THE TREATMENT OF WASTEWATERS WITH HIGH NUTRIENTS (N AND P) BUT LOW ORGANIC (COD) CONTENTS

Report to the
WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

1. MOTIVATION

High nutrient (nitrogen, N and phosphorus, P) low organic carbon (COD) wastewaters are wastewaters in which the carbon is greatly deficient relative to the nutrients N and P. These wastewaters are generated within a diversity of municipal waste treatment facilities. Such facilities include urban development schemes utilising alternative non-full waterborne sanitation systems, sanitary landfill sites and wastewater treatment plants with trickling filters, anaerobic sludge digestion, sludge treatment liquors and/or biological nutrient removal (BNR) activated sludge plants. Examples of specific wastewaters falling into this high nutrient low organic carbon (HNLC) group are:

(1) Septic tank effluents.
(2) Landfill leachates.
(3) Activated sludge de-watering liquors.
(4) Anaerobic digester supernatants, in particular from BNR activated sludge systems.
(5) Trickling filter effluents.
(6) Sludge disposal lagoon effluents.

(Oxidation pond effluents can also be included in this group, but oxidation ponds are implemented only in rural areas and are so few in number in South Africa that their effluents do not contribute significantly to surface water pollution and/or eutrophication).

These wastewaters will increasingly make a significant contribution to nutrient loads on surface water resources resulting in eutrophication and its associated problems. Accordingly, to limit eutrophication and maintain the quality of surface waters, the high nutrient low organic carbon wastewaters will require treatment to remove the nutrients. However, this treatment is problematic: Conventional activated sludge BNR technology is not practical due to the imbalance between the organics (low) and nutrients (high); indeed wastewater types (3), (4) and (6) above are themselves generated by BNR plants. Therefore alternative methods, processes and technologies need to be developed to treat these wastewaters.

To address the problems raised above, in January 1995 a three year contract "The treatment of wastewaters with high nutrients (N&P) but a low organic (COD) contents" (K5/692) was set up between the Water Research Commission (WRC) and the University of Cape Town (UCT). In this contract, it was proposed to conduct research into the first four of the high nutrient low organic carbon wastes listed above.

2. PRINCIPLE AIM

The principal aim of the contract was :

- To evaluate, investigate, develop and refine chemical, physical and biological processes and technologies to treat wastewaters with high nutrient (N and P) but low organic carbon contents.

3. MAIN TASKS

In terms of the priciple aim, four main tasks were identified to receive attention:

- Develop a fundamentally based mathematical model which will integrate the biological, physical and chemical processes that are operative in systems treating high nutrient low organic wastes.
- Review the literature to, (i) identify the origin and nature of these wastes, (ii) identify technologies currently used for the treatment of these wastes, (iii) identify new technologies that hold potential for the treatment of these wastes, and (iv) provide experimental data for calibration, testing and refinement of the mathematical model.
- Collect experimental data on the wastes and various treatment schemes. This will provide information on the feasibility of the schemes, and for the development, calibration and validation of the mathematical model.
- Evaluate and develop existing/new processes and technologies.

Each of these tasks is described below.

4. TASK 1: MODEL DEVELOPMENT

The objective of this task was to develop a fundamentally based mathematical model which integrates physical, chemical and biological processes. This task was prioritised since it was recognised that such a model would be particularly useful for application to the treatment of wastewaters where physical, chemical and biological processes play a significant role, such as the high nutrient low organic carbon (HNLC) wastewaters considered in the research project.

4.1 Background

The existing steady state design and dynamic kinetic models describing wastewater treatment systems have focussed on the biologically mediated processes that lead to the removal of, or change in the particular compounds of interest. By focussing on biological processes it is usually implicitly assumed that (i) the biological processes dominate the system response and that (ii) chemical and physical processes (e.g. precipitation and gas stripping respectively) play an insignificant role compared to the biological processes and accordingly can be neglected, (iii) compounds not directly involved in the biological processes or not of interest, even though present, do not significantly influence the behaviour, and (iv) the biological processes take place within a regime of constant pH. This has restricted application of these models to situations where the assumptions remain valid. However, in the treatment of a number of wastewaters the assumptions are not valid and the models cannot be applied. For example, in the nitrification of wastewaters with low buffer capacity and/or high N concentrations, or in the treatment of wastewaters where the generation or utilisation of short-chain fatty acids (SCFA), e.g. acetic, propionic, is significant, the assumption that the pH remains essentially constant no longer can be accepted. In particular, the models cannot be applied to situations where chemical and physical processes do play a significant role, and so cannot be neglected. One such category of wastewaters are the high nutrient low organic carbon (HNLC) wastewaters investigated in this project, i.e. where the organics are present at relatively low concentrations compared to the nutrients. To include chemical and physical processes requires the pH is incorporated in the model and accurately determined, as pH is of fundamental importance in these processes.

From the discussion above, it is evident that the application of the existing biological models can be enhanced by including pH as a ***parameter/compound***. Further, including pH will facilitate (i) the integration of chemical and physical processes with the biological models and (ii) the development of models for simulating the kinetic response of physical/chemical processes.

Thus, the main preliminary task identified for modelling was to find ways of including pH as a parameter/compound in the model. Once this was completed, the model was developed in stages namely, (i) single phase aqueous systems, (ii) two phase systems (solid-aqueous and gaseous-aqueous) and (iii) three phase systems (solid-aqueous-gaseous) which is a combination of the first two. Where possible, each section of the model was validated with data from the literature. However, not all sections of the model could be validated with data from the literature requiring an experimental investigation to collect suitable data for model validation.

4.2 Including pH as a compound in the model

The equilibrium chemistry approach that includes the mass parameter of alkalinity for the weak acid/base species, forms the basis on which most chemical conditioning algorithms have been developed. However, in the model developed here this approach, although possibly feasible, was found to present practical difficulties in implementation because of the presence of a number of weak acid/base systems and a number of processes acting simultaneously on the species concentrations of these weak acid/bases. This makes selection of the reference species for the solution alkalinity problematic, and finding an efficient solution procedure to solve the repeated calculations necessary to reach steady state very difficult and cumbersome.

To overcome these difficulties, a kinetic approach was developed, which formulates the weak acid/base equilibria in terms of the kinetics of the forward and reverse reactions for dissociation. This enabled the parameter (H^+) and all the individual species of the various weak acid/base systems to be explicitly included in the model so that pH is calculated directly from $pH = -\log (H^+)$. The advantages of the kinetic approach over the equilibrium-based approach are (i) kinetics are used throughout and this expedites integration of weak acid/base processes with existing biological kinetic models and (ii) the approach is general and can be applied to include any weak acid/bases of interest.

4.3 Development of single phase aqueous systems model

With a kinetic-based model including the carbonate, phosphate, nitrogen and acetic acid (for the short chain fatty acids, SCFA) weak acid/base systems, a good correlation was obtained at different steady states for all the species and pH compared with results obtained from equilibrium based algorithms in the literature. This validated both the kinetic approach to include pH and the single phase aqueous systems model.

The biological processes of carbon and nitrogen removal from the IAWQ Activated Sludge Model No.1 (ASM1) were then integrated with the single phase weak acid/base model. Where required, the interactions between the chemical species and biological processes were included e.g. CO_2 uptake for autotrophic nitrifier growth and NH_4^+ uptake for heterotrophic growth and nitrification. Also, literature information on the effect of pH on the maximum specific growth rates of nitrifiers was included. Data in the literature on aerobic batch tests with municipal wastewaters were simulated and a good correlation was obtained between the measured and predicted results and with results predicted by the original ASM1. However, in these tests even though the weak acid/base systems were included, these had little effect on the biological processes because the aqueous phase was well buffered against pH changes. Accordingly, rigorous validation was carried out later in the investigation with data obtained from an experimental investigation where the pH changed and the effect of this on the biological processes could be observed (see below).

4.4 Development of two phase systems model: Solid/aqueous

With the aid of information from the literature, kinetic equations for the precipitation of struvite ($MgNH_4PO_4$), newberyite ($MgHPO_4$), amorphous calcium phosphate [ACP, with a chemical formula similar to that of β-tricalcium phosphate, $Ca_3(PO_4)_2.xH_2O$], $CaCO_3$, and $MgCO_3$ were developed, and integrated with the weak acid/base chemistry model above. Ion pairing effects were also included in the model, by following a kinetic approach. Suitable data was obtained from the literature to validate the solid/aqueous phase model at different equilibrium states in sections, namely aqueous system with (i) $CaCO_3$ precipitation only, (ii) struvite precipitation only, and (iii) precipitation of ACP, $CaCO_3$ and $MgCO_3$. Time dependent data on the kinetics of precipitation were not available in the literature, and had to be collected in the experimental investigation (see below).

4.5 Development of two phase systems model: Gas/aqueous

The kinetics of gas exchange/stripping for CO_2 and NH_3 were included in the model. No suitable data was available from the literature to validate this gaseous/aqueous model, so that this data had to be collected in the experimental investigation (see below).

4.6 Development of the integrated three phase systems model (solid-aqueous-gaseous)

The solid precipitation and gas stripping kinetic reactions were integrated with the single phase combined biological and chemistry model, to give a combined physical, chemical and biological processes model. No suitable data could be found in the literature to validate all the processes in this integrated model. However, it was possible to validate some of the three phase chemical processes at the equilibrium state by comparing the model predictions with equilibrium chemistry algorithm results for $CaCO_3$ precipitation and CO_2 gas exchange from an example on conditioning of underground waters. This validated the masses of $CaCO_3$ precipitated and CO_2 stripped to reach equilibrium and the final state water composition, but not the rates of the processes. Information on these and other processes in the model were collected in the experimental investigation (see below).

4.7 Experimental investigation and model validation

During model development, the three phase systems model with weak acid/base systems reactions, biological processes, precipitation reactions of all solids and the processes of gas stripping could not be validated with data from the literature. This prompted an experimental investigation at

20°C to collect suitable data to validate most of the processes in the integrated model. Experiments in the form of aerated batch tests were carried out on four types of waste; (a) anaerobic digester liquor (ADL) from a biological nutrient removal (BNR) plant, (b) ADL from an upflow anaerobic sludge bed (UASB) reactor treating spent wine (c) a mixture of municipal raw sewage and waste activated sludge (WAS) from a nitrogen removal plant with and without chemical (Ca, Mg, P, and free and saline ammonia) addition and (d) a mixture of ADL from a BNR plant and WAS from a nitrogen removal plant. This enabled the model to be calibrated and validated by comparing model predictions with experimental results for physical and chemical processes only (with the first two wastes), biological processes only (with the third waste) and physical, chemical and biological processes of carbon and nitrogen removal, with the third and last type of waste. During aeration, the pH increased due to CO_2 stripping from about 7 up to 9.5 in batch tests on ADL, UASB supernatant and a mixture of ADL and WAS. In batch tests on a mixture of raw sewage and WAS with biological processes only, the pH remained nearly constant (7.6 - 8.0). In two of the three batch tests on a mixture of raw sewage and WAS with chemical addition, the pH decreased slightly (7.4 - 6.8) due to struvite precipitation and nitrification and in the third batch test, the pH was increased up to 9.0 through NaOH dosing.

In simulating the experimental results with the three phase kinetic model, after establishing (i) the minerals most likely to precipitate viz. struvite ($MgNH_4PO_4$), newberyite ($MgHPO_4$), amorphous calcium phosphate [ACP, $Ca_3(PO_4)_2$], $CaCO_3$ and $MgCO_3$ and (ii) their solubility products from the literature, the specific precipitation and gas stripping rate constants were determined by (i) trial and error visual fitting of predicted results to the experimental data and (ii) a parameter estimation facility which searches for the calibration constants that minimize the error between the model predictions and experimental results. A good correlation was obtained between model predictions and experimental results with both methods for all batch tests and while the second method may be superior, visually there was no discernable difference between the predicted results of the two methods. The good correlation between predicted and measured results enabled the kinetic model to be used to gain greater insight into the behaviour in the experiments, e.g. which minerals dominate in the precipitation and what masses precipitate, what stimulates the precipitation of the different minerals.

4.8 Discussion

The close correlation between predicted results and data available in the literature, and between predicted and observed results in the variety of batch tests undertaken in this investigation validated the kinetic model and the approach on which it is based. From the simulations it is evident that the kinetic model offers considerable advantages over equilibrium based models. Not only can it predict time dependent data, but also it can predict the final equilibrium state for situations with precipitation of multiple minerals which compete for the same species - equilibrium models are not capable of predicting either situation. Further, the kinetic modelling approach also allows the determination of the specific precipitation rates for a number of minerals simultaneously in an integrated manner from a single batch test. Also, the kinetic model provides greater insight into the processes operative in the system, and their interactions.

The three phase kinetic based weak acid/base chemistry model, and the approach on which it is based, is proving to be a useful tool for research into and design of wastewater treatment systems in which several weak acid/bases influence the behaviour and various combinations of biological, physical and chemical processes are operative. For research, the model helps to focus attention on issues not obvious from direct experiment and also allows determination of mineral precipitation rates for a particular wastewater from a single batch test. Once calibrated with the precipitation (and gas stripping if included) rates, this kind of model can be used to predict the performance of different treatment systems to identify for investigation those that appear technically and economically viable. For design, the model can be used to identify the critical design parameters and hence to optimize the design.

In conclusion, the kinetic based model developed in this research project constitutes a significant advance over the existing equilibrium chemistry based models for chemical processes, and the kinetic based models for biological processes. This kinetic model and the approach on which it is based can form a starting point for the development of a host of new models, for a variety of treatment systems in which pH and/or chemical and physical processes are of importance.

5. TASK 2: REVIEW OF LITERATURE

A review of the literature has been undertaken to identify technologies that are in use, or have potential for use in the treatment of the HNLC group of wastewaters. This review has indicated that a number of different treatment methods have been developed, which include biological, chemical and physical processes, usually separately:

- Precipitation methods usually aided by cation supplementation are in use in South Africa at Goudkoppies and Northern Works to remove nutrients from anaerobic digester liquors and activated sludge dewatering liquor respectively. This removes the phosphorus to relatively low values, but the ammonia concentrations in the anaerobic digester liquors may still be high (120mgN/ℓ), requiring further treatment.
- A number of treatment systems have been developed overseas that are not in use in South Africa. While each of these systems has its own particular advantages and disadvantages, in general the systems have been developed for the removal of N and not P. Only the Chemische Ammonium Fallung and Rezykherung (CAFR) system has the immediate potential for both N and P removal; however, evaluation in the Netherlands indicates that most likely the CAFR system will not be economically feasible.
- In this category of wastes, the imbalance between the nutrients (N & P) and organic carbon would suggest that treatment using combined biological, chemical and physical processes may be the best option for the removal of both N and P. Combined biological, chemical and physical processes are not well understood. In particular the interaction between the processes are poorly defined. It was considered therefore imperative that a model incorporating the biological, chemical and physical processes be developed to give a better understanding of the processes, to form a basis for design of treatment plants (see Task 1 above).
- Specific experiments to be undertaken were identified, namely, treatment of:
  - (i) Waste activated sludge dewatering liquors and anaerobic digestor supernatants, by combined chemical/physical and chemical/biological/physical methods.
  - (ii) Landfill leachates in activated sludge systems receiving municipal wastewaters.
  - (iii) Septic tank effluents in conventional BNR removal activated sludge systems.

  Research on these has been undertaken, and is reported in Task 3 below.

6. TASK 3: EXPERIMENTAL INVESTIGATION OF TREATMENT SCHEMES

Parallel to the development of the mathematical model, the feasibility of treating selected HNLC wastes was investigated. In terms of the contract proposals the wastes investigated were:

- Waste activated sludge dewatering liquors and anaerobic digestor liquors, by combined chemical/physical and chemical/biological/physical methods.
- Landfill leachates in activated sludge systems receiving municipal wastewaters.
- Septic tank effluents in conventional BNR removal activated sludge systems.

6.1 Waste activated sludge dewatering liquors and anaerobic digestor liquors

This experimental investigation was undertaken in conjunction with the development of the mathematical model, see **Task 1** above.

6.2 Landfill leachates in activated sludge systems receiving municipal wastewaters

Sanitary landfill sites are used for disposing solid refuse. In the past landfill sites were viewed only as solid waste disposal sites with little or no effort to promote the stabilization of the solids wastes. However, management and operation of landfill sites has now become a necessity due to (1) increased urban population resulting in a shortage of land for landfills and hence the need to maximise the life of a landfill, and (2) increased environmental awareness and the need to preserve the natural environment. The most serious environmental threat posed by a landfill site is the pollution of ground water caused by leachates. Leachates are formed by rain percolating through the solid waste. To avoid ground water pollution, leachate formed from sanitary landfills needs to be collected for treatment. Two types of leachates can be formed by a landfill, viz. stabilized leachate from a landfill in its methanogenic phase and acid leachate from a landfill in its acidogenic phase of decomposition. Acid leachate can be treated by discharging it onto methanogenic refuse to produce stabilized leachate (Novella, 1995). However, stabilized leachates are characterised by high organic and nitrogen contents (COD - 5 258 mg/ℓ; TKN - 440 mg/ℓ; Hansford and Ekama., 1993) and require further treatment.

Accordingly, a study was undertaken to provide additional information on the treatment of landfill leachates. In particular, the feasibility of adopting an integrated approach to municipal waste management by operating sewage treatment plants (liquid waste treatment) and sanitary landfill sites (solid waste management) in conjunction with each other was investigated. In terms of this approach, the liquid leachate stream produced in the landfill is treated in the sewage treatment plant and the waste activated sludge stream generated in the sewage treatment plant is disposed to the landfill. Two experimental studies have been undertaken:

(1) Treatment of stabilized landfill leachate in an N removal system.
(2) Treatment of an acid leachate in a nutrient (N&P) removal system.

In these laboratory-scale studies two identical systems were set up in parallel. Both systems received municipal wastewater as influent. Additionally, the appropriate landfill leachate was dosed into one selected system (experimental) while the parallel system did not receive leachate dose (control). By comparing the response of the experimental and control systems the effect of the leachate on the system behaviour could be determined.

With regard to treatment of stabilized landfill leachate in an N removal system, the results indicated that:

- The N and COD mass balances were generally good (better than 90%).
- 11.5% of leachate COD contributed to unbiodegradable soluble COD, increasing the effluent COD concentration from the experimental system by 13 mgCOD/ℓ (25%).
- 5.7% of leachate COD was unbiodegradable particulate, increasing the VSS concentration of the solids in the reactor by 75 mgVSS/ℓ (3%).
- 83% of the leachate COD was biodegradable and contributed to the biodegradable organics of the sewage.
- No noticeable difference between the effluent TKN concentration of the experimental and control systems could be detected, indicating that the leachate contains negligible soluble unbiodegradable organic N. Also nitrification was complete and all free and saline ammonia of the leachate was nitrified.
- The additional leachate biodegradable COD caused an increase in reactor VSS concentration of about 400 mgVSS/ℓ, i.e. 20% more than in the control. The biodegradable COD and TKN caused the oxygen utilization rate to increase by 5 mgO/ℓ/h i.e. also about 20% more than in the control system. These increases seem reasonable considering the leachate increased the organic and nitrogen load by 18%.
- The effluent nitrate concentration from the experimental system was *lower* than that from the control system. This implied, and detailed comparison on the denitrification performance of the two systems confirmed this, that the leachate not only was capable of denitrifying all the nitrate that was generated from its own TKN content, but also contributed to denitrification of nitrate generated from the sewage's TKN content.
- Sludge settleability in both systems *improved* from over 150 mℓ/g at the start of the investigation to below 60 mℓ/g at the end. The filaments in the sludge were the usual AA types (i.e. *M. Parvicella*, 0092, 0041, 0675) but were only present at common level. This indicated that leachate did not stimulate poor sludge settleability in N removal systems.

Addition of unstabilized (acid) leachate comprising 22.3% and 8.1% of the sewage COD and TKN loads respectively, to a biological nutrient removal activated sludge system (experimental) and comparing the response to an identical system not dosed (control) indicated that:

- Good COD (both experimental and control = 92%) and N (experimental = 90%; control = 88%) mass balances were obtained, supporting the reliability of the data.
- The acid leachate dose increased both the TSS and VSS concentrations in the reactor, by about 550 mgTSS/ℓ and 350 mgVSS/ℓ respectively (25 and 20% respectively).
- The acid leachate dose increased the OUR, by about 21%.
- The acid leachate dose did not increase the effluent COD concentration significantly, i.e. the unbiodegradable soluble COD concentration in the leachate is small, 2.2% of the leachate COD.
- The unbiodegradable particulate COD fraction of the leachate was close to zero.
- From the unbiodegradable soluble and particulate COD fractions, 98.7% of the leachate COD was biodegraded in the BNR activated sludge system.
- The acid leachate dose increased the influent TKN by about 7%, but did not increase the effluent TKN or FSA significantly, i.e. nitrification was complete and the unbiodegradable soluble organic N small, at 4.5% of the leachate TKN.

- The unbiodegradable particulate TKN fraction of the leachate was close to zero.
- From the unbiodegradable soluble and particulate TKN fractions, 98.7% of the leachate TKN was biodegraded in the BNR activated sludge system.
- Only 13.7% of the leachate COD was taken up in the anaerobic reactor for BEPR, the balance contributed to additional denitrification. The leachate COD taken up in the anaerobic reactor gave an increase in P removal of 4.3 mgP/ℓ (28.9%).
- The leachate denitrified all the nitrate generated from its own TKN and had the potential to denitrify an additional 4.9 mgN/ℓ generated from the sewage TKN due to a 19% higher denitrification rate.
- Leachate dosing had no effect on the nitrifier maximum specific growth rate or the sludge settleability.
- Not only did the particulate/colloidal metal complexes from the leachate accumulate in the activated sludge, but also significant concentrations of the soluble metal compounds, leaving the effluent with lower dissolved metal concentrations than the influent.

Thus, both investigations have demonstrated that, in addition to being treated, the leachate enhanced the nutrient removal capability of the activated sludge system. This would indicate that there is considerable merit in adopting an integrated approach to the management and treatment of municipal wastes, with soluble wastes generated in a landfill being treated in the municipal wastewater treatment plant (MWWTP), and the solid waste generated in the MWWTP being treated in the landfill.

6.3 Septic tank effluents in conventional BNR removal activated sludge systems

To investigate the expected impact of septic tank effluents on existing BNR activated sludge systems, it was decided to collect information on the characteristics of septic tank effluents and to do a desk-top study on the response of BNR activated sludge systems to various septic tank effluent loads. Some data on the characteristics of septic tank effluents are available in the literature, e.g. Peters (1993), Ketley (1996), Theunessin (1993). However, a particular problem with the data is that the effluents from single septic tanks have been analysed, which raises doubts as to whether the data are representative. It would be more acceptable if the combined effluent from a number of septic tanks could be analysed. A site in Hermanus was identified where ±200 septic tanks are connected to a single sewer. Samples from this sewer were obtained and analysed using chemical and biological tests to characterise the septic tank effluent. Having derived data on septic tank effluents and their characteristics, a theoretical desk top study was undertaken on the effect of various septic tank effluent loads on BNR activated sludge systems. For this study, the septic tank effluent was dosed into the settled wastewater serving as influent to the UCT configuration BNR activated sludge system pilot-scale plant at Mitchell's Plain (Cape Town, South Africa), and the theoretical response simulated with the UCTPHO kinetic simulation model (Wentzel *et al.*, 1992). Two main scenarios were considered:

Scenario 1: Theoretically, increasing flows of the septic tank effluent were introduced into the influent to the pilot plant and the flow of settled domestic sewage that is normally treated in the pilot plant was reduced proportionately, so that the total flow that the pilot plant was initially designed for would be maintained (i.e. 2.4Mℓ/d).

Scenario 2: The settled sewage flow was kept constant at the design value (i.e. 2.4Mℓ/d), and the septic tank effluent flow added to this flow, so that the total flow increased as the septic tank effluent dose increased. For this scenario, two alternative recycle schemes were simulated:

> **Scenario 2a:** The recycle flow rates were kept constant at the values for **Scenario 1** above, i.e. as the total flow increased, the recycle flows remained constant and so the recycle ratios decreased.
>
> **Scenario 2b:** The recycle ratios were kept constant at the values for **Scenario 1** above, i.e. as the total flow increased, the recycle ratios remained constant and so the recycle flow rates increased.

Results from these simulation studies indicated that:

- In all three scenarios considered, septic tank effluents do not impact significantly on COD removal and nitrification. The effluent COD concentrations decreased slightly and effluent TKN and FSA remained essentially constant with increased flows of septic tank effluents.
- Depending on the scenario considered, the reactor VSS concentrations and oxygen utilization rates (OUR) either decreased (scenario 1, settled sewage flow decreased in proportion to septic tank effluent flow), or increased (scenario 2, settled sewage flow kept constant and septic tank effluent flow increased). In practice, it is likely that scenario 2 will apply, and hence provision will have to be made to accommodate the increased VSS concentrations and OURs with increased septic tank flow.
- Both denitrification and biological excess P removal decrease as the septic tank effluent flow increases. However, these decreases are only significant when proportionally large quantities of septic tank effluent are treated. The lowest impact of septic tank effluent on nutrient removal performance are for scenario 2.
- When septic tank effluent is treated by itself (scenario 1, 100% septic tank effluent), poor nutrient removal performance is achieved. This confirms that treatment of septic tank effluents in dedicated BNR plants is not a viable option.
- In practice if an activated sludge plant were to treat a blend of settled sewage and septic tank effluent the blend ratio can be selected depending on the standard of effluent that the plant is expected to meet in terms of legal requirements laid down by the Department of Water Affairs and Forestry.
- In this study, the septic tank effluent from a number of septic tanks sited at Hermanus was selected. From the characterization of this effluent it would appear that the concentrations (COD, N and P) are considerably lower (245 mgCOD/ℓ, 63 mgN/ℓ and 10.4 mgP/ℓ respectively) than those obtained elsewhere (typically > 4 000mgCOD/ℓ, > 1 000 mgN/ℓ and > 100 mgP/ℓ, see Section 6.1). This probably arises because the septic tanks at Hermanus have full water flush (10 - 15 ℓ/flush) while those in the quoted studies have restricted water flush (1ℓ/flush). This would imply that with low volume flush septic tanks deterioration in BNR nutrient removal performance would be experienced at much lower septic tank effluent flow rates than obtained in this study. This aspect requires further investigation.

7. TASK 4: EVALUATE/DEVELOP EXISTING/NEW TECHNOLOGIES

In Task 2 above, the literature was reviewed to identify promising new technologies for treatment of HNLC wastewaters. This review indicated that the majority of technologies developed overseas have as their principle objective the removal of nitrogen. This causes that these technologies will have limited application in South Africa to HNLC wastewaters, where the removal of phosphorus also is of fundamental importance. In South Africa, aeration stimulated precipitation methods usually aided by cation supplementation are in use at Goudkoppies and Northern Works to remove nutrients from anaerobic digester liquors and activated sludge dewatering liquor respectively. It would appear that this technology has considerable potential for more widespread application. Accordingly, the kinetic model developed in Task 1 above was applied to examine aeration as a treatment scheme for anaerobic liquors.

The batch tests in the model validation investigation (Task 1 above) were critically examined with the objective to provide greater insight into the biological, chemical and physical processes operating in plants treating anaerobic liquors by aeration. The example case selected for study was Goudkoppies Treatment plant (Johannesburg, South Africa) where anaerobically digested sludge is first aerated to strip CO_2 (to cause pH to increase and so stimulate struvite and calcium phosphate precipitation) and lime is added for further precipitation. The batch tests in the model validation investigation in effect duplicate the first aeration step at Goudkoppies. The data from these batch tests were examined in detail and the following was concluded:

- In batch tests with anaerobic digester and UASB liquors, aeration caused CO_2 stripping and this resulted in pH increase from ±6.95 to 8.93 and 9.53 respectively.
- The increase in pH caused precipitation of predominantly struvite and ACP, reducing concentration of both nutrients N and P to around 380 gN/m^3 and 15 gP/m^3 respectively for anaerobic digester liquor and 30 gN/m^3 and 20 gP/m^3 respectively for UASB liquor.
- In both liquors, the ammonia was present in excess for struvite precipitation, and so the concentrations of ammonia were still relatively high (380 gN/m^3 for anaerobic digester liquor and 30 gN/m^3 for UASB liquor).
- Struvite precipitated very quickly within the first 20 to 45 minutes of aeration and ACP within 60 to 90 minutes of aeration.
- Ammonia is relatively non volatile so that the rate of ammonia removal via gas stripping is not a practical treatment alternative under the conditions present in the batch tests.
- Addition of WAS to the anaerobic digester liquor resulted in nitrification of the ammonia. However, this nitrification proceeded at a very slow rate (maximum specific growth rate of the nitrifiers, $\mu_{A20,pH7.2} = 0.03$ to 0.04 /d). Further, addition of WAS had the undesirable effect of reducing the rate of struvite precipitation, by up to two orders of magnitude.

The results above would indicate that the aeration of anaerobic liquors for nutrient removal should be a two stage process: (i) aeration for CO_2 stripping and pH increase, followed by (ii) addition of WAS for nitrification. In the nitrification step, care must be taken to ensure that the pH does not decrease below 7 to cause struvite redissolution.

8. CLOSURE

The imbalance between the nutrients and the organic carbon in the high nutrient low organic carbon category of wastewaters considered in this project causes that treatment of these wastewaters in conventional BNR activated sludge systems is not a viable option. This is clearly demonstrated in the theoretical desk top study on the treatment of septic tank effluents. For the treatment of these wastewaters, unit processes that incorporate combined chemical, physical and biological processes would seem essential. In this project a mathematical kinetic model has been developed that simulates the behaviour of such systems. From the simulations it is evident that the kinetic model offers considerable advantages over equilibrium based models. Not only can it predict time dependent data, but also it can predict the final equilibrium state for situations with precipitation of multiple minerals which compete for the same species - equilibrium models are not capable of predicting either situation. Further, the kinetic modelling approach also allows the determination of the specific precipitation rates for a number of minerals simultaneously in an integrated manner from a single batch test. Also, the kinetic model provides greater insight into the processes operative in the system, and their interactions.

The three phase kinetic based weak acid/base chemistry model, and the approach on which it is based, is proving to be a useful tool for research into and design of wastewater treatment systems in which several weak acid/bases influence the behaviour and various combinations of biological, physical and chemical processes are operative. For research, the model helps to focus attention on issues not obvious from direct experiment and also allows determination of mineral precipitation rates for a particular wastewater from a single batch test. Once calibrated with the precipitation (and gas stripping if included) rates, this kind of model can be used to predict the performance of different treatment systems to identify for investigation those that appear technically and economically viable. For design, the model can be used to identify the critical design parameters and hence to optimize the design.

In conclusion, the kinetic based model developed in this research project constitutes a significant advance over the existing equilibrium chemistry based models for chemical processes, and the kinetic based models for biological processes. This kinetic model and the approach on which it is based can form a starting point for the development of a host of new models, for a variety of treatment systems in which pH and/or chemical and physical processes are of importance.

9. RECOMMENDATIONS

With regard to the mathematical model:

1. Although a remarkable degree of constancy was found for precipitation rate constants of the minerals in each type of waste, definitive reasons could not be advanced for the variability in the struvite precipitation rate constant and deviation in the rate constants of ACP and $CaCO_3$. Further experimental work needs to be done to obtain more data on the precipitation rate constants of these minerals in different wastes and establish the factors that affect the precipitation rate constants of these minerals.

