the unbiodegradable particulate organic (UPO) fraction determined for the AS and AD systems. The aim (primary objective) of this study was categorised into various secondary objectives to ensure that all aspects related to this study are achieved. The objectives of, and modelling approaches utilized in, this study are largely similar to those reported by Söttemann *et al.* (2005a,b,c) in the development of the steady state model describing the anaerobic digestion of primary sludge (PS). Consequently, the steady state AD model of Söttemann *et al.* (2005a) is extended in this study to include the phosphorus and counter-ion metal components (Mg, K, Ca) contained by NDEBPR WAS in this steady state AD model. The development of this steady state AD model was divided into two sections, which are (i) the characterization of the WAS from the NDEBPR AS system and, (ii) the extension and amendment of the Söttemann *et al.* (2005a) steady state AD model to describe the anaerobic digestion of the NDEBPR WAS.

Each of these sections can then be divided further into secondary sections or parts. Figure 2.1 is a diagrammatical representation of these different stages in the development of the steady state AD model and gives directions to the chapters of this work dealing with the detailed specific topics by Harding *et al.* (2009).

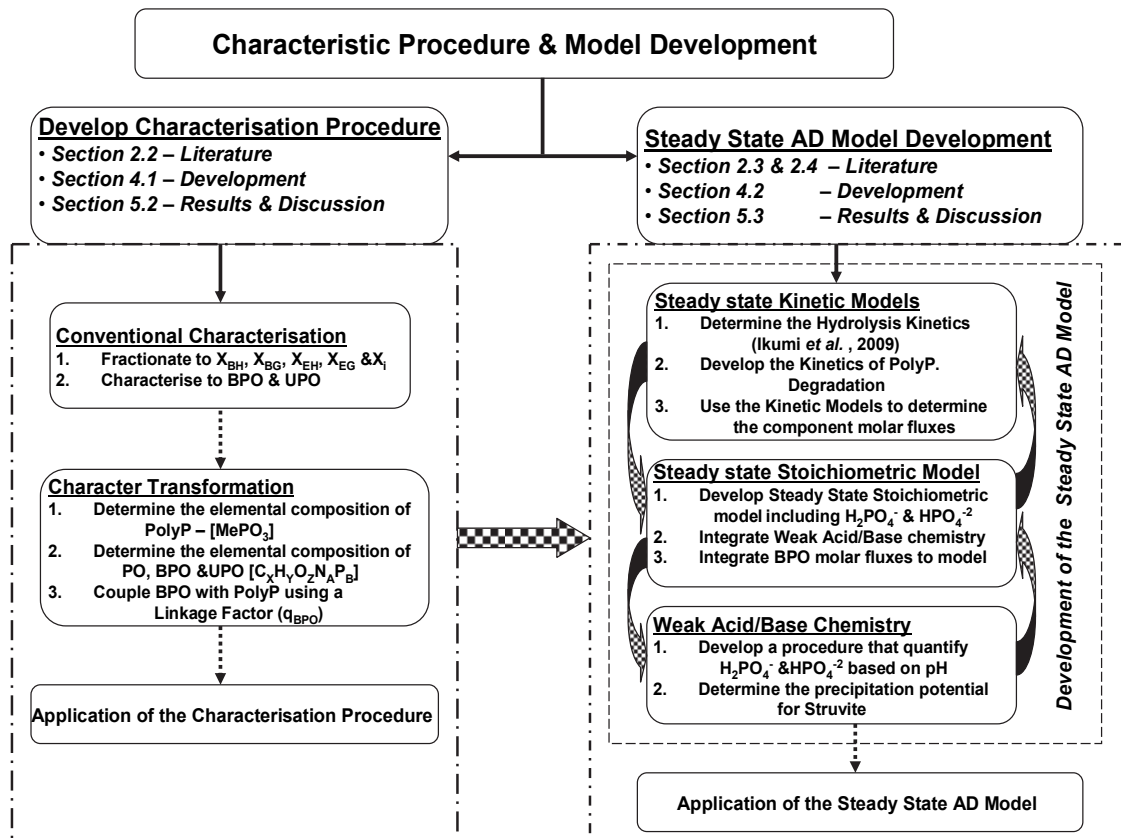


Figure 2.1: General structure of the study of Harding *et al.* (2009) (Report W132).

Firstly a characterization procedure was developed in this study that characterizes NDEBPR WAS to its elemental composition, which is the required form of the input variables to the stoichiometric part of the steady state AD model. This characterization procedure consists of two steps. (1) The fractionation of NDEBPR WAS into its active mass (OHO and PAO), endogenous mass (OHO and PAO) and inert organic mass content using the steady state AS model of Wentzel *et al.* (1990) and ISS (Ekama and Wentzel, 2004) model. These AS models require measured data from the experimental UCT MBR AS system as input variables. The OHO and PAO live biomass VSS concentrations from the fractionation of NDEBPR WAS are then grouped into the biodegradable particulate organic (BPO) and unbiodegradable particulate organic (UPO) components of the VSS (or equivalently particulate organic (PO) component) of the NDEBPR WAS. (2) The characterization procedure centres on transforming the PO, UPO and BPO components determined in the first step to molar elemental composition in terms of carbon (C), nitrogen (N), hydrogen (H), oxygen (O), phosphorus (P) and counter-ion metals (Me) content using their COD/VSS, OrgN/VSS and OrgP/VSS mass ratios. The organic part of WAS is characterized in the form $C_xH_yO_zN_A P_B$ while the inorganic polyphosphate stored in the PAOs is characterized as an additional $MePO_3$ compound linked to the PAOs, where Me is disaggregated into Mg, K and Ca with the aid of measurements on the WAS source UCT MBR system.

Although the polyphosphate part is not essentially biodegradable, it is hydrolysable and so its transformation during the AD process mimics that of the organic part of the BPO component

(but at a different rate) in that it changes from a stored and particulate form (based on analytical measurements) to a dissolved form in the AD system liquor. The kinetics that describes the hydrolysis rate of the organic part and polyphosphate part during AD is different. For this reason polyphosphate is characterized as separate part of the BPO component but linked to it with a linkage factor (q_{BPPO}) resulting in the elemental composition $\text{C}_x\text{H}_y\text{O}_z\text{N}_a\text{P}_b$. $q_{\text{BPPO}} [\text{MePO}_3]$. This elemental composition is also applied to the PO component because it contains the BPO component but with decreased linkage factor (q_{PO}) to account for the dilution of the polyphosphate concentration in relation to the larger organic concentration of the PO (PO = BPO + UPO where UPO contains no polyphosphate). The molar elemental composition is the required form of the input feed composition to the steady state AD model that was developed. Without full element mass balanced stoichiometry of biodegradable organics and polyphosphate, it is not possible to speciate the aqueous phase to determine pH.

The steady state AD model development includes the extension and modification, as required, of the three parts of the Sötemann *et al.* (2005a) model describing the AD of PS to include biomass phosphorus and the polyphosphate and the counter-ion metal components related to NDEBPR WAS. The three parts of the Sötemann *et al.* (2005a) AD models are (i) a COD based hydrolysis kinetic part, (ii) a CHONP stoichiometric part and (iii) a weak acid/base chemistry part. The kinetic part of this AD model deals with the determination of the kinetic rate describing the hydrolysis of the BPO component and was developed in the parallel study by Ikumi *et al.* (2014) (Chapter 3). This kinetic part of the AD model is used to quantify the extent of digestion of the feed WAS BPO and, thus, the residual BPO at different sludge ages. In addition, the kinetics for polyphosphate hydrolysis was determined in this study.

The stoichiometric part of the AD model focuses on determining the stoichiometry for the biochemical reactions that describe the anaerobic digestion of NDEBPR WAS including phosphate accumulating organisms (PAOs). This reaction stoichiometry, used in the Sötemann *et al.* (2005a,b) AD model, was initially developed by McCarty (1974, 1975) and is extended to full element stoichiometry in this study to accommodate biomass P and PAO polyphosphate with its counter-ion metals. The AD products therefore are methane (CH_4), carbon dioxide (CO_2), ammonium (NH_4^+), bi-carbonate (HCO_3^-), anaerobic biomass (assumed at $\text{C}_5\text{H}_7\text{O}_2\text{NP}_{0.114}$), Mg, K and Ca counter-ion metals and phosphate split between the H_2PO_4^- and HPO_4^{2-} forms. The method used in extending this reaction stoichiometry is that described by McCarty *et al.* (1975), Takács and Vanrolleghem (2006) and Ekama (2009). In adding P, cognizance needed to be taken of the $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$ pK value (~ 7.0) near the operating pH range of the experimental AD systems. This result in complexities concerning the phosphorus species, both H_2PO_4^- and HPO_4^{2-} concentrations being present within the AD system and the concentrations of these species changing with changes to the system pH. This problem is solved by using a factor f_{PT} that relates the aqueous phase phosphate species to the system pH (and vice versa), splitting the phosphates generated into $f_{\text{PT}} \text{H}_2\text{PO}_4^-$ and $(1-f_{\text{PT}}) \text{HPO}_4^{2-}$, which defines the pH depending on the f_{PT} value. The gaseous CO_2 and CH_4 set the p_{CO_2} , which together with the dissolved CO_2 (HCO_3^- or H_2CO_3^* Alk.) define the AD pH for the inorganic carbon system. The p_{CO_2} and HCO_3^- concentration are also affect the pH. The pH that meets the requirements for both the inorganic carbon and ortho-P subsystems defines the f_{PT} value and established the pH in the digester.

In the weak acid/base chemistry part of the AD model, the predicted results from the stoichiometric part are evaluated to determine the likelihood of mineral precipitation within the digester. Literature from Loewenthal *et al.* (1994) and Musvoto *et al.* (2000) suggest that struvite is the most likely precipitant with the AD of NDEBPR WAS. To evaluate the likelihood for struvite precipitation, the ionic product of the aqueous phase ions included in struvite are compared with its thermodynamic solubility product (K_{spm}). However, this method does not quantify the struvite formed but models developed by Loewenthal *et al.* (1994) and Musvoto *et al.* (2000) and software like Stuvite (Loewenthal and Morrison 1997), can be applied for this purpose (Harding *et al.*, 2011). The development and inclusion of a third solid phase that describes and quantifies the mineral precipitation are beyond the scope of steady state models but were included in the dynamic model plant wide model developed in this project (PWM_SA) – see Chapter 3.

2.2 METHODS

The experimental setup used in this research consists of a membrane (MBR) UCT NDEBPR AS system and a completely mixed flow through AD system that was fed the AS system P rich WAS.

The NDEBPR UCT AS system was fed a basic 600 mgCOD/l settled wastewater with 200 mgCOD/l acetate added to increase the EBPR capacity of this AS system. Also, to avoid P limitation di-potassium hydrogen orthophosphate (K_2HPO_4) was added to the feed to provide potassium and to increase the P concentration to 40mgP/l and when required NH_4Cl was added to increase the TKN/COD ratio to 0.1 mgN/mgCOD (before acetate addition). The reactor (zone) volumes (and mass fractions) of the NDEBPR UCT AS system were 19 l (0.13) anaerobic, 21 l (0.37) anoxic and a 35 l (0.60) aerobic. The aerobic zone comprised two reactors – a 32 l membrane reactor and a 3 litre side stream aeration tank for OUR measurement. The membrane tank was fitted with KubotaTM A4 size membranes through which the final effluent was produced. The membrane panels were fitted vertically in the bottom section of the main aerobic tank. Continuous coarse bubble aeration was supplied at the base of the reactor. The air bubbles were forced to rise between the membrane panels to provide scour and minimize fouling. The 3 l side stream aeration reactor was fitted with a DO controller/ OUR meter to measure the OUR. The flow rate from the anoxic reactor to side stream reactor was set to give the same actual retention time as in the MBR reactor. The solids concentrations in the side stream aerobic reactor was same as that in the anoxic reactor, hence the effective volume of the aerobic reactor at its higher solids concentration was lower than 35 l. This was taken into account when calculating the total sludge mass in the system and the anaerobic, anoxic and aerobic sludge mass fractions.

The UCT system was operated with one multi-channel peristaltic pump set to deliver the influent feed volume of 150 l in 23.5 to 24 h. The mixed liquor recycles were set at 3:1 (3 channels) for the as-recycle from the aerobic to the anoxic and 1:1 (1 channel) for the r-recycle from the anoxic to the anaerobic reactors. For the fixed volume reactors the anaerobic, anoxic and aerobic mass fractions are set by the recycle ratios. The relationships between the mass and volume fractions in terms of the recycle ratios are given by Ramphao *et al.* (2005). The anaerobic, anoxic and side stream aeration tanks were fitted with stirrers for mixing while the main aerobic MBR reactor was mixed by continuous coarse bubble aeration.

The AD was fed the WAS directly from the UCT-MBR AS system (~ 10g TSS/l) on a once daily batch feeding basis with the feed volume adjusted to give the required retention time. The AD was a flow through continuously stirred tank reactor (CSTR) with a total reactor volume of 20 litres and an operating volume of 16 litres. A feeding port was fitted on the side at the base of the tank and gas outlet and metering ports on the top lid. The gas metering pipe was connected to a wall-mounted gas meter. The AD was operated at a temperature of approximately 35 °C, optimal for mesophilic organisms. This temperature was controlled by means of heating coils wrapped around the outside of the digester walls and connected to temperature controller with a temperature probe in the reactor mixed liquor. The AD was completely sealed except for the provision of the gas outlet pipe and the access port, which was closed during normal operation. The access port was opened only once daily to measure the pH. The sludge inlet/ outlet pipe at the base of the AD, controlled by a valve, was only opened during feeding process when waste sludge was withdrawn and new feed sludge added. The AD system was operated at 7 different sludge ages i.e. 10, 12, 18, 20, 25, 40 and 60 days. The results of the 10, 18, 25, 40 and 60 day sludge ages are used to calibrate the steady state AD model while the 12 and 20 day sludge age results used to validate the AD model.

2.3 SUMMARY OF RESULTS

The samples taken from the experimental UCT MBR AS system were averaged over a Sewage Batch and named after the Sewage Batch number fed to the AS system. The experimental AD system was operated at different steady state AD sludge ages of 10, 12, 18, 20, 25, 40 and 60 days and the samples measured over a particular sludge age were averaged and named after the sludge age. The average results collected from the experimental AS and AD system were evaluated by performing COD, N, P and counter-ion metals (Mg, K and Ca) mass balances over these experimental systems. Also, Carbon mass balances were performed at the different sludge ages for the AD system based on the assumed carbon content (f_C , gC/gVSS) allocated to the VSS (PO) and UPO components of 0.52 and 0.51 respectively from which the f_C of BPO component was calculated. These mass balances were performed for the 11 Sewage Batches (Sewage Batches 3 to 14) of the AS system and the corresponding seven AD steady state sludge ages.

- 1 The COD mass balances for all the sewage batches of the AS system remained within 10% of the 100% balance and the AD system remained within 3% of the 100% for the COD. The accuracy of the COD mass balance is important in this study because COD it is used to calibrate the steady state AD model. The mass balances achieved throughout this study were very good, in fact better than those achieved in several previous AS and AD studies at UCT and so are acceptable for use in this study.
- 2 The phosphorus (P) is important in this study as it differentiates this steady state AD model from that previously developed by Söttemann *et al.* (2005a). The phosphorus mass balance also varies within 10% of the 100% balance for both the AS and AD systems for almost all balances. It was concluded that the P mass balances of the measured data from both systems were acceptable for use in this study.
- 3 The nitrogen (N) mass balances the measured data of both systems varied over a wider range (80-100%) than those of the COD and P. However, these variations did not significantly influence the results obtained from the use of the measured data because most of the N balance error arise from estimating the nitrate removal in the AS system, which does not affect the AD.

- 4 The C mass balance over the AD system averaged 92.7% (excluding about 3% for the AD biomass) and so deviates less than 10% from the target 100%. These good mass balance results for the C content validate the assumed C content (f_C) for the PO and UPO from which the f_C of the BPO was calculated by difference.
- 5 The mass balances for the polyphosphate counter-ion metals (Mg, K and Ca) varied within 20% of 100%. A possible source of error for these metals is the high dilution required in their analysis. Nevertheless, they are deemed acceptable for this study.

The quality of the data collected from the UCT membrane AS system during the experimental stage of this research were found to be consistent for the COD, TP and TOC and acceptable for the TKN and counter-ion metals.

The overall objective of the characterization procedure developed and applied in this study is to determine the elemental compositions for the VSS (PO), UPO and BPO components of NDEBPR WAS because this is the required form of the input variables for use in the stoichiometric part of the steady state AD model. The wastewater characteristics and reactor VSS fractions obtained from the characterization and fractionation step of procedure conformed to other studies on the UCT MBR AS system applying the steady state AS model of Wentzel et al. (1990) and the ISS model (Ekama and Wentzel, 2004).

The different VSS fractions of the NDEBPR WAS are grouped to determine the BPO and UPO components the VSS (PO) concentrations for AD. This was done because the UPO component of the WAS, ideally (one of the objectives is to confirm this for AS and AD system), remains unchanged during the AD and, consequently, only the BPO components takes part in the reactions within the AD process. The UPO content ($S_{up(AS)}$) of the WAS was determined as the sum of its (i) inert mass (X_I) which enters with the influent as S_{upi} and accumulates in the AS system, (ii) the endogenous residue mass of the OHOs and PAOs (X_{EH} and X_{EG}) and the unbiodegradable part of the active mass of the OHOs and PAOs (X_{BH} and X_{BG}), which in terms of the death regeneration model is 8%. The UPO fraction (f_{upWAS}) of NDEBPR WAS was found to be 0.535 (on average) which is significantly higher than PS and the 10 day sludge age ND system WAS operated in the parallel study to this investigation by Ikumi et al. (2014) (Chapter 3), at 0.33 to 0.36 (on average for PS and ND WAS). The BPO content of the WAS was determined from the difference of the PO and UPO components.

The second step of the characterization procedure transforms the form COD/VSS (f_{cv}), OrgN/VSS (f_N) and OrgP/VSS (f_P) mass ratios and the polyphosphate content of the PAOs of NDEBPR WAS to the required elemental compositions. The elemental compositions were determined for the PO (VSS) and BPO components in the forms $C_xH_yO_zN_aP_b-q\phi[MePO_3]$ and for the UPO component in the form $C_xH_yO_zN_aP_b$ where Φ is replaced by OP or BPO depending on the component against which the polyP is expressed.