2. For practical application of the model to a treatment scheme, the air flow rates and gas transfer rate coefficients (K_{La}) should be measured through the established methods and

then applied to the model.

3. Further experimental work needs to be done to investigate (i) the validity of the μ_A-pH relationship for the maximum specific growth rate of nitrifiers proposed in the model and (ii) the effect of increased pH above the optimum range for biological activated sludge systems on the rates of utilisation of RBCOD and hydrolysis of enmeshed COD and come up with formulations similar to the ones for the effect of pH on the maximum specific growth rate of nitrifiers.

4. Since the approach for including weak acid/base dissociation reactions is general, it can be applied to model development in other areas of wastewater treatment and biotechnology research.

5. The combined model presented in this research can be used to provide a basic understanding of the mechanisms operating in treatment schemes, and to theoretically refine the treatment process for practical implementation. The AQUASIM programme is flexible enough to model any combination of completely mixed or plug flow reactors with split influent flows, chemical addition, recycle flows and sedimentation tanks. It is therefore possible to simulate an anaerobic digester supernatant treatment system with the integrated chemical, physical and biological model developed in this research provided the reactor conditions such as air flow and gas transfer rates are known.

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TABLE OF CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

Symbol/abbreviation	Description
ADL	Anaerobic digestor liquor
BEPR	Biological excess phosphorus removal
BNR	Biological nutrient removal
CAFR	Chemische Ammonium Fallung and Rezkherung (Chemical ammonium precipitation and recirculation)
COD	Chemical oxygen demand
DSVI	Diluted sludge volume index
f_{CV}	Mixed liquor COD/VSS ratio
f_N	Mixed liquor TKN/VSS ratio
FSA	Free and saline ammonia
HNLC	High nutrient low organic carbon
IAWPRC	International Association for Water Pollution Research and Control
IAWQ	International Association on Water Quality (formerly IAWPRC)
MAP	Magnesium ammonium phosphate (struvite)
MLOSS	Mixed liquor organic suspended solids
MLSS	Mixed liquor suspended solids
N	Nitrogen
OUR	Oxygen utilization rate
P	Phosphorus
PST	Primary settling tank
SCFA	Short-chain fatty acids
SS	Sewage sludge
SSD	Sample standard deviation
TKN	Total Kjeldahl Nitrogen
TSS	Total suspended solids
UCT	Univerity of Cape Town
UASB	Upflow anaerobic sludge bed
VSS	Volatile suspended solids
WAS	Waste activated sludge
WRC	Water Research Commission
X_H	Heterotrophic active biomass

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CHAPTER 1

INTRODUCTION

1.1 MOTIVATION

High nutrient (nitrogen, N and phosphorus, P) low organic carbon (COD) wastewaters are wastewaters in which the carbon is greatly deficient relative to the nutrients N and P. These wastewaters are generated within a diversity of municipal waste treatment facilities. Such facilities include urban development schemes utilising alternative non-full waterborne sanitation systems, sanitary landfill sites and wastewater treatment plants with trickling filters, anaerobic sludge digestion, sludge treatment liquors and/or biological nutrient removal (BNR) activated sludge plants. Examples of specific wastewaters falling into this high nutrient low organic carbon (HNLC) group are:

(1) Septic tank effluents.
(2) Landfill leachates.
(3) Activated sludge de-watering liquors.
(4) Anaerobic digester supernatants, in particular from BNR activated sludge systems.
(5) Trickling filter effluents.
(6) Sludge disposal lagoon effluents.

(Oxidation pond effluents can also be included in this group, but oxidation ponds are implemented only in rural areas and are so few in number in South Africa that their effluents do not contribute significantly to surface water pollution and/or eutrophication).

These wastewaters will increasingly make a significant contribution to nutrient loads on surface water resources resulting in eutrophication and its associated problems. Accordingly, to limit eutrophication and maintain the quality of surface waters, the high nutrient low organic carbon wastewaters will require treatment to remove the nutrients. However, this treatment is problematic: Conventional activated sludge BNR technology is not practical due to the imbalance between the organics (low) and nutrients (high); indeed wastewater types (3), (4) and (6) above are themselves generated by BNR plants. Therefore alternative methods, processes and technologies need to be developed to treat these wastewaters.

To address the problems raised above, in January 1995 a three year contract "The treatment of wastewaters with high nutrients (N&P) but a low organic (COD) contents" (K5/692) was set up between the Water Research Commission (WRC) and the University of Cape Town (UCT). In this contract, it was proposed to conduct research into the first four of the high nutrient low organic carbon wastes listed above.

1.2 PRINCIPLE AIM

The principal aim of the contract was :

- To evaluate, investigate, develop and refine chemical, physical and biological processes and technologies to treat wastewaters with high nutrient (N and P) but low organic carbon contents.

1.3 MAIN TASKS

In terms of the aim, four main tasks were identified for completion (Schematically shown in Figure 1.1):

Task 1: Model Development

- Develop a fundamentally based mathematical model which will integrate the biological, physical and chemical processes that are operative in systems treating high nutrient low organic wastes.

Development of an integrated, internally consistent mathematical model was prioritized. It was recognized that this model and its development would provide a defined structural framework to direct the research. By providing quantitative descriptions, mathematical models allow predictions of the response of a system. From the predictions, design and operational criteria can be identified for optimization of system performance. Also, by evaluating model predictions, it is possible to test hypotheses on the behaviour of the treatment system (e.g. biological processes, their response to system constraints, etc.) in a consistent and integrated fashion. This directs attention to issues not obvious from physical experimental systems, and leads to a deeper understanding of the fundamental behaviour controlling the system response.

In the treatment of the HNLC category of wastes, in addition to biological processes, both chemical and physical processes play an important role. Thus, the model had to integrate all three process types, namely biological, physical and chemical. This constitutes a significant advance over previous models for wastewater treatment systems, which have concentrated on the biological processes.

Once a rudimentary model had been developed, experimental information was used to calibrate, test and refine the model. Wherever possible experimental data in the literature was used (see Task 2). Where the necessary information was not available in the literature, experiments were undertaken to collect the data (see Task 3).

Development of the model is reported in detail in Chapter 3, and experiments to validate the model in Chapter 4.

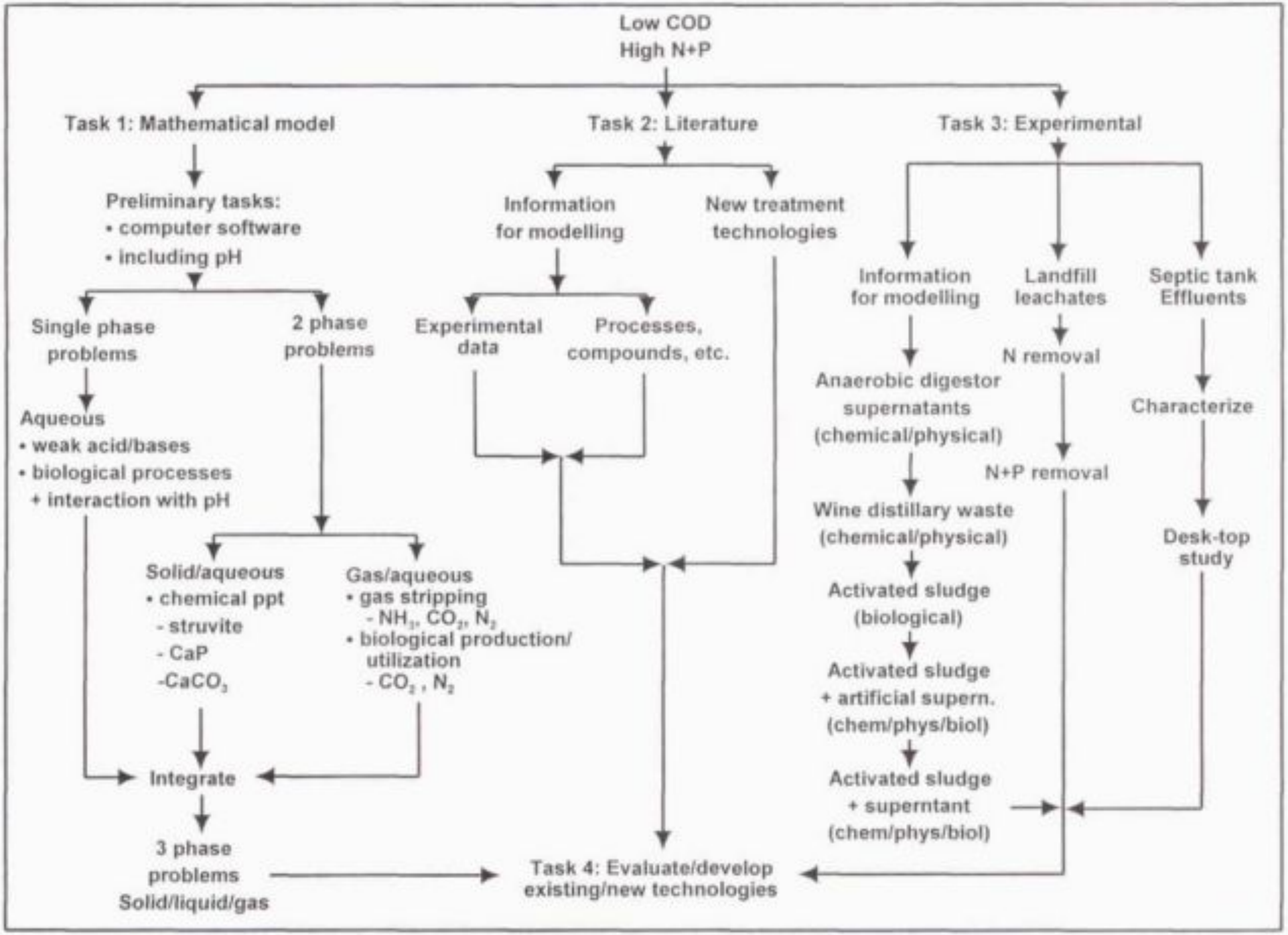


Fig 1.1: Flow scheme showing research tasks to be completed.

Task 2: Review of literature

- Review the literature to, (i) identify the origin and nature of these wastes, (ii) identify technologies currently used for their treatment, (iii) identify new technologies that hold potential for their treatment, and (iv) provide experimental data for calibration, testing and refinement of the mathematical model.

In this report, aspects (i), (ii) and (iii) are described in Chapter 2, while aspect (iv) is described in Chapter 4 together with the validation of the mathematical model.

Task 3: Experimental investigation

- Collect experimental data on the wastes and various treatment schemes. This will provide information on the feasibility of the schemes, and for the development, calibration and validation of the mathematical model.

Parallel to the development of the mathematical model, an experimental investigation has been undertaken into the feasibility of treating selected high nutrient low organic wastes in various treatment schemes. Specifically, experimental investigations have been undertaken on the treatment of:

(i) Waste activated sludge dewatering liquors and anaerobic digestor supernatants, by combined chemical/physical and chemical/biological/physical methods.

(ii) Landfill leachates in activated sludge systems receiving municipal wastewaters.

(iii) Septic tank effluents in conventional BNR removal activated sludge systems.

Item (i) is reported in Chapter 4 together with the validation of the mathematical model, item (ii) is reported in Chapter 5 and item (iii) in Chapter 6.

Task 4: Evaluate/develop existing/new technologies

- Evaluate and develop existing/new treatment processes and technologies.

As the modelling progresses and a deeper understanding of the fundamental processes is gained, existing and new treatment systems can be evaluated/developed. Also, as noted in Task 2 above, the literature will be reviewed to identify promising technologies.

1.4 ANCILLARY TASK

In addition, progress is also reported on an ancillary task:

- Heterotrophic active biomass component of activated sludge mixed liquor.

This task does not fall directly under the current contract, but progress is reported to keep the WRC and readers informed of the work being done in this area, see Chapter 7.

CHAPTER 2

THE ORIGIN AND TREATMENT OF HIGH NUTRIENT LOW ORGANIC WASTES

2.1 INTRODUCTION

High nutrient (N&P) low organic carbon wastewaters are generated in a diversity of municipal waste treatment facilities. Examples of specific wastewaters falling into this group are:

(1) Septic tank effluents.
(2) Landfill leachates.
(3) Activated sludge de-watering liquors.
(4) Anaerobic digester supernatants, in particular from BNR activated sludge systems.
(5) Trickling filter effluents.
(6) Sludge disposal lagoon effluents.

The nature, origin and some current methods of disposal of the six wastewaters above are described briefly in this Chapter. Also, an overview is given of the proposed experimental work on selected treatment schemes for these wastes. Further, the literature is reviewed to identify and evaluate innovative alternative treatment technologies.

2.2 DESCRIPTION OF WASTEWATER ORIGINS AND THEIR DISPOSAL

2.2.1 Septic tank effluents

Surveys in South Africa in 1993 have indicated that nearly 50% of the population do not have adequate sanitation and nearly 30% do not have adequate water, i.e. 18.6 and 10.8 million people respectively (Palmer Development Group and University of Cape Town, 1993). In urban areas, 64% of the population have full waterborne sanitation and less than 5% have adequate alternative non-waterborne sanitation; more than 30% of the population in urban areas (i.e. some 7 million people) have no or inadequate sanitation. About 20% of the urban population (i.e. nearly 5 million people) do not have adequate water supply at or near their place of residence. Therefore, over the next decade water supply and sanitation provision are going to be priorities in infrastructure development programmes. To provide affordable and sustainable water supply and sanitation, while restricting the increased demand on limited water resources, will require far greater application of alternative (non-full waterborne) sanitation systems. The low volume flush septic tank type system (called the aquaprivy) has been identified as one such system that has considerable merit. This system is a relatively low cost, but sustainable non-full waterborne sanitation system. Also, since the system requires a small amount of water per flush (about 1ℓ), it can be used for situations where communal water supplies only are available (i.e. where households are required to collect and cart water for on-site use). In the system, the waste is flushed to a digestor where the particulate matter settles and remains to be digested. This results in a considerable reduction in the organic content of the waste, but little reduction in the soluble nutrients (Peters, 1993). The supernatant from the digestor (effluent) requires disposal. Effluent disposal from septic tanks is usually on-site to soakaways but can be off-site (via low flow small bore sewer systems) depending on water quantity, soil type, plot size, etc. Currently in South Africa, most septic tank effluents are disposed of on-site in soakaways. It is therefore critical that the soakaways function effectively all the time. However, soakaway failure due to high water tables, clogging and overloading frequently occurs, especially in high density housing areas. This has been identified to be a major cause for failure of the septic tank system (Peters, 1993). Soakaway failure has major public health implications, causing diseases, smells, and unhealthy living conditions. Furthermore, the effects of septic tank effluent disposal in soakaways on soil and ground water quality are still unknown, but thought to be undesirable.

To eliminate the problems associated with soakaways, the effluents from septic tanks can be collected in small bore sewers for off-site treatment (e.g. the South African low volume flush, on-site anaerobic digester linked to a solids-free reticulation system-LOFLOS, Peters, 1993). In South Africa, this arrangement is still relatively uncommon with only a few systems installed (Palmer Development Group and University of Cape Town, 1993). However, it is expected that the merits of the system will cause it to be increasingly considered for application. Implementation of small bore sewers may be impeded by a lack of knowledge on how to treat the collected wastewater to comply with effluent quality discharge standards. These systems characteristically produce an effluent of about 15ℓ/person/d with a COD of 4 000 - 9 000mgCOD/ℓ and nutrient concentrations of about 1 000 - 2 000mgTKN-N/ℓ and 100 - 180mgTotal-P/ℓ (Peters, 1993), i.e. TKN/COD = 0.25mgN/mgCOD and TP/COD = 0.03mgP/mgCOD, compared to "normal" municipal wastewater TKN/COD ≈ 0.1mgN/mgCOD and TP/COD ≈ 0.02mgP/mgCOD. The imbalance between the organics and nutrients will cause their treatment in separate BNR wastewater treatment systems to be problematic. Further, should these wastewaters be discharged to conventional BNR treatment plants receiving wastewaters from full waterborne sanitation systems, they will increase the nutrient loads on these plants. The magnitude and effect of this increase are not known.

The mechanisms and technology for the treatment of wastewaters in BNR activated sludge systems are well understood and, provided the wastewater characteristics are well defined, the expected response of a system can be quantified through existing steady state design (Wentzel *et al.*, 1990) or kinetic simulation (Wentzel *et al.*, 1992; Henze *et al.*, 1995) models. Accordingly, to investigate the expected impact of septic tank effluents on existing BNR activated sludge systems, it was decided to collect information on the characteristics of septic tank effluents and to do a desk-top study on the response of BNR activated sludge systems to various septic tank effluent loads. More details on this study are reported in **CHAPTER 6: TREATMENT OF SEPTIC TANK EFFLUENTS**.

2.2.2 Landfill leachates

Sanitary landfill sites are used for disposing solid refuse. In the past landfill sites were viewed only as solid waste disposal sites with little or no effort to promote the stabilization of the solids wastes. However, management and operation of landfill sites has now become a necessity due to (1) increased urban population resulting in a shortage of land for landfills and hence the need to maximise the life of a landfill, and (2) increased environmental awareness and the need to preserve the natural environment. The most serious environmental threat posed by a landfill site is the pollution of ground water caused by leachates; leachates are formed by rain percolating through the solid waste. To avoid ground water pollution, leachate formed from sanitary landfills needs to be collected for treatment. Two types of leachates can be formed by a landfill, viz. stabilized leachate from a landfill in its methanogenic phase and acid leachate from a landfill in its acidogenic phase of decomposition. Acid leachate can be treated by discharging it onto methanogenic refuse to produce stabilized leachate (Novella, 1995). However, stabilized leachates are characterised by high organic and nitrogen contents (COD - 5 258 mg/ℓ; TKN - 440 mg/ℓ; Hansford and Ekama, 1993) and require further treatment.

A number of options for the treatment of landfill leachates have been proposed, e.g. biological pretreatment (nitrification and denitrification with added methanol) followed by two-stage reverse osmosis with evaporation and granular drying of the concentrates (Hippen *et al.*, 1997); pressure staged reverse osmosis followed by nanofiltration and precipitation (Peters, 1996); combined biological treatment with adsorption by activated carbon or oxidation with ozone (Peters, 1996). As an alternative to these relatively high technology high cost disposal methods, one option is to adopt an integrated approach to municipal waste management: Sewage treatment plants (liquid waste treatment) and sanitary landfill sites (solid waste treatment) are operated in conjunction with each other. In terms of this approach, the liquid leachate stream produced in the landfill is treated in the sewage treatment plant together with the municipal sewage, and the solids sludge stream generated in the sewage treatment plant is disposed to the landfill. The effect of disposing sludge from the sewage treatment plant to the landfill has been investigated (Novella, 1995). In this contract, the effect of adding landfill leachate to the sewage treatment plant was investigated. Two experimental studies were undertaken:

(1) Treatment of stabilized landfill leachate in a N removal activated sludge system.
(2) Treatment of acid landfill leachate in a BNR activated sludge system.

More details on these studies are set out in section **CHAPTER 5: EXPERIMENTAL INVESTIGATION: TREATMENT OF LANDFILL LEACHATES**.

2.2.3 Activated sludge de-watering liquors and anaerobic digester supernatants

In biological N and N & P removal wastewater treatment plants, the disposal of activated sludge de-watering liquors and anaerobic digestor supernatants is problematic. In N removal plants, during anaerobic digestion considerable quantities of N are released so that the liquors from subsequent sludge dewatering and drying can contain high concentrations of N: If these liquors are recycled to the head of the works (as is a usual practise), even though they only contribute about 2% of the flow to the treatment plant, they can contribute up to 25% of the total N load (Janus and van der Roest, 1997).

In BNR plants, waste activated sludge (WAS) contains considerable N and P, which will be released during thickening and dewatering, and during both acid and conventional anaerobic digestion (Pitman *et al.*, 1991). Also, primary sludge will release both N and P during both acid and conventional digestion. For example, N and P concentrations in sludge liquors from works in Johannesburg (South Africa) are shown in Table 2.1 (Pitman, 1995). Furthermore, in BNR systems these waste streams also contain high Mg concentrations, which combined with the high N and P concentrations can cause struvite (magnesium ammonium phosphate) precipitation. This may result in operational problems, such as pipe blockages (Pitman *et al.*, 1989). Calcium phosphates are also precipitated if the conditions are favourable.

Table 2.1: Typical ortho-phosphate, ammonia and suspended solids concentrations for liquors from treatment plants in Johannesburg (South Africa) (Pitman, 1995).

Liquor Type	Phosphate (mgP/ℓ)	Ammonia (mgN/ℓ)	Suspended solids (mg/ℓ)
Primary sludge			
- raw	15	20	-
- acid digested	50	170	-
Waste activated sludge			
- dissolved air floatation liquor	0.5	1.2	60
- belt press liquors	15	10	-
- gravity thickener overflow	1.8	1.2	8
Mixed sludge			
- anaerobically digested	150	800	-

Clearly, it would be advantageous to implement some kind of treatment scheme for these waste streams, and so prevent/minimize the internal recycling of nutrients. For the removal of N from the waste streams generated in N removal plants, considerable research has been done in the Netherlands on possible treatment options; these are reviewed in **Section 2.3** below.

For the removal of P or N and P from the waste streams generated in N and P removal plants, the precipitation of phosphates, especially struvite, would seem to provide a ready means for treatment: If the struvite precipitation reaction already noted in anaerobic digestors at these plants can be controlled, it will result in the removal of all three (N, P and Mg) problematic elements, in the mass ratio 1.71 Mg: 1.0 N: 2.21 P (molar ratio 1:1:1). It appears that the trigger mechanism for the precipitation of struvite is a reduction in total pressure or partial pressure of carbon dioxide, which causes carbon dioxide stripping from the aqueous phase with a concomitant increase in pH. This pH increase may give rise to a state of supersaturation with respect to struvite that is sufficiently high to cause precipitation of this mineral (Loewenthal *et al.*, 1994). A decrease in temperature also increases the precipitation potential (Pitman, 1982).

In a typical anaerobic digester supernatant, for the precipitation of struvite ammonia is present in excess quantities but magnesium is deficient (except in very hard waters) to precipitate all the phosphate present. Simultaneous precipitation of calcium orthophosphates by addition of lime has been used to remove substantial phosphate (Pitman *et al.*, 1989). Thus, supplementation of the cations magnesium or calcium would have to be used to achieve additional phosphate removal. Salutsky *et al.* (1972) showed that if digested sludge was degassed and metal cations such as Ca^{2+} and Mg^{2+} added, a valuable fertilizer (struvite and calcium phosphate) could be precipitated out.

Pitman and coworkers at Johannesburg have undertaken extensive experimental work investigating phosphate precipitation in digested sludge, digested sludge supernatants and dewatering liquors. Laboratory experiments on anaerobic digester supernatant samples (Pitman *et al*., 1989) showed that aeration stripped CO_2, increased the pH and caused phosphate to precipitate, as struvite. The increased pH also caused ammonia to volatilise. Addition of lime or ferric chloride to aerated samples showed that the phosphorus concentration could be reduced even further. In further laboratory experiments, Pitman *et al*. (1991) reported an increase in pH due to CO_2 stripping and a decrease in orthophosphate, also after aerating laboratory samples of digested sludge. Pitman *et al.* (1991) further showed that aeration of mixtures of digested sludge and thickened waste activated sludge caused a significant decrease in ammonia-N concentrations due to nitrification. If the aeration intensity was reduced, denitrification of the resultant nitrate took place.

From the experimental investigations of Pitman and co-workers, in South Africa chemical precipitation of phosphorus is now being used to treat anaerobic digester sludge at the Goudkoppies plant and sludge thickening dewatering liquor at the Northern Works plant in Johannesburg (Pitman, 1995). At Goudkoppies, waste activated sludge is thickened in a dissolved air floatation unit and primary sludge in gravity thickeners before undergoing combined anaerobic digestion. The anaerobically digested sludge is aerated to strip CO_2 (to cause the pH to increase and so stimulate struvite and calcium phosphate precipitation), lime is then added (for further precipitation) and the limed liquor is dewatered on belt presses. The liquors from the belt presses are clarified in separate thickeners and recycled to the head of the treatment plant. Table 2.2 shows the results from Goudkoppies plant as reported by Pitman (1995); the recycled digested liquors are low in P (1.1 mgP/ℓ) but still relatively high in N (120 mgN/ℓ). Methods therefore need to be devised to improve the N removal in these streams.

Table 2.2: Average results from Goudkoppies digested sludge conditioning plant (Pitman, 1995)

Parameter	Digested Sludge	Aerated sludge	Lime treated sludge	Liquors	Liquor thickener overflow
o-Phosphate (mgP/ℓ)	250	170	5.8	1.5	1.1
Ammonia (mgN/ℓ)	660	510	420	120	120
pH	7.1	7.7	9.2	8.9	8.9

At the Northern Works plant, after thickening in separate gravity thickeners, primary sludge and waste activated sludge are mixed via coarse bubble aeration. Lime is then added and the limed sludge is dewatered on belt presses. The liquor from the presses is clarified in gravity thickeners before recycling to the inlet of the primary settling tanks. Table 2.3 shows the quality of these dewatering liquors as reported by Pitman (1995). In this scheme both the concentrations of P and

N are relatively low (1.1mgP/ℓ and 9.4mgN/ℓ respectively). The lower N concentration than at Goudkoppies is probably due to the absence of anaerobic digestion at Northern Works which means the N content of the dewatering liquors will be lower (see Table 2.1).

Table 2.3: Quality of clarified dewatering liquors at Northern Works (Pitman, 1995).

Parameter	**Concentration (mg/ℓ)**
Suspended solids	23
Nitrate as N	0.5
o-Phosphate as P	2.2
Total Phosphorus as P	2.8
Ammonia as N	9.4
Kjeldahl Nitrogen as N	14

Clearly, the treatment schemes developed in Johannesburg by Pitman and co-workers are options for treating activated sludge de-watering liquors and anaerobic digester supernatants that have considerable merit. The successful implementation at full-scale would indicate that these options are practical. What is required is a greater understanding of the mechanisms operative in the systems, so that they can be optimally designed and operated. For this objective, the development of a mathematical model that incorporates the chemical, physical and biological processes operative in the scheme would be advantageous. The development of such a model and an experimental investigation into these type of treatment schemes to collect data required to calibrate and validate the model, are described in **CHAPTER 4: DEVELOPMENT OF A MATHEMATICAL MODEL** and **CHAPTER 5: EXPERIMENTAL INVESTIGATION: VALIDATION OF KINETIC MODEL**.

2.2.4 Trickling filter effluents

About half the sewage in sensitive catchments is treated in trickling filters, which do not remove significant concentrations of the nutrients N and P. The effluent from trickling filters therefore cannot be discharged directly to the receiving streams without further treatment. In 1985, a study was carried out on the removal of P and N compounds from trickling filter effluents (Brodisch, 1985). The study dealt with laboratory experiments on chemical P removal and bench and pilot plant studies on the removal of N by biological means. From this study it was concluded and recommended that:

- Orthophosphate can be effectively removed by chemical precipitation through pre-treatment, post-treatment or split treatment, the choice depending on the concentration of condensed phosphates at the point of chemical addition.

- Removal of nitrogenous compounds, especially through biological denitrification should be seen as part of a comprehensive upgrading process comprising facilities for chemical removal of P and COD and the possibility for biological denitrification. A pre-denitrification unit is recommended. Trickling filter effluent is recycled to the head of the works where it should be mixed with raw or settled sewage. In a following flash mixer, chemicals will be added to remove P and to improve floc forming in the subsequent denitrification tank. The raw sludge/denitrification solids should be removed in the primary settling tanks (PST) and the solids recycled to the denitrification reactor. The PST effluent should then go on to the trickling filters.

- Research is required on full-scale application of pre-biological filter denitrification, especially on the problem of settleability of the sludge and the capacities of the primary settlers to handle the increased flows and loads.

At present no data has been collected on full-scale treatment of trickling filter effluents. Innovative ways of utilizing old trickling filters when upgrading treatment works therefore need to be investigated and developed. This does not form part of this contract, but forms part of a proposal for a future research contract between WRC and UCT (K5/970).

2.2.5 Sludge disposal lagoon effluents

Waste sludge from small BNR treatment plants often is simply lagooned. Sludge lagoon supernatant, being high in N and P, is disposed of by irrigation around a treatment plant site as the only economic option. This practice can result in runoff contributing to surface water pollution. Also, in the long term, considerable ground water pollution can occur. For example, the surface P load at a 5 Mℓ/d plant irrigating a 1 ha site, is 70 times greater than that of applying non BNR sewage sludge at a maximum application rate of 8 t/ha/year. Solutions therefore need to be found for better treatment and disposal of these supernatants.

Treatment of these wastes is not considered in this contract, but the models and technologies developed in the contract for the other wastes above should find application to these types of wastes also.

2.3 ALTERNATIVE TREATMENT SYSTEMS - TECHNOLOGY EVALUATION

A review of the literature has been undertaken to identify possible alternative treatment systems, and is presented below.

2.3.1 STOWA sponsored investigation

From 1998 all wastewater treatment plants in the Netherlands have to meet strict guidelines for Total N removal; <10mgN/ℓ Total N for plants >20 000pe and <15mgN/ℓ Total N for plants <20 000pe. In examining options to improve N removal, from mass balance considerations at full-scale N removal treatment plants, it was found that anaerobically digested sludge dewatering and drying liquors (called reject waters) contained considerable N. Conventionally these liquors are recycled to the head of the treatment works and, even though they only contribute 2% of the flow to the works they can contribute up to 25% of the total N load to the activated sludge system (Janus and van der Roest, 1997). From a preliminary desk study of treatment options for the N-rich recycle stream, it was concluded that separate treatment of these streams probably would be more economical than upgrading the activated sludge system (RIZA/STOWA, 1992; Janus and van der Roest, 1997). Accordingly, the Dutch Foundation for Applied Water Research (STOWA) sponsored pilot-scale research with the objective of undertaking a technological and economic feasibility evaluation of various treatment processes to remove N from wastewater treatment plant reject liquor, such as activated sludge dewatering liquors, or anaerobic digestor supernatants. This was a broad based collaborative programme involving a number of Dutch local authorities (Utrecht, Amsterdam, Sluisjesdijk), consulting offices (DHV Water, Grontmij) and equipment manufacturers (NOELL, WATERGROUP, PAQUES and NALVA). Five different process technologies were evaluated experimentally at pilot scale (1-5 m^3 reactor sizes) viz.

(1) Membrane bioreactor.
(2) Biofilm airlift suspension reactor.
(3) Ammonia stripping (both air and stream stripping).
(4) Magnesium ammonium phosphate (MAP, i.e. struvite) precipitation with optional recycle (CAFR).
(5) Bioreactor without sludge recycling.

A series of seven reports (in Dutch) outlining technical process operating details and performance results have been produced by STOWA (STOWA, 1995a,b,c,d,e,f,g). These reports show the programme to have been thorough, detailed and comprehensive and undertaken at a scale that, from a financial point of view, could not readily managed in South Africa. The main features of the treatment schemes and some results from the pilot-scale studies are summarized below (for details the reader is referred to the series of reports):

(1) Membrane bioreactor

A drawback of the conventional activated sludge system is that the mixed liquor concentration limits the volumetric loading, with a concentration of 4-8gMLSS/ℓ being the maximum (this is primarily due to the operation of the secondary settling tank). Consequently, these systems require relatively large bioreactors. The use of membrane bioreactors overcomes this problem. In this system a membrane filtration unit is used instead of a secondary settling tank to separate the mixed liquor from the effluent. The use of membranes means (Van Dijk and Roncken, 1997):

- High biomass concentrations can be maintained in the bioreactor, 15-50gMLSS/ℓ; higher concentrations cause problems with viscosity, membrane fluxes and oxygen transfer.