This study compares various elemental compositions for PS and ND WAS determined from studies within the WRG as well as those found from studies in the literature. This is done to determine the possible range for their elemental composition and as such place the results of this investigation within the context of other findings. No values for the elemental compositions for UPO and BPO of NDEBPR WAS were found in the literature so it was compared with those of PS and ND WAS.

Within this study the elemental composition for all the components were based on the molar composition of 7 for hydrogen ($y=7$) in $C_xH_yO_zN_aP_b$. If the molar composition required based on Carbon $x=1$, then the molar compositions of the H, O, N and P became $CH_{y/x}O_{z/x}N_{a/x}P_{b/x}$. The results for the PO VSS (BPO + UPO) composition of NDEBPR WAS ranges from $C_{5.00}H_7O_{2.11}N_{0.76}P_{0.12}-0.29[MePO_3]$ to $C_{5.33}H_7O_{2.34}N_{0.74}P_{0.14}-0.36[MePO_3]$, which is slightly higher in terms of carbon and oxygen molar content than that found by Ekama *et al.* (2006b) from the van Haandel *et al.* (1998) ND WAS data, reported at $C_{4.96}H_7O_2N_{0.773}$.

The results for the BPO composition ranged from $C_{4.90}H_7O_{1.61}N_{1.09}P_{0.12}-0.61[MePO_3]$ to $C_{5.58}H_7O_{1.91}N_{1.18}P_{0.13}-0.75[MePO_3]$. The BPO compositions of WAS were found to range from $C_{4.8}H_7O_2N_{0.77}$ (Dold *et al.*, 1980) to $C_{5.67}H_7O_2N_{0.865}$ (Ekama *et al.*, 2006b). The organic phosphorus content reported by Volcke *et al.* (2006), in the composition $C_{5.02}H_7O_{2.04}N_{0.95}P_{0.113}$, was found to be similar to that found in this study. Generally, the elemental compositions of the organic parts of the BPO determined in this study compare well with those found for ND WAS in other studies (Ramdani *et al.*, 2012).

In this investigation the UPO composition was determined from measurements on the effluent from the 60 day AD and ranged from $C_{5.11}H_7O_{2.63}N_{0.44}P_{0.12}$ to $C_{5.21}H_7O_{2.65}N_{0.45}P_{0.14}$. These show significantly lower AS biomass nitrogen and phosphorus compositions than that reported by Volcke *et al.* (2006) as $C_{5.44}H_7O_{2.04}N_{0.75}P_{0.038}$. This may be due to the influent UPO composition being significantly different in this study. However, the composition of the UPO from this study is reasonably similar to that obtained from the PS studies reported by Wentzel *et al.* (2006) i.e. low N and P content (Ramdani *et al.*, 2012).

Generally, the elemental compositions determined in this study are similar to those found from comparative studies. This provides some confidence in the quality of elemental composition results obtained for the NDEBPR WAS in this study.

Results from the application of the three part steady state AD model developed in this research, i.e. (i) the kinetic part describing the organic and polyphosphate hydrolysis, (ii) the stoichiometry part describing the AD products produced from NDEBPR WAS AD and (iii) the mixed (inorganic carbon and phosphate weak acid/base chemistry part, and compared with the measured results are presented below.

The hydrolysis rate (kinetic part of the AD model) of the organic part of BPO component (in this study) were determined by Ikumi *et al.* (2014). The kinetic equations used to describe the BPO concentration utilisation are the Monod kinetics and Saturation kinetics. These kinetic models were calibrated using the influent and effluent COD measured data and is presented in Chapter 3.

Literature indicated that all the P contained by polyphosphate was released at sludge age < 7 days (Jardin and Pöpel, 1994) and this was validated by batches tests in this study. Five AD Batch tests over 11 days at different dilutions to limit precipitation showed that P was released in less than 5 days. In the continuous ADs the extent of polyphosphate P release could not be observed directly because P mineral precipitation took place during the AD of NDEBPR WAS. Instead the potassium (K) contained in polyphosphate that is linearly related to P content and does not precipitate was used to determine the extent of polyphosphate P

release. This K concentration release indicated that all the polyphosphate was released at a sludge age ≥ 10 days. Because 10 days was the shortest sludge age considered in this study all the polyphosphate P content of the WAS was released at all sludge ages (10-60d) considered. The kinetic rate of polyphosphate hydrolysis therefore is much faster than that of the biodegradable particulate organics of the OHO and PAO organics in NDEBPR WAS.

To deal with the different kinetic rates for the organic and polyphosphate hydrolysis in the steady state AD model, the total BPO and utilized BPO concentrations relating to the different sludge ages were converted to molar fluxes and the entire PAO PP content linked to these. The molar fluxes for the influent BPO (J_{BPO}) and utilized BPO ($J_{\text{BPO(U)}}$) were incorporated into the stoichiometry part of the AD model to ensure that the AD products were related to the hydrolysis kinetics that govern the utilization of BPO. The volumetric fluxes (l/d) determined for this study were 1.6, 1.333, 0.889, 0.8, 0.64, 0.4 and 0.267 at the different sludge ages of 10, 12, 18, 20, 25, 40 and 60 days respectively. The influent BPO fluxes (J_{BPO} , gCOD/d) were 39.4, 32.5, 25.4, 21.2, 18.8, 11.1 and 7.6 and the utilized BPO fluxes ($J_{\text{BPO(U)}}$, gCOD/d) were 17.6, 15.1, 14.3, 13.2, 12.5, 9.0 and 7.1 at the above stated sludge ages, respectively.

The application of the stoichiometry part of the steady state AD model predicted the concentration for the AD products at the different sludge ages i.e. results for the methane (CH_4) and carbon dioxide (CO_2) gas generated, ammonium (NH_4^+), bi-carbonate (HCO_3^-), counter-ion metals (Mg^{+2} , K^+ and Ca^{+2}), phosphates (H_2PO_4^- and HPO_4^{-2} , dependent on AD system pH) and biomass. The predicted concentrations not affected by mineral precipitation (mainly struvite) i.e. methane gas, potassium and CO_2 (aqueous (HCO_3^-) and gaseous) compared well with measurements. The predicted CH_4 gas was 50.7 mmol/d compared with 45.1 mmol/d measured at the 10 day sludge age and 17.8 mmol/d (predicted) versus 17.9 mmol/d (measured) at the 60 day sludge age. All the CH_4 gas fluxes are predicted within 10% of the measured fluxes.

However, the CO_2 gas was under-predicted for all sludge ages but this result was accompanied by the over-prediction of the HCO_3^- concentration. The variance in the measured and predicted CO_2 gas and aqueous HCO_3^- could be explained with mixed weak acid/base chemistry, which shows the interdependency of the CO_2 gas, H_2CO_3^* Alkalinity (closely equal to HCO_3^- concentration or between pH 7 and 8) and pH. Because mineral precipitation changed the digester pH, the steady state AD model over predicted the CO_2 in the gaseous phase and under predicted the CO_2 in the aqueous phase (HCO_3^-) measured as the system H_2CO_3^* alkalinity.

The measured and predicted carbon concentrations were determined for each of the components of the influent and effluent that contain carbon by using the assumed f_C values of 0.52 and 0.51 for the influent VSS (PO) and UPO components respectively. The f_C value for the BPO component was determined by difference from the assumed f_C for the PO and UPO. For the feed WAS, the PO (VSS) carbon content contributed more than 98% of the total influent carbon concentration with the less than 2% contained by the influent H_2CO_3^* alkalinity. The C concentration of the UPO remains unchanged from the influent to the effluent, as it is not affected by the AD processes and accounts for 53% of the C concentration exiting the AD system for both the measured and predicted results. The effluent

residual BPO accounts for 24% of the exiting C concentration at the 10 day sludge age but decreases to only 4% at the 60 day sludge age. In contrast, the C concentration of the CH₄ and CO₂ exiting the AD system were 11% and 7%, respectively, at the 10 sludge age but increased to about 22% and 11% respectively at the 60 day sludge age. This shows the increase in the transfer BPO carbon to the AD gaseous products, CH₄ and CO₂. The effluent C concentration contributed by the HCO₃⁻ or H₂CO₃* alkalinity remained a small portion (like the case of the influent) but shows an increasing trend from 2% at the 10 day sludge age to about 5% in the 60 day sludge age of the AD system effluent.

However, significant differences between the predicted and measured results for Mg, ortho-P and FSA concentrations were observed at the different AD test sludge ages. These differences were due to struvite precipitation, which increased with sludge age. Struvite precipitation was confirmed with the calculated ionic product of the measured molar aqueous concentrations of Mg⁺², FSA and PO₄⁻³ (determined from the measured Ortho-P and the equilibrium equations) were close to the thermodynamic solubility product (K_{spm}) of struvite. Quantification of the struvite precipitant is beyond the scope of this study. Struvite precipitation affected the pH of the experimental ADs, which affect the partial pressure of the gas and H₂CO₃* Alkalinity of the inorganic carbon system. Modelling struvite precipitation is discussed in Chapter 3.

Comparing the predicted results obtained from the application of the steady state AD model with those measured on the experimental system it was observed that the results of the compounds that are not affected by struvite precipitation, and consequently pH, compare reasonably well with the measured results. The AD model therefore determines the expected result for the components of struvite precipitation does not occur.

As a secondary objective, this study compares the UPO fractions determined for the NDEBPR AS system ($f_{up(AS)}$) with that determined from the AD system ($f_{up(AD)}$) to assess whether the UPO content of WAS in the NDEBPR AS system remains unbiodegradable when this WAS is digested in an AD system. The UPO of the NDEBPR WAS ($f_{up(AS)}$) fed to the AD system was calculated from the measured NDEBPR system performance to be 0.533, 0.533, 0.521, 0.533, 0.53, 0.529 and 0.551 at 10, 12, 18, 20, 25, 40 and 60 day AD sludge ages respectively. This resulted in a mean $f_{up(AS)}$ of 0.533 during the period of AD tests. From AD performance data (influent and effluent COD) Ikumi *et al.* (2014, see Chapter 3) used regression plots of the correlation coefficients (R^2) vs. f_{up} (in the expected UPO range) for the first order, specific first order, Monod and saturation hydrolysis kinetics to obtain the best $f_{up(AD)}$ at the maximum R^2 . The $f_{up(AD)}$ so determined was 0.54. Assuming the residual BPO and biomass BPO are zero, the $f_{up(AD)}$ was also measured on the 60 day sludge age effluent and found to be 0.55. All three NDEBPR WAS UPO fractions are reasonably similar, proving that the UPO content of the AS system remains unbiodegradable in the AD system and the UPO of NDEBPR WAS is the same for activated sludge systems and anaerobic digesters.

2.4 PRINCIPAL CONCLUSIONS AND RECOMMENDATIONS

The principal conclusions for this study are the following:

- (1) Mass balances for the COD, N, P, C and metals were performed over the AS and AD systems and found to be good.
- (2) The organics characterization procedure developed by Ekama *et al.* (2006b) has been extended in this study to include P as part of the elemental composition of the PO, UPO and BPO components.
- (3) PAO polyphosphate is coupled to the BPO part of NDEBPR WAS using a linkage factor but its hydrolysis and release during the AD process is much faster than the hydrolysis of the WAS BPO components.
- (4) The steady state AD model of Sötemann *et al.* (2005a) has been extended and amended in this study to describe the AD of NDEBPR WAS.
- (5) The stoichiometry part of the AD model predicted very well the concentration of the AD products that are not affected by struvite precipitation and consequently pH. However, because the AD model does not include struvite precipitation the concentrations affected by precipitation and pH were not predicted well.
- (6) Struvite precipitation took place during the normal operation of the AD system fed NDEBPR WAS.

Further research is recommended to extend the stoichiometric part of the steady state AD model developed in this study to quantify the mineral precipitation that took place in the AD of NDEBPR WAS during the operation of the experimental AD system because it strongly affects digester pH. This could be achieved by incorporating principles from the studies of Mustovo *et al.* (2000) and Loewenthal and Morrison (1997) to the steady state AD model developed in this project (Harding *et al.*, 2011). Also, there is a need to analytically measure the TOC content of the PO, UPO and BPO components to confirm the f_C values obtained from the C balance in this study.

Further detail of the research reported in this chapter can be found in:

Harding TH, Ikumi DS, Wentzel MC, and Ekama GA (2008) A stoichiometric steady state model describing phosphorus release during the anaerobic digestion of waste activated sludge for a phosphorus removal activated sludge system. Procs. 10th biennial WISA conference and exhibition, Suncity, 18-22 May.

Harding TH, Ikumi DS, and Ekama GA (2009) A steady state stoichiometric model describing the anaerobic digestion of biological excess phosphorus removal waste activated sludge. Research Report No W132, Dept of Civil Engineering, Univ of Cape Town, Rondebosch, 7701, Cape, South Africa.

Harding TH, Ikumi DS and Ekama GA (2011) Incorporating phosphorus into plant wide wastewater treatment plant modelling – Anaerobic digestion. 8th IWA Watermatex conference, San Sebastian, Spain, 20-22 June.

CHAPTER THREE

THE DEVELOPMENT OF A THREE PHASE DYNAMIC PLANT-WIDE MATHEMATICAL MODEL FOR SEWAGE TREATMENT

3.1 INTRODUCTION

Municipal wastewater usually contains a large quantity of nitrogen (N) and phosphorus (P), which if not removed is one of the main causes of eutrophication that negatively affects natural water bodies by excessive algae and plant growth. In general, phosphorus is removed in biological nutrient removal (BNR) wastewater treatment plants (WRRFs) through the use alternating anaerobic and aerobic conditions, which stimulate the growth of phosphorus accumulating organisms (PAOs) that mediate enhanced biological P removal (EBPR) in activated sludge systems. There is a need to find the most cost effective methods for the design and operation of WRRFs to minimize energy consumption and cost while maximizing nutrient recovery and effluent quality.

This required research into design procedures that were based on the behavioural patterns of microorganisms mediating the N and P removal processes of the WRRF. This research led to the development of a number of activated sludge kinetic theories and dynamic mathematical models, which were coded into computer simulation programmes. Also, simpler steady state models that use explicit algebraic equations, were developed to complement the dynamic models by allowing the WRRFs to be sized and/or wastewater characteristics to be determined before performing simulations, thereby obviating the inefficient trial and error use of dynamic models.

Previous steady state and dynamic simulation models concentrated mainly on the activated sludge (AS) unit operation because it is from this part of the WRRF that the effluent is produced. However, the mutual interaction between all the connected unit operations of the WRRF has recently triggered research interest in the development of mass balance based plant-wide WRRF models, which model all the unit operations of the WRRF together, linked with their connecting flows.

An integrated steady state model for the whole WRRF comprising nitrification-denitrification (ND) AS, anaerobic digestion (AD) of primary sludge (PS) and anoxic-aerobic digestion of waste activated sludge (WAS) was developed by Sötemann *et al.* (2006) and Ekama (2009) by coupling of the various existing WRRF individual unit operation steady state models. This model is being extended and modified as new information is added to it. Extending this plant-wide steady state model by adding P and inorganic settleable solid (ISS) with anoxic-aerobic and/or anaerobic digestion of the P-rich WAS is one of the objectives in this investigation.

The PAOs introduce several complex issues, which required investigation. For instance, the PAOs have a lower endogenous respiration rate compared with ordinary heterotrophic organisms (OHOs) and this affects the N and P nutrient releases in aerobic and anaerobic digestion (Sötemann *et al.*, 2006). Also, the release of P from polyphosphate (PP) could stimulate mineral precipitation in both aerobic or anaerobic digestion so three phase (aqueous-gas-solid) mixed weak acid/base chemistry needs to be considered.

3.2 PROJECT OBJECTIVES

The general project goal is to develop three phase (aqueous-gas-solid) steady state and dynamic mathematical models for the anaerobic and aerobic digestion of WRRF sludge, including waste activated sludge (WAS) produced by NDEBPR plants, in a plant-wide setting. To accomplish this goal the following four objectives were established:

- (1) Carry out an experimental investigation to generate the data required for both steady state and dynamic model development: The experimental set up was large, to mimic three real WRRF types at laboratory scale, as shown in Figure 3.1 below.
- (2) Develop a steady state AD model including P: From the experimental data of the ADs operated at five different sludge ages, determine the hydrolysis kinetics of PS, ND AS system waste activated sludge (WAS) and NDEBPR AS system WAS for inclusion into the stoichiometric AD model developed by Harding (2009) (Chapter 2). Since it was noted that mineral precipitation took place in the AD of NDEBPR WAS containing PAOs, the steady state mixed weak acid/base chemistry part of the AD model needs extension to include three phases (aqueous-gas-solid).
- (3) Develop a plant-wide dynamic model that includes P from NDEBPR WAS: A dynamic AD model has previously been developed by Sötemann *et al.* (2005b) but this model was (i) two phase (aqueous-gas), (ii) applied to only a PS and ND system WAS and (iii) included only one biodegradable particulate organic (BPO) for PS or WAS digestion. Therefore the planned AD dynamic model is to include three phase (aqueous-gas-solid) mixed weak acid/base chemistry to include mineral precipitation and multiple organic types for anaerobic digestion to facilitate AD of primary sludge (PS) together with WAS within the plant-wide framework. Due to the significant increase in size and complexity to model the WRRF as a whole, the NDEBPR activated sludge system and the tertiary treatment processes of AD and aerobic digestion (AerD), both fed NDEBPR WAS, required coding in WEST®, which is a program capable of simulating many bioprocesses in various unit operations assembled into a WRRF.
- (4) Develop a three phase AS dynamic model by extending an existing EBPR AS model, such as UCTPHO (Wentzel *et al.*, 1992) or ASM2 (Henze *et al.*, 1995) and ensuring its compatibility with the AD dynamic model mentioned in objective 3 for the plant-wide model development. In addition, this three phase AS model with EBPR is to be extended to plant-wide simulation of EBPR AS with anoxic-aerobic digestion of P-rich WAS with mineral precipitation to produce concentrated dewatering liquor with low N and P.