- The temperature in the system is high, 35-40°C, because *inter alia* 80% of the energy input for membrane filtration is converted to heat; this temperature is optimal for most biological processes.

- Effluent suspended solids concentrations are low, due to the high efficiency of membrane separation.

The research on membrane bioreactors for the treatment of reject waters sponsored by STOWA took place at the sludge treatment plant at Sluisjesdijk. A schematic of the system used is shown in Fig. 2.1. The system consisted of separated nitrification denitrification reactors in-series with external carbon (methanol) addition for denitrification and alkalinity (NaOH) addition for pH control. Both reactors were pressurized to 2-5 Bar to (i) improve oxygen transfer efficiency of the aeration systems and (ii) drive the cross flow membrane filtration system for effluent extraction. The reactors operated at a temperature of 33-38°C due to the reasons set out above.

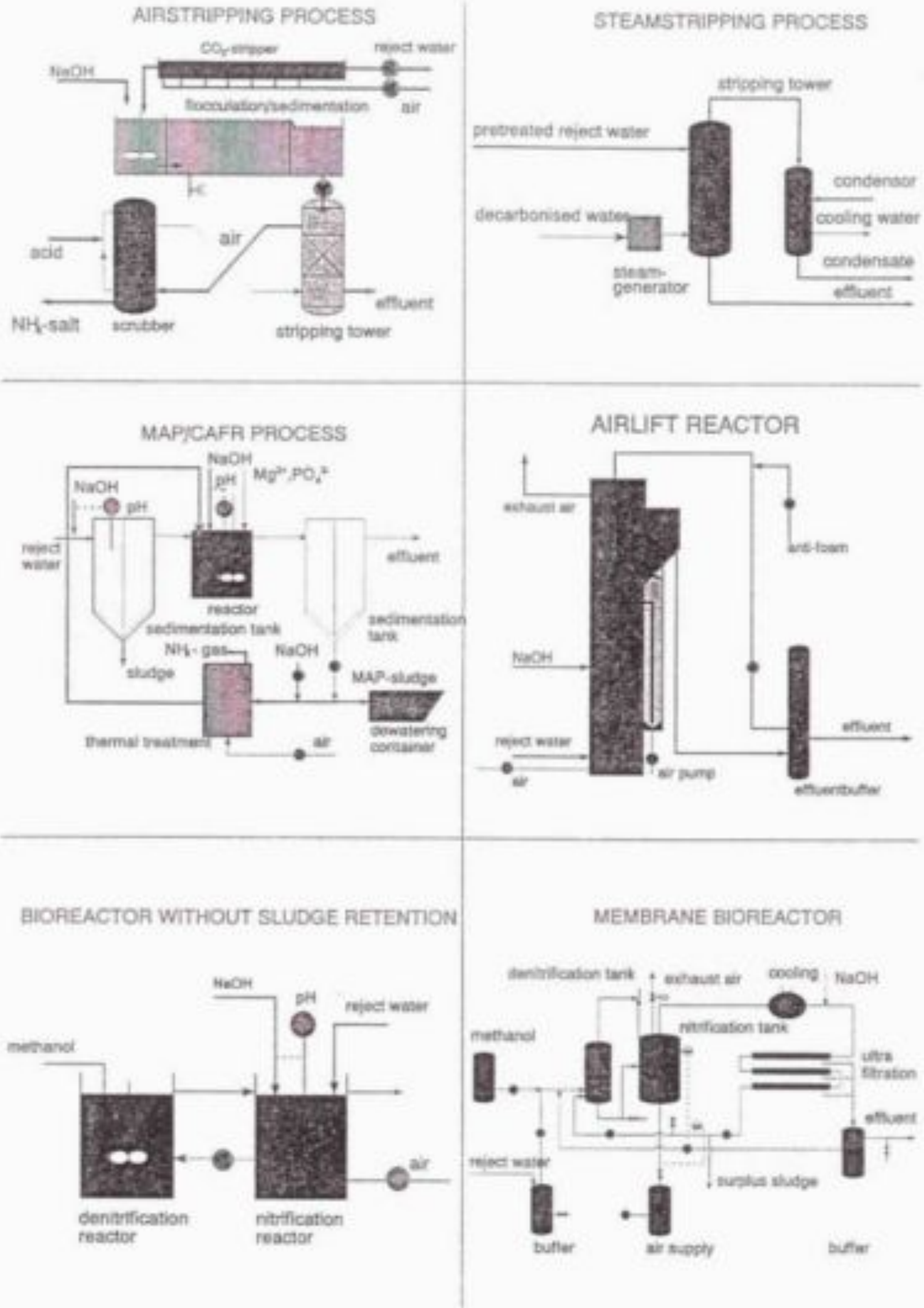


Fig 2.1: Schematic layout of treatment systems examined as part of the STOWA sponsored investigation into the treatment of reject water (Janus and van der Roest, 1997).

The research investigated maximum N load, variation in N concentration and the ultrafiltration (Janus and van der Roest, 1997). Oxygen transfer was found to be the limiting factor for nitrification. At an oxygen transfer rate of $1kgO_2/(m^3.h)$ the maximum N load for complete nitrification was $4.4kgN/(m^3.d)$. Maximum denitrification capacity was $9.8kgNO_3\text{-}N/(m^3.d)$.

(2) Airlift reactor

This is a fluidized bed system in which the biomass is adhered to a carrier material. The system consists of two parts, an airlift reactor with a three phase separator on top, see Fig. 2.1 (Tijhuis, 1994; Janus and van der Roest, 1997). The airlift reactor consists of two concentric tubes. Air is injected into the bottom of the inner tube (riser). The introduction of air in the riser (i) causes the mixed liquor and carrier medium supporting the biomass to flow upwards, (ii) mixes the three phases present in the riser (water, air and carrier material), and (iii) provides oxygen for biological oxidation of organics and for nitrification. At the top of the airlift reactor, the air, carrier medium/biomass (solids) and effluent are separated in a three phase separator. The carrier medium/biomass flows downward in the anoxic outer tube (down comer) where methanol is dosed for denitrification. In the airlift reactor, the biomass concentration can be up to 20 times higher than in conventional activated sludge systems.

Research into the airlift reactor took place at Utrecht. During the first phase the maximum nitrogen load at 90% nitrification was determined, and during the second phase the effect of varying the influent N concentration was studied.

Results indicated oxygen transfer as the limiting factor for nitrification. In the pilot plant (8m high), at 90% nitrification the maximum N load was $2.8kgN/(m^3.d)$. In scale-up, the increase in oxygen transfer with the increased height needs to be taken into account. For a full-scale installation 15m high, at 90% nitrification the maximum N load was estimated to be $3.3kgN/(m^3.d)$. During the research, denitrification could not be achieved. Consequently, if nitrate removal is required, a separate denitrification reactor would have to be installed.

(3) Ammonia stripping

The principle for ammonia stripping is as follows: Nitrogen in reject waters is mainly present as ammonium (NH_4^+). By increasing the pH, the ammonium is converted to ammonia (NH_3). When the water is contacted with a gas phase, the NH_3 will be transferred from the water to the gas phases (stripping). This stripping process usually takes place in a stripping tower, in which the water and gas flows are in opposite directions, i.e. counter current. The tower contains some kind of packing material to ensure a high contact surface area and so improves the stripping rates.

Both air and steam stripping were researched, see Fig. 2.1 (Janus and van der Roest, 1997). The difference between these two processes lies essentially in (i) use of air versus steam for stripping and (ii) the treatment of the ammonia rich gaseous stream. In air stripping, the ammonia rich gas stream is either scrubbed with acid to produce an ammonia salt, or combusted to produce nitrogen gas. In steam stripping, the gas stream is condensed to produce aqueous ammonia which is concentrated by reflux. It is essential for ammonia stripping towers that CO_2 is removed before stripping to avoid chemical fouling of the towers with calcium carbonate.

The research took place at Utrecht and Amsterdam. During the research the effects of the following process conditions were studied:

- pH
- temperature
- gas/liquid ratio
- N concentration

The experimental results were used to derive design guides for dimensioning the stripping processes. The height of the stripping tower is given by the specific height of one mass transfer unit (HTU) and the number of transfer units (NTU). For air stripping at 50°C a value for HTU of 0.7-1.0m was determined. For steam stripping, the HTU was 0.4m. The NTU was dependent on the influent N concentration and the required removal efficiency. Acid scrubbing at pH<3.5 resulted in almost complete removal of NH_3 from the ammonia rich gas stream. The results of catalytic combustion indicated that at combustion temperatures > 275°C the NH_3 removal from the gas stream was complete. At temperatures >310°C, the NO_x concentration no longer complied with Dutch regulations. In the application of steam striping, about 70% of the heat capacity available in the NH_3 vapour could be reused, resulting in considerable energy savings.

(4) Magnesium ammonium phosphate (MAP, i.e. struvite) precipitation with optional recycle (CAFR).

This system is based on forming an insoluble magnesium ammonium phosphate (MAP, $MgNH_4PO_4$) precipitate which is then settled out from the water stream. The process in effect operates as an ammonium concentrator, see Fig. 2.1. In the first stage, the ammonia is captured in solid MAP: The pH of the reject water is increased with NaOH to 8.5-10 where the solubility product of MAP is exceeded and MAP will accordingly precipitate. The precipitate is settled in a gravity settler. The reject water then flows to a reactor. Since the reject water contains high concentration of ammonium, but low concentrations of magnesium and phosphate, these compounds are added to the reject water in the reactor, to remove the remaining ammonium. With NaOH addition, the pH is again adjusted and MAP precipitates. The solid MAP is then separated by gravity settling. In order to save chemicals the Chemische Ammonium Fallung and Rezykherung (Chemical ammonium precipitation and recirculation) process (CAFR) was developed and is used as the second stage. Here the concentrated MAP is redissolved at 90°C, the ammonia is stripped and captured as condensate and the Mg and PO_4 rich water is recycled to the reactor thereby reducing the quantity of these chemicals that has to be added.

The research focussed on finding the optimal process conditions for the MAP process and the feasibility of recycling the treated MAP sludge in the CAFR process. The experiments were done at laboratory-scale. From the results it was concluded that at pH>9.5 the removal efficiency exceeds 90%. The optimum molar ratio of Mg:N:P was 1.1:1:1. Thermal treatment of the MAP sludge resulted in re-usable chemicals. Due to practical problems the CAFR process could not be tested at pilot-scale: In the configuration of the pilot plant, most of the NH_3 in the treated MAP sludge was recycled to the MAP reactor, which resulted in poor performance.

(5) Bioreactor without sludge recycling

This is a continuos flow-through (i.e. no sludge settling and recycle) system with separate nitrification and denitrification reactors, see Fig. 2.1. The reject water enters the aerobic nitrification reactor, which is dosed with NaOH for pH control. The nitrified reject water flows to a denitrification reactor where methanol is dosed for denitrification. The process is operated at elevated temperature to increase nitrification and denitrification rates.

The system was studied at pilot-scale. A stable and optimal TKN removal of 95% was achieved under the following conditions:

- aerobic hydraulic retention time: 2.5d
- anoxic hydraulic retention time: 1.25d
- process temperature: 35°C
- pH: 7.0

Economic evaluation

DHV were commissioned by STOWA to evaluate the different research projects (STOWA, 1995g; Janus and van der Roest, 1997). Based on results from the research projects, full-scale installations for the different treatment options were designed. For treatment capacities of 100 000pe and 400 000pe, investment and operating costs were calculated. The different treatment options were compared based on:

- cost,
- chemical requirements,
- energy requirements,
- operational experience, and
- process reliability.

For example, in Fig. 2.2, the cost per kgN removed for the capacity of 400 000pe is shown for different influent nitrogen concentrations. At low influent N concentrations (<≈800mgN/ℓ), air stripping and the bioreactor without recycle are most cost effective, while at higher influent N concentrations steam stripping and the membrane bioreactor system are also attractive options.

2.3.2 Technical University of Delft systems

Also in response to the Dutch national water quality standards, the Technical University of Delft has developed two new biological processes for removal of N:

(1) SHARON :- **S**ingle reactor system for **H**igh activity **A**mmonia **R**emoval **O**ver **N**itrite (Brouwer, 1995), and
(2) ANAMMOX :- **An**oxic **amm**onium **ox**idation process (van de Graaf and Robertson, 1994).

The principles of these two systems are described below:

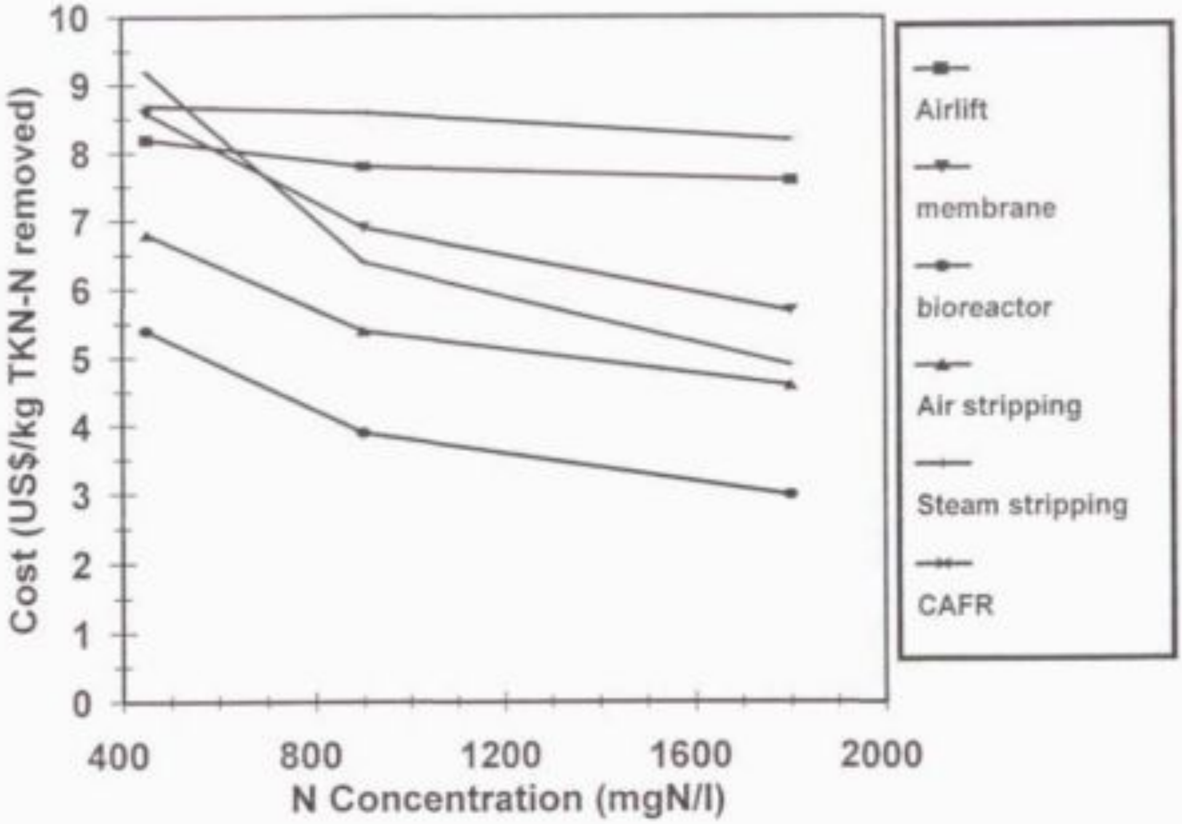


Fig 2.2: Cost per kgN removed versus nitrogen concentration for the options examined as part of the STOWA sponsored investigation into the treatment of reject water; capacity 400 000p.e. (Janus and van der Roest, 1997).

(1) SHARON

In this biological process ammonia is selectively oxidized to nitrite by preventing the subsequent (usual) oxidation of the nitrite to nitrate. This is achieved by operating the system such that the nitrite oxidizers are "washed out" of the system; the system is operated at a high temperature (30-40°C) and pH (7-8). Under these conditions the nitrite oxidizers have lower specific growth rates that the ammonia oxidizers, and thus by controlling the solids retention time (sludge age) the ammonia oxidizers can be selectively maintained in the system while the nitrite oxidizers are washed out. The system is operated as flow-through (without sludge settling and recycle) so that the sludge age equals the hydraulic retention time; because of the high temperature the retention time is relatively short (≈1-2d). By nitrifying to nitrite only there is considerable saving on aeration costs. However, due to the high half saturation coefficient for ammonium the effluent ammonium concentration can be quite high (≈100mgN/ℓ). Therefore SHARON is best suited to treat warm wastewaters with high ammonia concentrations (>500mgN/ℓ), Jetten *et al.* (1997).

The resultant nitrite from the SHARON process can be denitrified conventionally to dinitrogen thereby saving on carbon or the system can serve as the nitrite generator for the anammox system, described below.

(2) ANAMMOX

This is a biological system where ammonia serves as an electron donor and nitrite as electron acceptor giving rise to ammonia removal and nitrite denitrification respectively in the absence of oxygen (Strous *et al.*, 1997a,b). The mechanism is:

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \tag{2.1}$$

This process has potential application to wastes with high nitrogen and low carbon concentrations, since denitrification can be achieved without the need for organics. Unfortunately, the process requires a long solids retention time (>50d) since the organisms have very low growth rates and biomass yields, nitrite is required to serve as electron acceptor (usually not readily available) and nitrite can be toxic to the system.

2.3.3 Other processes

Removal of nitrate nitrogen by denitrification using elemental sulphur as electron donar has been proposed (Neytzell-De Wilde, 1979; Koenig and Liu, 1996). This process is mediated by *Thiobacillus denitrificans* as follows (Koenig and Liu, 1996):

$$NO_3^- + 1.10S + 0.40CO_2 + 0.76H_2 + 0.08NH_4^+ \rightarrow 0.5N_2 + 1.10SO_4^{2-} + 1.28H^+ + 0.08C_5H_7O_2N \tag{2.2}$$

From the equation above, potential problems may be the production of sulphate, and that the nitrogenb must be in the nitrate form, i.e. the process requires a preceding nitrification step.

2.4 DISCUSSION

The brief review above indicates that a number of different methods have been developed for the treatment of high nutrient low organic carbon wastewaters:

- Precipitation methods usually aided by cation supplementation are in use in South Africa at Goudkoppies and Northern Works to remove nutrients from anaerobic digester supernatant and activated sludge dewatering liquor respectively. This removes the phosphorus to relatively low values, but the ammonia concentrations in the anaerobic digester liquors may still be high (120mgN/ℓ), requiring further treatment.

- A number of treatment systems have been developed overseas that are not in use in South Africa. While each of these systems has its own particular advantages and disadvantages, in general the systems have been developed for the removal of N and not P. Only the CFAR system has the immediate potential for both N and P removal; however, evaluation in the Netherlands indicates that most likely the CFAR system will not be economically feasible.

- In this category of wastes, the imbalance between the nutrients (N & P) and organic carbon would suggest that treatment using combined biological, chemical and physical processes may be the best option for the removal of both N and P. Combined biological, chemical and physical processes are not well understood. In particular the interaction between the processes are poorly defined. It is therefore imperative that a model incorporating the biological, chemical and physical processes be developed to give a better understanding of the processes, to form a basis for design of treatment plants; this aspect is reported on in Chapter 3.

- Specific experimental investigations to be undertaken have been identified, namely, treatment of:
  - (i) Waste activated sludge dewatering liquors and anaerobic digestor supernatants, by combined chemical/physical and chemical/biological/physical methods.
  - (ii) Landfill leachates in activated sludge systems receiving municipal wastewaters.
  - (iii) Septic tank effluents in conventional BNR removal activated sludge systems.

  Research on (i) is reported in Chapter 4 together with the validation of the mathematical model, research on (ii) is reported in Chapter 5 and on (iii) in Chapter 6.

Fig 2.1: Schematic layout of treatment systems examined as part of the STOWA sponsored investigation into the treatment of reject water (Janus and van der Roest, 1997).

Fig 2.2: Cost per kgN removed versus nitrogen concentration for the options examined as part of the STOWA sponsored investigation into the treatment of reject water; capacity 400 000p.e. (Janus and van der Roest, 1997).

CHAPTER 3

DEVELOPMENT OF A MATHEMATICAL MODEL

3.1 INTRODUCTION

For the design and operation of, and research into conventional biological wastewater treatment systems, mathematical models have proved to be invaluable as a process evaluation tool (e.g. Dold *et al.*, 1980, 1991; Henze *et al.*, 1987). Mathematical models provide quantitative descriptions of the wastewater treatment system. By providing quantitative descriptions, they allow predictions of the system response and performance to be made. From the predictions, design and operational criteria can be identified for optimization of system performance. Also, mathematical models are very useful as research tools. By evaluating model predictions, it is possible to test hypotheses on the behaviour of the wastewater treatment system (e.g. biological processes, their response to system constraints, etc.) in a consistent and integrated fashion. This may direct attention to issues not obvious from the physical system, and lead to deeper understanding of the fundamental behavioural patterns controlling the system response. In essence, mathematical models can provide a defined framework which can direct thinking (design, operation or research).

Recognising the usefulness of mathematical models, it was decided to develop a model that will include the processes that can be expected to be operative in systems treating high nutrient low organic carbon wastes. Research on this development is summarised in this Chapter; for details, the reader is referred to Musvoto *et al*. (1998).

3.2 MODELLING TASKS

To aid the design and operation of, and research into conventional biological suspended biomass wastewater treatment systems, a variety of mathematical models have been developed. With few exceptions, these models have focused almost exclusively on the biologically mediated processes that lead to the removal of, or change in, the particular compounds of interest. For example, models for the activated sludge system have progressively included the biologically mediated processes of COD removal, nitrification, denitrification and biological excess phosphorus removal (Dold *et al.*, 1980; 1991; Van Haandel *et al.*, 1981; Henze *et al.*, 1987; Wentzel *et al.*, 1992; Henze *et al.*, 1995). In this group of models, by focusing on the biological processes usually it is implicitly assumed that: (i) The biological processes dominate the system response and that (ii) chemical and physical processes (e.g. precipitation and gas stripping respectively) play an insignificant role compared to the biological processes and accordingly can be neglected, (iii) compounds not directly involved in the biological processes or not of interest, even though present, do not significantly influence the behaviour, and (iv) the biological processes take place within a regime of constant pH. This has restricted application of these models to situations where the assumptions remain valid. For the activated sludge system treating municipal or similar types of wastewaters, where the organics are present at relatively high concentrations compared to the nutrient (N & P) concentrations, these assumptions usually are valid. For example, in the nitrification of municipal wastewaters it usually is reasonable to assume that the biological processes dominate and that there is sufficient buffer capacity present to absorb the generation of hydrogen ions (H^+) and loss of CO_2 so that the pH does remain approximately constant; some of the models have included the parameter "Alkalinity" to check that this condition is in fact true (e.g. Dold *et al.*, 1991). However, in the treatment of a number of wastewaters the assumptions are not valid and the models cannot be applied. For example, in the nitrification of wastewaters with low buffer capacity and/or high N concentrations, or in the treatment of wastewaters where the generation or utilisation of short-chain fatty acids (SCFA), e.g. acetic, propionic, is significant, the assumption that the pH remains essentially constant no longer can be accepted.

In particular, the models cannot be applied to situations where chemical and physical processes do play a significant role, and so cannot be neglected. One such category of wastewaters are the high nutrient low organic carbon wastewaters being investigated in this project, i.e. where the organics are present at relatively low concentrations compared to the nutrients. As noted in Chapters 1 and 2, these wastewaters are generated in a number of municipal waste treatment operations such as trickling filter effluents, anaerobic digester supernatants, activated sludge dewatering liquors, landfill leachates, septic tank effluents and waste sludge lagoon effluents. From the review in Chapter 2, in the treatment of these wastewaters, chemical and physical processes can be expected to play a significant role and no longer can be neglected; these processes and their interactions with each other and with the biological processes will have to be included in any model of these treatment systems. In other words, a model integrating the biological, physical and chemical processes of importance will be required. Deterministic models that quantitatively describe the stoichiometry and kinetics of the biological processes are well advanced, e.g. IAWQ Model No. 1 (Henze *et al.*, 1987; Dold *et al.*, 1991) and No. 2 (Henze *et al.*, 1995). Similar models need to be developed for the chemical and physical processes, and integrated with the biological models. Models including chemical and physical processes will require that the pH parameter/compound is incorporated and accurately determined, as pH is of fundamental importance in these processes, significantly influencing them.

From the discussion above, it is evident that application of the existing biological models can be enhanced by including ***pH as a parameter/compound***. Futher, including the pH will facilitate the integration of chemical and physical processes into the biological models, and the development of independent physical/chemical models. Including pH requires that all the weak acid/bases present that influence the pH (e.g. carbonate system, SCFA) have to be included. Also, any interactions between the biological, chemical and physical processes and the pH and weak acid/bases have to be included.

Thus, to develop an integrated biological/chemical/physical model describing the treatment of high nutrient low organic carbon wastes, the following general tasks can be identified:

- Identify approaches/mechanisms to include pH as a compound in the model.
- Identify the biological, chemical and physical processes that can be expected to be operative in the treatment of these wastes, and the compounds on which these processes act. In particular, attention will have to be given to the interaction between the processes and the compound pH.
- Conceptualize a mechanistic model that qualitatively describes the kinetic and stoichiometric behaviour of the processes and compounds.
- Formulate mathematically the kinetic rates for the biological, chemical and physical

processes, and their stoichiometric interactions with the compounds.
- Combine the biological, chemical and physical processes into an integrated model.
- Set up a solution procedure that includes process rates, stoichiometry and transport.
- Calibrate, refine and validate the integrated model, by comparing predictions against experimental data. Wherever possible data available in the literature should be used; where this is not available experiments will have to be conducted to gather the data.

These tasks can not be completed sequentially, but rather the model tends to evolve with the tasks being undertaken interactively. For example, to identify processes and compounds, one needs to have some initial conceptualization of the system behaviour, i.e. a rudimentary conceptual model. As more information becomes available from model application and testing, aspects of the rudimentary model are improved as new compounds and processes are identified for inclusion, or processes already included are modified. This certainly was the case for the integrated model developed here.

3.3 RESEARCH APPROACH

The complexity of the integrated model caused that it could not be developed as a single entity, but it had to be developed in sections which were integrated as the model progressed. The following sections were identified for development:

1. **Single phase aqueous systems only, viz.:**
    1.1 Aqueous mixed weak acid/base systems including carbonate, phosphate, ammonia and SCFA species without phase (liquid/gas, liquid/solid) changes.
    1.2 Biological processes of carbon (C), nitrogen (N) and phosphorus (P) removal and their interaction with alkalinity/pH/weak acid/bases.

2. **Two phase systems:**
    2.1 solid/aqueous
        - chemical precipitation - particularly, calcium carbonate, struvite and calcium phosphate, but also any other compounds of relevence.
    2.2 gas/aqueous
        - gas stripping of ammonia, carbon dioxide and nitrogen gas
        - biological production /utilization of carbon dioxide and nitrogen gases

3. **Three phase systems:**
    3.1 Solid/liquid/gas
        - integration of the above.

3.4 PRELIMINARY TASKS

Before modelling could commence, two preliminary tasks had to be completed:
- How to solve the complex model equations.
- How to incorporate pH as a parameter/compound in the model.

Completion of these tasks is described in this section.

3.4.1 Solution procedure

To integrate the biological, physical and chemical transformation processes with the system parameters (e.g. inflows, reactor configuration, operation), and solve the resultant complex equations, a computer programme is required. Two options were considered; commercially available software and writing a computer programme specific for the model being developed. These options are discussed below.

(1) Using existing commercially available computer programs

There are two types of commercially available programmes; in the first type the model is coded into the programme and can not be changed (e.g. SIMWORKS, GPX, BIOWIN) and in the second type the model itself forms part of the input to the programme. Since a new model was being developed, only the second type option was considered. Two existing computer programs of this type were identified for further investigation: Activated sludge SIMulation program (ASIM, Gujer and Larsen, 1995), and the computer program for the Identification and Simulation of Aquatic Systems (AQUASIM; Reichert, 1994).

ASIM was developed for use as a teaching tool for courses on the simulation of the dynamic behaviour of modern nutrient removal activated sludge systems. It allows for the definition of a biokinetic model, the flow scheme, process control strategies and load variation (Gujer and Larsen, 1995). To define and input the biokinetic model, the user selects from a list of possible kinetic expressions. The listed expressions are first and second order kinetics, Monod kinetics, adsorption kinetics and inhibition kinetics. The user is limited to use these specific kinetic expressions and there is no facility to put in alternative expressions. This restriction has made ASIM unsuitable for the proposed model, where expressions other than those available in ASIM were required to fully describe the chemical processes.

AQUASIM was developed to allow its users to perform simulations using different models, to assess their applicability and to estimate the values of model parameters (using measured data), and to estimate prediction uncertainty (Reichert *et al.*, 1995). The user can define the spatial configuration of the system to be investigated as a set of compartments (which can be connected by links) and specify any set of state variables and transformation processes to be active within the compartments. This flexibility in specifying the variables and transformation processes made AQUASIM ideally suited for the proposed model development. AQUASIM was purchased for solving the model and has proved capable of incorporating all the biological, chemical and physical processes identified for inclusion in the model.

(2) Writing a computer program to suit the model

Writing one's own programme code is enormously time consuming with relatively little of this time devoted to the main point of interest, i.e. integrated chemical, physical and biological modelling - most of the time is required for peripheral coding, such as management of data input and output, graph plotting, etc. Accordingly, since the commercially available programme AQUASIM was suitable for our use, this option was not followed.

3.4.2 Including pH as a compound in the model

In formulating the model, integration of the biological, physical and chemical processes presented perhaps the greatest challenge. In particular, including chemical and physical processes meant that the pH had to be included in some fashion in the model: The rates of the precipitation/dissolution and gas stripping reactions depend on the concentrations of the specific chemical species, which in turn depend on the total species concentration and pH. Including the pH in turn required that all the weak acid/bases present that influence the pH (e.g. carbonate, SCFA) also had to be included. That is, weak acid/base chemistry had to form an integral part of the model. To include weak acid/base chemistry and pH, initially it was thought that perhaps an equilibrium chemistry based approach could be followed.

3.4.2.1 Equilibrium chemistry based approach to include pH in the model

Conventionally, in working with mixed weak acid/base systems one is confronted with three types of problems (Loewenthal *et al*., 1989), viz.:

- estimation of the concentrations of the species of each of the weak acid/base systems, called characterization;
- estimation of the amount and type of chemicals to be added/removed to change the pH and/or species concentration to desired values, called dosing estimation; or conversely,
- estimation of the final state of a water after addition/removal of a known amount of a specified chemical to/from a known initial state.

Including weak acid/base chemistry and pH in models for application to waste-water treatment systems would encompass elements of all three types of problems. Both numerical and graphical solution procedures to address these types of problems have been developed (e.g. Loewenthal *et al*., 1989; 1991). These procedures are based on equilibrium chemistry. The basis for these procedures will be described *briefly* below, to assess their potential for use; the intention is not to provide an exhaustive review, the reader is referred to the cited texts for details.

On addition to water a weak acid/base will dissociate; for example, consider the weak acid/base HA:

$$HA \rightleftharpoons H^+ + A^- \qquad (3.1)$$

The degree of dissociation will depend on the pH, dissociation constants, the total species concentration of the weak acid/base and the ionic strength of the solution. Conventionally, it is accepted that the rate of dissociation is so rapid that the weak acid/base is at equilibrium, with the rates of the forward and reverse dissociation reactions being equal. Accepting the equilibrium condition, by using equilibrium chemistry the weak acid/base individual species concentrations can be formulated in terms of total species concentration, dissociation constants and pH (Loewenthal *et al*., 1989). Thus, if the total species concentrations of each of the weak acid/bases present are known and the pH has been measured, then the concentrations of the dissociated and undissociated species for each of the weak acid/bases can be calculated via the appropriate dissociation and mass balance equations. With each of the weak acid/base species determined, the solution is completely characterized.

Thus, to completely characterize the solution, the pH and total species concentrations of all the weak acid/bases are required. Usually the pH is available via potentiometric pH measurement; total species concentrations for each of the weak acid/bases in solution can be measured by conventional wet chemical techniques (e.g. ammonia, phosphate, SCFA) or by specialized techniques such as chromatography (e.g. SCFA) and inorganic carbon analyser (total carbonate species). However, measurement of total carbonate (C_T) using the inorganic carbon analyser presents problems - the instrument is highly specialized, difficult to operate and only available in large laboratories. Furthermore, measurements of C_T with this instrument are very likely to be in error, due to CO_2 loss/gain on sampling. The practical difficulties in measuring C_T have led to the development using equilibrium chemistry of a substitute parameter, $H_2CO_3^*$ alkalinity; if $H_2CO_3^*$ alkalinity and pH are known, C_T can be determined (Loewenthal and Marais, 1976; Loewenthal et *al.*, 1986). Methods to determine $H_2CO_3^*$ alkalinity from a total alkalinity titration of solutions containing only the carbonate weak acid/base and mixtures of weak acid/bases have been developed (Gran, 1952; Loewenthal *et al.*, 1989; Moosbrugger *et al.*, 1992). The $H_2CO_3^*$ alkalinity has the merit that CO_2 loss does not affect its value (provided that carbonate precipitation does not take place).

Accordingly, with mixtures of weak acid/bases in solution, provided the appropriate measurements (pH, total species concentrations, total alkalinity, and hence $H_2CO_3^*$ alkalinity) are available, through the use of equilibrium chemistry it is possible to completely characterize the solution. Having characterized the solution, the next important aspect is to determine the chemical type and dosage to achieve a final desired state (also called dosing estimation) or conversely to determine the final state of a water after addition/removal of a known amount of a specified chemical; both these problems are collectively termed chemical conditioning and are of direct relevence to the model being developed here. ***In chemical conditioning the principle difficulty is that the pH does not change in a simple stoichiometric fashion*** with changes in concentrations of the weak acid/bases, that is, with addition or removal of strong or weak acid/base species. To overcome this problem, chemical conditioning estimation procedures have been developed using equilibrium chemistry (e.g. Loewenthal *et al.*, 1991). In terms of these procedures, it is recognized that the *solution* alkalinities do change in a simple stoichiometric fashion with chemical dosing, as do the total species concentrations of the weak acid/bases. Knowing the *solution* alkalinity and the total species concentration of each weak acid/base, the pH can be calculated from equilibrium chemistry, or, knowing the pH and all capacity parameters except one (e.g. one total species concentration), the unknown capacity parameter can be calculated from equilibrium chemistry.

From the above, for aqueous systems where only chemical and physical processes take place, by using an equilibrium-based chemistry approach that includes the concepts of alkalinity, chemical conditioning problems can be largely resolved. This would suggest that a similar approach may be successful for integrating weak acid/base chemistry into the kinetically based biological models. In concept this approach would be as follows (see Fig. 3.1): Solution alkalinity would be included as a compound in the model. Any kinetic transformation would act on the compounds and the solution alkalinity, changing their concentrations. Knowing the new solution alkalinity and total species concentrations of all the weak acid/base systems present (e.g. SCFA, ammonium, phosphate, carbonate), the pH can be calculated using equilibrium chemistry. The calculated pH then can be used to speciate the weak acid/bases, i.e. determine the concentrations of the individual species making up the weak acid/base (e.g. NH_4^+ and NH_3 making up the ammonia/ammonium weak acid/base). The kinetic transformations, the rates of which depend on the concentrations of individual weak acid/base species, then act on the compounds (including the weak acid/base species) and the solution alkalinity. The cycle is repeated at every time/space step until a "steady state" solution is reached (i.e. constant compound concentrations and pH for the time/space step). However, although in concept this approach is feasible, it does present practical difficulties in implementation:

- The equilibrium-based chemical conditioning algorithms have been developed for situations where the total species concentration of a single or few weak acid/bases is changed in a simple fashion by adding or removing species; in the integrated weak acid/base chemistry and biological models, a number of different processes will act on the total species concentrations of a number of weak acid/bases simultaneously. This makes solution of the equilibrium-based algorithms difficult.

- In the equilibrium-based chemical conditioning algorithms, the reference species for the solution alkalinity have to be carefully selected, so that the solution alkalinity stays constant or changes in a simple stoichiometric fashion with dosing (Loewenthal *et al.*, 1991). However, in the integrated models to be developed it may not prove possible to select reference species *ab initio*, since there is no surety as to which species will change. Furthermore, the species that do change will vary from situation to situation, so that new reference species would have to be selected for each particular case, an undesirable event. Lastly, processes may act on both the dissociated and undissociated weak acid/base species simultaneously so that selection of the correct reference species may not be obvious, or even possible.

- Combining equilibrium chemistry with kinetic-based models is neither convenient nor efficient: The repeated calculations necessary to reach a "steady state" solution between the kinetics and equilibrium chemistry probably would cause any solution procedure to be unacceptably slow; in fact, there is not even surety that a "steady state" solution would be reached.

Due to the difficulties with the traditional equilibrium chemistry based approach to modelling weak acid/base systems as described above, it was decided to develop a new approach, based on kinetics.

3.4.2.2 Kinetic based approach to include pH in the model

As an alternative to the traditional equilibrium chemistry-based models for mixed weak acid/base systems, a kinetic-based model would seem to offer considerable advantages: Using a kinetic-based modelling approach will resolve the difficulties identified above with the equilibrium chemistry approach; in particular, a kinetic-based model would expedite integration with the existing biological models, and extension to include chemical and physical processes, both important requirements identified for the model. In this section the principles of such an approach are described.

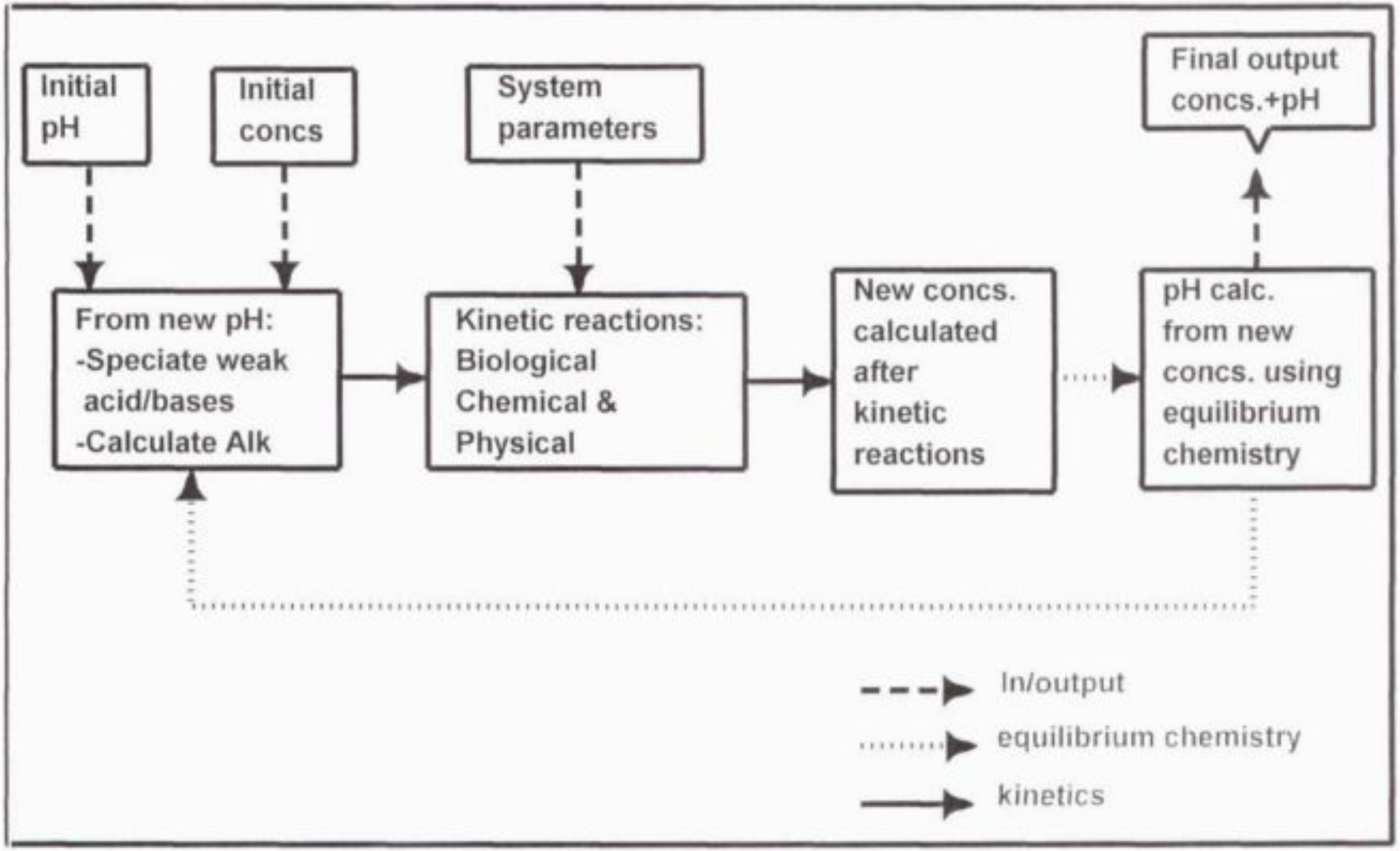


Fig 3.1: Schematic representation of Alkalinity approach to including pH in the model.

From the discussion in the previous sections above, it is evident that the principle requirement for a mixed weak acid/base chemistry model is that the pH is accurately determined. In a kinetic-based modelling approach, H^+ is included explicitly in the model as a compound (in mole units); pH can be calculated directly from H^+ via $pH = -\log (H^+) = -\log f_m [H^+]$. Further, all weak acid/base species that significantly influence the pH are included as compounds (in mole units), and weak acid/base equilibria are described in terms of the kinetics of the forward and reverse reactions for the dissociation of these weak acid/bases. For example, consider the dissociation for the ammonium/ammonia weak acid/base. The dissociation equation is given by:

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \tag{3.2}$$

The rate of the forward reaction is:

$$r_f = K_f(NH_4^+) = K_f f_m [NH_4^+] \tag{3.3a}$$

$$= K_f'[NH_4^+] \tag{3.3b}$$

where:

r_f = rate of forward reaction
K_f = specific rate constant for the forward reaction
$()$ = activity
f_m = monovalent activity coefficient (see Loewenthal *et al.*, 1989 and Musvoto *et al.*, 1998)
$[\,]$ = molar concentration
K_f' = apparent specific rate constant for the forward reaction

and the rate of the reverse reaction is:

$$r_r = K_r (NH_3)(H^+) = K_r f_m [NH_3] f_m [H^+] \tag{3.4a}$$

$$= K_r' [NH_3][H^+] \tag{3.4b}$$

where:

r_r = rate of reverse reaction
K_r = specific rate constant for the reverse reaction
K_r' = apparent specific rate constant for the reverse reaction.

The dissociation equation for the ammonia/ammonium weak acid/base can be represented by these two half reactions and both kinetic equations are included in the model as separate processes. Similarly, the kinetics of the forward and reverse dissociation equations for all weak acid/bases of importance are included. The apparent specific rate constants of the forward and reverse dissociation reactions are selected such that the rates are so rapid that equilibrium can be considered to be reached effectively instantaneously. Further, the ***relative*** values for the apparent specific rate constants will determine what that equilibrium condition will be. Thus, through careful selection of the apparent specific rate constants of the forward and reverse reactions for all the weak acid/base dissociation reactions, the concentrations of all the weak acid/base species will effectively be at a "pseudo-equilibrium", and their "equilibrium" concentrations can be made to correspond to those determined by true equilibrium chemistry. Since H^+ (and correspondingly pH) is included as a compound in the model, and also is included in the kinetic equations for the dissociation reactions, its value at the "pseudo-equilibrium" also will be calculated. If any of the weak acid/base species is added or removed from solution (including H^+), the kinetic equations for the forward and reverse dissociation reactions will cause the relative species concentrations (including H^+) to readjust very rapidly (effectively instantaneously) to the new condition. Since all the weak acid/bases have the species H^+ in common, all would be influenced and so readjust. In this manner a new "pseudo-equilibrium" condition is established.

The values of the apparent specific rate constants for the forward and reverse reactions that give rise to weak acid/base species concentrations that correspond to true equilibrium chemistry can be determined from the equilibrium constant. For the same ammonia/ammonium system, from the law of mass action, at equilibrium:

$$r_f = r_r \tag{3.5a}$$

$$K_f' [NH_4^+] = K_r' [NH_3] [H^+] \tag{3.5b}$$

$$\therefore K_f'/K_r' = [NH_3] [H^+]/[NH_4^+] = K_n' \tag{3.5c}$$

where:

K_n' = apparent equilibrium constant for the ammonium system.

Since the forward and reverse dissociation reactions are very rapid, the rate of the reactions cannot be measured. However, from a practical point of view, the exact actual value for the reaction rate is of little importance. In selecting values for the apparent specific rate constants, to ensure the reactions are effectively instantaneous, one of the rate constants (K_r') was given a very high theoretical value such that the new "equilibrium" was achieved in < 2 s. To ensure that the kinetically established equilibrium corresponds to true equilibrium chemistry, the value for the other rate constant (K_f') was calculated through the relationship with the apparent equilibrium constant, Eq. (3.5c), i.e. $K_f' = K_n' \cdot K_r'$. (More details on selection of the rate constants are given by Musvoto *et al*., 1998).

One advantage of this approach over the alkalinity/equilibrium chemistry approach is that kinetics are used throughout; kinetic expressions can be readily incorporated into the computer programme AQUASIM. Furthermore, ***the approach is general, and can be applied to include any weak acid/base in the model.***

3.5 MODEL DEVELOPMENT

Having successfully resolved the problems of solving the model and including H^+ (pH) as a compound, attention could be focussed on model development. As noted above in **Section 3.3 RESEARCH APPROACH**, the model was developed in sections, which then were integrated. Development of these sections and their integration is described below.

3.5.1 Single phase aqueous systems

3.5.1.1 Mixed weak acid/base systems

Since pH is to be incorporated in the model as a compound (via H^+), the interactions in the aqueous state between the weak acid/bases and pH also need to be included. The approach to do this using kinetics for the forward and reverse weak acid/base dissociation equations has been described above. Following this approach, in this task a model was developed to predict the chemical state of a single phase aqueous solution containing carbonate, ammonium, phosphate, and SCFA weak acid/bases. The model, represented in matrix notation is shown in Table 3.1(a). Kinetic constants for model simulations are listed in Tables 3.1(b) and (c); details on selection of the kinetic constants are given by Musvoto *et al.* (1998).

The validity of this model and the approach on which it is based needed to be tested. This was done by applying the model to chemical conditioning problems. Chemical conditioning of a solution involves determining, (i) the chemical type and dosage to achieve a desired change in the chemical state of a solution, and (ii) the final solution state after dosing a known amount of a specified chemical. In single phase aqueous problems, chemical conditioning is used mainly for (i) adjustment of pH/alkalinity/acidity of solutions by addition of weak or strong acids and bases, or salts of these (e.g. carbonate system in stabilisation of water supplies) and (ii) assessment of transient solution states during which precipitation/dissolution or gas exchange takes place (e.g. kinetics of precipitation/dissolution of solid $CaCO_3$). In the past, solving chemical conditioning problems has been achieved by using equilibrium chemistry based procedures (e.g. Loewenthal and Marais, 1976, 1983; Loewenthal *et al.*, 1986, 1991). These procedures have been extensively evaluated against a wide range of experimental data. Accordingly, to evaluate the model developed here using the kinetic based approach, the predictions were compared to the values calculated using the equilibrium based approach of Loewenthal and co-workers. The solution procedures of Loewenthal and co-workers have been applied to solve chemical conditioning problems in:

(1) **Systems dominated by the carbonate weak acid/base system**: (Loewenthal and Marais, 1976; Loewenthal *et al.*, 1986; 1988; Friend and Loewenthal, 1992)

(2) **Systems containing a mixture of weak acid/base systems**: (Loewenthal *et al.*, 1991)

The model was evaluated with both types of chemical conditioning problems. All model predictions were made using the computer program AQUASIM (Reichert, 1994; Reichert *et al.*, 1995). A number of comparisons were made between predictions with the kinetic based approach and those with the equilibrium based models of Loewenthal and co-workers for a wide range of conditions; in all cases excellent agreement was obtained. To illustrate, two examples of prediction for mixed weak acid/base systems using the model are given below:

Table 3.1(a): Matrix representation of the kinetic model for an aqueous mixture of weak acid/base systems. (Carbonate, ammonia, phosphate, short-chain fatty acid).

Compound → Process ↓		1 NH_4^+	2 NH_3	3 $H_2CO_3^*$	4 HCO_3^-	5 CO_3^{2-}	6 H^+	7 OH^-	8 H_3PO_4	9 $H_2PO_4^-$	10 HPO_4^{2-}	11 PO_4^{3-}	12 HA	13 A^-	Rate
1	Forward dissociation of NH_4^+	-1	1				1								$K'_{fn}[NH_4^+]$
2	Reverse dissociation of NH_4^+	1	-1				-1								$K'_{rn}[NH_3][H^+]$
3	Forward dissociation of $H_2CO_3^*$			-1	1		1								$K'_{fc1}[H_2CO_3^*]$
4	Reverse dissociation of $H_2CO_3^*$			1	-1		-1								$K'_{rc1}[HCO_3^-][H^+]$
5	Forward dissociation of HCO_3^-				-1	1	1								$K'_{fc2}[HCO_3^-]$
6	Reverse dissociation of HCO_3^-				1	-1	-1								$K'_{rc2}[CO_3^{2-}][H^+]$
7	Forward dissociation of H_3PO_4						1		-1	1					$K'_{fp1}[H_3PO_4]$
8	Reverse dissociation of H_3PO_4						-1		1	-1					$K'_{rp1}[H_2PO_4^-][H^+]$
9	Forward dissociation of $H_2PO_4^-$						1			-1	1				$K'_{fp2}[H_2PO_4^-]$
10	Reverse dissociation of $H_2PO_4^-$						-1			1	-1				$K'_{rp2}[HPO_4^{2-}][H^+]$
11	Forward dissociation of HPO_4^{2-}						1				-1	1			$K'_{fp3}[HPO_4^{2-}]$
12	Reverse dissociation of HPO_4^{2-}						-1				1	-1			$K'_{rp3}[PO_4^{3-}][H^+]$
13	Forward dissociation of HA						1						-1	1	$K'_{fa}[HA]$
14	Reverse dissociation of HA						-1						1	-1	$K'_{ra}[A^-][H^+]$
15	Forward dissociation of water						1	1							K'_{fw}
16	Reverse dissociation of water						-1	-1							$K'_{rw}[H^+][OH^-]$
	Units	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	

Table 3.1(b): Kinetic constants for weak acid/bases in mixed weak acid/base model [Table 3.1(a)]; f_m, f_d and f_t are mono-, di- and trivalent activity coefficients respectively, see Loewenthal *et al.*(1989); for pK values, see Table 3.1(c).

PROCESS	SPECIFIC RATE CONSTANTS					
	FORWARD DISSOC. REACTION		REVERSE DISSOC. REACTION		EQUILIBRIUM CONSTANT	
	Symbol	Value	Symbol	Value	Symbol	Value
Ammonia $NH_4^+ \rightleftharpoons NH_3 + H^+$	K'_{fn}	$K'_{rn} \cdot K'_n$	K'_{rn}	10^{12} (/s)	K'_n	10^{-pKn}
Carbonate 1 $H_2CO_3^* \rightleftharpoons HCO_3^- + H^+$	K'_{fc1}	$K'_{rc1} \cdot K'_{c1}$	K'_{rc1}	10^{10} (/s)	K'_{c1}	$10^{-pKc1}/f_m^2$
Carbonate 2 $HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	K'_{fc2}	$K'_{rc2} \cdot K'_{c2}$	K'_{rc2}	10^{12} (/s)	K'_{c2}	$10^{-pKc2}/f_d$
Phosphate 1 $H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$	K'_{fp1}	$K'_{rp1} \cdot K'_{p1}$	K'_{rp1}	10^{8} (/s)	K'_{p1}	$10^{-pKp1}/f_m^2$
Phosphate 2 $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$	K'_{fp2}	$K'_{rp2} \cdot K'_{p2}$	K'_{rp2}	10^{12} (/s)	K'_{p2}	$10^{-pKp2}/f_d$
Phosphate 3 $HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$	K'_{fp3}	$K'_{rp3} \cdot K'_{p3}$	K'_{rp3}	10^{15} (/s)	K'_{p3}	$10^{-pKp3} \cdot f_d/(f_t \cdot f_m)$
SCFA $HA \rightleftharpoons A^- + H^+$	K'_{fa}	$K'_{ra} \cdot K'_a$	K'_{ra}	10^{7} (/s)	K'_a	$10^{-pKa}/f_m^2$
Water $H_2O \rightleftharpoons OH^- + H^+$	K'_{fw}	$K'_{rw} \cdot K'_w$	K'_{rw}	10^{17} (/s)	K'_w	$10^{-pKw}/f_m^2$

Table 3.1(c): Values for pK constants in mixed weak acid/base model (Tables 3.1a and b). (T is temperature in Kelvin).

pK CONSTANT	FORMULATION
1940s Data base (Loewenthal and Marais, 1976. Loewenthal *et al.*, 1989)	
pK_n	$2\,835.8/T - 0.6322 + 0.00123 \cdot T$
pK_{c1}	$3\,404.7/T - 14.8435 + 0.03279 \cdot T$
pK_{c2}	$2\,902.4/T - 6.498 + 0.02379 \cdot T$
pK_{p1}	$799.3/T - 4.5535 + 0.01349 \cdot T$
pK_{p2}	$1\,979.5/T - 5.3541 + 0.01984 \cdot T$
pK_{p3}	12.023
pK_a	$1\,170.5/T - 3.165 + 0.0134 \cdot T$
1980s Data base (Friend and Loewenthal, 1992)	
pK_{c1}	$356.309 + 0.0609196 \cdot T - 21\,834.4/T - 126.834 \cdot \log T + 1.68492 \cdot 10^6/T^2$
pK_{c2}	$107.887 + 0.0325285 \cdot T - 5\,151.79/T - 38.9256 \cdot \log T + 563\,714/T^2$
$pK_{H,CO2}$	$-2\,025.3/T - 0.0104 \cdot T + 11.365$
pK_w	14.00

Example 3.1: ***Chemical dose for specified dosage type and specified initial and final solution states***

A water has carbonate, ammonium and phosphate weak acid/base subsystems present in solution, with $C_T = 0.005$ mol/ℓ, $N_T = 0.004$ mol/ℓ and $P_T = 0.003$ mol/ℓ, ionic strength (μ) = 0.01 and temperature = 20°C. Determine the strong base required to adjust pH from 6.50 to 8.50 (see Table 3.2).

Table 3.2: Comparison of results obtained with the kinetic model and the equilibrium chemistry-based algorithms of Loewenthal *et al.* (1991).

Parameter	**Unit**	**KINETIC MODEL**	**EQUILIBRIUM ALGORITHM**
$H_3PO_4/H_2CO_3^*/NH_4^+$ alkalinity	mol/ℓ	0.01142	0.01144
OH^- dose	mol/ℓ	0.004812	0.004812

Example 3.2: ***Final state for a specified initial state and a specified chemical dose and dosage type***

For the raw water in Example 3.1, determine the final pH for a carbonate (CO_3^{2-}) dosage of 0.004865 mol/ℓ (see Table 3.3).

Table 3.3: Comparison of results obtained with the kinetic model and the equilibrium chemistry-based algorithms of Loewenthal *et al.* (1991).

Parameter	**Unit**	**KINETIC MODEL**	**EQUILIBRIUM ALGORITHM**
$H_3PO_4/H_2CO_3^*/NH_4^-$ alkalinity	mol/ℓ	0.01634	0.01636
pH		8.52	8.50

The kinetic model predicted change in pH with time was very rapid, with adjustment to the new equilibrium condition in ~2s.

In both Examples 3.1 and 3.2, very good agreement was obtained between results from the kinetic- based model and the equilibrium-based algorithms of Loewenthal *et al.* (1991). This provides evidence that validates both the mixed weak acid/base kinetic model and the approach on which it is based.

3.5.1.2 Biological processes of carbon and nitrogen removal and their interaction with pH.

A number of mathematical models describing variously biological carbon, nitrogen and phosphorus removal by the activated sludge system have been developed over the years, e.g. the constant flow and load aerobic nitrification model by Marais and Ekama (1976), the dynamic aerobic model by Dold *et al*. (1980), the nitrification-denitrification (ND) model by van Haandel *et al*. (1981) and Dold *et al.* (1991), the "Activated Sludge Model No.1" proposed by the IAWQ Task Group on Mathematical Modelling for Design and Operation of Biological Wastewater Treatment (Henze *et al*., 1987), the nitrification-denitrification biological excess phosphorus removal (NDBEPR) model by Wentzel *et al*. (1992), and the NDBEPR model "Activated sludge model No. 2" by the IAWQ Task Group (Henze *et al*., 1995). Various commercial programmes (e.g. ASIM, Gujer and Henze, 1991; UCTOLD, Dold *et al*., 1991) based on these models have also been developed and these enabl simulations to be done under different operating conditions.

These existing biological models were accepted as a basis for the biological model developed here. However, the existing models were developed for wastewater treatment systems where the biological degradation of organic matter dominates the system response and the background pH remains approximately constant. In the treatment of high nutrient low organic carbon (HNLC) wastewaters the weak acid/base species of the carbonate, ammonia, sulphide, phosphate and SCFA weak acid/bases may be present in significant concentrations. Also, chemical and physical processes will be significant and must be included in any model for these wastewaters. Both these factors have a marked effect on the pH (and in turn are influenced by the pH). Thus, for the biological transformations the background pH no longer can be assumed to be constant, and it must be included as a compound. The kinetic based approach to include pH in the model has been described above, and was followed to include pH as a parameter in the biological models. Including pH as a compound in the model has a number of consequences on the biological models that must be taken into account:

- All weak acid/bases that influence the pH must be included in the models.
- Including the carbonate weak/acid base means that the influence of the biological transformations on this weak acid/base has to be modelled, i.e. the production and utilization of CO_2 has to be included.
- Weak acid/bases already in the biological model must be divided into the individual weak acid/base species. For example, in the existing biological models the ammonia/ammonium weak acid/base is included as a single species, with the concentration equal to the total species concentration; the individual ammonia and ammonium species must be included separately.
- The phosphate weak acid/base must also be included, so also the uptake of phosphorus for organism growth; the non-P removal models do not include this.
- The effect of pH on the biological processes must be included where these are expected to be significant, e.g. nitrifier growth rates.
- The effect of biological processes on the pH must be included, e.g. production of H^+ in nitrification.

For the model developed for this research, the biological processes as described in the IAWQ Activated Sludge Model No. 1 (see Henze *et al*., 1987; Dold *et al*., 1991) were integrated with the processes describing weak acid/base equilibrium chemistry [see 3.5.1.1 above; Table 3.1] giving rise to a combined biological/chemical model for single phase aqueous systems which takes into account the considerations listed above. This aqueous system model is shown in matrix notation in Table 3.4(a, b and c). The biological processes' kinetic rate equations have been modified to take into account the effect of pH where this effect is significant: This was done in two ways; (i) where there is a direct influence of pH on the process rate, pH was included in the kinetic formulation, and (ii) specific weak acid/base species were included in the model and so the kinetic rates were reformulated to reflect this; in the current models the individual species for each weak acid/base are lumped into the total species concentration and this concentration influences the kinetic rate - in the model developed here a specific weak acid/base species influences the kinetic rate, e.g. for nitrification, in the current models the nitrification rate is influenced by the total inorganic nitrogen species concentration (ammonia+ammonium), whereas in the model developed here the rate is influenced by the ammonium concentration only. Further, new stoichiometric coefficients were added and adjustments to existing ones made where applicable to take into account the use of specific inorganic carbon, nitrogen and phosphorus species during organism growth. Details of these modifications to the rates of biological processes and stoichiometric coefficients are given by Musvoto *et al*. (1998). Also, the units for the weak acid/base chemistry section of the model were converted from mol/ℓ (Table 3.1a) to g/m^3 (Table 3.4a) to facilitate integration with the biological processes. The model was incorporated into the AQUASIM computer programme, and a number of simulations done to evaluate the model predictions; one example is given below.

Table 3.4a: Matrix representation of the weak acid/base processes from Table 3.1 which were combined with the biological processes (Table 3.4b above) to give the combined single phase aqueous systems model. Note that the units for weak acid/base species have been changed.

	Compound →	1	2	3	4	5	6	7	8	9	10	11	12	13	
Process ↓		NH_4^+	NH_3	$H_2CO_3^*$	HCO_3^-	CO_3^{2-}	H^+	OH^-	H_3PO_4	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	HA	A^-	Rate
1	Forward dissociation of NH_4^+	-1	1				1/14								$K'_{fn}[NH_4^+]$
2	Reverse dissociation of NH_4^+	1	-1				-1/14								$K'_{rn}[NH_3][H^+]$
3	Forward dissociation of $H_2CO_3^*$			-1	1		1/12								$K'_{fc1}[H_2CO_3^*]$
4	Reverse dissociation of $H_2CO_3^*$			1	-1		-1/12								$K'_{rc1}[HCO_3^-][H^+]$
5	Forward dissociation of HCO_3^-				-1	1	1/12								$K'_{fc2}[HCO_3^-]$
6	Reverse dissociation of HCO_3^-				1	-1	-1/12								$K'_{rc2}[CO_3^{2-}][H^+]$
7	Forward dissociation of H_3PO_4						1/31		-1	1					$K'_{fp1}[H_3PO_4]$
8	Reverse dissociation of H_3PO_4						-1/31		1	-1					$K'_{rp1}[H_2PO_4^-][H^+]$
9	Forward dissociation of $H_2PO_4^-$						1/31			-1	1				$K'_{fp2}[H_2PO_4^-]$
10	Reverse dissociation of $H_2PO_4^-$						-1/31			1	-1				$K'_{rp2}[HPO_4^{2-}][H^+]$
11	Forward dissociation of HPO_4^{2-}						1/31				-1	1			$K'_{fp3}[HPO_4^{2-}]$
12	Reverse dissociation of HPO_4^{2-}						-1/31				1	-1			$K'_{rp3}[PO_4^{3-}][H^+]$
13	Forward dissociation of HA						1/12						-1	1	$K'_{fa}[HA]$
14	Reverse dissociation of HA						-1/12						1	-1	$K'_{ra}[A^-][H^+]$
15	Forward dissociation of water						1	1							K'_{fw}
16	Reverse dissociation of water						-1	-1							$K'_{rw}[H^+][OH^-]$
	Units	gN/m^3	gN/m^3	gC/m^3	gC/m^3	gC/m^3	gH/m^3	gH/m^3	gP/m^3	gP/m^3	gP/m^3	gP/m^3	gC/m^3	gC/m^3	

Table 3.4b: Matrix representation of the biological processes which were combined with the weak acid/base processes (see Table 3.4a) to give the combined single phase aqueous systems model.