The new knowledge contributed by this research is directly tied to the research objectives, which include:

- 6 The development of a three phase plant-wide model that includes phosphorous. This involves:
 - 6.1 The development of the mixed weak acid/base chemistry part of the steady state AD model to include multiple mineral (struvite, magnesium hydrogen phosphate, tricalcium phosphate, calcium and magnesium carbonates), precipitation and digester pH prediction.
 - 6.2 The development of a three phase dynamic model that includes phosphorus and mineral precipitation processes in aerobic (and/or anoxic-aerobic) and anaerobic digestion of concentrated WAS.

- 7 Investigating the biodegradability of organics within the WRRF, including:
 - 7.1 The determination of organics biodegradability within the different unit operations of the WRRF, including primary settling tank (PST), AD and AS systems.
 - 7.2 The comparison of the influent unbiodegradable particulate organic (UPO) fraction calculated from the ND AS system and NDEBPR AS system, treating the same settled wastewater and AD of the WAS from these systems.
- 8 Inclusion of the hydrolysis of multiple organic types in the plant-wide model, for the treatment of municipal sewage.

3.3 MATERIALS AND METHODS

The experimental layout to accomplish this research project replicates at laboratory scale three full scale water resource recovery facility (WRRF) schemes, comprising (1) a Modified Ludzack-Ettinger (MLE) nitrogen (N) removal (ND) activated sludge (AS) system treating settled wastewater (WW) with the separate AD of PS, WAS and PS-WAS blends, (2) a MLE N removal AS system treating raw WW with AD of its WAS and (3) a University of Cape Town (UCT) N or P removal system treating settled WW with the AD of its WAS. All three AS systems were fed the same wastewater collected from the Mitchells Plain WRRF, in Cape Town. To ensure a consistent composition of the raw and settled wastewater, measured masses of macerated PS collected from the Athlone WRRF (in Cape Town) were added to the collected Mitchells Plain (settled) WW. Hence in this experimental programme, raw WW is Mitchell's Plain settled WW with added Athlone PS, and settled WW is Mitchell's Plain settled WW only. In order to increase the enhanced biological P removal (EBPR) in the UCT system 200 mg/l of acetate and 30 mgP/l KH_2PO_4 were dosed to its settled wastewater feed.

3.4 EXPERIMENTAL SET UP

A diagrammatic representation of the experimental layout is shown in Figure 3.1.

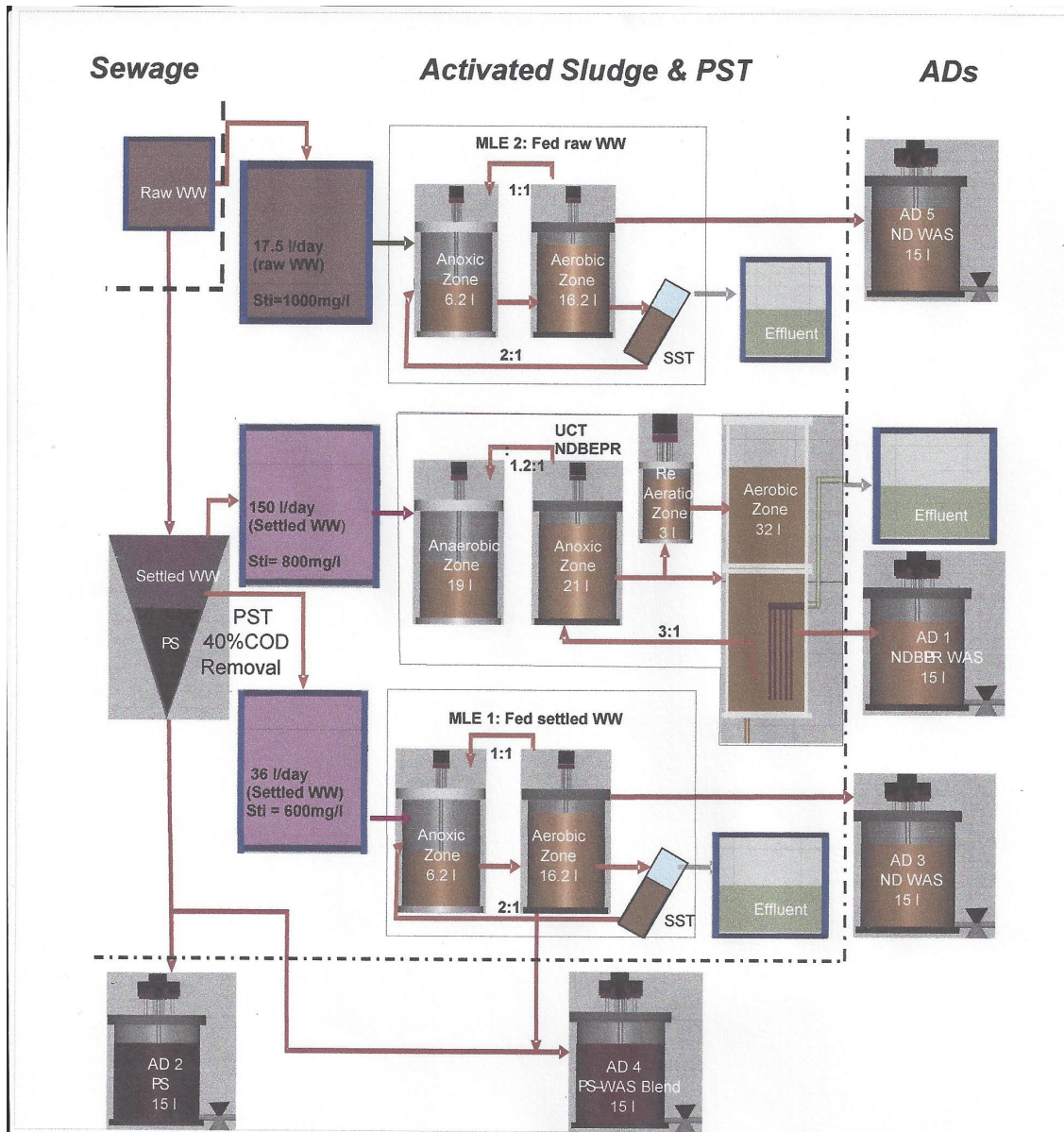


Figure 3.1: Experimental set-up.

Raw WW (18 l/d) was fed to one of the MLE systems (MLE 2) and settled WW to the UCT NDBEPR (150 l/d) and the other MLE system (MLE 1, fed at 36 l/d). The sludge age of all three AS systems was 10 days established by hydraulic control. The PS added to the collected WW to make the raw WW and the WAS from the three AS systems were fed to five completely mixed flow-through ADs: (1) UCT NDBEPR system WAS, (2) PS only, (3) settled WW MLE system (MLE 1) WAS, (4) MLE 1 WAS and PS blend and (5) raw WW MLE system (MLE 2) WAS.

Each digester was operated at five different sludge ages, i.e. 10, 18, 25, 40 and 60 days. The short sludge ages are useful to determine the hydrolysis rate of the different sludges and the very long 60-day sludge age is useful to determine the unbiodegradable fraction of the sludges, as recommended by Sötemann *et al.* (2005a). For the short and long sludge ages, once the time period of three sludge ages had elapsed, testing of the ADs commenced and continued for a period of about two weeks. The lab scale AS and AD systems, were operated over a two-year experimental period. The AS systems were also tested during this AD test period, because the source feed PS and WAS fed to the ADs was taken from them. During the periods when the systems were not intensively tested, random tests were performed on the AS and AD systems to check steady state conditions.

The results obtained in the experimental investigation were sufficiently reliable to provide data for (1) the development of a steady state model for the AD of PS, ND and NDEBPR WAS including P, (2) determination of the hydrolysis kinetic rates of the PS and WAS from the three AS systems and the PS-WAS blend and (3) experimental determination of whether or not the unbiodegradable particulate organics (UPO) from the influent wastewater and the unbiodegradable endogenous residue produced by the OHO and PAO biomass in the AS system, remain unbiodegradable under anaerobic digester conditions. If similar unbiodegradable fractions are obtained from the AS and AD systems, this would validate that unbiodegradable organics, as defined by the (aerobic) AS system remain unbiodegradable in the (anaerobic) AD system.

3.5 STEADY STATE KINETIC MODEL DEVELOPMENT

A steady state model for the anaerobic digestion (AD) of primary and secondary sludge from NDEBPR plants treating municipal wastewater was developed by modifying the existing steady state AD model for primary sludge of Sötemann *et al.* (2005a). This involved adding:

- 1 Phosphorus (P), both organically bound P (OrgP) and polyphosphate (PP) in phosphorus accumulating organisms (PAOs), into the stoichiometry, taking due consideration of the OP systems pK value near 7.
- 2 The hydrolysis of WAS from ND and NDEBPR systems in the AD model.
- 3 Anaerobic digestion of primary sludge (PS) and WAS blends.
- 4 Mineral precipitation, in particular struvite, which involves three phase (liquid-gas-solid) mixed weak acid/base chemistry of the inorganic carbon (IC) and ortho-phosphate (OP) systems.

This will extend the steady state AD model to be able to deal with all the main types of municipal sludge thereby extending the plant-wide WRRF steady state model of Ekama (2009) to:

- 1 Predict the release of N and P in AD of PS and WAS from ND or NDEBPR activated sludge (AS) systems.
- 2 Optimizing plant operation procedures to minimize effluent N and P concentrations.
- 3 Tracking the various compounds and elements- mainly carbon (C), hydrogen (H), oxygen (O), N, P, magnesium (Mg), potassium (K) and calcium (Ca) -through the unit operations of the WRRF and identifying areas where mineral precipitation problems can occur.

In the steady state and dynamic AD models of Sötemann *et al.* (2005a,b) the hydrolysis of particulate biodegradable organics (BPO) was modified so that the three different organic groups (proteins, carbohydrates and lipids) of the IWA ADM1 (Batstone *et al.*, 2002) to a single hydrolysis process acting on two generic biodegradable organics groups, viz. fermentable biodegradable soluble organics (FBSO) and biodegradable particulate organic (BPO) representing sewage sludge, i.e. $C_xH_yO_zN_aP_b$. Also included to make a total of five influent organics groups are the unbiodegradable soluble organics (USO), the unbiodegradable particulate organics (UPO) and the VFA. The five organics group types are also in the influent wastewater and therefore this AD influent characterization is aligned with plant wide modelling. While a composition (x, y, z, a, b) in $C_xH_yO_zN_aP_b$ is also assigned to the USO and UPO, these pass through the AD unaffected.

With complex organics like in WRRF sludges, the hydrolysis process is the rate-limiting step so that the AD processes that follow it, being much faster, can be dealt with stoichiometrically in steady state AD models to yield directly the digester end products, i.e. biomass, methane (CH_4), carbon dioxide (dissolved HCO_3^- and gaseous CO_2), ammonia (NH_4^+) and water. Thus, the extended steady state (SS) model also comprises three sequential parts:

- 1 A chemical oxygen demand (COD) based hydrolysis kinetic part from which the concentration of biodegradable COD utilized and methane and sludge production are determined for a given AD sludge age (R_s , which is also equal to hydraulic retention time for flow through ADs).
- 2 A COD, C, H, O, N, P and charge mass balance stoichiometry part from which gas production and composition (or partial pressure of CO_2), NH_4^+ released, biomass produced and alkalinity generated (HCO_3^- , $H_2PO_4^-$ and HPO_4^{2-}) are calculated from the biodegradable COD removal.
- 3 A three phase mixed inorganic carbon (IC) and ortho-phosphate (OP) weak acid/base chemistry part from which the digester pH and mineral precipitation is calculated.

3.6 AD KINETICS OF SLUDGE HYDROLYSIS

Like Sötemann *et al.* (2005a,b), in this investigation four kinetic equations were accepted to model hydrolysis/acidogenesis in the breakdown of BPO (the main biodegradable organic group >95% of biodegradable COD) in AD. These are (1) first order [$r_h = k_h S_{bp}$, where S_{bp} is the residual BPO COD concentration, gCOD/l and r_h = the volumetric hydrolysis rate, gCOD/(l.d)], (2) Specific first order ($r_h = k_H S_{bp} Z_{AD}$, where Z_{AD} the acidogenic biomass concentration gCOD/l), (3) Monod kinetics ($r_h = k_m S_{bp} / (K_s + S_{bp}) Z_{AD}$), and (4) saturation kinetics [$r_h = k_M (S_{bp} / Z_{AD}) / \{K_S + (S_{bp} / Z_{AD})\} Z_{AD}$]. In order to use these kinetic formulations, the hydrolysis kinetic rate constants (k_h , k_H , k_m , K_s , k_M and K_S) in ADs fed the different sludges were determined. For this, the most useful data was that from the short sludge age ADs while long sludge age AD data was useful to determine the unbiodegradable particulate COD fraction ($f_{SL,up}$) of the different sludges.

The Monod and saturation kinetic constants, calibrated to the measured experimental AD data for the PS and WAS types are listed in Table 3.1. It was observed that each of the hydrolysis kinetic equations yielded slightly different UPO fractions for best correlation against the experimental results over the sludge age range so it was not possible to select the best rate equation to model hydrolysis. The 1st order (k_h) and specific 1st order (k_H) rates were

quite well correlated to sludge age increasing as sludge age increases so these rates are given in Table 3.1 as linear equations in sludge age with their correlation coefficients (R^2). Also the correlation coefficients for the Monod and saturation kinetics, obtained using selected sludge age results for improved correlation, are given in Table 3.1 and can be used to model hydrolysis of PS and WAS over the wide range of AD sludge ages tested.

The different sludge types (PS, MLE 1 WAS, MLE 2 WAS, NDEBPR WAS and the PS-MLE 1 WAS blend) did not hydrolyse at the same rate. Although each sludge type has a unique hydrolysis rate, Figure 3.2 shows that the measured percentage biodegradable COD removed with sludge age for each of the sludges does not exhibit a very large difference between the PS and WAS. Therefore, from this investigation, AD of waste activated sludge (WAS) together with primary sludge (PS) does not have a significant impact on the hydrolysis rate of WAS compared with anaerobically digesting the WAS by itself.

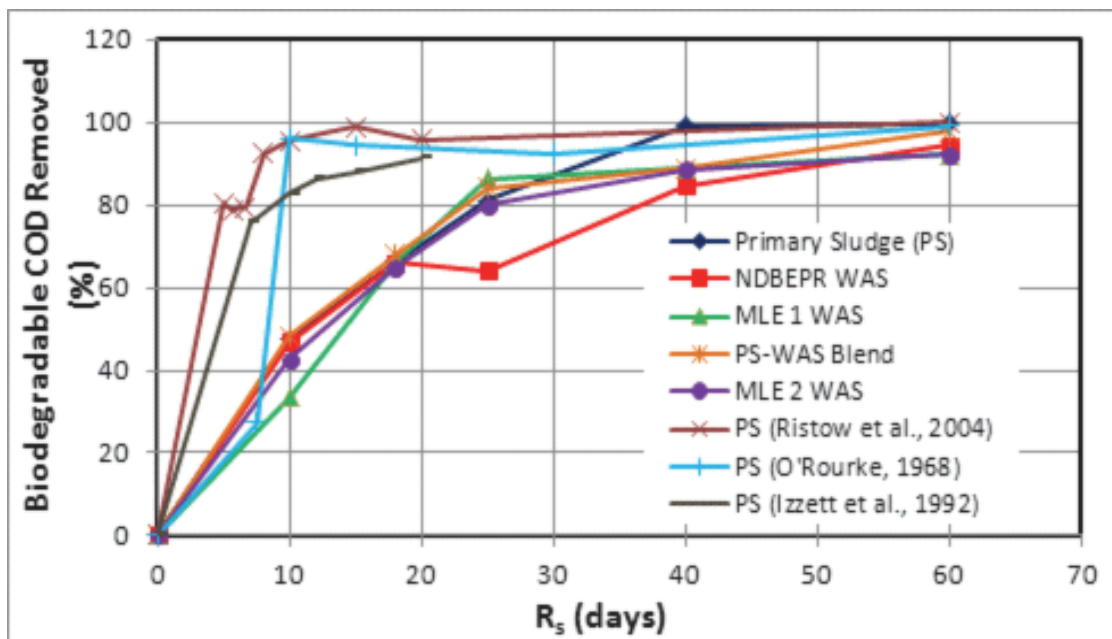


Figure 3.2: The percentage biodegradable COD removed, calculated from measured results with increasing sludge age (R_s) for the different sludge type.

Table 3.1: Unbiodegradable Particulate Organic (UPO) Fractions and Hydrolysis Kinetic Determined by the Different Methods in the Experimental Investigation

Parameter		PS	WAS	WAS	WAS	PS -WAS	PS ¹	PS ²	PS ³
		Author	MLE1	MLE2	NDEBPR	PS + MLE1	Izzett	O'Rourke	Ristow
UPO value	Hydrolysis Kinetics Value	0.31	0.47	0.62	0.54	0.37	0.36	0.34	0.34
	60-day AD value	0.31	0.53	0.66	0.58	0.40			
	AS performance Value	0.30	0.47	0.62	0.53	0.36			
Hydrolysis kinetic rates	1st Order k_h								
	mk_h	0.013	0.003	0.003	0.033	0.015	0.0065	0.398	23205
	ck_h	-0.077	0.041	0.070	0.004	-0.165	0.432	1.030	-221130
	R^2	0.924	0.842	0.820	0.895	0.981	0.780	0.762	0.922
	Specific 1st order k_H								
	mk_H	0.372	0.096	0.092	0.216	0.430	0.007	0.2042	139.79
	ck_H	-0.303	0.970	1.147	0.131	-4.331	0.228	-1.5004	-1332.12
	R^2	0.852	0.974	0.980	0.872	0.956	0.780	0.874	0.922
	Monod								
	k_m	4.300	2.094	2.482	2.465	5.153	3.340	2.004	0.243
	k_s	1.523	0.408	0.626	0.607	1.710	6.760	0.355	640
	R^2	0.930	0.963	0.948	0.826	0.960	0.900	0.429	-
	Saturation								
	k_M	1.796	1.603	1.524	1.951	1.919	5.270	2.047	11.2
k_S	7.962	5.387	4.838	9.109	7.723	7.980	0.263	13.0	
R^2	0.942	0.951	0.951	0.919	0.970	0.900	0.428	-	

3.7 STOICHIOMETRIC MODEL FOR AD OF NDEBPR WAS

Sötemann *et al.* (2005a) developed a two phase (aqueous-gas) steady state model to describe the anaerobic digestion of organics, based on C, H, O, N and COD mass balanced stoichiometry developed with the method described by McCarty (1975). In the extension of this stoichiometric model, Harding (2009) added biomass P and polyphosphate (PP), with its associated Mg, K and Ca, into this mass balance stoichiometry. The complexities of including P into the mass balanced stoichiometry of the different WRRF unit operations were

considered to hinge around (1) the different rates at which PP and organically bound P are released in anoxic/aerobic and anaerobic digestion, (2) the effect of the 2nd dissociation constant of the OP weak acid/base system ($pK_{p2} \sim 7$), and (3) the precipitation of metal phosphates resulting from the high metal (Mg^{2+} , K^+ , Ca^{2+}) content which is also released with the OP in aerobic and anaerobic digestion. Harding et al. (2011) noted that at AD sludge ages of five days or longer, only a part of the biodegradable organics of the NDEBPR WAS biomass was degraded but all of the PP in the PAOs was released. Also, the way in which PP is released affects the weak acid/base chemistry of the AD system and hence the pH.