Process↓	Compound→	1	3	6	10	14	15	16	17	18	19	20	21	22	Rate
		NH_4^+	$H_2CO_3^*$	H^+	HPO_4^{2-}	Z_{BH}	Z_E	Z_{BA}	S_{enm}	S_{bs}	NO_3^-	N_{obs}	N_{ous}	O	
17	Aerobic growth of Z_{BH} with NH_4^+	$-f_{ZB,N}$	$(1-Y_{ZH})/(3Y_{ZH})$	$f_{ZB,N}/14-2f_{ZB,P}/31$	$-f_{ZB,P}$	1				$-1/Y_{ZH}$				$-(1-Y_{ZH})/Y_{ZH}$	$\mu_H\left[\frac{S_{bs}}{K_{SH}+S_{bs}}\right]\left[\frac{H.Air}{On}\right]\left[\frac{NH_4^+}{limit}\right]Z_{BH}$
18	Aerobic growth of Z_{BH} with NO_3^-		$(1-Y_{ZH})/(3Y_{ZH})$	$-f_{ZB,N}/14-2f_{ZB,P}/31$	$-f_{ZB,P}$	1				$-1/Y_{ZH}$	$-f_{ZB,N}$			$-(1-Y_{ZH})/Y_{ZH}$	$\mu_H\left[\frac{S_{bs}}{K_{SH}+S_{bs}}\right]\left[\frac{H.Air}{On}\right]\left[\frac{1-NH_4^+}{limit}\right]\left[\frac{NO_3^-}{limit}\right]Z_{BH}$
19	Anoxic growth of Z_{BH} with NH_4^+	$-f_{ZB,N}$	$(1-Y_{ZH})/(3Y_{ZH})$	A'	$-f_{ZB,P}$	1				$-1/Y_{ZH}$	$-(1-Y_{ZH})/(2.86Y_{ZH})$				$\mu_H\left[\frac{S_{bs}}{K_{SH}+S_{bs}}\right]\left[\frac{H.Air}{Off}\right]\left[\frac{NH_4^+}{limit}\right]\left[\frac{NO_3^-}{limit}\right]Z_{BH}\,\eta_G$
20	Anoxic growth of Z_{BH} with NO_3^-		$(1-Y_{ZH})/(3Y_{ZH})$	C'	$-f_{ZB,P}$	1				$-1/Y_{ZH}$	B'				$\mu_H\left[\frac{S_{bs}}{K_{SH}+S_{bs}}\right]\left[\frac{H.Air}{Off}\right]\left[\frac{1-NH_4^+}{limit}\right]\left[\frac{NO_3^-}{limit}\right]Z_{BH}\,\eta_G$
21	Death of Z_{BH}			$2(f_{ZB,P}-f_E f_{ZE,P})/31$	$f_{ZB,P}-f_E f_{ZE,P}$	-1	f_E		$1-f_E$			$f_{ZB,N}-f_E f_{ZE,N}$			$b_H\,Z_{BH}$
22	Hydrolysis of S_{enm}								-1	1					$K_H\left[\frac{(S_{enm}/Z_{BH})}{K_X+(S_{enm}/Z_{BH})}\right]\left(\left[\frac{H.Air}{On}\right]+\eta_h\left[\frac{H.Air}{Off}\right]\left[\frac{NO_3^-}{limit}\right]\right)Z_{BH}$
23	Hydrolysis of N_{obs}											-1	1		$HydrolysisS_{enm}\,(N_{obs}/S_{enm})$
24	Ammpnification of N_{ous}	1		-1/14									-1		$K_R\,N_{ous}\,Z_{BH}$

Process ↓	Compound →	1	3	6	10	14	15	16	17	18	19	20	21	22	Rate
		NH_4^+	$H_2CO_3^*$	H^+	HPO_4^{2-}	Z_{BH}	Z_E	Z_{BA}	S_{bsa}	S_{us}	NO_3^-	N_{obs}	N_{ous}	O	
25	Aerobic growth of Z_{BA}	$-(1/Y_{ZA})$ $-f_{ZB,N}$	-3/8	$f_{ZB,N}/14+$ $1/(7Y_{ZA})$				1			$1/Y_{ZA}$			$-(4.57-Y_{ZA})$ $/Y_{ZA}$	$\mu_A\left[\frac{NH_4^+}{K_{NA}+NH_4^+}\right]\begin{bmatrix}A\ Air\\On\end{bmatrix}Z_{BA}$
26	Death of Z_{BA}						f_E	-1	$1-f_E$			$f_{ZB,N}-f_E f_{ZE,N}$			$b_A Z_{BA}$
27	Units	gN/m^3	gC/m^3	g/m^3	gP/m^3	gCOD $/m^3$	gCOD $/m^3$	gCOD $/m^3$	gCOD $/m^3$	gCOD $/m^3$	gN/m^3	gN/m^3	gN/m^3	gCOD $/m^3$	

$A^+ = -\frac{1-Y_{ZH}}{14\cdot 2.86Y_{ZH}} + \frac{f_{ZB,N}}{14} - 2\cdot\frac{f_{ZB,P}}{31}$ $\quad B^+ = -\frac{1-Y_{ZH}}{2.86Y_{ZH}} + f_{ZB,N}$ $\quad C^+ = -\frac{1-Y_{ZH}}{14\cdot 2.86Y_{ZH}} - \frac{f_{ZB,N}}{14} - 2\cdot\frac{f_{ZB,P}}{31}$

Table 3.4c: Switching function parameters used in the biological processes of the combined single phase aqueous systems model (Table 3.4b).

Switching function	Formulation	Switching function	Formulation
$\begin{bmatrix}H\,Air\\On\end{bmatrix}$	$\frac{O}{K_{OH}+O}$	$\begin{bmatrix}NH_4^+\\limit\end{bmatrix}$	$\frac{NH_4^+}{K_{NA}+NH_4^+}$
$\begin{bmatrix}H\,Air\\Off\end{bmatrix}$	$\frac{K_{OH}}{K_{OH}+O}$	$\begin{bmatrix}1-NH_4^+\\limit\end{bmatrix}$	$\frac{K_{NA}}{K_{NA}+NH_4^+}$
$\begin{bmatrix}A\ Air\\On\end{bmatrix}$	$\frac{O}{K_{OA}+O}$	$\begin{bmatrix}NO_3^-\\limit\end{bmatrix}$	$\frac{NO_3^-}{K_{NO}+NO_3^-}$

Example 3.3: ***Aerobic batch test***

The aerobic batch test described by Dold *et al.* (1991) was used to check the model. In this batch test mixed liquor drawn from a nitrifying activated sludge system was mixed with raw municipal wastewater and aerated. Because the total species concentrations of the carbonate, phosphate, ammonia and SCFA systems were not measured by Dold *et al.* (1991), values for these parameters had to be estimated for input to the model. The initial conditions in the batch test given by Dold *et al.* (1991) and the estimated total species concentrations are set out in Table 3.5(a). The input kinetic and stoichiometric constants given by Dold *et al.* were accepted for the combined weak acid/base chemistry and biological processes model are shown in Table 3.5(b).

Table 3.5(a): Initial conditions in the aerobic batch test given by Dold *et al.* (1991) and used as input to the single phase aqueous weak acid base chemistry and biological processes model.

Parameter	**Description**	**Value**	**Units**
Z_{bh}	heterotroph active biomass	460	g COD m^{-3}
Z_e	endogenous mass	442	g COD m^{-3}
Z_{ba}	autotroph active biomass	25.40	g COD m^{-3}
S_{enm}	enmeshed COD	173.96	g COD m^{-3}
Z_i	particulate unbiodegradable COD	17.44	g COD m^{-3}
N_{obp}	particulate biodegradable N	1.77	g N m^{-3}
S_{bs}	soluble biodegradable COD	9.16	g COD m^{-3}
N_a	ammonia N)	14.17	g N m^{-3}
N_{obs}	soluble organic N	4.56	g N m^{-3}
NO_3	nitrate N	9.40	g N m^{-3}
Alkalinity		7.50	mole m^{-3}
S_{us}	soluble unbiodegradable COD	17.44	g COD m^{-3}

Table 3.5(b): Estimated total species concentrations in the aerobic batch test given by Dold *et al.* (1991) and used as input to the single phase aqueous weak acid base chemistry and biological processes model.

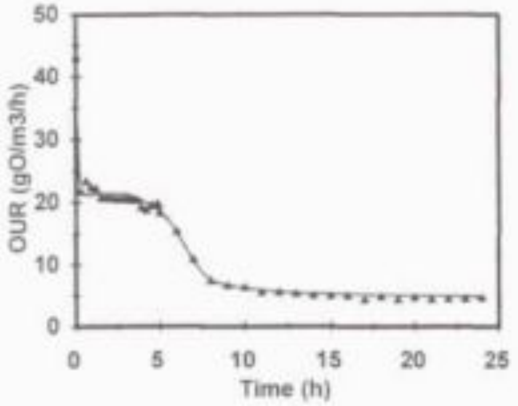
Parameter	**Description**	**Value**	**Units**
C_{Ti}	initial total carbonate species	40	g C m^{-3}
P_{Ti}	initial total phosphate species	12	g P m^{-3}
A_{Ti}	initial total SCFA species	0	g C m^{-3}
N_{Ti}	initial total ammonia/ium species	14.17	g N m^{-3}
TKN_i	initial TKN concentration	20.5	g N m^{-3}
pH_i	initial pH	7.6	

Figs. 3.2a to 3.2c show respectively the oxygen utilization rate (OUR), nitrate and TKN concentrations predicted using the combined weak acid/base biological model developed here (simulations using AQUASIM) compared with those predicted using the original IAWPRC model of Dold *et al.* (1991), and the experimental data. The predictions of the two models compare favourably and with the experimental data. The close correlation between predictions with the two models is to be expected since the simulations were done for municipal wastewaters where, despite their inclusion in the model developed here, the weak acid/base systems have no significant effect on the biological processes. No suitable data on biological treatment of wastewaters where the weak acid/base systems and pH play a significant role could be found in the literature to adequately validate the model. Rigorous model validation was carried out with data from experiments which were conducted later in the research.

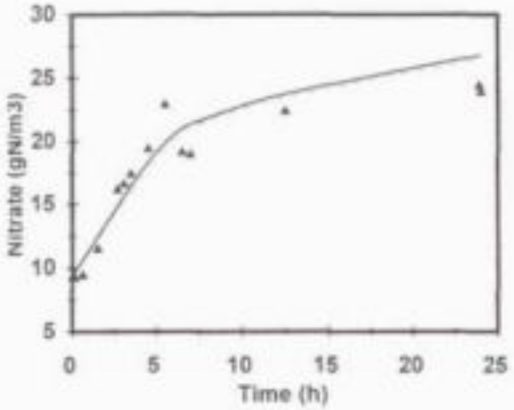
A note on the COD mass balance of the model

Mass balances are performed over a model or experimental system to check its accuracy. Strictly speaking, the COD mass balance performed on biological processes only models (see Dold *et al.*, 1991) is no longer possible for the combined chemical and biological processes model, because inorganic carbon (as CO_2) is changed to organic nitrifier VSS unless this contribution is specifically excluded. In reality, the contribution of the inorganic carbon is so small that it does not affect the value of the COD mass balance significantly for domestic wastewaters where the growth of autotrophs is very small compared to the growth of heterotrophs. However, for wastewaters which have a high ammonia content relative to the organic content (e.g. HNLC wastewaters) the growth of autotrophs will be significant compared with the growth of heterotrophs and COD mass balances greater than 100% will be obtained if the autotrophic biomass is included in the VSS component of the mass balance.

(a) OUR



(b) Nitrate



(c) TKN

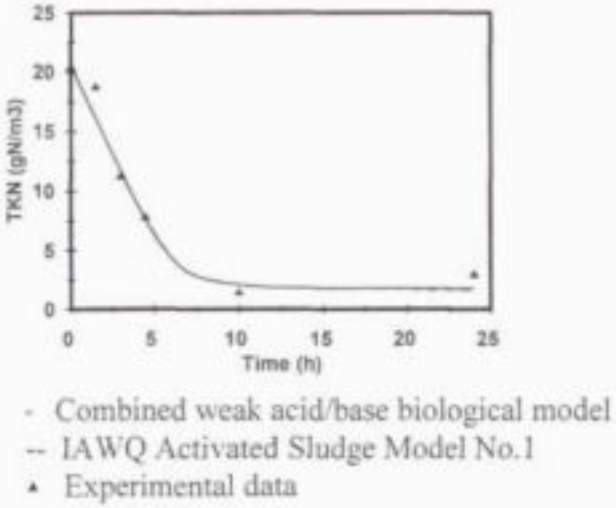


Fig 2.4 Comparison of the predicted oxygen utilization rate (OUR), Nitrate and TKN concentrations in aerobic batch test with nitrification (Example 2.3) with the batch version of IAWQ Activated Sludge Model No.1 (Dold *et al.*, 1991) and the combined biological and weak acid/base chemistry kinetic model.

3.5.2 Two-phase systems: Solid/Aqueous

The solid/aqueous two phase systems required consideration of the chemical precipitation of sparingly soluble salts. The precipitation of sparingly soluble salts can be used as a means for removal of P and N from wastewaters. The main ions considered for this purpose are calcium, iron and magnesium. In some HNLC wastewaters, magnesium and calcium can be present at concentrations sufficient to precipitate considerable amounts of P and N without external cation supplementation (e.g. anaerobic digestor supernatant). The main phosphate salts precipitated are magnesium phosphates, such as magnesium ammonium phosphate (struvite), and various calcium phosphates. Other salts like calcium carbonate and magnesium carbonate are also precipitated under the same conditions that the phosphates are precipitated. The precipitation kinetics for sparingly soluble salts are not well defined and the literature gives a wide variation of how these kinetics can be modelled. Details of the precipitation kinetics used in the model developed here are given by Musvoto *et al.* (1998), and are summarized in Appendix A. With the information and concepts from the literature, this section of the model was developed stepwise: First, the precipitation of calcium carbonate only from aqueous systems containing a mixture of weak acid/bases systems was developed. Then the same was done for struvite. Once these two precipitation models had been validated with experimental data from the literature, the two models were combined and then extended to include the precipitation of the other salts, such as calcium phosphate and magnesium carbonate.

3.5.2.1 Modelling of calcium carbonate precipitation:

Development and validation of calcium carbonate ($CaCO_3$) precipitation kinetics was the first stage in developing the two phase solid/aqueous systems model, because data are available in the literature to validate this process. For surface-controlled precipitation processes, such as $CaCO_3$ precipitation, the rate can be formulated by following the theory of Koutsoukos *et al.* (1980): For many sparingly soluble salts $M_{v+}A_{v-}$ the rate of crystallization can be expressed by an equation of the form (Koutsoukos *et al.*, 1980):

$$\frac{d}{dt}M_{v+}A_{v-} = -k's[([M^{m+}]^{v+}[A^{a-}]^{v-})^{\frac{1}{v}} - ([M^{m+}]_0^{v+}[A^{a-}]_0^{v-})^{\frac{1}{v}}]^n \qquad (3.6)$$

where:

- $[M^{m+}]$, $[A^{a-}]$ and $[M^{m+}]_0$, $[A^{a-}]_0$ are the concentrations in mole units of crystal lattice ions in solution at time t and at equilibrium respectively. At equilibrium $[M^{m+}]_0^{v+}[A^{a-}]_0^{v-} = K_{sp}'$, where K_{sp}' is the apparent solubility product of the salt.
- k' is the apparent precipitation rate constant
- s is proportional to the total number of available growth sites on the added seed material
- v^+ is the total number of cationic species
- v^- is the total number of anionic species
- $v = v^+ + v^-$
- The number n is determined experimentally and equals 2 for a number of divalent sparingly soluble salts

Applying this equation to the precipitation of $CaCO_3$, where :

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_{3(s)} \tag{3.7}$$

and $v^{+} = 1$, $v^{-} = 1$ and $v = 2$, then:

$$\frac{d}{dt}\,[CaCO_3] = -k'_c s\,\left[[Ca^{2+}]^{\frac{1}{2}}\,[CO_3^{2-}]^{\frac{1}{2}} - K'^{\frac{1}{2}}_{sp}\right]^2 \tag{3.8}$$

where:

k_c' = apparent precipitation rate constant for $CaCO_3$

s = constant proportional to the total number of available growth sites on the added seed material

K'_{sp} = apparent solubility product for $CaCO_3$

In Eq. (3.8), accepting that no seed material has been added, the rate no longer depends on the available number of growth sites (s) so that the rate constant k_c's can be replaced by a single precipitation rate constant K'_{rCaCO3}. This equation can also be derived by using the hypothesis of Davies and Jones (Benjamin *et al*., 1976; Sturrock *et al*., 1976) and, accordingly, has been accepted for use in the model. The equation applies only to the precipitation of $CaCO_3$ and not to the dissolution; in the model the equation is valid only if $[Ca^{2+}]^{½}\,[CO_3^{2-}]^{½} > K'^{½}_{sp}$ - **this condition must be checked**.

The above calcium carbonate precipitation equation [Eq. (3.8)] was integrated with the mixed weak acid/base chemistry model in Table 3.1, together with the stoichiometric coefficients determined from Eq. (3.7) (i.e. $Ca^{2+} = -1$; $CO_3^{-} = -1$; $CaCO_3$ solid = +1). To test the model, examples obtained from Loewenthal *et al.* (1986) were simulated. The results obtained with the kinetic-based model (in AQUASIM) were compared with the equilibrium based results obtained from the graphical Modified Caldwell Lawrence (MCL) diagrams (Loewenthal *et al.*, 1986) and from the computer programs STASOFT I (Loewenthal *et al.*, 1988) and STASOFT III (Friend and Loewenthal, 1992). The MCL diagrams are based on equilibrium constants derived from data obtained in the 1940s, while the equilibrium constants in STASOFT III are based on data obtained in the 1980s; STASOFT I includes the option to use either set of equilibrium constants. To evaluate the kinetic model, results from the MCL diagrams, STASOFT I and the kinetic model were compared using the same 1940s-based equilibrium constants, and the results from STASOFT I, STASOFT III and the kinetic model were compared using the same 1980s-based equilibrium constants; in all cases very good agreement was obtained. To illustrate, examples are given below.

Example 3.4: ***Assessment of initial state***

Analysis of a water gives alkalinity = 80 mg/ℓ, Ca^{2+} = 100 mg/ℓ (both as $CaCO_3$), pH = 8.6, ionic strength (μ) = 0.005 (TDS = 200 mg/ℓ) and T = 20°C. Determine the saturation state of the water and the mass concentration of $CaCO_3$ which potentially can precipitate from the water (see Table 3.5).

Table 3.5a: Results for Example 3.4 obtained with the equilibrium constants from the 1940s database

Parameter	Units	KINETIC MODEL	MCL	STASOFT I
$H_2CO_3^*$ alkalinity	mg/ℓ as $CaCO_3$	75.9	75	75.9
Ca^{2+}	mg/ℓ as $CaCO_3$	95.9	95	95.9
pH		8.13	8.13	8.12
$CaCO_3$ precipitation potential	mg/ℓ as $CaCO_3$	4.1	5	4.1

Table 3.5b: Results obtained with equilibrium constants from the 1980s database

Parameter	Unit	KINETIC MODEL	STASOFT I	STASOFT III
$H_2CO_3^*$ alkalinity	mg/ℓ as $CaCO_3$	74.3	74.9	74.2
Ca^{2+}	mg/ℓ as $CaCO_3$	94.3	94.9	94.2
pH		7.97	8.00	7.94
$CaCO_3$ precipitation potential	mg/ℓ as $CaCO_3$	5.7	5.1	5.7

The results obtained using the kinetic-based model compare very well with those obtained using the equilibrium chemistry-based MCL diagrams, STASOFT I and STASOFT III.

Example 3.5: *Calcium softening using lime*
Analysis of a water gives: $H_2CO_3^*$ alkalinity = 300 mg/ℓ, calcium = 280 mg/ℓ (both as $CaCO_3$), pH = 7.2, $\mu = 0.01$ (TDS = 400 mg/ℓ) and temperature 20°C. Determine the $Ca(OH)_2$ dose to soften the water to $Ca^{2+} = 100$ mg/ℓ (as $CaCO_3$) (see Table 3.6).

Table3.6a: Results obtained with equilibrium constants from the 1940s database

Parameter	**Unit**	**KINETIC MODEL**	**MCL**	**STASOFT I**
$H_2CO_3^*$ alkalinity	mg/ℓ as $CaCO_3$	120	120	120
Ca^{2+}	mg/ℓ as $CaCO_3$	100	100	100
pH		7.97	7.95	7.96
$Ca(OH)_2$ dose	mg/ℓ as $CaCO_3$	257.5	270	265.3

Table 3.6b: Results obtained using equilibrium constants from the 1980s database

Parameter	**Unit**	**KINETIC MODEL**	**STASOFT I**	**STASOFT III**
$H_2CO_3^*$ alkalinity	mg/ℓ as $CaCO_3$	120	120	120
Ca^{2+}	mg/ℓ as $CaCO_3$	100	100	100
pH		7.78	7.84	7.77
$Ca(OH)_2$ dose	mg/ℓ as $CaCO_3$	253.1	264.0	253.6

Again results from all calculations correlate closely. The above two examples validated the $CaCO_3$ precipitation kinetics in the model.

3.5.2.2 Modelling of struvite precipitation:

Similarly to the kinetics of $CaCO_3$ precipitation described above, a kinetic equation was developed for struvite (magnesium ammonium phosphate, $MgNH_4PO_4$) precipitation (for details of struvite precipitation kinetics, see Musvoto *et al*., 1998), using the general precipitation equation [Eq. (3.6)], to give:

$$\frac{d}{dt}\,[Struv.] = -k'ppt_{struvite}\,[[Mg^{2+}]^{\frac{1}{3}}\,[NH_4^+]^{\frac{1}{3}}\,[PO_4^{3-}]^{\frac{1}{3}} - K'sp_{Struv.}^{\frac{1}{3}}]^3 \qquad (3.9)$$

The struvite precipitation kinetics were integrated with the mixed weak acid/base model in Table 3.1 and the resultant struvite precipitation model was evaluated. In simulations, an arbitrary value for the rate of precipitation of struvite had to be used in the model because no rates were available from the literature for precipitation from unseeded solutions. However, the equilibrium conditions predicted by the model could be evaluated. This was done by comparing the model predictions of equilibrium conditions against those predicted by the equilibrium chemistry model of Loewenthal *et al*. (1994) for struvite precipitation.

Example 3.6: ***Struvite precipitation***
Loewenthal et al. (1994) developed an equilibrium chemistry based model for struvite precipitation which was subsequently coded into a computer programme called Struvite 3.1 by Loewenthal and Morrison (1997). Equilibrium conditions predicted by this programme, for the two solutions discussed by Loewenthal et al. (1994) were compared with the predictions of the kinetic model developed above. The TDS concentrations of the two solutions, which are required as input to Struvite 3.1, were calculated from the ionic strength of the ammonium chloride, magnesium chloride and potassium phosphate species making up the solutions and the TDS - ionic strength (μ) relationship given by Loewenthal et al. (1989), i.e. $\mu=2.5\cdot10^{-5}(TDS-20)$; viz., $\mu=0.0826$ giving a TDS of 3325 mg/ℓ for Solution 1 and $\mu=0.0706$ giving a TDS of 2844 mg/ℓ for Solution 2 (see Table 3.7a). The initial total species concentrations of the phosphate (P_T), short chain fatty acid (A_T) and ammonia (N_T) systems, the magnesium concentration (Mg), the partial pressure of CO_2 (which fixes the total species concentration of the carbonate system, C_T) and pH for the two solutions are listed in Table 3.7a. The weak acid/base pK values and their temperature sensitivities, and the solubility product for struvite (no temperature correction) included in Struvite 3.1 are those given by Loewenthal et al. (1994) (see also Loewenthal et al., 1989 or Musvoto et al., 1997). These were included also in the kinetic model as model constants (not changed). The initial total alkalinities (T Alk) were calculated by the Struvite 3.1 equilibrium model as 1284 and 990 mg/ℓ as $CaCO_3$ for Solutions 1 and 2 respectively, and are with respect to the most protonated species of each of the weak acid/base systems, viz. the $H_2CO_3^*/H_3PO_4/NH_4^+/HAc$ alkalinity. The initial $H_2CO_3^*/H_3PO_4/NH_4^+/HAc$ alkalinity (T Alk) calculated by the kinetic model was 1275 mg/ℓ as $CaCO_3$ (0.0255 mol/ℓ) for Solution 1 and 981 mg/ℓ as $CaCO_3$ (0.0196 mol/ℓ) for Solution 2. Thus, Struvite 3.1 and the kinetic model give virtually identical initial $H_2CO_3^*/H_3PO_4/NH_4^+/HAc$ (total) alkalinity values for both solutions. This indicated that the initial conditions specified in both models were virtually identical.

In Struvite 3.1, the ionic strength (μ), the mono-, di- and tri-valent ion activity coefficients (f_m, f_d, f_t), and hence the pK′ values for non-ideal solutions, are determined from the input TDS, and the first iteration to calculate the equilibrium condition is based on this initial μ. A revised μ is then calculated taking into account the change in ionic species due to precipitation of struvite. A revised equilibrium condition is then determined from the revised μ and this equilibrium condition is accepted as the final condition. In the kinetic model the ionic strength, mono-, di- and tri-valent ion activity coefficients (f_m, f_d, f_t), and hence the pK′ values for non-ideal solutions, are embedded within the equations for the kinetic constants of the model and therefore any change in ionic strength due to precipitation is taken into account at each integration step in an integrated and seamless way.

The initial and final equilibrium conditions predicted by Struvite 3.1 and the kinetic model for the two solutions are listed in Table 3.7a. It can be seen for Solution 1, which does not contain carbonate system species, the kinetic model predicts lower dissolved species concentrations (by about 0.0006 mol/ℓ) and a lower pH by 0.19 units. Also the concentration of struvite precipitated is almost 20% more in the kinetic model. The difference in the species concentrations and struvite precipitated between that predicted by the kinetic model and by Struvite 3.1 is smaller for Solution 2, viz. 0.0002 mol/ℓ lower and 7% more struvite precipitated with the kinetic model. However, the pH difference is greater, viz. 0.23 pH units lower in the kinetic model. In seeking the reason for these differences, ionic speciation at the final conditions predicted by the two models was undertaken. It was found that for both solutions the struvite ionic product calculated from the final condition predicted by Struvite 3.1 was somewhat greater than the solubility product (see Table 3.7b). This indicated that the Struvite 3.1 predicted final condition was not at equilibrium. For the kinetic model the struvite ionic product calculated from the final condition was equal to the solubility product for both solutions indicating that an equilibrium condition had been correctly reached. To check whether or not the Struvite 3.1 predicted final condition was at equilibrium, this final condition for the two solutions was given as initial conditions to the kinetic model, taking due account of the ionic strength. The results predicted by the kinetic model, including the struvite ionic and solubility products, are given in Table 3.7b. For both solutions, precipitation is predicted to continue with a further 68 and 58 mg/ℓ struvite predicted to precipitate from Solution 1 and 2 respectively to reach equilibrium. The pH of this revised equilibrium condition is only 0.02 pH units from that predicted by the kinetic model from the initial conditions (Table 3.7a) and the ionic product is equal to the solubility product (Table 3.7b).

From the comparison above of the Struvite 3.1 equilibrium model and the kinetic model, it can be concluded that the kinetic model identifies the equilibrium condition for a single precipitate accurately and precisely, and that the differences between this condition and the equilibrium condition predicted by Struvite 3.1 lie in the handling of ionic strength and in the algorithm for estimating the equilibrium pH in Struvite 3.1. The advantage of the Struvite 3.1 programme is that it is very simple to use and gives an answer very quickly (< 1 sec), which although not exact, is attractive to practising engineers and scientists in the wastewater treatment field. In contrast, the kinetic model is more accurate but requires significant lead-in time to master confidently, particularly if the three phase mixed weak acid/base kinetic model as described in this paper has to be coded from scratch into a computer programme such as Aquasim (Reichert, 1994).

Table 3.7a: Initial and final concentrations for the two struvite precipitation solutions given by Loewenthal et al. (1994) comparing the kinetic model predictions with the Struvite 3.1 equilibrium struvite precipitation model of Loewenthal and Morrison (1997). Ion pairing not included in both models.

Parameter	Solution 1 (T=20°C, [1]TDS=3325 mg/ℓ)						Solution 2 (T=20°C, [1]TDS=2844 mg/ℓ)					
	Initial Conditions		Final Struvite 3.1		Final Kinetic Model		Initial Conditions		Final Struvite 3.1		Final Kinetic Model	
	mg/ℓ	mol/ℓ	mg/ℓ	mol/ℓ	mg/ℓ	mol/ℓ	mg/ℓ	mol/ℓ	mg/ℓ	mol/ℓ	mg/ℓ	mol/ℓ
[2]T Alk	1284	0.0257	734	0.0147	620	0.0124	990	0.0198	554	0.0111	507	0.0102
N_T	300	0.0214	249	0.0178	238	0.0170	250	0.0179	209	0.0149	207	0.0148
P_T	400	0.0129	286	0.0092	264	0.0085	300	0.0097	210	0.0068	203	0.0066
Mg	200	0.0083	111	0.0046	96	0.0040	200	0.0083	129	0.0054	125	0.0052
pH	8.04		7.04		6.85		7.96		7.11		6.88	
pCO_2	0		0		0		0.00037		0.00037		0.00037	
Struvite Precipitated (mg/ℓ)			503		601		-		399		426	

1.Total dissolved solids (TDS) concentration was calculated from the ionic strength of the ammonium chloride, magnesium chloride and potassium phosphate species making up the solution and the TDS - μ relationship given by Loewenthal et al. (1989), i.e. $\mu=2.5\times10^{-5}(TDS-20)$; for Solution 1, $\mu=0.0826$ and for Solution 2 $\mu=0.0706$.
2.Total Alkalinity (T Alk) with respect to the $H_2CO_3^*/H_2PO_4^-/NH_4^+/HAc$ reference species as given by Struvite 3.1. In these two solutions the total HAc concentration (A_T) was zero.

Table 3.7b: Speciation results of the Struvite 3.1 struvite precipitation equilibrium model final condition (Table 3.7a) and the kinetic model (KinM) results using this final condition as initial condition.