In the anaerobic reactor of the NDEBPR system, PAOs take up short chain fatty acids and convert them to poly-3-hydroxyalkanoates (PHA), which are energy storage compounds that can be broken down aerobically by the PAOs to carry out their growth and respiration metabolism. In the dynamic AD model, PAOs fed to the AD, upon entering the environment are deemed capable of carrying out the same P-release mechanisms as in the anaerobic reactor of the NDEBPR AS system. However, the PAOs cannot complete their life cycle because they require aerobic conditions to supply a terminal electron acceptor (oxygen) for their growth on the PHA and respiration. Therefore, the PAOs die at a rate much faster than the hydrolysis of their biomass, releasing all remaining PP and PHA. So in the AD kinetic model, both the PP release with PHA formation, as mediated in the anaerobic reactor of the NDEBPR system, and PP and PHA release upon the death of PAOs is included. The hydrolysis of the dead PAO biomass is the slowest rate controlling process in the AD and governs the rate of release of organically bound P and N.

In the steady state model, PP, with its associated metals, is assumed to be released instantaneously, which restricts the model to sludge ages larger than 5 days. The release of P and N from the hydrolysis of biomass biodegradable organics is modelled with the same hydrolysis/ acidogenesis kinetics in the steady state and dynamic kinetic models and is the rate determined from the experimental results. The release of PP and metals Mg^{2+} , K^+ and Ca^{2+} to high concentrations cause the precipitation of mainly struvite but also other minerals. Therefore, steady state and dynamic kinetic AD models for digestion of P rich sludge containing PP requires three phase (solid-liquid-gas) weak acid/base stoichiometry to be included.

3.8 WEAK ACID/BASE CHEMISTRY AND THE INCLUSION OF A SOLID PHASE

The process of anaerobic digestion produces various aqueous chemical species at different molar concentrations within the AD liquor. These species belong to several weak acid/base sub-systems that are simultaneously present in solution. A methanogenic AD typically includes the carbonate, phosphate, ammonia, acetate and water weak acid/ base subsystems. Loewenthal *et al.* (1989) noted that each weak acid/base system requires characterization through measurement of the P_T , N_T , C_T and A_T weak acid total species concentrations before they can be speciated at a specific pH (distributing the total concentrations between their ionic species). From the AD steady state model (described in Chapter 2 of this report), the digester product concentrations and pH are completely defined by the influent organics composition and so the aqueous concentrations of the different weak acid/base species and pH (HCO_3^- , $H_2PO_4^-$, HPO_4^{2-} , NH_4^+ , Ac^- and H^+) can be speciated from the measured influent characteristics. These species concentrations in turn are used to determine the digester pH.

Sötemann *et al.* (2005b) noted that the pH established within AD systems treating PS and ND WAS is primarily affected by the inorganic carbon system. Although other weak acid/base systems are present such as the ammonia (N_T), phosphate (P_T) and VFA sub-systems, these do not significantly affect pH, either because their concentration is low (as for the P system) or their pK values are far outside the normal 6.5 to 8.0 pH range of ADs (as for the VFA [$pK_a = 4.7$] and ammonia [$pK_n = 9.1$] systems) (Loewenthal *et al.*, 1994).

When the phosphate species are included in the AD stoichiometry, such as for the AD of NDEBPR WAS with high P concentrations, it is necessary to include the P_T system, since it significantly influences the AD pH via (1) its 2nd dissociation constant pK_{p2} at ~ 7.0 , (2) the form in which it is released ($H_2PO_4^-$ from PP or H_3PO_4 from biomass P) and (3) precipitation of phosphate minerals, in particular struvite. These factors all affect the H_2CO_3 alk, partial pressure of CO_2 (p_{CO_2}) and the P_T concentration and hence the AD pH, causing it to decrease.

3.8.1 Calculation of Struvite Precipitation

The steady state model can also deal with mineral precipitation and because struvite is the main precipitant from the Mg co-released with the PP. The aqueous species concentrations and p_{CO_2} predicted by the complete element mass balanced stoichiometry by the steady state AD model are all at infinite solubility. The struvite precipitation and AD pH can be calculated from these concentrations with the software STRUVITE (Loewenthal and Morrison, 1997) based on the algorithm of Loewenthal *et al.* (1994). The problem with STRUVITE is that p_{CO_2} is required as input to predict the pH and is assumed constant with struvite precipitation. From the 3-phase dynamic AD model developed in this project, struvite precipitation in the AD causes the p_{CO_2} to increase (slightly, <5%) which results in a lower AD pH (and hence less precipitation). A (not so simple) spreadsheet method was developed to solve for the AD pH and p_{CO_2} with struvite precipitation. This requires simultaneous solution of the AD stoichiometry and 3 phase mixed weak acid/base chemistry of the inorganic carbon (IC) and OP systems Harding *et al.* (2010).

3.9 THREE PHASE PLANT-WIDE DYNAMIC MODEL DEVELOPMENT

A plant-wide aligned three phase AD dynamic model was developed in the simulation program WEST® in this project. The initial step in the preparation of this plant-wide aerobic and anaerobic digestion model was the selection of a general set of components, which are universal to all the unit operations of the plant. For this, 38 components were identified in mass concentrations (with the units of milligrams per litre) but further provisions were made to parameterise the component descriptions in terms of their COD and molar concentrations (molalities). Thereafter, ASM2 and UCTSDM1 dynamic models were extended and linked to construct the integrated plant-wide tailored “supermodel”. These extensions include:

- 1 An algebraic equation based aqueous ionic speciation model (Brouckaert *et al.*, 2010) model, which includes dissociation constant (K) adjustment for temperature and non-ideal ionic strength with the Butler (??) equation and ion pairing effects (Musvoto *et al.*, 2000).
- 2 The ASM2 (Henze *et al.*, 1995), modified to include the ionic speciation model (Brouckaert *et al.*, 2010) and the Inorganic Settleable Solids (ISS) model of Ekama and Wentzel (2004).
- 3 The three phase anaerobic digestion model (ADM-3P), including the hydrolysis of multiple biodegradable particulate organic (BPO) types to cater for PS, ND WAS,

NDEBPR WAS and PS-WAS blends, the Ekama and Wentzel (2004) ISS model, the Brouckaert *et al.* (2010) ionic speciation model and multiple mineral precipitation. This ADM-3P model extends the UCTSDM1 model developed by Sötemann *et al.* (2005b) by adding:

- 3.1 Additional soluble and particulate biodegradable organic components to represent organics which might be combined from different sources in the WRRF and fed to the anaerobic digester.
- 3.2 Hydrolysis kinetics of the polyphosphate for the AD of waste activated sludge (WAS) from EBPR systems.
- 3.3 Precipitation of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ (struvite), $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (K-struvite) and $\text{Ca}_3(\text{PO}_4)_2$ (ACP).
- 3.4 Modelling separately as algebraic equations, the “instantaneous” aqueous phase equilibrium and ion-pairing reactions to increase computational efficiency and reduce simulation run times, while the usual kinetic differential equation used for the slower biological, gas exchange and mineral precipitation processes.
- 3.5 Parameterised full element mass balanced stoichiometry for the bioprocesses for the various organics compositions entered as x, y, z, a and b values in $\text{C}_x\text{H}_y\text{O}_z\text{N}_a\text{P}_b$ and polyphosphate entered as $\text{Mg}_c\text{K}_d\text{Ca}_e\text{PO}_3$. When linked, these parameter values are passed between the AD and AS systems.
- 3.6 A pre-processor routine which transforms measured influent parameters such as FSA, OP, H_2CO_3 alk., VFA, pH and TDS to model components and the correct ionic strength for activity coefficient determination and a post-processor transforms predicted model components back to predicted “measured” concentrations for comparison with the actual measured concentrations.
- 4 An integrated plant-wide dynamic model that combines the ASM2-3P and ADM-3P models.

3.9.1 Ionic Speciation Routine and Inter-Phase Transfers

The ionic speciation routine, common in both the ASM2-3P and ADM-3P models, provides a general algebraic approach to modelling the very rapid ionic dissociation and ion pairing equilibrium reactions separately from the slower biological and physical processes. Forty-four species were selected to represent the distribution of the mixed weak acid/base system species and ion pairs that can form from 14 ionic components (of the 38 universally selected model components). The 14 basic components represent the total concentrations of the various weak acid/base systems and are applied in the model material balance calculations. The input pre-processor links to the ionic speciation routine as follows: Measured influent concentrations {OP (P_T), FSA (N_T), Mg^{2+} , K^+ , Ca^{2+} , pH and the H_2CO_3^* alkalinity and VFA (A_T)} and TDS and temperature are entered into the ADM-3P. The pre-processor adds NaCl to achieve the correct ionic strength (TDS), calculates the ionic activity coefficients and disaggregates the total concentrations into the sub-species for each weak acid/base system at the given influent pH. The charge represented by this ionic state forms the reference charge state of the model initial conditions against which all changes in charges are based. The post-processor does the reverse, aggregating the various species concentrations to totals, H_2CO_3^* alkalinity and pH at the effluent ionic strength (TDS).

3.9.2 The Three phase ASM2 (ASM2-3P) Model

The ASM2 is widely accepted and widely applied in NDEBPR system design, operation and process optimisation and forms a basis for further model development (Vanrolleghem *et al.*,

2005). The ASM2, which was developed for NDEBPR AS systems, can also be applied to anoxic-aerobic digestion (AnAerD) because, at least theoretically, AnAerD is a continuation of the AS system endogenous respiration process of OHOs and PAOs. However, this may require calibrating the kinetic rates of some of the bioprocesses and (if necessary) adjusting some of the kinetic and stoichiometric constants (Sötemann *et al.*, 2006).

The ASM2-3P model is calibrated against (1) the NDEBPR UCT activated sludge system of this investigation and (2) the modified Ludzack-Ettinger (MLE) AS systems of this investigation (all systems shown in Figure 3.1) and ASM1 in the absence of EBPR, (3) the batch aerobic digestion (AerD) tests on NDEBPR WAS conducted by Mebrahtu *et al.* (2007, 2008) and (4) the anoxic-aerobic digester (AnAerD) tested by Vogts *et al.* (2012, 2014a,b), which was fed concentrated (2x) and dilute (1/3x) WAS from the same the NDEBPR UCT AS system as fed to the ADs in this investigation.

3.9.3 The Three phase UCTADM (ADM-3P) Model

Figure 3.3 shows a schematic overview of the three phase AD model chemical, physical and biological processes.

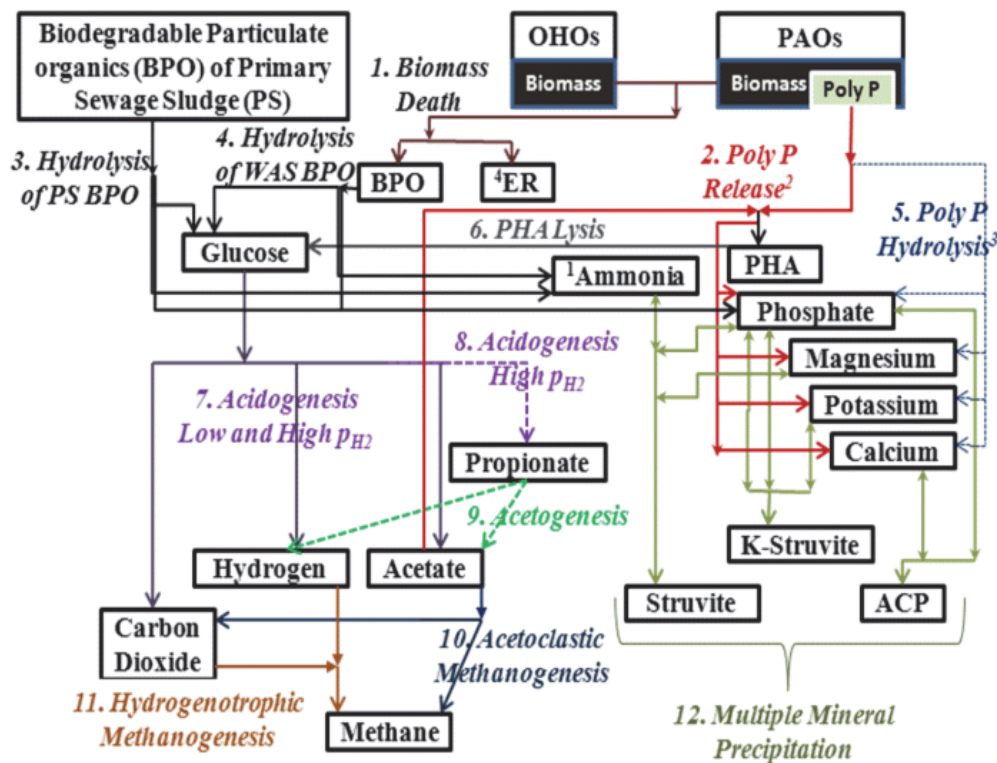


Figure 3.3: Process scheme for the ADM-3P model, as extended from the UCTSDM1 model of Sötemann *et al.* (2005b). Note that (1) ammonia is released in the NH_3 form and picks up a proton from H_2CO_3 to form NH_4^+ , (2) Process 2 is for PP release with the uptake of acetate and (3) process 5 is for the PP hydrolysis with the death of the PAOs, (4) ER stands for the endogenous residue of biomass. Process 12 only shows for P precipitates, but other precipitates (i.e. calcite and magnesite, which are less likely to form) are also included in the model.

The ADM-3P model was calibrated against the ADs of this investigation, i.e. the AD of PS, MLE 1 WAS, MLE 2 WAS, PS-WAS (MLE 1) blend and NDEBPR WAS (the last with both continuous and batch AD tests to ensure that the P release is accurately modelled). The ADM-3P was also validated with PS AD results of Izzett *et al.* (1992) and the predictions of the 2 phase UCTSDM1 of Sötemann *et al.* (2005a,b), which was calibrated against the Izzett *et al.* (1992), O'Rourke (1967) and Ristow *et al.* (2004) experimental data.

The models were verified by checking that 100.00% material (COD, C, H, O N, P, Mg, K and Ca) mass balances were obtained. Calibration of the models generally involved matching the model results to measured variables on the different systems during selected steady state periods. Because the AS and AD systems were operated at steady state, the main calibration effort was determining the hydrolysis kinetic rates of the different sludges. This was accomplished with the COD based hydrolysis (first) part of the steady state model as detailed by Ikumi *et al.* (2014). Because the hydrolysis /acidogenesis process is the slowest, all subsequent processes need to be fast enough to produce a low component residual concentration. Therefore, the methanogenic bioprocesses (acetoclastic and hydrogenotrophic) were not actually calibrated – the yield coefficient endogenous respiration rate and Monod growth kinetic constants of these processes were taken directly from UCTSDM1 by Ikumi *et al.* (2014). This means the ADM3P, while capable of simulating dynamic, start up and overloaded (failure) conditions, has not been calibrated for such conditions. Calibration for dynamic, start up and overloaded (failure) conditions is being undertaken in current (2014 and 2015) research projects at UCT.

In calibration work, the unbiodegradable particulate COD fractions of the different sludge types were kept the same throughout all sludge ages. Its composition also was kept unchanged at elemental composition (i.e. the x, y, z, a and b values of $C_xH_yO_zN_aP_b$) that suited all the sludge ages best. The reason for this was because the AS systems were fed from the same wastewater and PS source throughout the investigation. It was deemed more important to observe that the model was predicting similar trends to experimentally measured results and to provide reason for any observed discrepancies, rather than to correct the discrepancies by changing the elemental formulation at each of the different experimental periods.

After separate calibration, the ASM2-3P and ADM-3P models were combined to build an integrated three phase plant-wide WRRF model in WEST with NDEBPR activated sludge, anaerobic digestion of PS and anoxic-aerobic digestion or anaerobic digestion of concentrated WAS. Therefore, since the ASM2-3P and ADM-3P models already had matching model components, the parameters and stoichiometric processes from the two models were easily combined into one Gujer matrix to form the integrated plant-wide model. However, in the WEST experimentation environment (where the model simulations are performed), it was ensured that only the AS reaction rates were activated in the simulation of AS system and only those of the AD were activated in simulation of the AD unit.