Parameter	Solution 1				Solution 2			
	Struvite 3.1 final condition as KinM initial condition		Kinetic Model final condition		Struvite 3.1 final condition as KinM initial condition		Kinetic Model final condition	
	mg/ℓ	mmol/ℓ	mg/ℓ	mmol/ℓ	mg/ℓ	mmol/ℓ	mg/ℓ	mmol/ℓ
T Alk	734	0.0147	706	0.0141	554	0.0111	476	0.0095
N_T	249	0.0178	242	0.0173	209	0.0149	203	0.0145
P_T	285	0.0092	270	0.0087	210	0.0068	198	0.0064
Mg	110	0.0046	86	0.0041	129	0.0054	119	0.0050
pH	7.04		6.86		7.11		6.90	
Ionic Product	$8.7\cdot10^{-12}$		$4.8\cdot10^{-12}$		$8.4\cdot10^{-12}$		$4.5\cdot10^{-12}$	
Solublity Product	$5.1\cdot10^{-12}$		$4.8\cdot10^{-12}$		$4.6\cdot10^{-12}$		$4.5\cdot10^{-12}$	
pCO_2	0		0		0.00037		0.00037	
Struvite Precipitated	0		68		0		58	

3.5.2.3 Ion Pairing Effects

Before the calcium carbonate and struvite precipitation models could be integrated and extended to include the precipitation of other sparingly soluble salts, ion pairing effects had to be taken into account. The most common ion pairs formed in solutions containing calcium and magnesium in the presence of the carbonate, phosphate and ammonia weak acid/base system species are listed in Table 3.8a together with their stability constants. To include ion pairing in the kinetic model, it was noted that the equilibrium equations for ion pair formation are similar to those representing the dissociation equilibria of weak acid/bases. Accordingly, the ion pairing equilibria were described in terms of the kinetics of the forward and reverse reactions and included in the model in the same manner as outlined by Musvoto et al. (1997) for weak acid/bases. Including the 11 identified ion pair compounds extends the model matrix by 13 compounds from 23 to 35, i.e. calcium (compound 23), magnesium (compound 24) and the 11 ion pair compounds (25 to 35), and the number of processes by 22 from 26 to 47, i.e. one forward and one reverse dissociation process for each ion pair. The ion pair section of the matrix, which is added to the existing model matrix given in Table 3.1, is shown in Table 3.8b. It should be noted that not all the compounds and processes associated with the ion pairs identified for inclusion in the model (Table 3.8a) are shown in Table 3.8b, only the first and last two of the 11 ion pairs in Table 3.8a and one generic ion pair are given for illustrative purposes. Also, some of the columns representing the compounds are duplicated from Table 3.1, i.e. columns 5, 8, 10 and 11 for CO_3^{2-}, OH^-, HPO_4^{2-} and PO_4^{3-} respectively, because these compounds also appear in the ion pairing processes. The ion pairing process rates are defined on the right hand side of Table 3.8b. The process rate constants were determined in the same manner followed for the weak acid/base dissociation constants (Musvoto et al., 1997), i.e. the rate for the forward ion pair reaction was selected at a very high value (10^7/s, Table 3.8c) and the rate for the reverse ion pair reaction was then calculated from the appropriate ion pair stability constant (Table 3.8c); this procedure ensures rapid equilibrium and that the equilibrium species concentrations correspond to those determined by equilibrium chemistry. The ion pair stability constants (pK_{ST}, Table 3.8c) were regarded as model constants and were not changed in the simulations. The values incorporated in the model are from the literature and are listed in Table 3.8a; the calculation procedures to adjust these values for Debye-Hückel ionic strength effects using mono-, di- and tri-valent activity coefficients (f_i), are given in Table 3.8c. The ion pair stability constants could not be adjusted for temperature, as no information is available in the literature on this.

3.5.2.4 Combined model for the precipitation of sparingly soluble salts:

Following the successful application of the individual calcium carbonate and struvite precipitation models and the development of kinetic equations for ion pairing effects, a combined model was developed for the precipitation of various calcium and magnesium salts from solutions containing the carbonate, ammonium and phosphate weak acid/base systems. In the presence of magnesium and calcium species, apart from struvite (magnesium ammonium phosphate) and calcium carbonate (calcite), the solids most likely to precipitate are newberyite (magnesium hydrogen phosphate), amorphous calcium phosphate (ACP) and magnesium carbonate (magnesite). These minerals were identified from an extensive review of the literature; for details see Musvoto *et al.* (1998) and a summary in Appendix A. Kinetic equations for the precipitation of the minerals were developed from the general precipitation rate equation [Eq. (3.6)]. The precipitation kinetics for the minerals are shown in matrix format in Table 3.9.

Table 3.8a: Common ion pairs formed in solutions containing calcium and magnesium with carbonate, phosphate and ammonia weak acid/bases present and their stability constants (pK_{ST}) at 25°C (activity scale). Those from Ferguson and McCarty (1971) in column (a) were included in the model.

No	Ion pair reaction - Ca and Mg	Stability Constants pK_{ST} - Sources		
		a	d	e
26	$Ca^{2+} + OH^- \rightleftharpoons CaOH^+$	-1.37^b	-1.15	-1.22
28	$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3(aq)$	-3.2^b		-3.21
30	$Ca^{2+} + HCO_3^- \rightleftharpoons CaHCO_3^+$	-1.26^b		-2.71
32	$Ca^{2+} + PO_4^{3-} \rightleftharpoons CaPO_4^-$	-6.46^c	-6.5	
34	$Ca^{2+} + H PO_4^{2-} \rightleftharpoons CaHPO_4(aq)$	-2.73^c	-2.7	
36	$Ca^{2+} + H_2PO_4^- \rightleftharpoons CaH_2PO_4^+$	-1.41^c	-1.4	
38	$Mg^{2+} + OH^- \rightleftharpoons MgOH^+$	-2.2^b	-2.56	-2.56
40	$Mg^{2+} + CO_3^{2-} \rightleftharpoons MgCO_3(aq)$	-3.4^b		-2.98
42	$Mg^{2+} + HCO_3^- \rightleftharpoons MgHCO_3^+$	-1.16^b		-4.90
44	$Mg^{2+} + HPO_4^{2-} \rightleftharpoons MgHPO_4(aq)$	-2.5^b	-2.5	
46	$Mg^{2+} + PO_4^{3-} \rightleftharpoons MgPO_4^-$	-3.13^b		

(a) Ferguson and McCarty (1971) from (b) Sillen and Martell (1964) and (c) Chughtai *et al*. (1968);
(d) Stumm and Morgan (1981); (e) Nordstrom *et al*. (1990).

Table 3.8b: Matrix representation of the ion pairing reactions of the most common Ca^{2+} and Mg^{2+} ion pairs in solutions containing carbonate and phosphate species. Ion pair stability constants and equilibrium equations are given in Tables 3.8a and 3.8c respectively.

Compound Number →		5	8	10	11	23	24	25	26	27....	....	33	34	35	
Process Number ↓		CO_3^{2-}	OH^-	HPO_4^{2-}	PO_4^{3-}	Ca^{2+}	Mg^{2+}	$CaOH^+$	$CaCO_3^0$	A^{X+}	B^{Y-}	AB^{X+Y-}	$MgHPO_4$	$MgPO_4^-$	Process Rate
26	Assoc. of Ca^{2+}, OH^-		-1			-1		+1							$K'_{fca1}\,[Ca^{2+}][OH^-]$
27	Dissoc. of $CaOH^+$		+1			+1		-1							$K'_{rca1}\,[CaOH^+]$
28	Assoc. of Ca^{2+}, CO_3^{2-}	-1				-1			+1						$K'_{fca2}\,[Ca^{2+}][CO_3^{2-}]$
29	Dissoc. of $CaCO_3^0$	+1				+1			-1						$K'_{rca2}\,[CaCO_3^0]$
....	Assoc. of A^{X+}, B^{Y-}									-1	-1	+1			$K'_{fST}\,[A^{X+}][B^{Y-}]$
....	Dissoc. of AB^{X+Y-}									+1	+1	-1			$K'_{rST}\,[AB^{X+Y-}]$
44	Assoc. of Mg^{2+}, HPO_4^{2-}			-1			-1						+1		$K'_{fmg4}\,[Mg^{2+}][HPO_4^{2-}]$
45	Dissoc. of $MgHPO_4^0$			+1			+1						-1		$K'_{rmg4}\,[MgHPO_4](aq)$
46	Assoc. of Mg^{2+}, PO_4^{3-}				-1		-1							+1	$K'_{fmg5}\,[Mg^{2+}][PO_4^{3-}]$
47	Dissoc. of $MgPO_4^-$				+1		+1							-1	$K'_{rmg5}\,[MgPO_4^-]$
	Units	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	

Table 3.8c: Specific rate constants for ion pair reactions in Tables 3.8a and 3.8b. See Loewenthal *et al.* (1989) for calculation of activity coefficients (f_i) for the different ionic species. The stability constants pK_{ST} values at infinite dilution are given in Table 1a.

No	Process	Specific rate constants					
		Ion pair association reaction		Ion pair dissociation reaction		Stability constant pK_{ST}	
		Symbol	Value	Symbol	Value	Symbol	Value
26..27	$Ca^{2+} + OH^- \rightleftharpoons CaOH^+$	K'_{fca1}	$K'_{rca1} \bullet K'_{CaOH+}$	K'_{rca1}	10^7 (/s)	K'_{CaOH+}	$10^{-pKCaOH+} \cdot f_m \cdot f_d / f_m$
28..29	$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3^0$	K'_{fca2}	$K'_{rca2} \bullet K'_{CaCO3}$	K'_{rca2}	10^7 (/s)	K'_{CaCO3}	$10^{-pKCaCO3} \cdot f_d \cdot f_d$
30..43	$A^{X+} + B^{Y-} \rightleftharpoons AB^{X+Y-}$	K'_{fST}	$K'_{rST} \bullet K'_{ST}$	K'_{rST}	10^7 (/s)	K'_{ST}	$10^{-pKST} \cdot f_{A(X+)} \cdot f_{B(Y-)} / f_{AB(X+Y-)}$
44..45	$Mg^{2+} + HPO_4^{2-} \rightleftharpoons MgHPO_4^0$	K'_{fmg4}	$K'_{rmg4} \bullet K'_{MgHPO4}$	K'_{rmg4}	10^7 (/s)	K'_{MgHPO4}	$10^{-pKMgHPO4} \cdot f_d \cdot f_d$
46..47	$Mg^{2+} + PO_4^{3-} \rightleftharpoons MgPO_4^-$	K'_{fmg5}	$K'_{rmg5} \bullet K'_{MgPO4-}$	K'_{rmg5}	10^7 (/s)	K'_{MgPO4-}	$10^{-pKMgPO4-} \cdot f_d \cdot f_t / f_m$

Table 3.9: Matrix representation of the processes of precipitation included in the two phase (solid/aqueous) mixed weak acid/base kinetic model. The single phase aqueous forward and reverse dissociation processes of weak acid/base species and the three phase processes of the carbonate system are given in Table 3.1 with the same numbering of the compounds.

No	Compound→ Process↓	1 NH_4^+	2 NH_3	3 $H_2CO_3^*$	4 HCO_3^-	5 CO_3^{2-}	6 H^+	7 OH^-	8 H_3PO_4	9 $H_2PO_4^-$	10 HPO_4^{2-}	11 PO_4^{3-}	12 HA	13 A^-	23 Ca^{2+}	24 Mg^{2+}	Rate
48	Precipitation of $CaCO_3$					-1									-1		$K'ppt_{CaCO3}([Ca^{2+}]^{\frac{1}{2}}[CO_3^{2-}]^{\frac{1}{2}}-K'_{spCaCO3}{}^{\frac{1}{2}})^2$
49	Precipitation of $MgNH_4PO_4$	-1										-1				-1	$K'ppt_{Struv}([Mg^{2+}]^{\frac{1}{3}}[NH_4^+]^{\frac{1}{3}}[PO_4^{3-}]^{\frac{1}{3}}-K'_{spStruv}{}^{\frac{1}{3}})^3$
50	Precipitation of $MgHPO_4$										-1					-1	$K'ppt_{Newb}([Mg^{2+}]^{\frac{1}{2}}[HPO_4^{2-}]^{\frac{1}{2}}-K'_{spNewb}{}^{\frac{1}{2}})^2$
51	Precipitation of $Ca_3(PO_4)_2$											-2/3			-1		$K'ppt_{ACP}([Ca^{2+}]^{\frac{3}{5}}[PO_4^{3-}]^{\frac{2}{5}}-K'_{spACP}{}^{\frac{1}{5}})^2$
52	Precipitation of $MgCO_3$					-1										-1	$K'ppt_{MgCO3}([Mg^{2+}]^{\frac{1}{2}}[CO_3^{2-}]^{\frac{1}{2}}-K'_{spMgCO3}{}^{\frac{1}{2}})^2$
	Units	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	

Example 3.7: ***Precipitation of mixed salts***

Ferguson and McCarty (1971) report data on precipitation of Ca and Mg minerals from solutions containing carbonate and phosphate system species, and the kinetic model predictions were compared with this data. The data of Ferguson and McCarty includes ion-pairing so this was included in the kinetic model (processes 26 to 47, Table 3.8b). Struvite precipitation (process 49 in Table 3.9) was not included because the solutions did not contain NH_4^+ species. Precipitation of Newberyite ($MgHPO_4$) (process 50 in Table 3.9) was also not included because it precipitates significantly only at low pH (<7), significantly lower than the pH range of the Ferguson and McCarty experiments, pH>8 - in the anaerobic digestor liquors (ADL) aeration batch tests described below ($7 < pH < 9.5$), $MgHPO_4$ precipitation was included and it formed less than 0.3% of the precipitate formed. Ferguson and McCarty accepted that the calcium phosphate mineral formed in their experiments was hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$, see Appendix A). However, in reviewing the literature on calcium phosphate mineral precipitation (Musvoto *et al.*, 1998; Appendix A), it is concluded that amorphous calcium phosphate (ACP, $Ca_3(PO_4)_2 \cdot xH_2O$) would be a more likely precipitant. Also, x-ray diffraction by Ferguson and McCarty indicate the presence of tricalcium phosphate, which has the same formula as ACP. Therefore, the precipitation of ACP (process 51 in Table 3.9) rather than HAP was included in the model. Calcite ($CaCO_3$) and magnesite ($MgCO_3$) also can be expected to precipitate in the Ferguson and McCarty experiments (processes 48 and 52 in Table 3.9 respectively). Thus, processes included in the model were 1 to 16 (Table 3.1) for the forward and reverse weak acid/base dissociations, processes 26 to 47 (Table 3.8b) for ion-pairing, and 48, 51 and 52 (Table 3.9) for the precipitation of Calcite ($CaCO_3$), ACP and Magnesite ($MgCO_3$) respectively.

Experiments 4 (Exp 4) and 5 (Exp 5) were selected from Ferguson and McCarty for simulation, because these two appeared the most suitable for multi precipitate formation modelling and the most internally consistent of the six experiments reported. These experiments were conducted at 29°C. The pK values and their temperature sensitivities for the water, carbonate, phosphate, ammonia and short chain fatty acid weak acid/base systems were included in the model as model constants (not changed); values were those given by Loewenthal et al. (1989) (see also Loewenthal et al., 1994 or Musvoto et al., 1997) which are the same as those used in the comparison with the Struvite 3.1 model described above. The stability constants for the 11 ion pairs (not adjusted for temperature) are those from Ferguson and McCarty and are given in Table 3.8a under column a. These were also included in the model as model constants (not changed).

The initial ionic strength (μ) was calculated from the ionic species making up the solutions and for Exps 4 and 5 this was 0.057 and 0.067 respectively. The solubility product values given as input to the model for the three minerals that were identified to precipitate were obtained from Ferguson and McCarty ($CaCO_3$ and $MgCO_3$) and Hoffmann and Marais (1977) (ACP) and are given in Table 3.10, i.e. for Exp 4 ($pH < 9$) $CaCO_3$ 6.8, $MgCO_3$ 6.7 and ACP 25.46 and for Exp 5 ($pH > 9$) $CaCO_3$ 6.5, $MgCO_3$ 6.6 and ACP 25.46. These values were not adjusted for temperature. The values for the first two minerals are the activity product (pA) values (which include adjustment for ionic strength) at equilibrium measured by Ferguson and McCarty. The activity product values are equivalent to the thermodynamic solubility product (Ferguson and McCarty, 1971) and accordingly were given as input to the model as such; in the model these are appropriately adjusted for ionic strength to give the apparent solubility products which are in terms of the molar concentrations used in the model. The measured activity product values were considered more suitable for simulating the experiments than the 7.8 and 7.9 solubility product values at infinite dilution quoted for pure solutions of $CaCO_3$ and $MgCO_3$ respectively by Ferguson and McCarty (1971) (see Appendix A), because the solubility products for $CaCO_3$ and $MgCO_3$ are influenced by the presence of Mg and Ca respectively, and the activity products were measured for the experiments being simulated and take these effects into account. The value for ACP is the activity product value from Hoffmann and Marais (1977) (see Appendix A). During the simulation, the ionic strength was continually calculated to take due consideration of changes in ionic concentrations as a result of mineral precipitation. Hence, the dissociation, stability and solubility constants/products were continually adjusted for ionic strength as the simulation proceeded to equilibrium. In order to keep the pH constant at the initial values as reported by Ferguson and McCarty, OH^- or H^+ dosing was included in the simulations.

With regard to precipitation rate constants, Ferguson and McCarty did not report time dependent data, only the initial and final (equilibrium) concentrations. Thus, only the final steady state (equilibrium) results of the model could be evaluated, not the mineral precipitation rates. However, in the experiments of Ferguson and McCarty minerals precipitate which compete for the same species, e.g. ACP and $CaCO_3$ both include Ca. In situations where competing minerals precipitate, it is possible that the final equilibrium condition will be influenced by the relative rates of precipitation of the competing minerals. Thus, in simulating the data of Ferguson and McCarty, although only the initial and final equilibrium states are given, the rates of precipitation were varied to evaluate the effect on the predicted final equilibrium state. From these simulations it was found that for the selected experiments the final equilibrium state was relatively independent of the precipitation rate constants, provided the precipitation rate constant for ACP was much larger than those for $CaCO_3$ and $MgCO_3$. Accordingly, the precipitation rates used for the simulations of both experiments were ACP 350/d, $CaCO_3$ 0.05/d and $MgCO_3$ 0.05/d. These rates were determined by visually fitting simulated to experimental data.

The measured and predicted final species concentrations remaining in solution for Exps 4 and 5 are given in Table 3.10. Also given in Table 3.10 for both experiments are the concentrations of Ca, Mg, P_T and C_T precipitated, as calculated from the difference between the kinetic model predicted initial and final concentrations, and as given by Ferguson and McCarty from measurements with x-ray diffraction. In comparing the kinetic model predicted results with those measured by Ferguson and McCarty, a difficulty is the lack of consistency in the measured data. For the kinetic model predictions, the concentration of Ca, Mg, P_T and C_T precipitated can be reconciled with the precipitated minerals (since these are calculated from the difference between initial and final soluble concentrations). However, in the measured results the concentrations of species precipitated are not equal to the difference between the initial and final soluble concentrations, e.g. in both experiments the measured precipitated P_T concentrations (2.57 and 2.95 mmol/ℓ respectively) are both greater than the difference between the measured initial and final P_T concentrations (1.67 and 1.87 mgP/ℓ respectively). The inconsistencies in the experimental results make a very close correlation between predicted and experimental results unrealistic. Taking the above into account, from Table 3.10 the predicted and measured final concentrations and concentrations of species precipitated match reasonably closely. Also, the kinetic model predicts correctly the expected precipitation behaviour; from Table 3.10, in both experiments 4 and 5 about 0.93 mmol/ℓ ACP was formed and, as expected, a significantly larger $CaCO_3$ and $MgCO_3$ concentration precipitated at high pH (Exp 5) than at low pH (Exp 4). Taken overall it appeared that the kinetic model performed well with multiple mineral precipitation and therefore was deemed sufficiently robust and stable to model the unsteady state behaviour of multiple mineral precipitation in aeration treatment of ADL.

Table 3.10: Initial and final concentrations for two Ferguson and McCarty (1971) mineral precipitation experiments (4 and 5) comparing the kinetic model predictions with experimental observation. With ion pairing. Temperature = 29°C.

Parameter	Experiment 4			Experiment 5		
	Initial Conditions	Final Ferg & McC	Final Kinetic Model	Initial Conditions	Final Ferg & McC	Final Kinetic Model
	mmol/ℓ	mmol/ℓ	mmol/ℓ	mmol/ℓ	mmol/ℓ	mmol/ℓ
μ	0.057	-	0.043	0.067	-	0.053
Ca_T	5.0	1.85	1.39	5.0	0.5	0.65
Mg_T	2.0	1.65	1.72	2.0	1.2	0.68
P_T	2.0	0.33	0.16	2.0	0.13	0.33
C_T	30.0	25.0	28.88	30.0	29.0	26.8
Na_T	40.0	-	-	59.5	-	-
Cl_T	14.0	-	-	14.0	-	-
pH	8.11	8.11±0.2[*1]	8.11	10.06	10.06±0.2[*1]	10.06
Concentrations precipitated (mmolℓ)						
Ca	-	3.52	3.61	-	4.55	4.35
Mg	-	0.29	0.28	-	0.88	1.32
P	-	2.57	1.84	-	2.95	1.67
C_T	-	1.35	1.12	-	2.74	3.16
Minerals precipitated as predicted by kinetic model (mmol/ℓ)						
ACP	-	-	0.92	-	-	0.84
$CaCO_3$	-	-	0.84	-	-	1.84
$MgCO_3$	-	-	0.28		-	1.32
Solubility product values (pK_{sp})						
ACP	-	-	25.46[*2]	-	-	25.46[*2]
$CaCO_3$	-	6.8[*3]	6.8[*3]	-	6.5[*3]	6.5[*3]
$MgCO_3$	-	6.7[*3]	6.7[*3]	-	6.6[*3]	6.6[*3]

[*1] Ferguson and McCarty (1971) state that the final pH was within 0.2 pH units of initial pH.

[*2] From Hoffmann and Marais (1977) - see Table 2.

[*3] Activity product values (which include correction for ionic strength) measured by Ferguson and McCarty (1971). The kinetic model results are based on these pK_{sp} values.

3.5.3 Two phase systems: Gas/Aqueous

The model developed above for the precipitation of sparingly soluble salts was extended to include the stripping of carbon dioxide and ammonia gases. Details of the rate equations used for gas stripping are given in Musvoto *et al*. (1998) and Appendix B. Kinetics and stoichiometry for the gas stripping processes are shown in matrix format in Table 3.11, processes 53 and 54 for CO_2 and 55 for NH_3. No data were available in the literature to check the combined two phase model which includes gas stripping.

3.5.4 Three-phase systems

Initially, the separate models for single phase mixed weak acid/base aqeous systems (Table 3.1), calcium carbonate precipitation (process 48, Table 3.9) and carbon dioxide gas exchange (processes 53 and 54, Table 3.11) were combined to give a simple three phase model, i.e. aqueous/solid/gas phases, with no biological processes. Values for the kinetic constants are listed in Tables 3.1(b and c) and 3.12(a and b). This was done because some data are available in the literature to test this model, so that the approach to modelling three phase systems could be evaluated.

To test the model, examples obtained from Loewenthal *et al.* (1986) were used. Predictions with the kinetic based model (in AQUASIM) were compared with those using the equilibrium-based Modified Caldwell Lawrence (MCL) graphical solution procedure (Loewenthal *et al.*, 1986) and the equilibrium-based computer programs STASOFT I (Loewenthal *et al.*, 1988) and STASOFT III (Friend and Loewenthal, 1992). The MCL diagrams use equilibrium constants derived from data obtained in the 1940s, while those used in STASOFT III are based on data obtained in the 1980s; STASOFT I includes the option to use either set of equilibrium constants. To evaluate the kinetic model, results from the MCL diagrams, STASOFT I and the kinetic model were compared using the same 1940s-based equilibrium constants, and the results from STASOFT I, STASOFT III and the kinetic model were compared using the same 1980s-based equilibrium constants; examples are given below.

Table 3.11: Matrix representation of the processes of gas stripping processes included in the three phase mixed weak acid/base kinetic model..

No	Compound→ Process↓	1 NH_4^+	2 NH_3	3 $H_2CO_3^*$	36 $CO_2(g)$	Rate
53	Dissolution of CO_2			1	-1	$K'_{rCO2}[CO_2(g)]$
54	Expulsion of CO_2 from solution			-1	-1	$K'_{rCO2}[H_2CO_3^*]$
55	Stripping of NH_3		-1			$K'_{rNH3}[NH_3]$
	Units	mol/ℓ	mol/ℓ	mol/ℓ	mol/ℓ	

Table 3.12(a): Constants for CO_2 exchange and $CaCO_3$ precipitation in mixed weak acid/base model; for pK values, see Table 3.12(b).

PROCESS	CONSTANTS			
	DESCRIPTION	SYMBOL	VALUE	UNITS
$CaCO_3$ precipitation $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)}$	Specific rate of ppt	K'_{rCaCO}	0.0171	/s
	Equilibrium constant	$K'_{spCaCO3}$	$10^{-pKspCaCO3}/f_d^2$	-
CO_2 exchange $CO_2gas \leftrightarrow H_2CO_3^*$	Dissolution of CO_2	K'_{rCO2}	$K'_{rCO2} \cdot K'_{eqCO2}$	/s
	Expulsion of CO_2	K'_{rCO2}	10^4	/s
	Equilibrium constant	K'_{eqCO2}	$K_{H,CO2} \cdot RT$	-
	Henry's law constant	$K_{H,CO2}$	$10^{-pKH,CO2}$	mol/ℓ/atm
	Universal gas constant	R	$8.20575 \cdot 10^{-2}$	ℓatm/K/mol

Table 3.12(b): Values for pK constants for $CaCO_3$ precipitation and Henry's law for CO_2 in the carbonate system three phase mixed weak acid/base model. (T is temperature in Kelvin).

pK CONSTANT	FORMULATION
1940s Data base (Loewenthal and Marais, 1976; Loewenthal *et al.*, 1989)	
$pK_{spCaCO3}$	$0.01183 \cdot T + 8.03$
1980s Data base (Friend and Loewenthal, 1992)	
$pK_{H,CO2}$	$-2\,025.3/T - 0.0104 \cdot T + 11.365$

Example 3.8: ***Determining the final state of an underground water after three-phase equilibrium is attained***

Analysis of an underground water to be pumped to the surface, gives $H_2CO_3^*$ alkalinity = 320 mg/ℓ, calcium = 210 mg/ℓ (both as $CaCO_3$), pH = 7.4, μ = 0.02 (TDS = 800 mg/ℓ) and temperature 15°C. The water is exposed to air. Determine the chemical state of the water after it has (1) achieved equilibrium with air, and (2) attained equilibrium with air and solid $CaCO_3$ (see Table 3.13).

Table 3.13a: Results for Example 3.8 obtained with equilibrium constants from the 1940s database after equilibrium with air

Parameter	**Unit**	**KINETIC MODEL**	**MCL**
$H_2CO_3^*$ alkalinity	mg/ℓ as $CaCO_3$	320	320
Ca^{2+}	mg/ℓ as $CaCO_3$	210	210
pH		8.95	8.83
$CaCO_3$ precipitation potential	mg/ℓ as $CaCO_3$	55.6	50
CO_2 expelled	mg/ℓ as $CaCO_3$	86.1	80

Table 3.13b: Results obtained with equilibrium constants from the 1980s database after equilibrium with air

Parameter	**Unit**	**KINETIC MODEL**	**STASOFT III**
$H_2CO_3^*$ alkalinity	mg/ℓ as $CaCO_3$	320	320
Ca^{2+}	mg/ℓ as $CaCO_3$	210	210
pH		8.95	8.92
$CaCO_3$ precipitation potential	mg/ℓ as $CaCO_3$	67.4	67.3
CO_2 expelled	mg/ℓ as $CaCO_3$	86.1	83.6

Note that STASOFT I cannot be used to predict the transient state of the water after equilibrium with air, and so cannot be included in the comparison in Tables 3.13 (a and b).

Table 3.14a: Results obtained for Example 3.8 with equilibrium constants from the 1940s database after equilibrium with air and solid $CaCO_3$ in solution.

Parameter	Unit	KINETIC MODEL	MCL	STASOFT I
$H_2CO_3^*$ alkalinity	mg/ℓ as $CaCO_3$	142.3	140	142.2
Ca^{2+}	mg/ℓ as $CaCO_3$	31.9	30	32.2
pH		8.62	8.52	8.59
$CaCO_3$ precipitated	mg/ℓ as $CaCO_3$	178.1	180	177.8
CO_2 expelled	mg/ℓ as $CaCO_3$	240.5	245	240.8

Table 3.14b: Results obtained with equilibrium constants from the 1980s database after equilibrium with air and solid $CaCO_3$ in solution.

Parameter	Unit	KINETIC MODEL	STASOFT I	STASOFT III
$H_2CO_3^*$ alkalinity	mg/ℓ as $CaCO_3$	133.1	134.5	131.8
Ca^{2+}	mg/ℓ as $CaCO_3$	23.1	24.5	21.8
pH		8.59	8.56	8.56
$CaCO_3$ precipitated	mg/ℓ as $CaCO_3$	188.4	185.5	188.2
CO_2 expelled	mg/ℓ as $CaCO_3$	249.7	247.8	-

From Tables 3.13 and 3.14, close correlation between the equilibrium and kinetic based approaches were obtained. This implies that the approach to modelling three phase systems is valid. Accordingly, the separate models for single phase aqueous systems (weak acid/base chemistry and biological processes, Table 3.4) and two phase systems (chemical precipitation, Table 3.9 and gas stripping, Table 3.11) were combined to give a complete three-phase systems model, i.e. aqueous/solid/gas phases. This model incorporates the biological as well as the physical/chemical processes most likely to occur in the treatment of HNLC wastewaters. Validation of this complete three phase model was hindered by the lack of experimental data in the literature. Accordingly, an experimental investigation was initiated to collect appropriate data to validate the model, see below.

3.6 CLOSURE

In this Chapter a three phase (aqueous/solid/gas) kinetic model has been developed to describe the combined biological, physical and chemical reactions that are likely to occur in the treatment of high nutrient low organic carbon (HNLC) wastewaters. This development has taken place in sections, with the sections being integrated as the modelling progressed. Wherever possible, as the various sections of the model were completed, these were validated using experimental data or model data available in the literature. In the validation, close correlation between kinetic model predicted results and literature data was obtained. However, complete model validation has been hindered by the lack of suitable data in the literature. Accordingly, an experimental investigation was initiated to collect appropriate data to validate the model, see Chapter 4.

CHAPTER 4

EXPERIMENTAL INVESTIGATION: VALIDATION OF KINETIC MODEL

4.1 INTRODUCTION

In Chapter 3, a kinetic model has been developed for three phase (aqueous/solid/gas) biological, physical and chemical processes. Rigorous validation of this kinetic model was hindered by lack of suitable data in the literature. To facilitate validation, experiments in the form of batch tests were run to collect the necessary data. The batch tests were divided into two categories, namely:

1. **Batch tests to validate the model for chemical and physical processes of precipitation and gas stripping**

To validate the model for chemical and physical processes, batch tests were conducted on anaerobic digestor liquors (ADL) from:

- A digestor treating a blend of primary and biological excess removal (BEPR) waste activated sludge (WAS).
- An upflow anaerobic sludge bed (UASB) digestor treating spent wine distillery effluent.