3.10 CONCLUSIONS

In this project, three phase (aqueous-gas-solid) plant-wide kinetic steady state and dynamic mathematical models were developed to simulate the anaerobic, aerobic and anoxic-aerobic digestion of sewage sludge including waste activated sludge (WAS) produced by enhanced biological phosphorus Removal (EBPR) plants. Determining whether or not the

unbiodegradable organics of the influent wastewater and waste activated sludge (WAS) remained unbiodegradable also in the anaerobic digester was considered an important issue in the model development, when coupling the primary settling tank (PST), activated sludge (AS), aerobic digestion (AerD) and AD unit operations. Experimental observations carried out in this investigation led to the following conclusions regarding the fate of influent unbiodegradable particulate organics (UPO) and activated sludge generated (endogenous residue) unbiodegradable particulate organics in the water resource recovery facility (WRRF) (Ikumi et al., 2014):

- 1 The biodegradability of the influent wastewater organics remains closely consistent throughout the WRRF, i.e. the influent UPO component as established by the fully aerobic or ND AS systems remains unbiodegradable in the AD systems. The influent unbiodegradable soluble organics (USO) concentration is low enough (<50mgCOD/l) to be of little concern.
- 2 The material that is unbiodegradable in AS systems (i.e. endogenous residue and influent UPO) also is not further degraded in the AD system, even at very long sludge ages (60d). Hence, unbiodegradable material (influent UPO and AS generated) is conserved throughout the plant, within experimental system operation error.
- 3 The remaining influent organic material that is biodegradable (particulate and soluble) gets transformed to active organisms (OHO) in the fully aerobic and ND AS systems, part of which undergoes endogenous respiration to form endogenous residue (which becomes part of the UPO in WAS). The OHO in WAS undergoes further endogenous respiration in the anoxic-aerobic digestion (AnAerD) sludge treatment. In AD the BPO of the PS and WAS undergoes hydrolysis/acidogenesis to form acetate and hydrogen which is utilized by the AD biomass for growth, forming CH₄ and CO₂ gas as products. The concentration of BPO not hydrolysed depends on the kinetic rate of sludge hydrolysis and the sludge age of the AD. With complex organics like those found in WRRF sludge, the hydrolysis process is the rate-limiting step so that the AD processes that follow it, being much faster, invariably reach completion. The hydrolysis kinetic rate and unbiodegradable particulate organic (UPO) fraction of the different sludges were determined from the measured AD influent and effluent COD concentrations of the sludge age range of 10-60 days. The WAS UPO (assuming 8% of OHO and PAO biomass was unbiodegradable) measured on the 60d AD and determined from the hydrolysis kinetics calibration matched reasonably closely to the UPO determined for the WAS from measured activated sludge performance.
- 4 From 3 above, the higher UPO in the NDEBPR WAS (relative to that of the MLE system fed the same settled WW) is real and not an artifice of the NDEBPR AS model compared with the ND AS model. This has been a repeated observation in the UCT research (see Ekama and Wentzel, 1999). Determining where this extra UPO comes from was beyond the scope of this investigation. Because the NDEBPR system comprises a mixed culture of OHOs and PAOs, it becomes complex to account for this higher UPO. The endogenous residue fraction of OHOs ($f_{EH} = 0.2$, equivalent to 0.08 in death regeneration) used for modelling endogenous respiration and for determination of the unbiodegradable fraction of WAS has been validated in several investigations over the past decades (Marais and Ekama, 1976; van Haandel *et al.*, 1998; Ekama *et al.*, 2006a; Ramdani *et al.*, 2011, 2012). Accounting for the higher NDEBPR WAS UPO by changing the UPO of PAOs (f_{EG}) distorts the f_{EG} value

beyond a reasonable range of that observed in enhanced PAO culture EBPR so this cannot be the reason for the difference.

- 5 The influent inorganic settleable (fixed) solids (ISS) is deemed not to take part in any reactions and is conserved through the plant as already investigated by Sötemann *et al.* (2006) and Ekama *et al.* (2006a). Hence, it simply is enmeshed in the sludge mass and increases with sludge age. Moreover, as modelled by Ekama and Wentzel (2004), some influent inorganic dissolved solids (IDS) are taken up by the OHO and PAO and add to the mixed liquor (fixed) ISS concentration when VSS samples are dried. Therefore, the total reactor ISS comprises the ISS content of the OHO, PAO and ANO biomass (i.e. $ISS_{BM} = 0.15 \text{ mgISS/mg biomass}$), the PAO stored PP (3.23 mgISS/mgP), all precipitates formed (struvite, amorphous calcium phosphate (ACP) and K-struvite ($MgKPO_4$)) and the influent ISS that is enmeshed with sludge. However, although the metals (Magnesium (Mg), potassium (K) and calcium (Ca)) and ortho-phosphate (OP) are taken up aerobically (from where the WAS is withdrawn), to make up polyphosphate (PP), and released anaerobically in the AS system, the mineral precipitation and dissolution of the influent ISS was found to be negligible in the AS systems. In contrast, significant phosphorus mineral precipitation does occur in the AD system fed concentrated WAS from the NDEBPR system ($\sim 10 \text{gTSS/l}$), increasing as the P removal of the parent NDEBPR system and concentration of the feed WAS increases.
- 6 Because polyphosphate (PP), a high-energy compound in the PAOs, is non-cell bound intracellular part of the biomass, it is released much faster than hydrolysis releases the organically bound biomass P (and N) during anaerobic digestion. This PP release from PAOs has no direct relation to the kinetics of hydrolysis/acidogenesis of the PAO (and OHO) biomass, and so the hydrolysis kinetics of the EBPR WAS are not significantly different from that of the WAS from fully aerobic or N removal AS systems. Aside from the PP, the composition of the OHO and PAO BPO material, which requires hydrolysis in the AD, was modelled to be the same because the experimental investigation did not allow these to be differentiated.

3.10.1 Some Observations from the Plant-Wide Model Development

The ASM2-3P and ADM-3P models were verified and validated individually before merging to construct the integrated plant-wide model. This model can be applied to simulate the whole WRRF plant comprising a NDEBPR AS system linked to an AD or an anoxic-aerobic digestion (AxAerD) for WAS stabilisation.

The following aspects were noted when modelling the anoxic-aerobic systems (AS, AerD and AnAerD) with the ASM2-3P model:

- 1 Since the MLE system with ND does not stimulate EBPR, its effluent P comprises mainly the OP that was not utilized by the biomass (mainly OHOs) for growth. This growth is limited by the flux of influent biodegradable COD available. With no PAO growth, no PP gets stored. Hence, the WAS produced from this type of system is not likely to cause struvite precipitation during sludge treatment, even with significant thickening before digestion.
- 2 The aeration that occurs in the aerobic zone of AS systems strips out most of the CO_2 generated by the bioprocesses. Consequently, this biologically generated CO_2 does not have a significant impact on the pH of the system – pH of the AS system reactors depends mostly on the loss and gain of alkalinity via protein hydrolysis (gain), nitrification (loss), denitrification (gain) and PP storage (loss). Provided the H_2CO_3

- alk remains above 40 mg/l as CaCO₃, the degree of CO₂ super-saturation has little effect on pH.
- 3 In MLE systems with little or no nitrification taking place, high quantities of P and acetate in the unaerated ('anoxic') zone will result in the growth of PAOs rather than OHOs (and ANOs) only as expected in fully aerobic or nitrogen (N) removal systems. The concentration of acetate available for this PAO growth (and consequential excess P removal) depends on the rate of fermentation of fermentable biodegradable soluble organics (FBSO) that occurs and the concentration of nitrate that gets recycled to the anaerobic reactor in these systems. This can also take place in 3 and 5-stage Bardenpho systems – during the winter months when denitrification is lower than in the summer, the nitrate concentration recycled to the anaerobic reactor can be sufficiently high to suppress EBPR, in which case the WAS is not P-rich and AD of the WAS will not result in mineral precipitation even if thickened to 4 or 5% by flotation. In contrast, in summer the nitrate recycled to the anaerobic reactor is low resulting in EBPR in this system and mineral precipitation in AD and sludge dewatering systems. This happened at the Cape Flats WRRF in Cape Town, where the WAS was thickened to 3 to 4% by dissolved air flotation and anaerobically digested with PS. Seasonal EBPR in the 5-stage Bardenpho system caused mineral precipitation in the AD sludge dewatering centrifuges (van Rensburg *et al.*, 2003). The problem was solved by adding aeration to the post AD sludge storage tank to raise the digester liquor pH by CO₂ stripping to stimulate mineral precipitation before discharge to the dewatering centrifuges. While not quantitatively validated the plant-wide ASM2-AD-3P does qualitatively predict this behaviour correctly.
 - 4 In anoxic-aerobic digestion (AxAerD), the absence of VFA and an anaerobic period renders the PAOs unable to compete with the OHOs. Consequently, the PAOs do not grow and undergo endogenous respiration. The PAOs eventually die, releasing their stored PP that contains Magnesium, Calcium, potassium and OP. Struvite (MgNH₄PO₄) precipitation occurs when the concentration of Mg, ammonia and OP is high enough (i.e. the struvite is supersaturated) in the mixed liquor. If the ammonia is low (< 1mgN/l), due to nitrification, the Mg and P combine with K to form K-struvite (MgKPO₄). The precipitation of FSA-struvite and K-struvite is limited by the Mg concentration, which is usually the lowest of the Mg, K, FSA and P. Once the Mg is limited, no further OP reduction takes place. About one-third of the P released by PP precipitates with the co-released Mg. This was observed in both aerobic and anaerobic digestion (see Chapter 4).
 - 5 From the application of the ASM2-AerD-3P model to the diluted (4gTSS/l) aerobic batch tests of Mebrahtu *et al.* (2007, 2008), in which mineral precipitation did not take place, it appears that the PAOs retain their PP until they 'die' at their very slow endogenous respiration rate (0.04/d). This means that after 20d aerobic digestion, a considerable proportion of PAOs, with a high PP content, are still "alive" (> 50%). If the WAS is concentrated (> 2% TSS) FSA-struvite and K-struvite precipitation will take place but will be limited by the co-released Mg. The P release behaviour in aerobic digestion is therefore distinctly different to that in anaerobic digestion, where all the PP is released in less than 5 days. The FSA and OP concentrations in dewatering liquor from aerobic digestion of P-rich WAS are therefore much lower than those from AD of P-rich WAS.

- 6 Application of the model to the 20 day retention time semi continuous flow though anoxic-aerobic digester fed concentrated P-rich WAS of Vogts et al. (2012, 2014a,b) validated that the effluent FSA and nitrate were very low ($< 1\text{mgN/l}$) and that about $1/3^{\text{rd}}$ of released P was precipitated as struvite with co-released Mg. While Vogts *et al.* (2012, 2014a,b) also tested the effect of Ca and Mg dosing to the AxAerD on the aqueous OP concentration, this was not simulated but will be done in further work. Also, the P release in the semi-continuous digester was faster than that in the batch tests of Mebrahtu et al. (2007) resulting in complete PP release in 20d, an aspect that requires further evaluation of this projects results.

The following aspects were noted when modelling the AD systems using the steady state and dynamic (ADM-3P) three phase AD models:

- 1 In the AD of PS, biodegradable particulate organics (PS BPO) are directly available. For AD of WAS, the biomass (OHOs and/or PAOs) die and are converted to BPO rapidly – much faster than their aerobic endogenous respiration rate. The WAS BPO is hydrolyzed at a distinct rate (which was measured in this investigation). This hydrolysis rate of PS BPO and WAS BPO dictates the rate of all bound FSA and OP release in AD. The COD removal associated with FSA and OP release increases with increased AD sludge age. This increase is due to the increased time available for the hydrolysis of BPO material and hence release of the organically bound N and P, as FSA and OP, into the AD liquor.
- 2 Methane is produced via the COD removal; hence, methane production depends only on the electron donating capacity of the biodegradable organics degraded (minus the very small amount, 2-5% of COD in the AD biomass produced). The C not included in CH_4 (minus the very small amount of C in the biomass) becomes CO_2 , either dissolved CO_2 (HCO_3^-) or gaseous CO_2 . Being insoluble at close to atmospheric pressure, methane usually all escapes as gas as soon as it is formed by the biological reactions. The mole fraction of the CO_2 in the gas phase [$\text{CO}_2 / (\text{CO}_2 + \text{CH}_4)$] sets the partial pressure of the gas phase (p_{CO_2}), which together with the various species of the different weak acid/base systems (IC, FSA, OP, VFA, H_2S) that make up the total alkalinity set the AD pH.
- 3 Organically bound N is released with the breakdown of biodegradable organics in the non-ionic NH_3 form, which are non-reference species for the ammonia weak acid/base system so the alkalinity increases by the concentration of NH_3 released. The NH_3 , in the 6-8 pH range of ADs, picks up a H^+ ion from the bulk liquid which is supplied by the dissolved CO_2 (H_2CO_3^*) forming HCO_3^- , according to $\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{HCO}_3^- + \text{NH}_4^+$. Therefore, the total alkalinity (T.Alk) remains unchanged but is transferred from the N containing organics fed to the AD FSA system to the inorganic carbon system in the aqueous phase in the AD. This is the main aqueous phase H_2CO_3^* alkalinity generation process in an AD treating PS or WAS that is not P-rich. For ADs fed P-rich WAS, the aqueous phase H_2CO_3^* alkalinity also depends on PP and cell bound P released.
- 4 Initially, polyphosphate (PP) release and PHA storage by PAOs takes place with the uptake of acetate, as would happen in the anaerobic part of the parent NDEBPR system. This results in increased alkalinity because the PP is released as H_2PO_4^- . Because the PAOs also require aerobic conditions to supply them with the terminal electron acceptor (oxygen) for their growth, they cannot grow in the AD. Therefore, the PAOs are modelled to “die” in AD at a rate faster than their endogenous

- respiration rate; releasing their PHA and rest of their stored PP, adding more H_2PO_4^- and alkalinity. Depending on the charge/proton balance requirements, some of the H_2PO_4^- species become HPO_4^{2-} species by reacting with HCO_3^- to form HPO_4^{2-} , H_2O and CO_2 . In this exchange, the T.Alk remains constant but the species concentrations that represent it change. This causes an additional transfer of alkalinity from the HCO_3^- of the IC system to the HPO_4^{2-} of the OP system and increases the CO_2 that exits the digester as gas and so increases the p_{CO_2} of the AD gas.
- 5 The organically bound P in the PAO (and OHO) biomass is released as H_3PO_4 at the much slower hydrolysis rate than the rapid PP release rate, which is complete in less than five days (Harding et al., 2009). Because H_3PO_4 is reference species for the OP weak acid/base system, the T.Alk does not change with this P release. In the AD pH range 7 to 8, the H_3PO_4 reacts with HCO_3^- to become H_2PO_4^- or HPO_4^{2-} species, the HCO_3^- becoming H_2O and CO_2 . So again the T.Alk does not change, the species that represent it do with a transfer of alkalinity from the HCO_3^- of the IC system to the H_2PO_4^- and HPO_4^{2-} species of the OP system. The CO_2 that would have been retained in the aqueous phase as HCO_3^- with low or no P now exits the AD as gas, which increases the p_{CO_2} of the gas phase because the CH_4 gas production remains unchanged as it is fixed by the COD of the utilized biodegradable organics.
 - 6 The rapid release of PP and associated Mg^{2+} and the slow release of biomass N and P generate high concentrations of P, NH_4^+ and Mg^{2+} species in the AD aqueous phase liquor, which promotes mineral, in particular struvite precipitation. This struvite precipitation decreases the T.Alk by $3 \times$ the struvite concentration precipitated due to the decrease in PO_4^{3-} species and so results in re-speciation of the IC and OP systems, increases p_{CO_2} (slightly) and decreases AD pH (Loewenthal *et al.*, 1994). If the T.Alk is low due to low N content of BPO and the P-rich WAS concentration high, precipitation of struvite results in decreased alkalinity and pH. However, the digester would not be at risk of failure, since for this precipitation to occur, the AD mixed liquor pH will be above that required for stable operation, i.e. > 6.8 – struvite precipitation commences at $\text{pH} > 7.5$ (Van Rensburg et al., 2003).
 - 7 Because the acetoclastic methanogens utilise only the associated form of VFA (HAc), all dissociated VFA fed to the AD, which is part of the influent alkalinity, increases the aqueous phase alkalinity by transferring to the IC system as follows: $\text{Ac}^- + \text{H}_2\text{O} + \text{CO}_2 = \text{HAc} + \text{HCO}_3^-$.
 - 8 The above demonstrates that the AD pH is defined by the composition of the influent organics. It is a consequence of the alkalinity intrinsically or measurably part of the influent organics, which when degraded, transfers to the aqueous phase by the release of N, PP and utilization of dissociated VFA. These three bioprocess aqueous phase alkalinity generating processes plus the influent H_2CO_3 alkalinity, establish the T.Alk in the AD. The T.Alk generated and p_{CO_2} of the gas phase and hence, AD pH are therefore completely defined by the composition of the organics digested and the type of bioprocess, in this case methanogenesis, which itself does not increase aqueous phase alkalinity like sulphate reduction does (Poinapen and Ekama, 2010). However, it is also notable that physical processes that enhance CO_2 gas stripping, e.g. vigorous stirring of the AD tank could cause increased CO_2 expulsion (hence higher p_{CO_2}), increased alkalinity and increased pH.

The material [COD, C, H, O, N, P, (S), Mg, K and Ca] mass balance based three phase (solid – aqueous – gas) steady state AD and dynamic AD models have been developed in three steps, i.e. kinetics of hydrolysis, model stoichiometry and mixed weak acid/base chemistry. The ASM2-3P model was also developed to which the ADM-3P model can be connected to allow plant-wide simulation. Similarly, the 3 phase steady state AD model can be used on its own or linked to a steady state NDEBPR model, such as that developed by Wentzel *et al.* (1990), to construct a steady state plant-wide model, which is useful to make design decisions for the wastewater treatment plant layout (Ekama, 2009). Spreadsheet plant wide model calculators were written in this project but are not ready for distribution at this time.

It was necessary to develop the steady state and dynamic models simultaneously because the steady state models were required to determine kinetic rates and sludge compositions for dynamic model input and calibration. This was possible because the steady state models and dynamic AS and AD models are based on the same basic principles, mass balances stoichiometry, just in simplified form without significant loss of accuracy. Therefore, steady state models are a useful complement to dynamic models. They allow the WRRF to be sized and optimized (i.e. for direct calculation of sludge age, reactor volumes and recycle flows) or wastewater characteristics to be determined before performing simulations and so obviate much of the trial and error use of dynamic models, which require the plant unit operations to be sized and wastewater characteristics to be defined before simulations can be run. Once the WRRF layout is established with steady state models, dynamic models can be applied to its operation to minimize energy consumption and cost while maximizing nutrient recovery and effluent quality.