2. **Batch tests to validate the model for chemical and physical processes (as in 1 above) as well as biological processes of the activated sludge**

To validate the model for combined chemical, physical and biological processes, the following mixtures of wastewaters were tested in these batch tests:

- WAS and raw sewage
- WAS and anaerobic digestor supernatant (ADS)
- WAS and raw sewage with Ca, Mg, P and free and saline ammonia (FSA) addition.

Details of these experiments are outlined below.

4.2 EXPERIMENTS TO EVALUATE THE MODEL FOR CHEMICAL AND PHYSICAL PROCESSES

Having completed a preliminary validation of the model for single and multiple mineral precipitation with information in the literature, the model was applied to describe the time dependent three phase weak acid/base reactions that occur when anaerobic digestor liquors (ADL) are aerated. No suitable data in the literature were available on this, so an experimental investigation was undertaken to gather the appropriate data. Aeration of ADL from (i) a spent wine UASB digester (UASBDL) and (ii) an anaerobic digester treating sewage sludge (SSADL) was investigated.

4.2.1 Experimental procedure for UASBDL

Liquor from a UASB digester treating grape wine distillery waste at Stellenbosch Farmers' Winery (Wellington, South Africa) was collected directly into sealed pressurised containers. Care was taken that CO_2 loss was minimized during collection, to limit precipitation of minerals before the start of experiments. The containers were stored in the laboratory at 20°C. Five litre samples of the liquor were placed in a batch reactor, again taking care to minimize CO_2 loss, and the liquor was aerated for at least 24 hours. At frequent intervals, 100 mℓ and 10 mℓ samples were drawn from the batch reactor for analysis. The pH in the reactor was recorded regularly throughout the experiment and the temperature controlled to 20°C.

Immediately after sampling, the 10 mℓ sample was directly analysed for FSA without prior filtration. Experience had shown that significant loss of ammonia occurred during filtration at high pH. The 100 mℓ sample was immediately vacuum filtered through 0.45μm filters and the filtrate was divided into two. To one filtrate sample, a few drops (≈1.5 mℓ) of concentrated nitric acid (HNO_3) were added to reduce the pH to below 2 and so prevent further precipitation. The acidified filtered sample was analysed for the following:

- Ca, Mg and Fe: By emission spectroscopy using the inductively coupled plasma (ICP) method (Standards Methods, 1985). The Fe concentration was found to be very low (<1 mg/ℓ) and its analysis was thus discontinued after the first few batch tests. In hindsight this was an error because it was later learned that the $CaCO_3$ precipitation rate is very sensitive to even low concentrations of Fe.
- Phosphate system species (P_T): Molybdate/vanadate colour reaction and/or ICP method (Standard methods, 1985).

The second filtered sample was not acidified and was analysed for:

- Carbonate system species (C_T): This parameter was calculated after directly measuring the $H_2CO_3^*$ alkalinity and pH with the 5-point pH titration method of Moosbrugger et al. (1992), which is based on the mixed weak acid/base characterization method of Loewenthal et al. (1989) and takes due account of the presence of ammonia (N_T), phosphate (P_T) and short-chain fatty acid (A_T) weak acid/base system species[1].
- Short chain fatty acids (SCFA, A_T): 5-point pH titration Moosbrugger et al. (1992).

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[1] Loss of CO_2 during vacuum filtration does not significantly affect the $H_2CO_3^*$ alkalinity. Determination of the $H_2CO_3^*$ alkalinity requires knowing the carbonic acid ($H_2CO_3^*$) equivalence point pH. While by definition the $H_2CO_3^*$ alkalinity is independent of CO_2 loss or gain, loss or gain of CO_2 does influence the $H_2CO_3^*$ equivalence point pH, which increases slightly with loss of CO_2 (or C_T decrease). However, the difference in $H_2CO_3^*$ equivalence point pH does not significantly affect the $H_2CO_3^*$ alkalinity because the $H_2CO_3^*$ equivalence point is in an area of low buffer capacity for the carbonate system. Moreover, the mixed weak acid/base characterization method of Loewenthal et al. (1989) does not require the $H_2CO_3^*$ equivalence point pH to be known to determine the $H_2CO_3^*$ alkalinity. The 5 pH point titration method of Moosbrugger et al. (1992) was developed not so much to obviated the use of expensive instrumentation for analysing inorganic carbon (C_T) and short chain fatty acids (A_T), but to have a measurement method for C_T that is insensitive to CO_2 loss.

4.2.2 Experimental procedure for SSADL

Anaerobically digested sludge liquor was obtained from the anaerobic digesters at Cape Flats Wastewater Treatment Plant (Cape Town, South Africa). These digesters (with retention time of 10 to 12 days) treat a blend of primary and secondary waste activated sludge (WAS) from a 5 stage modified Bardenpho biological nutrient (nitrogen and phosphorus) removal activated sludge system, treating 150 Mℓ/d of wastewater, primarily of domestic origin. Although originally designed for biological excess P removal (BEPR), little BEPR took place at the time of testing with the result that the ADL did not contain the elevated P and Mg concentrations characteristic of ADL from BEPR plants. The anaerobically digested sludge was collected directly from the digesters through a sampling port into gas tight collection containers (with a volume of 20ℓ) which were immediately sealed. During sample collection care was taken that a minimum of CO_2 was lost which would lead to precipitation of minerals before the start of the batch tests. The sealed containers were stored in the laboratory at 20°C for about three days during which time sludge settlement took place. Five litres of liquor was then carefully withdrawn from one container (once more taking care to minimise loss of CO_2) and placed in a batch reactor. Preliminary analysis of the liquor gave soluble (< 0.45 µm) concentrations of Ca = 50 - 60 mg/ℓ, Mg = 20 - 30 mg/ℓ and P_T = 15 - 30 mgP/ℓ. These concentrations were too low to be representative of those in typical BEPR waste activated sludge ADL and so were increased by adding 500 mg of Ca, Mg and P (as Ca, Mg and P from $CaC\ell_2{\cdot}2H_2O$, $MgC\ell_2{\cdot}6H_2O$ and K_2HPO_4 respectively) to the 5ℓ batch volume (i.e. 100 mg/ℓ batch volume of each)[2]. Immediately after dosing, the liquor was aerated for at least 24 hours, but usually up to 56 hours to enable the kinetics of ammonia stripping to be observed. Aeration was by means of compressed air passed through a diffuser stone at the bottom of the batch reactor. At frequent intervals, 100 mℓ and 10 mℓ samples were drawn from the batch reactor for Ca, Mg, P_T, C_T, A_T and N_T analysis with the same methods as outlined above for the UASBDL. The pH in the reactor was recorded frequently throughout the batch test and the temperature controlled to 20°C.

Table 4.1 shows the initial and final values of some of the parameters measured for the three batch tests on UASBDL (Batch tests 16, 17 and 18) and the four batch tests on the SSADL (Batch tests 11, 12, 13 and 14). Detailed results are given in Musvoto et al. (1998).

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[2] There were no anaerobic digesters in the Western Cape region treating BEPR waste activated sludge from which SSADL with high concentrations of Mg and P_T could be obtained.

Table 4.1: Initial and final concentrations for four aerobic batch tests (11 to 14) on anaerobic digester liquor (SSADL) from a digester treating blended sewage primary sludge and waste activated sludge and three aerobic batch tests (16 to 17) on liquor from a UASB digester treating wine distillery waste (UASBDL).

Parameter	**SSADL**								**UASBDL**					
	Batch Test 11		**Batch Test 12**		**Batch Test 13**		**Batch Test 14**		**Batch Test 16**		**Batch Test 17**		**Batch Test 18**	
	Initial	Final*	Initial	Final*	Initial	Final*	Initial	Final*	Initial	Final*	Initial	Final*	Initial	Final*
Calcium (g/m^3)	113	32.1	129	33.6	133	51	83.8	18.6	54.8	23.7	58.6	22.5	55.4	20.0
Magnesium (g/m^3)	125	3.7	116	3.5	128	5.4	128	4.6	81.8	8.0	67.6	6.4	64.6	6.1
Phosphate (gP/m^3)	190	15.9	185	14.6	200	13.3	177	13.3	128	28.8	106	19.8	104	17.0
FSA (gN/m^3)	714	361	770	490	812	353	781	386	128	11.5	128	46.8	127	42.0
Inorganic carbon (gC/m^3)	720	165	700	216	720	126	720	135	820	470	847	490	830	470
pH	6.94	8.77	7.05	8.78	7.09	8.91	7.09	8.93	7.03	9.53	6.95	9.37	6.97	9.48
Duration of test (days; h)	2.25; 54		2.25; 54		2.33; 56		2.25; 54		1.00; 24		1.00; 24		1.00; 24	

*For Ca, Mg and P_T final concentration is the mean of the last three (SSADL) or two (UASBDL) measurements.

4.2.3 Model preparation

The kinetic model consisted of the weak acid/base systems (Table 3.1), ion pairing effects (Table 3.8b), mineral precipitation (Table 3.9) and gas stripping (Table 3.11). The model was given as input the eight dissociation constants (pK) and their temperature sensitivities for the 16 forward and reverse dissociation processes for the water, carbonate, phosphate, SCFA and ammonia weak acid/base systems (Tables 3.1b and c) and the 11 stability constants (pK_{ST}) for the 22 forward and reverse dissociation processes for the ion pairs (Tables 3.8a and c). Also given as input were the solubility product (pK_{SP}) values from the literature for the five minerals identified to precipitate (see Appendix A and Table 4.2). These pK, pK_{ST} and pK_{SP} values were accepted to be model constants (not changed). With the measured initial conductivity, also given as input and converted internally in the model to an ionic strength value with the formulae given by Loewenthal et al. (1989) (see Table 3.7a), the input pK, pK_{ST} and pK_{SP} values were internally corrected for ionic strength with the appropriate mono-, di- and tri-valent ion activity coefficients, as indicated in the above mentioned tables. The input pK values were also internally adjusted for temperature; the pK_{ST} and pK_{SP} values could not be adjusted as information on temperature sensitivities for these is not available in the literature. The initial measured total species concentrations (C_T, P_T, N_T, Ca and Mg) and pH were also given as input to the model for the batch tests.

Table 4.2: Model input values for the solubility products of the five minerals identified to precipitate in the seven aeration batch tests on the SSADL and UASBDL and model simulation results giving the mineral precipitation and gas stripping rate constants determined by trial and error visual correlation and Aquasim parameter estimation. (Tests on SSALD run for 54h; on UASB for 24h).

Test		Visual estimation results								Aquasim Parameter estimation results							
		Str'vite	Nwb'ite	ACP	$CaCO_3$	$MgCO_3$	O_2	CO_2	NH_3	Str'vite	Nwb'ite	ACP	$CaCO_3$	$MgCO_3$	O_2	CO_2	NH_3
	pK_{SP}	13.16	5.8	26.0	6.45	7.00	$K'_{La,O2}$	$K'_{La,CO2}$	$K'_{La,NH3}$	13.16	5.8	26.0	6.45	7.00	$K'_{La,O2}$	$K'_{La,CO2}$	$K'_{La,NH3}$
	Refs*[1]	(1)	(1)	(2)	(3)	(4)	-	-	-	(1)	(1)	(2)	(3)	(4)	-	-	-
BT 11	Rate*[2]	300	0.05	150	50	50	300	273	1.1	177	0.01	241	14	13	286	260	1.1
SSADL	Conc*[3]	1236	3.8	140	58	0	-	580	239	1209	1.3	154	51	<0.1	-	580	241
μ=0.16	%	88	0.3	10	4.1	0	-	-	-	85	0.1	11	3.6	0	-	-	-
BT 12	Rate*[2]	300	0.05	150	50	50	225	204	1.2	293	0.06	168	46	57	225	205	1.2
SSADL	Conc*[3]	1140	2.8	170	46	0	-	545	226	1128	4.0	175	70	<0.1	-	545	228
μ=0.17	%	84	0.2	12.5	3.4	0	-	-	-	82	0.3	13	5.1	0	-	-	-
BT 13	Rate*[2]	300	0.05	150	2	50	550	500	1.05	357	0.01	249	0.6	15	510	464	1.35
SSADL	Conc*[3]	1250	2.8	160	43	0	-	618	330	1237	1.0	198	23	<0.1	-	619	334
μ=0.18	%	85	0.2	11.0	3.0	0	-	-	-	85	0.1	14	1.6	0	-	-	-
BT 14	Rate*[2]	300	0.05	150	50	50	600	545	0.9	267	0.07	165	68	68	588	538	1.0
SSADL	Conc*[3]	1270	2.6	50	98	0	-	596	292	1247	3.7	66	91	0.95	-	596	292
μ=0.16	%	89	0.2	3.5	6.9	0	-	-	-	89	0.3	4.7	6.5	0	-	-	-
BT 16	Rate*[2]	3000	0.05	350	0.5	50	670	610	1.92	2406	0	388	0.3	39	619	563	1.98
UASB	Conc*[3]	677	2.1	91	<0.1	30	-	389	49	675	0	91	0.5	31	-	389	49
μ=0.08	%	84	0.3	11.4	0	3.8	-	-	-	85	0	11	0.1	3.9	-	-	-
BT 17	Rate*[2]	3000	0.05	350	0.5	50	400	365	2.5	2309	0	371	0.3	39	453	412	2.5
UASB	Conc*[3]	532	1.2	98	<0.1	30	-	389	49	530	0	98	0.5	31	-	389	49
μ=0.08	%	80	0.2	14.8	0	4.5	-	-	-	80	0	15	0.1	4.7	-	-	-
BT 18	Rate*[2]	3000	0.05	350	0.5	50	670	610	1.92	1815	0	385	0.3	48	581	529	2.2
UASB	Conc*[3]	528	0	92	<0.1	21	-	389	49	504	0	93	0.4	29	-	389	49
μ=0.08	%	82	0	14.4	0	3.3	-	-	-	80	0	15	0.1	4.6	-	-	-

*[1] References: (1) JESS - Murray and May (1996); (2) Butler (1964); (3) Merrill and Jorden (1975); (4) Not from any specific reference - selected 7.00 from the range reported by Mamais et al. (1994) - see Table 2. *[2] Rates in per day. *[3] Mineral precipitant concentrations in mg/ℓ, CO_2 in mgC/ℓ and NH_3 in mgN/ℓ.

4.2.4 Model calibration - determination of mineral precipitation and gas stripping rates

Correction for ionic strength in the model is dynamic so that any changes in ionic strength due to precipitation of minerals as the simulation continues, automatically readjusts the pK', pK'_{ST} and pK'_{SP} values. By changing only the precipitation rate constants (K'_{ppt}) for the five minerals and the specific gas stripping rate constants (K_r') for CO_2 and NH_3 (the calibration constants), these seven rate constants were determined by trial and error fitting of theoretical model predictions to the experimental data. The results obtained by this "visual" data fitting are listed in Table 4.2. The Aquasim model includes a parameter estimation facility which searches for selected parameter values between given upper and lower limits that give the best correlation between experimental and theoretical results. To check the "visually" determined precipitation and gas stripping rate constants, these seven rate constants were searched for simultaneously with the parameter estimation facility for each of the four batch tests on SSADL and the three batch tests on UASBDL. The lower and upper limits specified for the seven rate constants were zero and double the visually determined values respectively (all parameter estimation values fell within this range). The rate constants and results from the parameter estimation simulations are given in Table 4.2. Also given in Table 4.2 are the concentrations of each mineral precipitated and the mass % these represent in the total concentration of minerals precipitated. Table 4.3 gives a summary of the *initial concentrations* of Ca, Mg and P_T in the batch tests as well as other parameters cited in the literature which affect the precipitation of the various minerals in wastewaters of this type. It should be noted that these initial concentrations and β ratios change rapidly as the pH increases due to CO_2 expulsion. Therefore, while, for example, $CaCO_3$ is initially undersaturated, it quickly becomes supersaturated and precipitates as the test progresses.

As examples, Figs 4.1 to 4.4 show the measured and predicted results from the parameter estimate simulations for batch tests 16 and 18 on the UASBDL and batch test 11 and 12 on SSADL respectively. (Comparisons for the other batch tests are given by Musvoto *et al*., 1998). It can be seen that a good correlation is obtained between experimental and theoretical model predictions for both liquors. Moreover, visually there is very little discernable difference between Figs 4.1 to 4.4 and the figures (not shown) of the results from the visually determined precipitation and gas stripping rates. A comparison of the predicted results from the visual calibration and parameter estimate simulations can be made from Table 4.2.

Table 4.3: Summary of some of the parameters that affect the precipitation of minerals for batch tests on SSADL and UASBDL.

Batch Test No.	ADL Type	Mg_i g/m^3	Ca_i g/m^3	P_{Ti} gP/m^3	Mg_i mol/l	Ca_i mol/l	P_{Ti} mol/l	Mg/Ca molar	Mg/P molar	Ca/P molar	β_{Ni}	β_{Si}	β_{Ni}/β_{Si}	β_{CaCO3i}
11	SSADL	125	113	190	0.0052	0.0028	0.0061	1.86	0.85	0.46	4.4	6.1	0.72	0.08
12	SSADL	116	129	152	0.0048	0.0032	0.0049	1.5	0.98	0.65	4.7	9.0	0.52	0.12
13	SSADL	128	133	200	0.0053	0.0033	0.0065	1.61	0.82	0.51	6.3	16.3	0.39	0.14
14	SSADL	128	83.8	177	0.0053	0.0021	0.0057	2.52	0.93	0.37	5.5	12.0	0.46	0.09
16	UASBDL	81.8	54.8	128	0.00034	0.0014	0.0041	2.43	0.83	0.34	2.4	0.9	2.7	0.05
17	UASBDL	67.6	58.6	106	0.0028	0.0015	0.0034	1.87	0.82	0.44	1.4	0.35	4.0	0.05
18	UASBDL	64.6	55.4	104	0.0027	0.0014	0.0034	1.93	0.79	0.41	1.4	0.35	4.0	0.05

Note: 1. β_{Ni}, β_{Si}, and β_{CaCO3i} are the initial supersaturation for newberyite, struvite and $CaCO_3$ respectively. Initial supersaturation is defined as the ratio of the initial ionic product to the solubility product e.g. for $CaCO_3$, $\beta_{CaCO3i} = (Ca^{2+}_i)(CO_3^{2-}{}_i)/K_{spCaCO3}$

2. Subscripts "T" = total ortho-phosphate species, and "i" = initial.

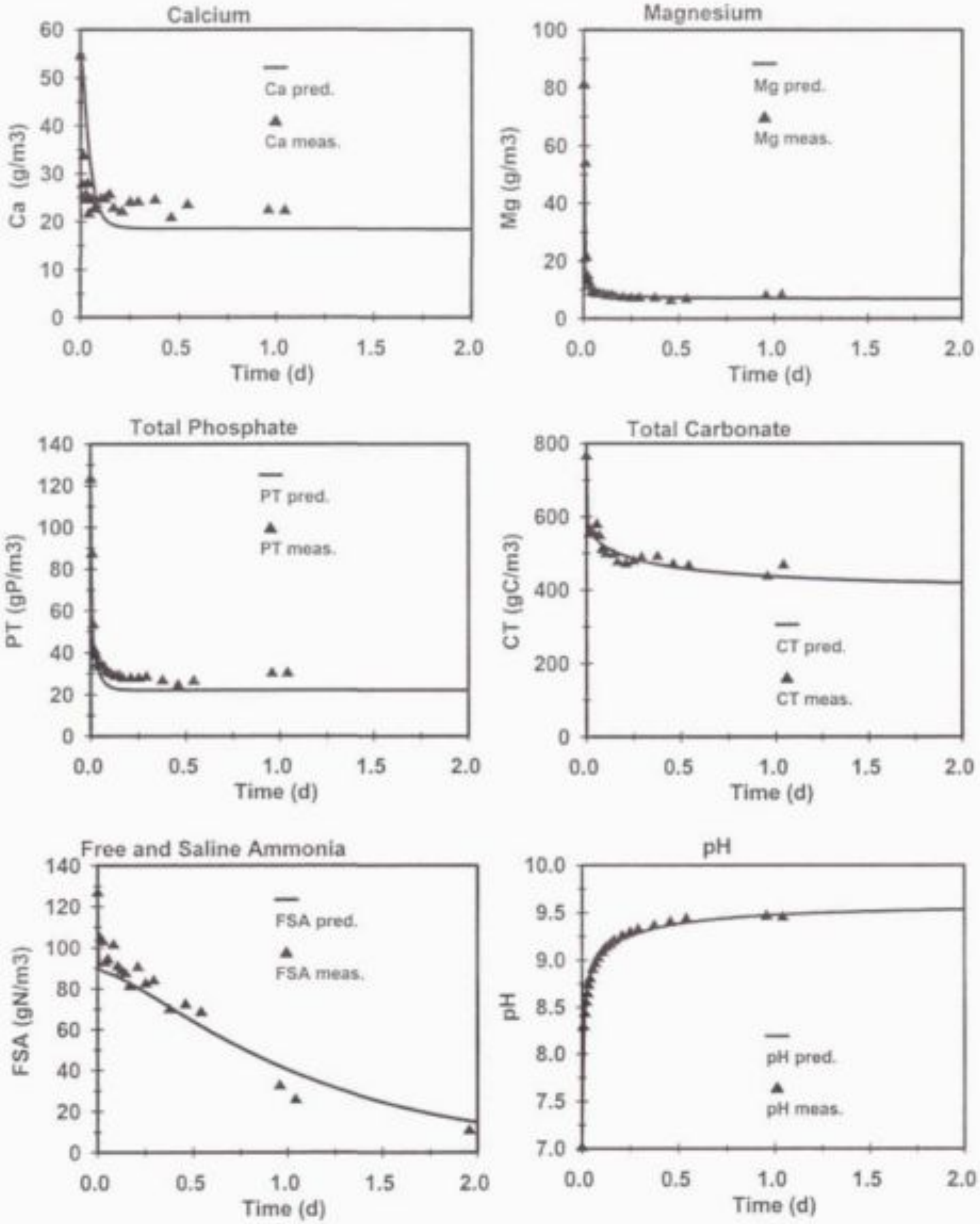


Fig 4.1: Predicted (parameter estimate results) and measured soluble concentrations for calcium (Ca, top left), magnesium (Mg, top right), total phosphate species (P_T, middle left), total carbonate species (C_T, middle right), free and saline ammonia (FSA, bottom left) and pH (bottom right) for aeration Batch Test 16 on ADL from Stellenbosch Farmers' Winery (Wellington, South Africa) spent wine UASB digester.

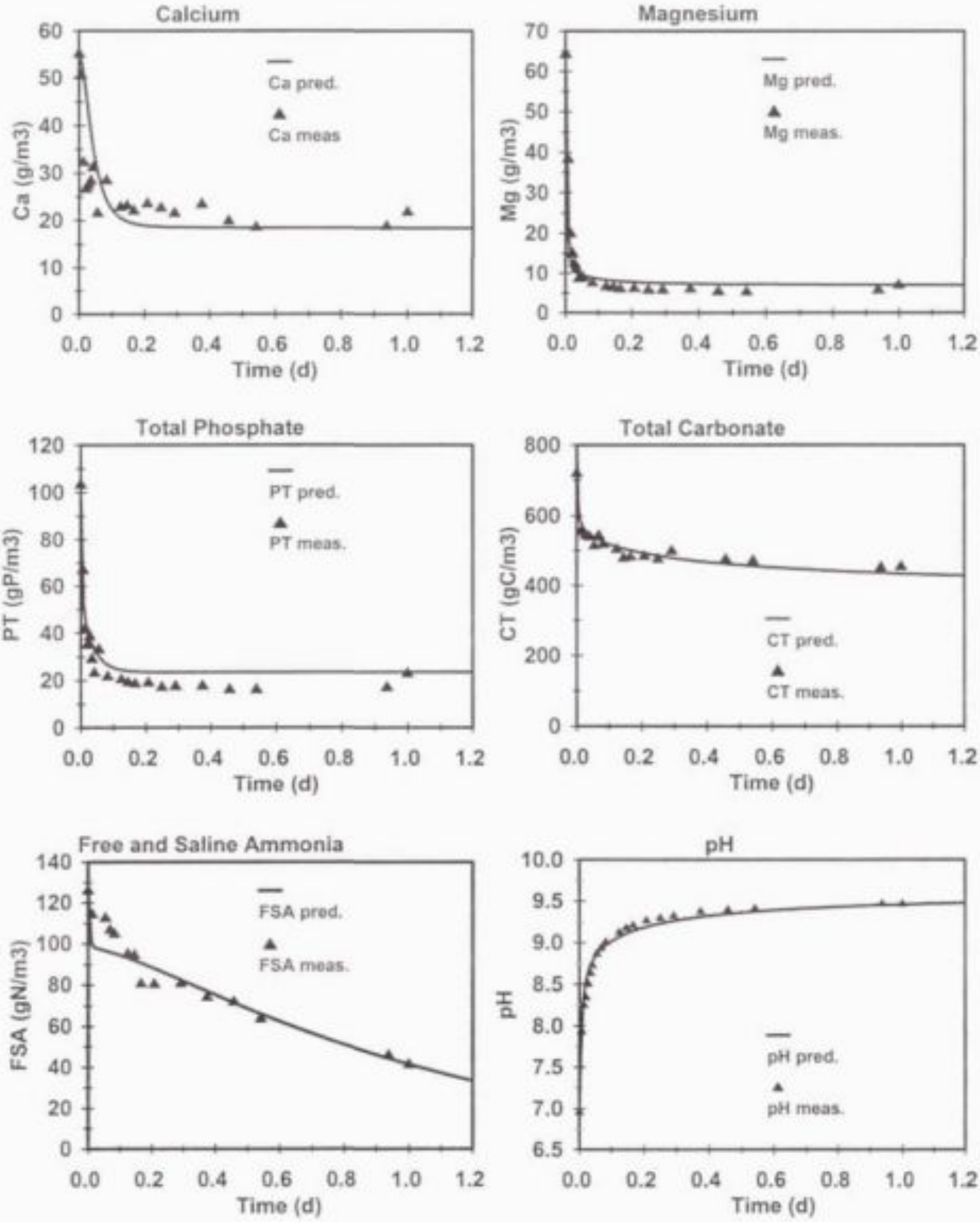


Fig 4.2: Predicted (parameter estimate results) and measured soluble concentrations for calcium (Ca, top left), magnesium (Mg, top right), total phosphate species (P_T, middle left), total carbonate species (C_T, middle right), free and saline ammonia (FSA, bottom left) and pH (bottom right) for aeration Batch Test 18 on ADL from Stellenbosch Farmers' Winery (Wellington, South Africa) spent wine UASB digester.

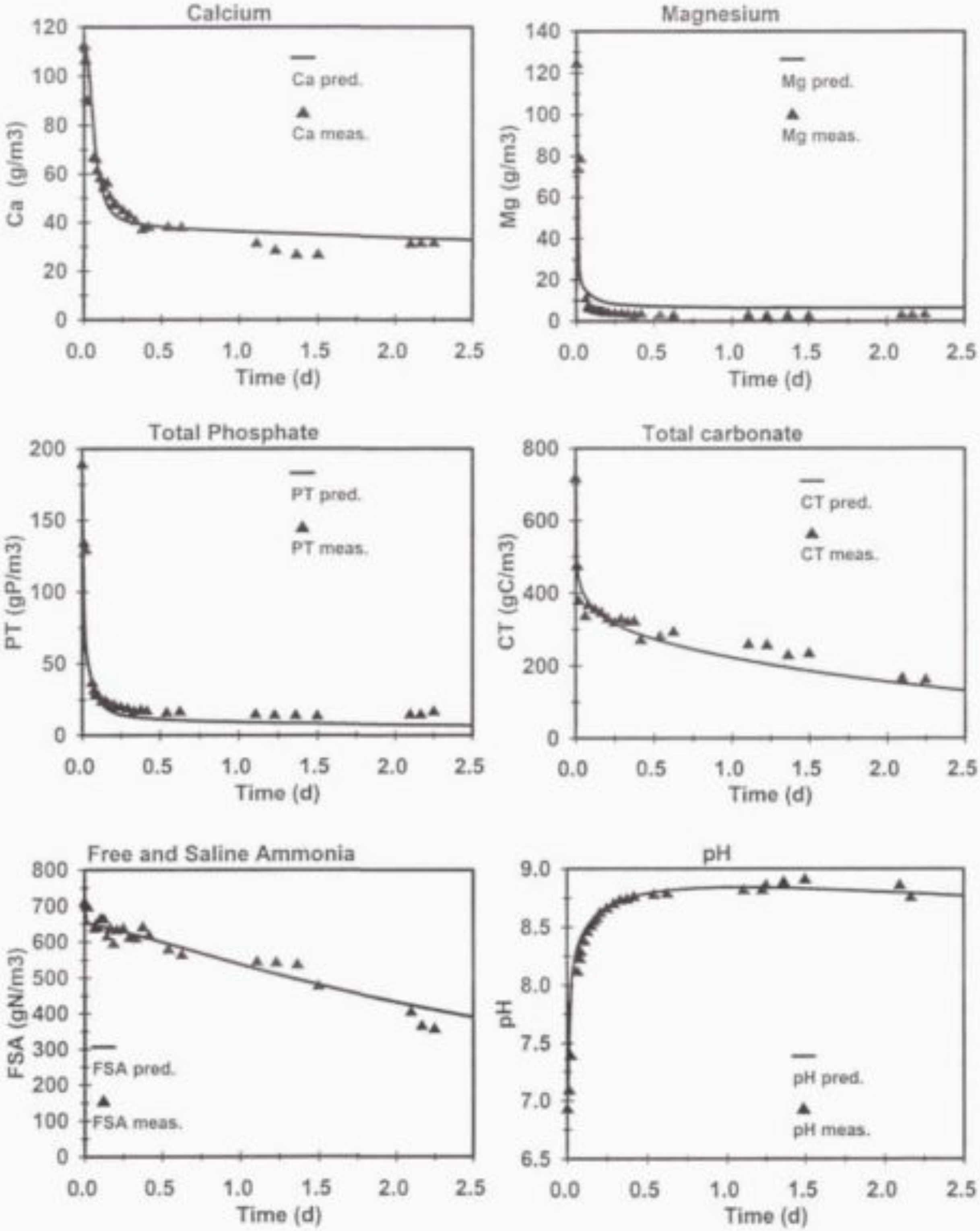


Fig 4.3: Predicted (parameter estimatation) and measured soluble concentrations for calcium (Ca, top left), magnesium (Mg, top right), total phosphate species (P_T, middle left), total carbonate species (C_T, middle right), free and saline ammonia (FSA, bottom left) and pH (bottom right) for aeration Batch Test 11 on ADL from Cape Flats Wastewater Treatment Plant (Cape Town, South Africa) digestor treating primary and waste activated sludge.