3.11 RECOMMENDATIONS

The steady state and dynamic three phase AD models developed have been incorporated into plant-wide settings. However, when developing these models, there were a few aspects that should be considered in future research. These include:

- 1 Investigation into the reason behind the influent UPO fraction ($f_{S'up}$) values, calculated from EBPR plants being higher than for ND systems treating the same wastewater, a phenomenon observed repeatedly in previous investigations (Ekama and Wentzel, 1997) and again in this one. Two possible causes for this higher $f_{S'up}$ fraction are: (1) incorrect allocation to the PAOs the same death regeneration unbiodegradable fraction ($f_{EG} = 0.08$) as for OHOs and/or the PAOs having sequestered some of the influent hydrolyzed biodegradable particulate organics (BPO) rather than only influent fermentable biodegradable soluble organics (FBSO) and (2) more unbiodegradable particulate organics (UPO) being enmeshed in the aerobic reactor (which has a higher sludge concentration and from which the waste sludge fed to the AD is taken) than the other reactors. To explore the validity of cause (1), the determination of f'_{EG} (the unbiodegradable fraction of PAO biomass) could be done experimentally by digesting enhanced cultures of PAOs at a long AD sludge age (about 60 days or more). The exploration on the validity of cause (2) can be done by investigating the biodegradability of sludge from aerobic, anoxic and anaerobic reactors of the NDEBPR system individually by feeding to ADs operated at a long sludge age (about 60 days or more).
- 2 It is important to stress that when dealing with systems under non-ideal conditions that are likely to have mineral precipitation, some parameters that do not ordinarily get tested require rigorous testing. These include influent (and effluent) pH and alkalinity, ionic conductivity and for P precipitation, the OP should be tested before

dissolution of precipitates and after dissolution to distinguish between P that is bound in PP from that bound in the precipitate.

- 3 The steady state and dynamic plant-wide AD models have been used to predict the output of laboratory scale systems only. However, when used to predict the output from full scale wastewater treatment plants, new challenges may arise, especially regarding the primary settling or fluid dynamics of reactors, which are assumed to be completely mixed and may not be. It would be interesting to explore how well the models predict full-scale systems and to see what type of modifications would be required to achieve this.

Note: This chapter is an edited version of the synopsis of the detailed report by Ikumi DS, Harding TH, Brouckaert CJ and Ekama GA (2014) Development of a three phase plant wide mathematical model for sewage treatment. Research Report W138.

CHAPTER FOUR

ANOXIC-AEROBIC DIGESTION OF P RICH WASTE ACTIVATED SLUDGE

4.1 INTRODUCTION

Biological nutrient removal (BNR) activated sludge (AS) systems produce a waste activated sludge (WAS) that is rich in nitrogen (N) and phosphorus (P). When this sludge is thickened to 3-6% TSS and then digested (aerobic or anaerobic), a high proportion of N and P are released to the bulk liquid resulting in high concentrations of N (ammonia in anaerobic and nitrate in aerobic) and ortho-phosphate (OP) up to several thousand mg/l (without denitrification or P precipitation).

Anaerobic digestion (AD) is often preferred over aerobic, but both have advantages and disadvantages. Anaerobic digestion has a high capital cost, is complex to operate and so requires skilled operators, has a very sensitive bioculture and needs specialized equipment. However, the methane can be used to generate electricity to help cover pumping and heating costs of the WRRF. It also generates little sludge (other than unbiodegradables in the feed) because AD cultures have a low yield coefficient (<5%). A major problem with AD, particularly with EBPR WAS, is the precipitation of minerals after the sludge exits the digester. Mineral precipitation often blocks pipes and unbalances centrifuges in post-digestion processes (Van Rensburg et al., 2003; Barat et al., 2009; Marti et al., 2008; Doyle and Parsons, 2002).

Aerobic digestion is simpler to operate and less sensitive to reactor conditions, having the same bacterial composition as AS. In developing countries with the skills shortage, aerobic digestion (AerD) is often preferable. However, it has the operational cost of aeration. Also the aerobic digestion of primary sludge (PS) is often a problem as digester volumes become large due to aeration and concentration limitations because PS is concentrated (both in biodegradable and unbiodegradable COD). However, when digesting EBPR WAS, both aerobic and anaerobic digesters have precipitation in the digester and produce dewatering liquors (DWL) high in N (NH_4^+ for anaerobic and NO_3^- for aerobic) and OP. P can be removed in anaerobic and aerobic digestion with additives for precipitation and nitrate can be removed in aerobic digestion by denitrification if anoxic zones or time periods are created. High N and P DWL cannot be released as effluent and if recycled to the influent of the AS system, will overload the system with N and P and result in high effluent N and P concentrations.

To avoid the complexity of N removal from digested sludge dewatering liquor, this research investigates N removal by nitrification and denitrification and P removal by P precipitation in anoxic-aerobic digestion of P rich BNR system WAS.

4.2 METHODS

The WAS feed for two anoxic-aerobic digesters and long term aerobic batch tests was provided by the same lab-scale University of Cape Town (UCT) NDEBPR system with submerged panel membranes in the aerobic reactor for solid-liquid separation, that was used in the study of Harding et al. (2009) (Chapter 2) and Ikumi et al. (2014) (Chapter 3). In this study the UCT system was operated at a sludge age of 10 days at an influent COD concentration of 800 mgCOD/l. This UCT system was fed 150l/d diluted real settled

wastewater. The settled wastewater was collected in 2m³ batches from Mitchell's Plain WRRF (in Cape Town, South Africa, which treats primarily domestic wastewater), trucked to the laboratory, macerated and stored in 400ℓ stainless steel tanks in a 4°C refrigerated room. Each sewage batch collected was numbered sequentially for this investigation from Feb 2009 to Nov 2010 and considered a steady state period for the UCT system. Each batch lasted 2 to 3 weeks. Daily, after thorough mixing, the required volume of wastewater was withdrawn from the storage tanks and diluted with tap water to a target feed COD concentration of 600mgCOD/ℓ. To increase EBPR, acetate, phosphate, magnesium and potassium were added to the influent. As Cape Town's tap water is lime and CO₂ dosed for stabilization, neither calcium nor alkalinity were dosed to the influent – the K₂HPO₄ and CH₃COONa were sufficient additional alkalinity. The additives to the daily 150ℓ diluted sewage were as follows: 200mg/ℓ sodium acetate i.e. 39g CH₃COONa; 100ml of 175g/ℓ MgCl₂.6H₂O solution and 34g of K₂HPO₄. Enough phosphate was dosed to ensure an effluent OP>5mgP/ℓ and the P removal achieved in the system was 25-30mgP/ℓ.

To observe the effect of anoxic-aerobic digestion and P precipitation on N and P removal, two 20ℓ digesters were set up and fed WAS from the above UCT NDEBPR system. One was fed concentrated WAS (2x = ~18gTSS/ℓ) to promote mineral precipitation, the other fed dilute WAS (1/3 = ~3gTSS/ℓ) to prevent precipitation. Both digesters were operated at the same 20 day sludge age and with the same intermittent aeration cycle (3h aeration on, 3h aeration off). The two semi-continuous (fed once daily) intermittently aerated digesters were operated over four experimental time periods, with different chemical additives to the WAS feed in each period (Table 4.1). The high TSS digester was started in 2008 and operated for about 16 months before the low TSS digester was started in January 2009. The low TSS digester reached steady state after 1 month and was tested for 5 months to June 2009. So for Period 1, the high TSS digester ran for about 21 (484 days) months and the low TSS digester for 5 months (96 days, Table 4.1). During Period 1, no chemicals were added for pH control were added and the digesters' pH during ranged from 6.3 to 6.7. Therefore, in Period 2, which lasted about 6 months, the pH was controlled at around 7.4 by the addition of sodium bicarbonate. In Period 3, which also lasted about 6 months, the dosing chemicals were NaOH and MgCl₂ [effectively Mg(OH)₂] to observe the increase in precipitation of phosphate. However, after a few days the MgCl₂ dosing to the low TSS digester was stopped because precipitation was not required in it, it was also taken off the intermittent aeration cycle and operated fully aerobic to check the N balance. In Period 4, which lasted about 5 months, pH continued to be controlled by dosing NaOH, with the low TSS digester as fully aerobic, but for the high TSS digester intermittent aeration was continued and NaOH and CaCl₂ were dosed [effectively Ca(OH)₂] to observe the effect of Ca on P precipitation. Throughout the three chemical dosing Periods 2 to 4 (Table 4.1), the pH of both digesters was maintained between 7.3 and 7.5. Both digesters were stopped at the end of October, 2010.

Table 4.1: The four anoxic-aerobic digester investigation periods.

Period	Dates	Sewage batch	High TSS digester			Low TSS digester		
			Days	Aeration	Dosing	Days	Aeration	Dosing
1	24 Jan 2008 ^b – 25 May 2009	1 to 3	484	Intermittent ^a	None	96	Intermittent	None
2	26 May 2009 – 25 Jan 2010	4 to 11	245	Intermittent	NaHCO ₃	245	Intermittent	NaHCO ₃
3	26 Jan 2010 – 19 July 2010	12 to 17	175	Intermittent	Mg(OH) ₂	175	Continuous	NaOH
4	20 July 2010 – 20 Oct 2010	18 to 21	93	Intermittent	Ca(OH) ₂	93	Continuous	NaOH

^a 3hour aeration on-3hour aeration off for all intermittent aeration

^b The low TSS digester was started on 18 February 2009. The results collected from the high TSS digester during 2008 will also be analysed in this report.

Initially, to observe P release and ND profiles during the daily cycle, samples were taken during the intermittent aeration cycle of both anoxic-aerobic digesters. For these tests both digesters were fed at the start of the 3hr aeration period as normal. A sample (from each digester) was taken before the feed was added (i.e. from that day's waste) and immediately after the feed was added. Samples were then taken every hour for a whole 6 hour cycle (i.e. 3h with aeration, 3h without) and finally a sample at the start of the second aeration cycle. The cycle immediately after feeding was selected because it would show the largest changes of the four 6h cycles per day. The first profile test (PT1) was over a 6h cycle. A second type (12h) of profile test was conducted in which the cycle time was extended to 12hrs (i.e. 6hr air on and 6hr air off) – PT2 and PT3. These profiles showed no discernable trends in ammonia, nitrate and OP concentrations and therefore batch tests on sludge harvested from the UCT and anoxic-aerobic digesters needed to be conducted to determine kinetics rates and system performance.

Accordingly, long term aerobic batch digestion batch tests were conducted (1) on UCT system WAS at low TSS concentration (BT2, BT4 and BT5) to observe the rate of polyphosphate (PP) and biomass P release in the absence of precipitation and the build-up of nitrate, where the latter, together with the cumulative oxygen utilized are good additional indicators of VSS removal, (2) on UCT system WAS at high TSS concentration (BT3) to observe the digestion behaviour with mineral precipitation, and (3) on effluent (waste) sludge from the high TSS digester to observe the digested sludge's residual capability of P release and PAO biomass digestion because EBPR WAS is less stable due to the 6x slower endogenous rate of PAOs at 0.04/d compared with OHOs (0.24/d). Short term (<24h) anoxic batch tests (BT1, BT6 and BT7) were conducted on high TSS digester effluent to observe its denitrification performance after 20d digestion. Also short term anaerobic-aerobic batch tests were also conducted on diluted high TSS digester effluent (BT8 and BT9) with acetate to observe if PAO P release and P uptake still occurred after 20d digestion and finally aerobic batch tests were also conducted on diluted (BT10) and undiluted (BT11) high TSS digester effluent with dosed ammonium chloride to measure the nitrification rate after 20d digestion. Table 4.2 summarizes the different batch tests that were conducted.

4.3 SUMMARY OF RESULTS

4.3.1 The UCT system

The lab scale NDEBPR activated sludge system operated for this project was very effective in N and P removal. The effluent ammonia and nitrate were at all times low, less than 5mgFSA-N/ℓ and between 6 to 12 mgNO₃-N/ℓ. The system's P removal was 25 to 30 mgP/ℓ with an effluent OP of 15 to 25 mgPO₄-P/ℓ due to the additional OP added to the influent. The WAS had a P content that increased from 0.10 to 0.19 mgP/mgVSS during the two year experimental period. The influent and effluent Ca concentrations were low (average 25 mgCa²⁺/ℓ and under 20 mgCa²⁺/ℓ respectively) but this did not limit polyphosphate uptake, which was significant, with a calculated molar polyphosphate cation ratio averaging 0.335: 0.247: 0.041:1 for Mg: K: Ca: P. During the 2 year operation, consistent anoxic P release was observed and denitrification of nitrate to nitrogen gas in the anoxic zone was complete. This constrained aerobic P uptake EBPR to take place in the UCT system and EBPR models that reflect this type of EBPR behaviour were used to evaluate and model the systems, viz. the steady model of Wentzel et al. (1990) and the dynamic model UCTPHO of Wentzel et al. (1992), in which the biodegradable particulate organics (BPO) do not take part in EBPR.

Table 4.2: Details of profile and batch tests.

Number	During Period	Date	Batch test type	Digester	Duration	Test TSS conc (g/ℓ)
PT 1	1	3-Mar-09	Profile test	high TSS	6 h	
PT 2	1	12-Mar-09	Profile test	both digesters	12 h	
PT 3	1	24-Mar-09	Profile test	both digesters	12 h	
PT 4	1	12-May-09	Profile test	both digesters	12 h	
BT 1A	2	11-Jun-09	Anoxic	high TSS	12 h	2.6
BT 1B	2	11-Jun-09	Anoxic	low TSS	12 h	1.6
BT 2	3	16-Mar-10	Aerobic	UCT WAS	20d	3.0
BT 3	3	11-May-10	Aerobic	high TSS	40d	14.8
BT 4	3	26-May-10	Aerobic	UCT WAS	20d	1.9
BT 5	3	20-Jun-10	Aerobic	UCT WAS	40d	1.6
BT 6	4	07-Oct-10	Anoxic	high TSS	24h	8.3
BT 7	4	10-Oct-10	Anoxic	high TSS	5.5h	8.4
BT 8	4	16-Oct-10	Acetate	high TSS	6h	8
BT 9	4	18-Oct-10	Acetate	high TSS	45min	7.6
BT 10	4	19-Oct-10	Aerobic	high TSS	24h	7.3
BT 11	4	20-Oct-10	Aerobic	high TSS	30h	14.8

The influent sewage and WAS characteristics were calculated with the EBPR model of Wentzel et al. (1990) and the method of Ekama and Wentzel (1999) accepting as steady state periods the 2 to 3 three week periods during which the 21 sewage batches were fed to the UCT system over the 2 years of operation. The procedure of Ekama and Wentzel (1999)

essentially calibrates the steady state model by finding the influent unbiodegradable particulate organics (UPO) fraction ($f_{S'_{up}}$) and PAO P content (f_{XBGP}) which sets equal the calculated masses of VSS and TSS in the system and the P removal to those measured. The PAO P content (f_{XBGP}) varied between 0.19 to 0.47 mgP/mgPAOVSS depending on the influent's own volatile fatty acid (VFA) and fermentable biodegradable organics (FBSO) concentrations and the influent UPO fraction ($f_{S'_{up}}$) varied between 0.15 and 0.21. These results are similar to those obtained in previous investigations (Ekama and Wentzel, 1999).

4.3.2 The anoxic -aerobic digesters

Even though the low TSS digester was fed dilute WAS (~3gTSS/l) so that mineral precipitation would not occur, precipitation of magnesium phosphate did occur at pH above 7. This meant that only the dilute batch tests (BT2, BT4 and BT5) and not the performance of this digester could be used to determine the rate of poly-phosphate (PP) release by PAOs under (anoxic) aerobic digestion. The very high P content of the WAS, together with high concentrations of co-released Mg and Ca, was the cause of this precipitation and shows that mineral precipitation is a consequence of both WAS P concentration (gP/gVSS) and WAS solids concentration (gVSS/l). The low TSS digester denitrified well. The effluent nitrate concentration was 6 to 12 mgNO₃-N/l, the same as that from the parent UCT system, which showed that at least all the nitrate produced from the endogenously released ammonia was denitrified. When the low TSS digester was operated completely aerobic in Period 3, the measured nitrate concentration was 42 mgNO₃-N/l and the steady state model calculated nitrate concentration matched this well. This validated (i) the steady state model endogenous respiration rates of the OHO (0.24/d) and PAO (0.04 /d) and (ii) that even at low TSS concentration, where dissolved oxygen (DO) concentration has a long persistence effect into the anoxic period, a 3h anoxic 3h aerobic cycle is sufficient to remove all the N produced by anoxic-aerobic digestion.

After an initial start-up period of two months, the high TSS digester (fed ~18gTSS/l) denitrified completely, with zero residual nitrate, which it maintained throughout the study, showing complete N removal by nitrification-denitrification. This digester also denitrified the low effluent nitrate concentration in the WAS feed from the UCT system (initially 10-20 mgN/l, later 5-10 mgN/l throughout the study). A parallel identical high TSS digester operated by Motlomelo (2010) fed the same UCT system WAS but also 600 ml/d undiluted men's urine, was capable of denitrifying additionally approximately as much nitrate from the dosed urine as released by the WAS. Because undiluted urine contains about as much FBSO COD as ammonia (both ~6000 mg/l), there is insufficient COD in the urine to remove the N. This showed that the intermittently aerated digester (3hr air on-3hr air off) fed concentrated WAS (in which the persistence effect of DO into the anoxic period is negligible) is capable of removing twice as much N as produced by the WAS making the digester a useful option for the co-treatment of a wastewater characteristically high in N and low in COD.

During Period 1 with no chemical dosing, the influent TP (unfiltered) fed to High TSS digester was 1350mgTP-P/l and the filtered OP (effluent) concentration was 215 mgPO₄-P/l. If the PP and organically bound P were released at the same rate as the PAO and OHO endogenous respiration rates ($b_G = 0.04/d$ and $b_H = 0.24/d$), the model predicted OP concentration should have been 430 mgPO₄-P/l. This shows significant P precipitation (about half of the released P) even at the low pH of 6.8. That precipitation took place was confirmed with the low TSS digester, in which the measured OP was higher (108 mgPO₄-P/l) than the

model predicted OP concentration (84 mgPO₄-P/ℓ). The higher measured than model predicted OP for the Low TSS digester indicated that PP was hydrolysed faster than the endogenous rate of the PAOs $b_G = 0.04/d$. The low TSS concentration batch tests (BT2 and BT4) discussed below confirmed this.

During Period 2 when sodium bicarbonate was dosed to control the pH between 7.1 and 7.4, the influent TP (unfiltered) to High TSS digester was 1280 mgTP-P/ℓ and the filtered OP concentration was 200 mgPO₄-P/ℓ. Again, if the PP and organically bound P were released at the same rate as the PAO and OHO endogenous respiration rates, the model predicted OP concentration should have been 469 mgPO₄-P/ℓ. The higher pH did not increase the P precipitation because P precipitation was limited by the availability of bulk liquid aqueous Mg and Ca cations, which were 49 mgMg/ℓ and 14 mgCa/ℓ respectively. That PP was released faster than the PAO endogenous rate was again observed in the low TSS digester, in which the measured OP concentration was higher (100 mgPO₄-P/ℓ) than that predicted by the model (78 mgPO₄-P/ℓ).

When Mg was dosed to the High TSS digester during Period 3, magnesite precipitated but the filtered aqueous Mg increased from 50 mgMg/ℓ to 150 mgMg/ℓ, which was not an efficient use of the dosing chemical. So in Period 4, the dosing chemical was switched to Ca, which was found to be a much more effective precipitator of OP than Mg. The filtered aqueous Ca concentration remained low (~50mgCa/ℓ) even when the OP was as low as 50 mgP/ℓ. During Period 4, the OP was successfully precipitated down to the same concentration of UCT system influent (30 to 50 mgPO₄-P/ℓ) – low enough for the dewatering liquor to be recycled to the influent without overloading the activated sludge system (equivalent to ~0.5 mgPO₄-P/ℓ influent sewage).

From mineral precipitation and mixed weak acid base chemistry calculations, the most common phosphate precipitates in the anoxic-aerobic digesters (and aerobic batch tests, see below) were found to be newberryite (MgHPO₄·3H₂O) and amorphous tricalcium phosphate (ACP or TCP, Ca₃(PO₄)₂·xH₂O). Struvite (MgNH₄PO₄·6H₂O) and potassium magnesium phosphate (KMP, MgKPO₄) were not found to precipitate in this investigation because ammonia was fully nitrified (<1mgFSA-N/ℓ), so the ionic product of K, Mg and OP concentrations did not exceed the solubility product of KMP, rendering it unavailable for precipitation with OP.

4.3.3 The batch tests

The ratio of PP cations taken up into PP in the UCT system was confirmed in PP release in dilute aerobic batch tests BT2 and BT5. In these batch tests, aerobic P uptake continued during the first day of aerobic batch digestion, where P and Mg were taken up but not K. Precipitation of released OP commenced after 15 to 20 days of digestion, even at low TSS concentrations (1.8gVSS/ℓ), due to the high P content of the WAS. Potassium was found to be a reliable non-precipitating indicator of PP release, which was exploited in the long term batch test and in the anoxic-aerobic steady state digesters to track PP release.

In the long term aerobic batch tests conducted on dilute WAS (BT2 and BT4), a linear release of PP was observed. When this linear rate of PP release is combined with the exponential loss of PAO (slow at 0.04/d) and OHO biomass (fast at 0.24/d), the PP content (f_{XBGPP}) of the

remaining live PAO biomass decreases parabolically, which was too complex to model because the PP content appeared unconnected to the remaining live PAO concentration. So the PP release was modeled as an exponential rate (like endogenous respiration) and a release rate (b_{GP}) of 0.1/d matched the BT2 and BT4 data best. While this exponential rate did not fit the data as well as the “unconnected” plain linear rate, it matched the data well enough to model the PAO PP release behaviour. This faster release of PP was confirmed with (i) the aqueous K concentration and (ii) nitrate and OP concentration versus cumulative oxygen consumed graphs, which were linear for nitrate but not for PP. This meant that under aerobic and anoxic aerobic digestion conditions, PAO release PP 2.5 times faster than their endogenous respiration rate (b_G of 0.04/d). This was confirmed in BT5 and with the filtered K concentrations of the anoxic-aerobic digesters. A faster PP release rate than their endogenous respiration rate by PAO was also observed by Wentzel et al. (1989) in the enhanced PAO culture behaviour that became the basis of ASM2 (Henze et al., 1995).

After 20d retention time in the High and Low TSS digesters, according to the aerobic digestion model, less than 10% of the initial OHO remains but more than 50% of the PAOs remain due to their slow endogenous respiration rate. The long term (40d) aerobic batch test (BT3) on high TSS digester waste sludge (BT3) showed an initial P release from 100 to 140 mgP/l over the first 5 days but then a gradual decrease over the next 20 days to 60 mgOP-P/l – the Mg concentration decreased from 100 to 40 mgMg/l confirming precipitation. None of this was deemed to be PP release because the K concentration did not increase but mineral precipitation must have taken place to decrease the Mg concentration. The VSS, TSS and ISS concentrations decreased 4270 mgVSS/l, 5850 mgTSS/l and 1600 mgISS/l respectively with the VSS/TSS ratio decreasing from 0.700 at the start to 0.678 at the end of the 40 days. From the ISS model of Ekama and Wentzel (2004) an ISS decrease is expected from the release biomass intracellular ions to the bulk liquid. The nitrate concentration increased from 0 to 219 mgNO₃-N/l indicating that PAO biomass was still decreasing with time, confirming the slow rate of endogenous respiration of PAOs.

The anaerobic-aerobic P release and uptake batch tests on the high TSS digester waste sludge (BT8) at 8.0 gTSS/l (4.0 gV SS/l) showed that the sludge could still release some PP (163 mgP/l in 6h, with concomitant increase in Mg and K of 31 and 34 mg/l) when dosed with acetate (1951 mgCOD/l) and take up some P (40 mgP/l) under subsequent aeration. The sludge was still showing a low EBPR behaviour but this was most likely from the PAOs most recently fed to the system. A second anaerobic-aerobic batch test (BT9) with much lower acetate addition (117 mgCOD/l) showed negligible P and cation release and subsequent P uptake.

The two short term anoxic batch tests on High TSS digester effluent sludge (BT6 and BT7) yielded 0.356 and 0.108 mgNO₃-N/(mgOHVSS.d). These rates are 1.4x and 0.42x faster than the K_{220} rate in the primary anoxic reactor of the NDEBPR activated sludge system. This cannot be the normal anoxic-aerobic digestion K_{420} rate, which was measured by Warner et al. (1986) at 0.048 mgNO₃-N/(mgOHVSS.d). With the denitrification rate so unexpectedly high, the results from these anoxic test results are inconclusive. A more reliable determinant of the N removal capacity of the concentration TSS anoxic-aerobic digester was the identical high TSS anoxic-aerobic digester operated in parallel to this investigation by Motlomelo et al. (2014), but to which 600 ml/d urine was added. This digester showed that twice more nitrate can be denitrified than is produced from the nitrification of the WAS released ammonia.

The two short term (24h) aerobic batch tests on High TSS digester effluent sludge (BT10 and BT11) yielded nitrification rate of 5.35 mgNO₃-N/(ℓ.h) or 1.07 mgNO₃-N/(mgVSS.d). Initially the rate was very low (10 mgNO₃-N/ℓ in 5h) but increased thereafter. This rate is 5 times faster than the FSA release rate by the endogenous respiration of OHO and PAO, which explains why the FSA concentration was always low on the anoxic-aerobic digesters, and any accumulation of FSA during the anoxic period is quickly nitrified upon conditions becoming aerobic.

4.4 CONCLUSION

Anoxic-aerobic digestion of concentrated (>2% TSS) with an aeration cycle of 3h air on and 3h air off and lime dosing to precipitate P has been proven to be an effective method of stabilising EBPR WAS that produces a dewatering liquor low in N and P (0-12 mgNO₃-N/ℓ and 20 mgPO₄-P/ℓ respectively). The N is effectively removed by nitrification and denitrification on self-generated endogenous organics and P was effectively precipitated stoichiometrically with the addition of lime.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 MODELS, COMPUTER CODE, MODELLING PLATFORMS/SOFTWARE.

The plant wide model developed in this project (called PWM_SA) accomplishes all the objectives of this project. While not completed (when is a model ever complete?), it links activated sludge (AS), anaerobic digestion (AD), and anoxic aerobic digestion (AerD). The capabilities and limitations of this model are summarised in Table 5.1.

A model is a set of equations and the set of equations making up the PWM_SA plant wide model is freely available to all in the reports produced in this project. This form of dissemination is the same as for the ASM and ADM models – these models are available in the IWA reports. Models are given expression in computer code executed within modelling platforms or software. The PWM_SA model is expressed in the WEST2014 modelling platform. This software is not freely available but can be purchased from MikebyDHI.

5.2 TECHNOLOGY TRANSFER

There appears to be a measure of frustration among consulting and municipal users. Modelling of WRRFs seem to be advancing further and further and in the process becoming less and less accessible and usable to users. The authors of PWM_SA understand this frustration and believe it is a residue from the time that researchers developed both models software (like UCTOLD, UCTPHO) which were available freely and therefore accessible. However, the days of researchers writing their own computer code are long gone for decades. WRRF simulation software is written by WRRF software developers and vendors. These days researchers use WRRF simulation platforms into which they code a new bioprocess model or model extension. There are many general simulation platforms, inter alia Matlab, Modelica (of which there is a free open source version available), and dedicated WRRF platforms like SIMBA, Biowin, WEST and SUMO. Research groups either buy their own modelling platform or are granted access to one for model development. The WRG at UCT and PRG UKZN use WEST for model developments under the WEST Development Centre agreement between these Universities and Mike by DHI.

In order for consultants, municipalities and industry users to gain access to WRRF modelling software, they need to (i) decide which platform to buy (yes, this is not a simple task and requires a present and future needs assessment), (ii) train staff to use the purchased software competently reliably and confidently. This will require a significant investment in people, which makes the cost of software negligible. WRRF software develops and progresses at a fast pace, like any other software. So it's best to select software that has the greatest potential for advancement and then continue to invest in dedicated bioprocess modellers to use this software effectively. This investment requires both high-level education and training (postgraduate) in (i) the principles on which these models are based and (ii) the details of the models themselves and (iii) the intricacies of the software which gives expression to the models of the different unit operations of the WRRF. As stated in the introduction (Chapter 1), models and software should never be a replacement for knowledge and understanding of WRRFs – without a deep and thorough understanding of WRRF in all their complexity and

detail, and the bioprocess models used to simulate them, simulation software will not be used effectively, reliably and accurately.

5.3 FUTURE WORK

The limitations listed in Table 5.1 also point to further model developments. These were written up by the IWA Plant Wide Modelling Task Group at the ICA2013 conference in Narbonne and presented at the WWTmod 2014 conference (30 Mar-2 Apr). It follows in Section 5.5 below. Projects currently active at UCT to complement and extend WRRF modelling are listed in Section 5.4 below.

Table 5.1: Capabilities and limitations of the PWM_SA plant wide model.

	Capabilities of PWM_SA	Limitations of PWM_SA
1	Includes models for activated sludge (AS), anaerobic digestion (AD), anoxic-aerobic digestion (AerD) and secondary settling tanks (SST) for nitrification denitrification (ND) and enhanced biological phosphorus removal (EBPR) based on ASM2 (>90% aerobic uptake EBPR) and UCTSDM1*.	Sludge storage tanks settling tanks and sludge thickeners non-reactive for example no be released. No denitrification by PAO's excluded not based on ASM 2-D.
2	Full element mass balances – intrinsic mass continuity C, H, O, N, P, S, COD and charge.	No detailed N conversions, i.e. neither nitrite nor gaseous denitrification intermediates; no greenhouse gases except CO ₂ and CH ₄ .
3	Includes primary settling tanks (non-reactive).	PST module needs attention – does not reflect observed PST behaviour of removing unbiodegradable particulate organics (UPO) in greater proportion (60-85%) than biodegradable particulate organics (BPO, 30-50%).
4	Three-phase (aqueous – gas – solid)	
5	Calculates pH in AD	Also calculates pH in AS reactors but this depends on the stripping rate by aeration which is site-specific must use low pH is flag for alkalinity problems as in ASM one.
6	Fast run times and stable integration. Separates fast (aqueous) and slow (bioprocess, gas exchange and precipitation) processes. Solves aqueous phase speciation with purpose coded algebraic speciation routine.	Does not include ammonia stripping. Minerals included only struvite, calcium phosphate, potassium struvite, Newberryite, calcium carbonate and magnesium carbonate.

	Capabilities of PWM_SA	Limitations of PWM_SA
7	Includes correction for non-ideal aqueous phase (Butler's ionic strength correction) and ion pairing.	pH calculation valid up to ionic strength ~0.10.
8	Supermodel approach. Variables selection tailored to suit WRRF plant wide modelling. Seamless connectivity between unit operations.	Doesn't require variable transformers translating state variables between unit operations.
9	Classic wastewater organics characterisation based on COD concentration of seven wastewater organics groups (HPr, HAc, FBSO, BPO, USO, UPO) and their compositions (x,y,z,a,b) in $C_xH_yO_zN_aP_b$ with ammonia and orthophosphate.	Does not use carbohydrates, proteins and lipids of ADM1 for organics characterization.
10	Includes influent wastewater transformation model that converts measured influent state variables to the model counterparts; similarly, a post processor transforms model state variables into reactor/effluent variables aligned with measured parameters.	
11	Requires characterisation of influent only and biomass composition for entire wastewater treatment plant	
12	Predicts nutrient concentrations in dewatering liquors	dewatering systems are point separators
13	Explicitly includes ISS from influent, biomass and polyphosphate and so predicts VSS and TSS.	
14	Experimentally validated	Only at laboratory scale
15	Tailored sludge digestion model specifically for sewage sludge digestion	Not as "general" as ADM1
16	Can form the basis for (i) mineral precipitation in AD and AerD to estimate nutrient recovery potential from dewatering liquors, (ii) pH control and (iii) CO ₂ stripping from dewatering liquors.	Does not include ammonia stripping.

	Capabilities of PWM_SA	Limitations of PWM_SA
17	Fully integrated into WEST library	
18	Full complement of WEST associated software available; ready connectivity to other water quality software such as sewer and river modelling.	
19	Implicitly includes primary sludge fermentation	Has not been tested/calibrated.

5.4 CURRENT (2014) ACTIVE MODELLING RESEARCH PROJECTS AT UCT.

Ghoor, Tasneem (Msc Eng) – Modelling the SANI system for saline sewage treatment.

Botha, Rudi (Msc Eng) – Augmenting the biomethane potential (BMP) test to also generate data for anaerobic digester performance assessment.

Wu, William (Msc Eng) – Developing a steady state plant wide WRRF design and analysis model for dynamic simulation model input data generation.

Haile, Fasil (Msc Eng) – Dynamic modelling of anaerobic digestion – start up, stability and control

Renaux, Fabian (Msc Eng) – Modelling nitrification of source separated urine.

5.5 THE FUTURE OF WASTEWATER TREATMENT PLANT MODELLING

Wastewater treatment plant design, modelling and operation wants P in plant wide models (PWM) – in fact it is a logical extension of PWN and long overdue because Benchmark Simulation Model No 2 (BSM2, Jeppsson et al., 2006) includes N only. The PWM_SA produced in this project is one to the first to have commenced this. However, to include P sufficiently realistically adds major, but unavoidable, *complexity* especially for anaerobic digestion (AD) models because it requires.....

- 1.1 Including mineral precipitation, which requires three-phase (aqueous, gas, solid) modelling which involves physico-chemical modelling, ion pairing, charge accounting, ionic strength tracking and pK value correction. Fortunately physico-chemical modelling is well specified and defined with kinetics and thermodynamics. For these processes thermodynamics define the endpoints of the kinetic processes so significant calibration is usually not required. But for bioprocesses and precipitation rates thermodynamics are not yet defined/known so kinetics have to define endpoints of reactions and this needs much calibration.
- 1.2 Including multi mineral precipitation which considers competition for cations by phosphate and carbonate.
- 1.3 Including pH modelling, which is very important for AD (useful but not essential for AS).
- 1.4 Linking ASM2 to an AD model. Cannot use ADM1 – transformers in continuity based interface modelling (CBIM) become very complex. Need a revised ADM tailored to PS and WAS sludge digestion. Best to use a pared down custom tailored supermodel which includes all variables (AS and AD) moving to all unit operations

whether active in a particular unit operation or not. For AD pH is very important but not so much for AS (except nitrification). This ADM doesn't need to predict strong AD dynamics because in WWTP layouts, AD loads are attenuated. Also only the slowest hydrolysis rate needs accurate calibration (data exists) because subsequent AD bioprocesses are faster (unless AD failure also needs to be predicted).

- 1.5 Full elemental mass balances CHONP, COD and charge to predict pH (*completely*). This needs expanded wastewater organics characterisation protocols and measurements with careful aligning of measurement frameworks for wastewater and characterization and modelling frameworks for continuity and mass balancing.
- (2) Including important reactions of P with Fe and Al. To be realistic, can't avoid including Fe/Al precipitation reactions – chemical P removal. Fe has important reactions with S, which, if included, brings its own physico-chemical and bioprocesses. How many of these S processes should be included? Biological sulphate reduction to sulphide has been included in the UCTSDM of Poinapen and Ekama (2010) but not the interaction between methanogens and sulphidogens. Also with Fe and Al, chemically enhanced primary treatment (CEPT) can be included, but all these reactions add more complexity.
- (3) An improved PST model. In current PWMs, the primary settling tank (PST) is a unit operation least realistically modelled – this needs major revision. It has been observed that greater proportions of unbiodegradable particulate organics (UPO) (60-80%) settle out in PSTs than biodegradable particulate organics (BPO 25-40%) (Wentzel et al., 2006), but PST models don't reflect this.
- (4) Include reactive storage tanks and settling tanks to predict P release in SSTs, gravity thickeners and EBPR WAS storage tanks. Often flotation units are used to for thickening EBPR WAS to prevent P release so models need include flotation units, not only gravity thickening.
- (5) Including P results in more complex AS plant layouts Bardenpho, UCT, JHB, BCFS. Also with EBPR (as for Chem P removal), P removal performance affects sludge production, i.e. the higher the P removal the higher the sludge production. This connects wastewater characterization and plant sludge production and oxygen demand in two ways, viz. via the influent unbiodegradable particulate organics (UPO), as in N removal plants, and via the P removal, which complicates determining the influent UPO fraction sludge production and oxygen demand. Hence dynamic models cannot (should not!) any longer be used in a trial and error way (as is often do these days) to find wastewater characteristics that match plant performance. It is better to use steady-state models (require less input information) to define plant layout for design or wastewater characteristics for capacity of existing plants.
- (6) New and expanded wastewater characterisation to include all added model variables, due to the large increase in state variables. Three most important wastewater characteristics that profoundly affect BNR system size and performance are maximum specific growth rate of nitrifiers (μ_{Am20}), influent UPO fraction and influent VFA and fermentable biodegradable soluble organic (FBSO) fractions. These are difficult to measure so usually are guessed, so WW characteristics about which there is greatest uncertainty also have greatest impact on size for design or capacity for exiting plant.
- (7) Steady-state pre-processing models
 - (7.1) to determine

(7.1.1) for design, AS system sludge age and configuration (anaerobic and anoxic mass fractions), recycle ratios, PST and SST areas, AD retention time and unit operation interconnecting flows, or

(7.1.2) for existing plants, wastewater characteristics (uAm20, UPO and BSO fractions) and sludge settleability, and

- (7.2) test different scenarios with steady state PWM until satisfied with plant layout or calculated parameters to match influent and plant measurements. In fact, much of what the IWA Good Modelling Practise (GMP) Task Group recommend as good modelling practice can be done with steady-state models (see Ekama, 2009, Wat Res, 43(8)2101-2120). So a steady state PWM pre-processor generates influent wastewater characteristics and plant layout specification files, which are read as input files by WWTP simulation models so creating a seamless integration between steady state models where high level decisions are made and simulation models where low level detailed simulation related evaluations are made (*continuity*).
- (8) Easily *connectivity* of future PWM to Receiving Water Quality Models (RWQM) and sewer models is becoming increasingly important.
- (9) Possibly fuzzy logic and neural networks allow connecting qualitative expert system type information to WWTP simulators. These can check the likelihood of e.g. activated sludge bulking or foaming to estimate the likelihood of maintaining a certain sludge settleability. Sludge settleability remains the least predictable parameter of the AS and has the greatest effect on WWTP size and capacity.

Some concluding views to close. Up to 1990, research groups (academics) developed models, simulation code and experimental data for calibration, e.g. ASM1 and ASM2. From 1985, software vendors wrote simulation code of bioprocess models (and many variations), e.g. Biowin, Simba, Stoat, West, Sumo etc., some with limited validation. Including P in models creates complexity which is unavoidable and probably beyond generalist consulting practice capability, unless they are large enough to support specialist modelling sections. Future modelling of WWTP is likely to become a specialist function and plant owners and consultancies will contract this specialist competence into their projects (as is currently with finite element modelling in structural engineering). Many 21st century wastewater treatment professionals only know AS and AD from models, not from reality and lack practical experience of real systems (small or large) to make the required judgements on whether or not simulation model outputs are reliable. Steady-state (algebraic spreadsheet) models can assist with this these by giving approximate results to check dynamic model outputs.

5.6 FURTHER MODEL DEVELOPMENTS

Towards BSM2-PGSX: A plant-wide benchmark simulation model not only for carbon and nitrogen, but also for phosphorus (P), sulphur (S), greenhouse gases (G), and micropollutants (X), all within the fence of WWTPs/WRRFs

Peter Vanrolleghem¹, Xavier Flores-Alsina², Lisha Guo¹, Kimberly Solon³, David Ikumi⁴, Damien Batstone⁵, Chris Brouckaert⁶, Imre Takács⁷, Paloma Grau⁸, George Ekama⁴, Ulf Jeppsson³ and Krist V. Gernaey²

¹modelEAU, Département de génie civil et de génie des eaux, Université Laval, Québec, QC, Canada, G1V 0A6.

²Center for Process Engineering and Technology (PROCESS), Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Building 229, DK-2800 Kgs. Lyngby, Denmark.

³Department of Measurement Technology and Industrial Electrical Engineering, Division of Industrial Electrical Engineering and Automation (IEA), Lund University, Box 118, SE-221 00 Lund, Sweden.

⁴Water Research Group, Department of Civil Engineering, University of Cape Town, Rondebosch, South Africa.

⁵Advanced Water Management Centre (AWMC), University of Queensland, St Lucia, QLD 4072, Australia.

⁶Pollution Research Group, School of Chemical Engineering, University KwaZulu-Natal, Durban, South Africa

⁷Dynamita, 7 Lieu-dit Eoupe, F-26110 Nyons, France.

⁸Department of Environmental Engineering, CEIT, Paseo Manuel Lardizábal 15, 20018 Donostia, Spain.

INTRODUCTION

Benchmarking WWTP/WRRF control strategies has turned out to be a very successful vehicle for development of consolidated models of whole facilities (Gernaey et al., 2013a). Over the last year a comprehensive thinktank of researchers that were already involved in this development have put together a wishlist of developments in WWTP/WRRF modelling. They want these ideas for BSM development to be exposed to the WWTP/WRRF modelling community, brought together at WWTmod2014. From a starting point that summarizes ongoing work on extending the Benchmark Simulation Model No.2 (BSM2) and the wish to extend the current BSM2 to include phosphorus aspects, the thinktank presents this abstract to outline the options lying ahead. The paper will present the underlying arguments for choosing among the identified modelling options, in order to get informed feedback from the WWTmod2014 audience that will allow defining a roadmap for future modelling efforts. It is believed that this way of guiding the combined (voluntary) efforts of model development will be beneficial to the WWTP/WRRF modelling community at large.

The developments in the benchmarking area this paper will discuss relate to:

- G. Greenhouse gases (GHG): Next to methane and CO₂ that are intrinsically part of the plant-wide benchmark simulation model, recent work has focused significantly on N₂O emissions, leading to considerable extensions to the details of the N-removal submodel of the BSM2;
- (p) Phosphorus: P-removal has been a focus of WWTP/WRRF design and operation, but its inclusion in whole plant models is lagging behind that of N-removal, due to the difficulties in modelling the precipitation processes that P is involved in, especially in the sludge train.
- 19. Sulphur: This element is receiving increased attention not only because of its role as a competitor for P and related impact on P-complexation and release, but also because new processes in seawater-based systems (e.g. the SANI-process) take advantage of sulphur as a reactive element. Efforts to control H₂S emissions and induced corrosion in sewer systems benefit from such S-focused modelling efforts as well.
- 24. Micropollutants: Recent interest in micropollutants has led to a diversity of model developments that would benefit from consensus-building and inclusion in the benchmark simulation platform. The diversity of micropollutants remains a challenge, but consensus can probably be found on modelling the overall fate-determining mechanisms (sorption, biodegradation, volatilization, hydrolysis, photolysis ...).

With these four themes combined, the name to be given to this extension of the plant-wide Benchmark Simulation Model No.2 could be BSM2-P/S/G/X, depending on which of the features (P,S,G and/orX) have been included.






To reach this goal, the following topics will have to be addressed: 1) new evaluation criteria; 2) new chemical and biochemical processes that should be taken into account; 3) new components involved in these processes that thus need to be modelled; 4) new influent wastewater characteristics; 5) modifications to the original BSM2 physical plant layout and new unit process models; 6) model integration; and, 7) new control handles/opportunities. These are shortly presented below.

The intention at the WWTmod2014 seminar is to select a number of the more clear-cut topics developed below, and get the opinion from the audience by presenting them with a clear choice and a way to directly provide feedback (colored cards or a SurveyMonkey on-line voting system).

DISCUSSION TOPICS










(1) New evaluation criteria

With the ambition to use benchmark simulation models to evaluate the control and monitoring performance of WWTP/WRRFs that go beyond what could be achieved with BSM1/2 (COD/N-removal) a new set of evaluation criteria needs to be put forth:

-  Is the approach for GHG-emission evaluation appropriate (Flores-Alsina et al., 2014)?
-  P-related criteria should be added, such as its contribution to the effluent quality index.
-  Given the interest in nutrient recovery, should evaluation criteria be developed that highlight production of (high quality) recovered nutrients from WWTPs/WRRFs?
-  Should sulphur compounds be considered in performance evaluation and in what way?
-  Do we consider ecotoxicity to evaluate micropollutant removal (Clouzot et al., 2013)?



(1) New chemical and biochemical transformations

Upgrading the BSM WWTP with the PSGX related transformations inevitably leads to a wide range of processes that need to be added. The level of complexity remains an open question though:

-  GHG-modelling has matured significantly over the last two years, but finalization is still required (e.g. Ni et al., 2013);
-  In GHG-models temperature dependency of reactions has been modelled using the Ratkowsky equation instead of Arrhenius, giving the advantage of being able to deal with decreasing rates at high temperatures. Is this to be applied to all kinetics or are there more appropriate ways to model temperature dependency?
-  Is ASM2d still adequate for modelling enhanced biological P-removal or do we need modifications, e.g. electron acceptor dependent decay, denitrification by specific substrates with special kinetics (methanol, glycerol, methane, ...), role of the ions Mg^{2+} , Ca^{2+} , K^{+} ;
-  Is it important to model the behaviour of PAO's when they enter the anaerobic digester with a consequent P-release, VFA uptake, storage? How must ADM1 be upgraded to account for phosphorus and treatment of Bio-P sludge? Is ADM1 the proper model (Ikumi et al., 2011)?
-  Is it important to include anoxic-aerobic digestion of Bio-P wastage sludge with lime or Mg dosing for P-precipitation (to achieve low N and P dewatering liquors) for sludge treatment and how must ASM2/2d be modified to also model this (Vogts and Ekama, 2012)?
-  Which precipitation reactions should we model, and which approach should we use?
-  How will the physico-chemical model look like (precipitation, acid-base reactions, pH, ion-pairing, ion activity, etc.) in terms of level of detail, equation structure and solver requirements, etc. (Batstone et al., 2012);
-  If S-containing components are considered important for P-modelling (e.g. competition for iron), which of the (bio)chemical S-related oxido-reduction processes need to be included and how is the competition with methanogens to be modelled?
-  Do the traditional micropollutant fate models (volatilization, sorption, photolysis, biodegradation) that only require standard chemical properties (Henry coefficients, Kow, ...) suffice or are dedicated models necessary for each micropollutant (Clouzot et al., 2013)?

(1) New components

If the above list of processes is all considered important, a wide range of new components will have to be added to the current set of components considered in the next generation of BSM models:

-  Inert inorganic suspended solids need to be added for proper TSS accounting;
-  P-related components (phosphate, PAO's, poly-P, PHA) and the components related to

precipitation and PAO hydrolysis (calcium, magnesium, potassium, iron, struvite, K-struvite, newberyite, calcium phosphate, iron phosphate, iron hydroxide, calcite, magnesite);

- ☰☞ S-related components (sulphate, sulphite, sulphur, H₂S, poly-S, iron and other sulphides);
- ☰☞ A multitude of micropollutants (and their transformation products);
- ☰☞ Components related to GHG emissions (methane, CO₂, NO, N₂O, NH₂OH).

(1) New influent wastewater characteristics

Evidently, when the set of state variables is extended, the inputs to the system will have to be extended too, including methane (G), phosphorus (P), sulphur (S), micropollutants (X). Are colloids important for the proposed configuration? Multiple approaches could be proposed:

- ⌚ Can we just use correlations with the traditional wastewater components in the influent files used so far (using TSS, COD and N-fractions as independent variables to correlate with)?
- ⌚ Do we need to develop new influent generation models that include, for instance, methane formation in the sewer (Guisasola et al., 2009), micropollutant release patterns (De Keyser et al., 2010, Snip et al., 2013), sulphur conversions, etc.?
- Do we need to provide detailed information on influent pH-dynamics and acid-base / ion composition to support the physico-chemical model that is required?

(1) New physical layout of BSM2 and unit process models

The suggested layout of the BSM2-PSGX WWTP is shown in Figure 1. The activated sludge section has been modified by including an anaerobic section for Bio-P removal. The actual volumes are still open for discussion and will be obtained through application of standard design guidelines, just as for BSM2 (Gernaey et al., 2013a). Some proposals have been made to extend the layout that this paper will put to the floor for feedback:

- ☰☞ Should we include a P-recovery unit process in the sludge train and how do we model it? Evidently, including such a process in the layout would attract a lot of attention to the BSM work, and in principle the physico-chemical model contains the necessary processes, but is there a “typical” P-recovery process that industry would accept as being representative?
- ☰☞ Sludge reject water treatment was already tried out in the BSM2 process layout (Volcke et al., 2006). Is it time to make this an integral part of a whole plant model?
- ☰☞ Should we also model the pumping station and grit chamber so as to really model all processes within the fence? A storage tank prior to the digester could allow for more control options and the addition of external organic material input to the system.
- ☰☞ The primary clarifier is receiving increased attention due to its potential role in separating organics for energy recovery by anaerobic digestion (Flores-Alsina et al., 2014). Should chemical enhancing of primary treatment (CEPT) be added to the BSMs (Tik et al., 2013)?
- ☰☞ Is a “fermenter” that generates VFA’s out of primary sludge a unit process to be included in the whole plant configuration to be studied in the future? It certainly would provide an interesting possibility for control.
- ⌚☞ Should the secondary settler model be upgraded to include compression and dispersion and to make its numerical solution consistent (Bürger et al., 2011)?
- ☰☞ Is it now time to explicitly consider the reactions in the secondary clarifier, in particular denitrification, and how would that best be done (fully reactive settler, separate reactor, etc. (Gernaey et al., 2006))? Must the same hold for thickeners and storage tanks?
- ☰☞ Should we add effluent polishing systems for nutrients (denitrifying filters) and TSS (disk filters) and can consensus on a representative technology and appropriate models be found?

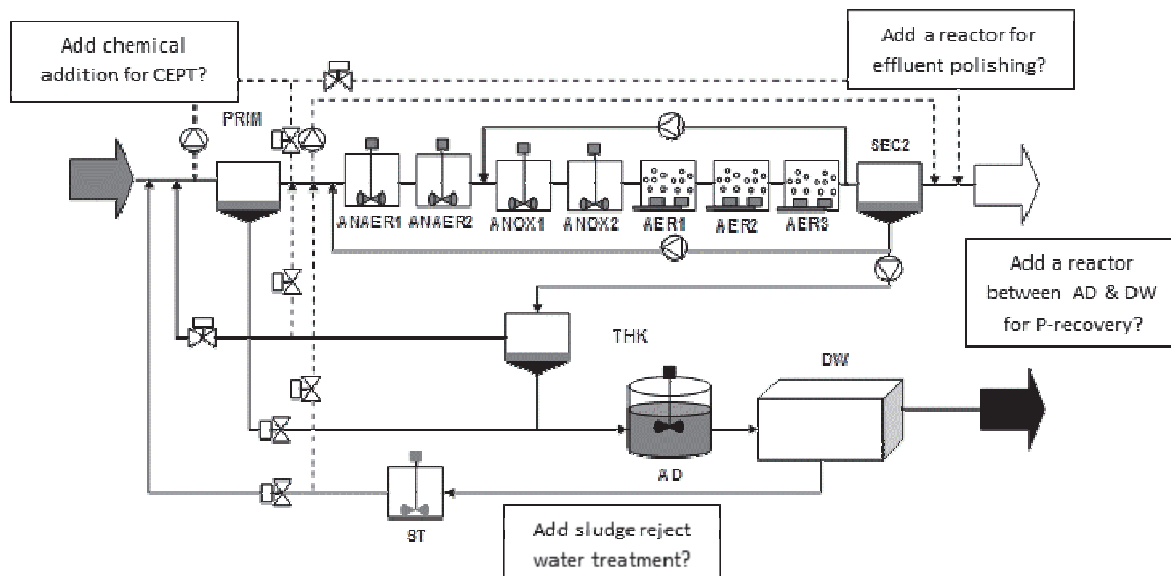


Figure 5.1. Plant layout of the proposed BSM2-PSGX. Some questions remain to be answered.

(1) Model integration

So far BSMs have used interfaces to integrate the submodels. As complexity increases, the following questions can be asked:

- 📁👉 Do we stick to the approach with submodels with individual component sets and mass continuity interfaces to connect them or do we move towards the plant-wide modelling concept or the Supermodel approach (Grau et al., 2009)?
- 📄👉 If we stick to interfaces, do we extend the existing interface or do we rigorously apply the continuity-based-interfacing-of-models (CBIM) approach (Vanrolleghem et al., 2005)?

(1) New sensors and control handles

Control of WWTP/WRRFs will require a new set of sensor models to measure, for example, phosphate concentrations. Also, more control handles will become available compared to BSM2.

- 📁👉 Models for P-analysers and nitrite measurement devices need to be established;
- 📄👉 Will off-gas analysis (methane, H₂S, O₂, N₂O, CO₂...) break through and how will we model these measuring systems with gas sample preparation?
- 📄👉 Models for actuators needed for CEPT may have to be developed, given their particularities;
- 📄👉 Which sensors and control handles can be modelled for nutrient recovery systems? For instance one could imagine on-line particle size distribution measurement combined with seeding as a control handle for struvite formation.

CONCLUSION

This abstract intends to allow the benchmarking community to get feedback from the wastewater modelling community regarding the requirements for the next generation benchmark simulation model. Given the many spin-offs that the benchmark modelling efforts have generated for the wastewater modelling community at large (Gernaey et al., 2013b), it is believed that streamlining the work that is planned to occur in this benchmarking framework should be guided by the specialists in the discipline.

Efforts have and will be deployed to make the interaction with the audience as efficient as possible by presenting only a selected number of key topics presented above and providing clear choices that can be answered during the time allocated for the presentation.

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