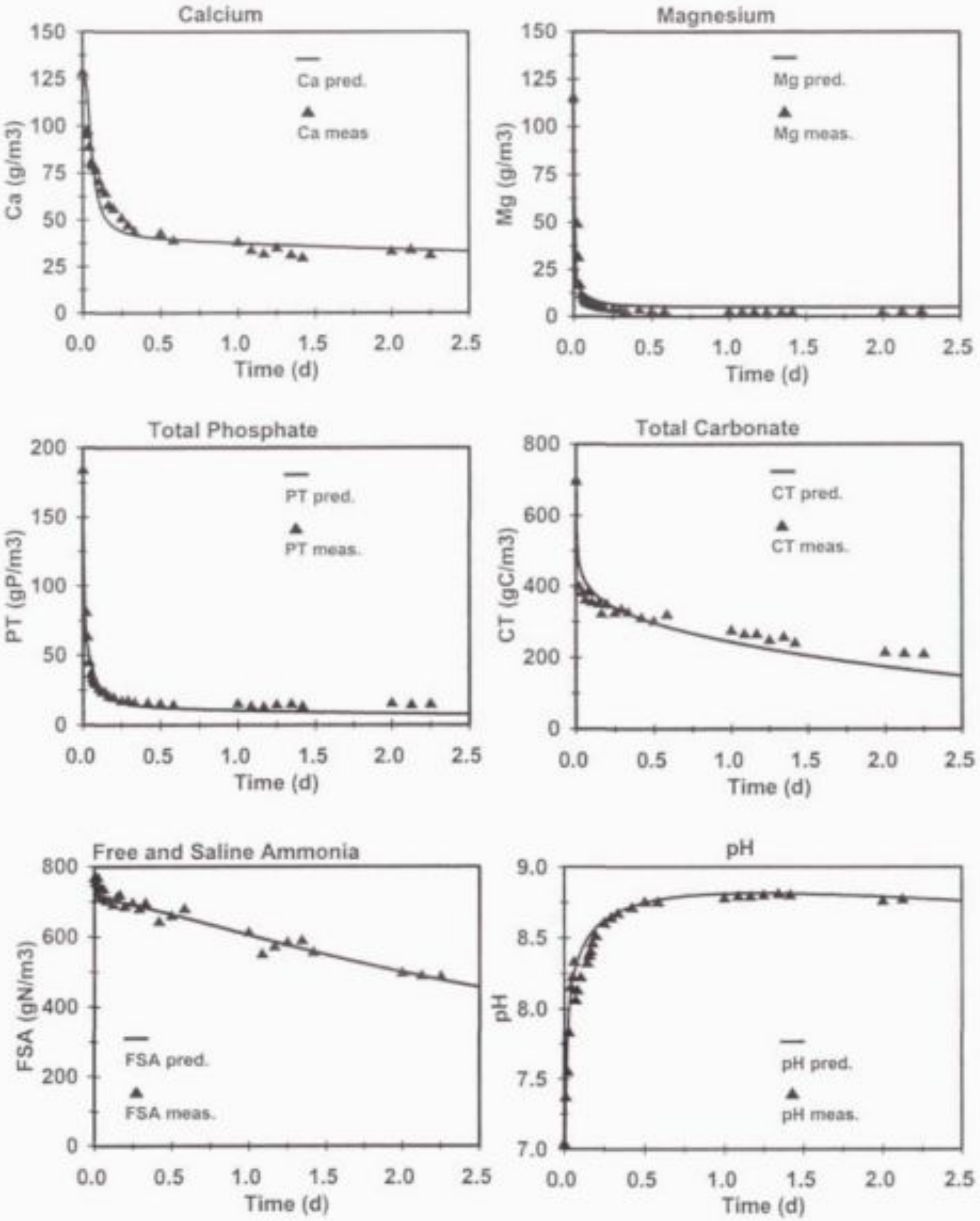


Fig 4.4: Predicted (parameter estimation) and measured soluble concentrations for calcium (Ca, top left), magnesium (Mg, top right), total phosphate species (P_T, middle left), total carbonate species (C_T, middle right), free and saline ammonia (FSA, bottom left) and pH (bottom right) for aeration Batch Test 12 on ADL from Cape Flats Wastewater Treatment Plant (Cape Town, South Africa) digester treating primary and waste activated sludge.

4.2.5 Results and discussion

The following conclusions can be drawn from a comparison of the simulation results for the two liquors (Tables 4.2 and 4.3):

1. Solids most likely to precipitate

The same solids, viz. struvite, ACP, newberyite, $CaCO_3$ and $MgCO_3$, were identified from the literature as most likely to precipitate in both SSADL and UASBDL and on this basis were included in the model. With these precipitants, the consistency between predicted and measured soluble species concentrations (Figs 4.1 to 4.4) indicates that no precipitants of importance have been omitted from the model. From the simulations, in both liquors struvite formed the bulk (80 to 89%) of the total mass of precipitate formed, followed by ACP (3.5 to 14.8%) (Table 4.2). $MgCO_3$ was predicted to precipitate in the UASBDL, but not in the SSADL. This is because the pH for the UASBDL increased to about 9.5 which is significantly higher than that for the SSADL, where the increase was to about 8.9; the higher pH stimulated $MgCO_3$ precipitation. This is in agreement with the literature where it is noted that at higher pH, $MgCO_3$ is likely to precipitate, but not at lower pH; from the simulations, at the lower pH the concentration of CO_3^{2-} species is too low for the solution to be supersaturated with respect to $MgCO_3$. In the UASBDL, $MgCO_3$ comprised 3.3 to 4.5% of the total mass of precipitate formed (Table 4.2). Conversely, $CaCO_3$ was predicted to precipitate in SSADL, but not significantly in UASBDL. This difference in precipitation behaviour between SSADL and UASBDL for $CaCO_3$ could only be taken into account in the simulations by significantly reducing the precipitation rate for the UASBDL batch tests (see below). In the SSADL, $CaCO_3$ comprised 3.0 to 6.9% of the total mass of precipitate formed. Newberyite was predicted to precipitate in small amounts from both liquors in the visual calibration simulations whereas in the parameter estimation simulations it was predicted to precipitate only in the SSADL; however, in all simulations it comprised only < 0.3% of the precipitate mass formed (Table 4.2). From information in the literature, this is expected because the pH, initial molar concentrations and the degrees of supersaturation for newberyite and struvite present during aeration favour the precipitation of struvite over newberyite, i.e. newberyite precipitates at pH < 6.0, P concentrations > 0.01M and $\beta_{Ni}/\beta_{Si} > 4$ (Abbona et al., 1982).

2. Solubility products (pK_{sp})

For each of the five minerals that precipitated, the pK_{sp} values were model constants (not changed) and were the same for both the SSADL and UASBDL (Table 4.2). All are within the range of accepted literature values commonly used in equilibrium based water chemistry (see Appendix A).

3. Specific rate constants for precipitation (K'_{ppt})

From the parameter estimation results (Table 4.2), in the UASBDL the K'_{ppt} for struvite and ACP, which together make up >95% of the precipitate mass, varied from 1815 to 2406 /d and 371 to 388 /d respectively. The K'_{ppt} for Newberyite and $CaCO_3$ were the same in all three batch tests at 0 /d and 0.3 /d respectively. The K'_{ppt} for $MgCO_3$ varied from 39 to 48 /d. Struvite and ACP precipitation were complete in three and eight minutes respectively. This can be seen in Fig 4.5 which shows the concentration of mineral precipitated with time for Batch Test 16 on UASBDL (parameter estimate prediction). The batch tests were continued for at least 24 hours to observe also the ammonia stripping rate (see below).

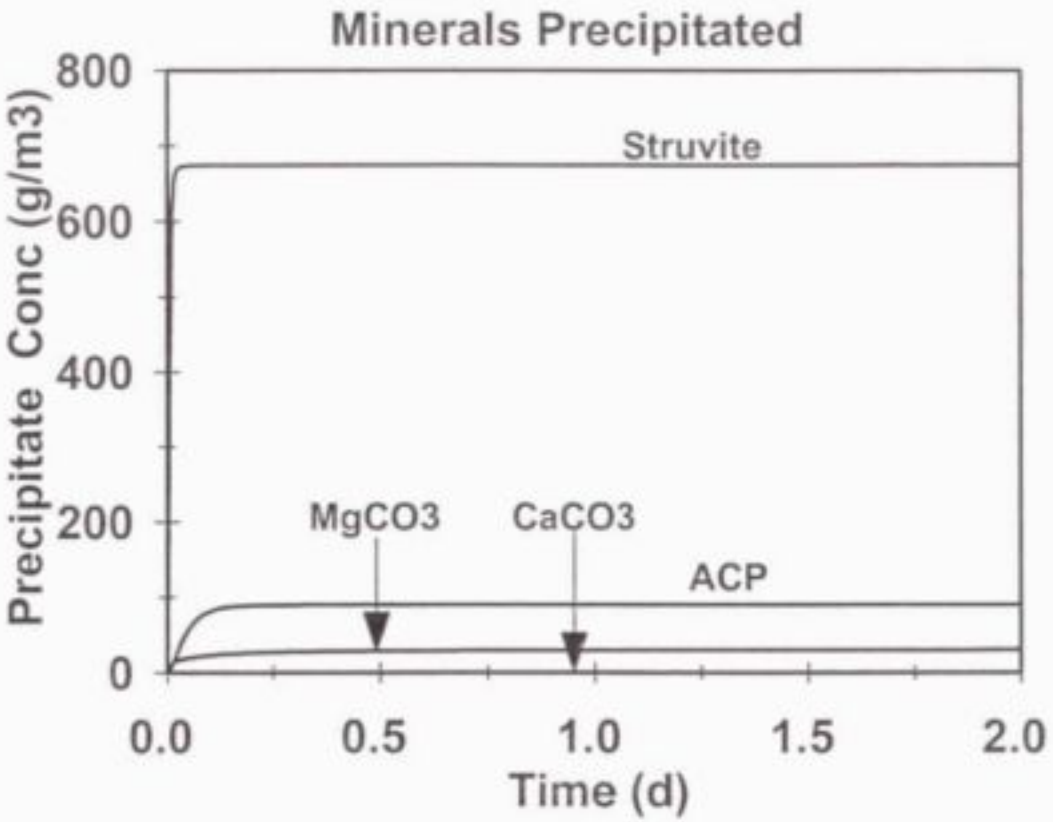


Fig 4.5: Predicted (parameter estimate results) concentrations of struvite, amorphous calcium phosphate (ACP), $MgCO_3$ and $CaCO_3$ precipitated with time in aeration Batch Test 16 on anaerobic digester liquor from Stellenbosch Farmers' Winery (Wellington, South Africa) spent wine UASB digester. Newberyite ($MgHPO_4$) too low to be included.

From the parameter estimation results (Table 4.2), in the SSADL the K'_{ppt} for struvite and ACP varied from 177 to 357 /d and 165 to 249 /d respectively. The K'_{ppt} for Newberyite was very low and varied from 0.01 to 0.07 /d. The K'_{ppt} for $CaCO_3$ varied between 14 and 68 /d with one very low value of 0.6 /d for Batch Test 13. The K'_{ppt} for $MgCO_3$ varied between 13 and 68 /d (however, the very small amount of $MgCO_3$ precipitated, < 1mg/ℓ, makes accurate estimation of this rate difficult). The reason for the very low K'_{ppt} for $CaCO_3$ in Batch Test 13 could not be established. For some reason that could not be determined, in both the visual fit and parameter estimation simulations Batch Test 13 with the very low K'_{ppt} for $CaCO_3$ differs from the other three tests on SSADL. The visually calibrated and parameter estimation simulation results for Batch Test 13 are shown in Figs 4.6 and 4.7 respectively. Because in the visual calibration a good correlation with pH was emphasised (Fig 4.6), the correlation for pH is good but for the FSA, Ca and C_T the correlation is not so good. In the parameter estimate simulations (Fig 4.7), this bias towards a good fit for pH was absent and the correlation between the predicted and observed results is improved for FSA, Ca and C_T, but the pH is consistently under predicted. As is evident above, this lack of fit with all the measured data is absent in the other 6 batch tests.

4. *Comparison of specific precipitation rates in UASBDL and SSADL.*

The specific precipitation rate constants (K'_{ppt}) found for struvite, ACP and $CaCO_3$ differ significantly between the SSADL and UASBDL (Table 4.2). The rates for struvite and ACP in both the visual and parameter estimation simulations are much higher in the UASBDL than in the SSADL. Conversely, in both sets of simulations the rate for $CaCO_3$ is lower for the UASBDL than for SSADL. The rates for Newberyite and $MgCO_3$ were similar in the UASBDL and SSADL, viz. 0.05/d and 50/d respectively for visual simulations and between 0 and 0.07 /d and 13 and 68 /d respectively for parameter estimation simulations. With regard to the K'_{ppt} for struvite and ACP, it is most likely that these differences are due to inhibition of the precipitation process through "poisoning" of the crystal growth sites. The presence of even small amounts of foreign organic and inorganic constituents, trace quantities of surfactants and other materials are known to alter significantly the growth rate of crystals and their morphology (Stumm and Morgan, 1981). The SSADL contained considerably more particulate organics than the UASBDL, which most likely acted as inhibitors (rather than providing more seed material surface area) and probably is the reason for the slower rates of precipitation of struvite and ACP in the SSADL than in the UASBDL.

With regard to the precipitation rate of $CaCO_3$, from the literature this is particularly sensitive to and inhibited by the presence of dissolved organic matter, polyphosphates, polyphenols, phosphoric acid derivatives, fulvic acid, magnesium, organic and inorganic phosphate and iron. Fe^{2+} is known to be the strongest inhibitor, reducing the $CaCO_3$ growth rate even at very low concentrations (Droomgoole and Walter, 1990). The inhibition by inorganic P depends on both the initial concentration and the initial degree of supersaturation of $CaCO_3$. The phosphate concentration in solution does not affect the kinetics of precipitation once crystal growth has started, but generally the rate of precipitation is lower if the initial supersaturation of $CaCO_3$ is lower (House, 1987). In the experiments, the initial Mg/Ca and Mg/PO_4-P ratios are not significantly different in the two liquors, though the initial Mg/Ca ratio tends to be higher in the UASBDL (Table 4.2). The initial $CaCO_3$ saturation is lower in the UASBDL than in SSADL, but initially both are strongly undersaturated with $CaCO_3$. Because in the batch test several minerals are precipitating and pH is rising, the relative ratios of the species concentrations and the saturation state change with time. Because struvite precipitates so rapidly and ACP more slowly, the P_T and Mg concentrations decrease very quickly, but the Ca concentration more slowly. This, with the rising pH, causes $CaCO_3$ to become supersaturated several minutes into the test. Therefore, by the time $CaCO_3$ starts precipitating, the Mg and P_T concentrations are already low. Under these conditions, it is difficult to assess the significance of the effect of initial condition parameters (concentration and β ratios such as in Table 4.3) on the precipitation rates.

Although the filtered COD concentration (which is an indication of soluble organics) was not measured for each batch test, measurements on a few samples showed a soluble concentration of 900 mg/ℓ for SSADL and 980 mg/ℓ for UASBDL. Measurements of Fe indicated low concentrations (0.2 to 0.7mg/ℓ) and that the concentrations did not differ significantly between SSADL and UASBDL; accordingly, this cannot account for the difference in $CaCO_3$ precipitation rates between the two liquors. The presence of compounds such as pyrophosphates, polyphenols and fulvic acid, which are known to inhibit $CaCO_3$ precipitation, were not determined in the two liquors. It therefore appears that the lower precipitation rate constant for $CaCO_3$ in the UASBDL may be due to: (i) higher concentrations of inhibiting compounds like pyrophosphates, (ii) a lower initial $CaCO_3$ β ratio and possibly, though unlikely, (iii) dissolved organic substances because the filtered COD of the UASBDL is slightly higher than the SSADL. Because all these effects are not taken into account directly in the model, they are reflected by a change in the specific precipitation rate constant. However, it is not possible to identify definitively the cause for the difference in $CaCO_3$ precipitation rates between the two liquors.

5. Gas stripping

The specific rates for gas stripping for both CO_2 and NH_3 differed for each individual batch test (Table 4.2). This is not unexpected because the aeration conditions (gas flow rates, mixing, solids, etc.) differed in each batch test. With the clarity of hindsight, the aeration rates in the batch tests should have been controlled to be the same for all the batch tests, which would have eliminated the specific gas stripping rate as a calibration constant for each batch test.

6. Comparison of CO_2 and NH_3 stripping rates.

The stripping rate for CO_2 is much higher, by two orders of magnitude, than that for NH_3. This is in agreement with the literature where it is evident that the volatility of NH_3 is much lower than that for CO_2. This is reflected in the value for the dimensionless Henry's constant (H_C). For NH_3, $H_C = 0.011$ whereas for CO_2, $H_C = 0.95$ (Loewenthal et al., 1986; Katehis et al., 1998). In the batch tests, the pH was raised by stripping CO_2. Because this process is relatively slow, the mineral precipitation rates may have been influenced by the pH rise rate. The effect of the gas stripping rate on the mineral precipitation rates was not examined in this investigation. In future work it is intended to measure the mineral precipitation rates in batch tests with lime or NaOH addition to rapidly increased the pH without aeration or with delayed aeration at controlled rates, to examine the effect of this on the mineral precipitation rates.

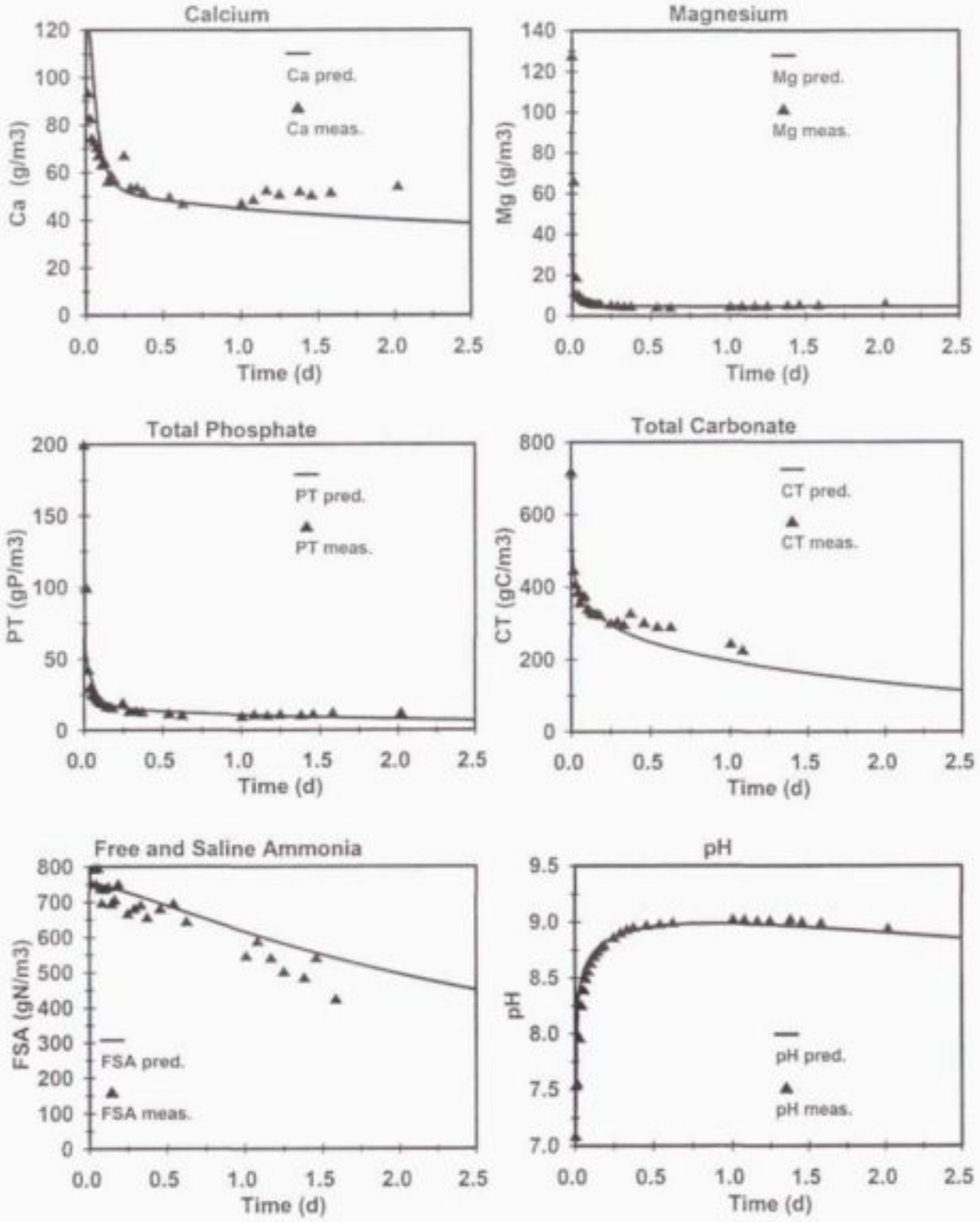


Fig 4.6: Predicted (visual calibration) and measured soluble concentrations for calcium (Ca, top left), magnesium (Mg, top right), total phosphate species (P_T, middle left), total carbonate species (C_T, middle right), free and saline ammonia (FSA, bottom left) and pH (bottom right) for aeration Batch Test 13 on ADL from Cape Flats Wastewater Treatment Plant (Cape Town, South Africa) digester treating primary and waste activated sludge.

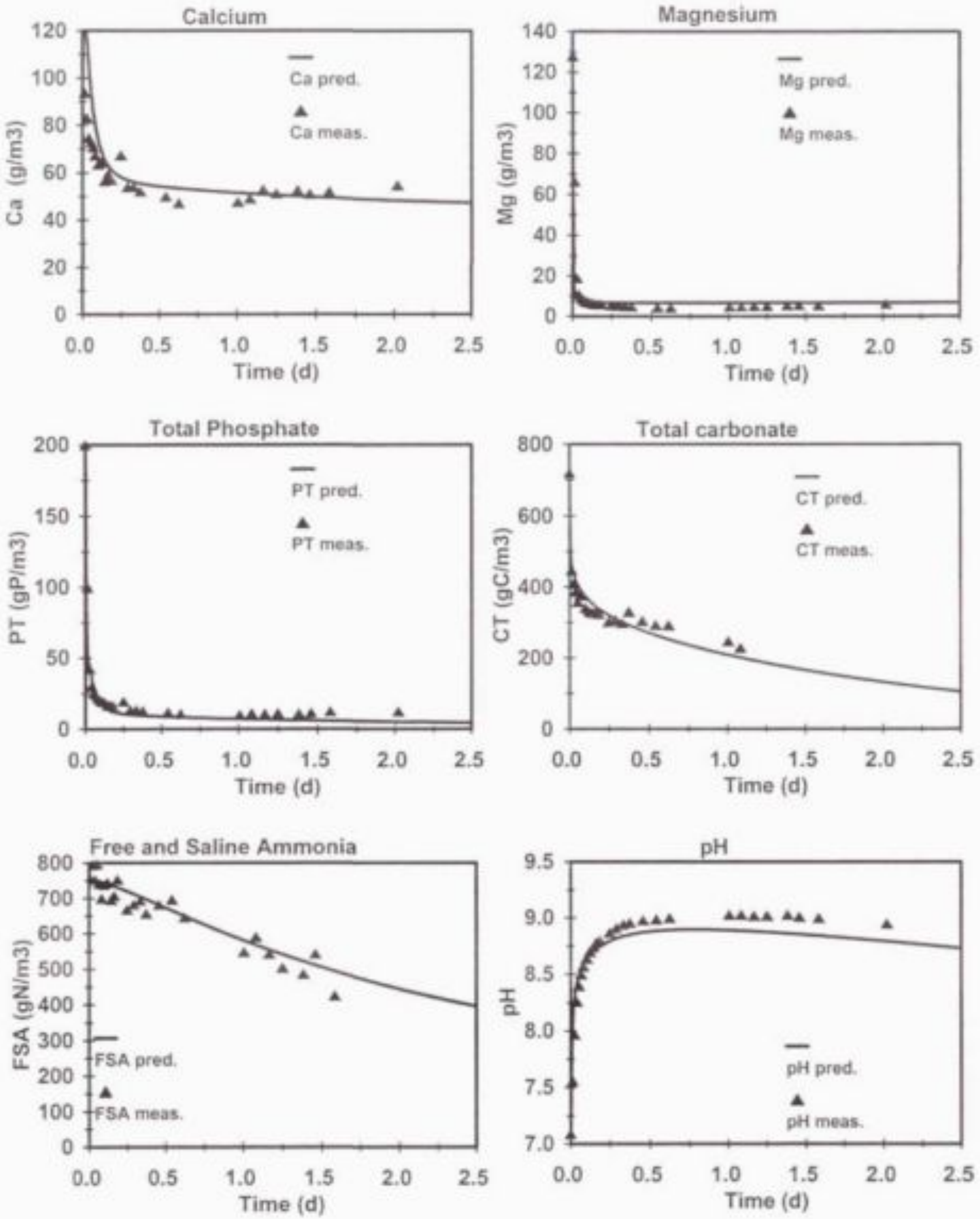


Fig 4.7: Predicted (parameter estimation) and measured soluble concentrations for calcium (Ca, top left), magnesium (Mg, top right), total phosphate species (P_T, middle left), total carbonate species (C_T, middle right), free and saline ammonia (FSA, bottom left) and pH (bottom right) for aeration Batch Test 13 on ADL from Cape Flats Wastewater Treatment Plant (Cape Town, South Africa) digester treating primary and waste activated sludge.

4.2.6 Conclusion

A three phase physical-chemical kinetic model was developed to include the phosphate, ammonia and short chain fatty acid weak acid/base systems in three phases with multi-mineral precipitation and multi-gas stripping. This specific kinetic model was developed to simulate the physical-chemical reactions which occur in the aeration treatment of anaerobic digester liquors (ADL). The processes that occur under these conditions are the dissociation of the weak acid/bases, precipitation of solids (struvite, newberyite, amorphous calcium phosphate, magnesium and calcium carbonate) and stripping of CO_2 and NH_3 gases. Ion pairing effects are also included in the model, because the ionic strength of the liquors tested was greater than 0.025.

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

To validate the time dependent performance of the model and determine the calibration constants, batch experiments were conducted by aerating two anaerobic digester liquors (ADL), viz. three batch tests on liquor from a spent wine UASB digester (UASBDL) and four batch tests on liquor from an anaerobic digester treating a blended primary sludge and waste activated sludge (SSADL). In these batch tests, Ca, Mg, PO_4-P (P_T), inorganic C (C_T, via the H_2CO_3* Alk), free and saline ammonia (FSA, N_T) and pH were measured over 24 to 54h. After establishing (i) the minerals most likely to precipitate viz. struvite ($MgNH_4PO_4$), newberyite ($MgHPO_4$), amorphous calcium phosphate [ACP, $Ca_3(PO_4)_2$], $CaCO_3$ and $MgCO_3$ and (ii) their solubility products from the literature, the specific precipitation and gas stripping rate constants were determined by (i) trial and error visual fitting of predicted results to the experimental data and (ii) a parameter estimation facility which searches for the calibration constants that minimize the error between the model predictions and experimental results. A good correlation was obtained between model predictions and experimental results with both methods for six of the seven batch tests and while the second method may be superior, visually there was no discernable difference between the predicted results of the two methods. The good correlation indicated that no mineral that precipitated significantly in the ADL were omitted from the model.

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

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

In conclusion, the three phase kinetic based weak acid/base chemistry model, and the approach on which it is based, has been validated for chemical and physical processes. This modelling approach now needs to be extended to include biological processes, such as those of anaerobic digestion or biological nutrient removal activated sludge. This is done in the next section.

4.3 EXPERIMENTS TO VALIDATE THE MODEL FOR CHEMICAL, PHYSICAL AND BIOLOGICAL PROCESSES

Having successfully validated the model for combined chemical and physical processes (Section 4.2 above), a series of experiments were conducted to extend the validation to include biological processes, on their own and in combination with chemical and physical processes. To achieve this, batch tests were conducted on mixtures of (i) waste activated sludge (WAS) and raw sewage, (ii) WAS and ADL, and (iii) WAS and raw sewage supplemented with Ca, Mg, P and FSA. This section describes these tests, and model application to the observed results.

4.3.1 Batch tests on a mixture of Waste Activated Sludge (WAS) and raw sewage

Only biological processes took place in these experiments, but these processes also interacted with the weak acid/base chemistry. Thus the model constituted biological and weak acid/base chemistry processes (Table 3.4). Although the biological processes (taken from Activated Sludge Model No.1, ASM1) have been fully calibrated and validated for municipal wastewaters treated in activated sludge systems (Dold *et al.*, 1991), it was necessary to carry out these batch tests in order to calibrate the kinetic and stoichiometric constants applicable to the particular WAS used in the experiments, because some kinetic parameters (e.g. specific maximum growth rates of nitrifiers and heterotrophs) differ from system to system and from wastewater to wastewater. Once the kinetic and stoichiometric constants had been established for the biological processes, they could then be applied to simulate the batch tests which include not only the biological processes, but also the physical and chemical processes. Also, the interaction of the biological processes with the weak acid/base chemistry needed to be tested.

The WAS for the batch tests was obtained from a steady state laboratory scale Modified Ludzack Ettinger (MLE) system fed with raw sewage from Mitchell's Plain sewage treatment plant (Cape Town, South Africa). The same Mitchell's Plain raw sewage was mixed with the MLE system WAS in the batch tests. The design and operating parameters for the MLE system are given below in Table 4.4. Details on the operation and performance of the MLE system are given by Ubisi *et al.* (1997b).

Table 4.4: Influent raw sewage characteristics and operating parameters for the laboratory scale MLE system from which WAS was obtained for the batch tests.

Parameter	**Value**
Influent Raw sewage:	
Source	Mitchell's Plain
COD concentration	± 750 mg COD/ℓ
Flow	10 ℓ/d
TKN concentration	60 - 100* mgN/ℓ
Phosphate concentration	15 - 24* mgP/ℓ
Operating parameters:	
Sludge age	20 days
Temperature	20°C
pH of mixed liquor	7.2 - 8.2
DO in aerobic reactor	3 mgO/ℓ
Volume of anoxic reactor	2.5 ℓ
Volume of aerobic reactor	7.5 ℓ
Mixed liquor r - recycle	2:1
Underflow s - recycle	1:1

Note:

* Values varied between sewage batches

4.3.1.1 Experimental procedure

Two litres each of raw sewage and WAS were mixed and placed in a batch reactor and an initial sample of the mixture was taken for measurement of the total initial COD and VSS concentrations. The initial COD and TKN of the raw sewage were also measured. The mixture was then aerated continuously for at least 24 hours. At regular intervals, 50 mℓ samples were drawn from the batch reactor and a few drops of mercuric chloride were immediately added to stop further biological activity. The reactor pH and the oxygen utilisation rate (OUR) were recorded throughout the experiment. The OUR was automatically recorded with the OUR meter developed by Randall *et al*. (1991).

The 50 mℓ samples drawn from the batch reactor were divided into two. One part was filtered through 0.45μm and analysed for nitrate and COD concentrations (Standard Methods, 1985). The unfiltered part was analysed for FSA. Two batch tests were conducted, the detailed results of which are given by Musvoto *et al*. (1998).

4.3.1.2 Model calibration

The constants for the weak acid/base chemistry section of the model were taken unmodified from Table 3.1(b and c). The characteristics of the raw sewage and WAS used in the batch tests, as well as the kinetic and stoichiometric parameters, are required as inputs to the model. The raw sewage and WAS characteristics were determined with the aid of the theory for the activated sludge system (see Ekama *et al*., 1986; Dold *et al*., 1991 and Still *et al*., 1996). The active fraction for heterotrophs and nitrifiers with respect to the VSS (f_{XBH} and f_{XBA} respectively) were then calculated (see Musvoto *et al*., 1998). With these fractions, and the MLVSS measured on the day of the test, the initial concentrations of the heterotrophs and nitrifiers present at the start of the batch test conducted within that particular steady state period were calculated. Details of the steady state periods for the MLE system are given in Musvoto *et al*. (1998). The initial characteristics of the raw sewage and WAS mixture for the two batch tests are given in Table 4.5.

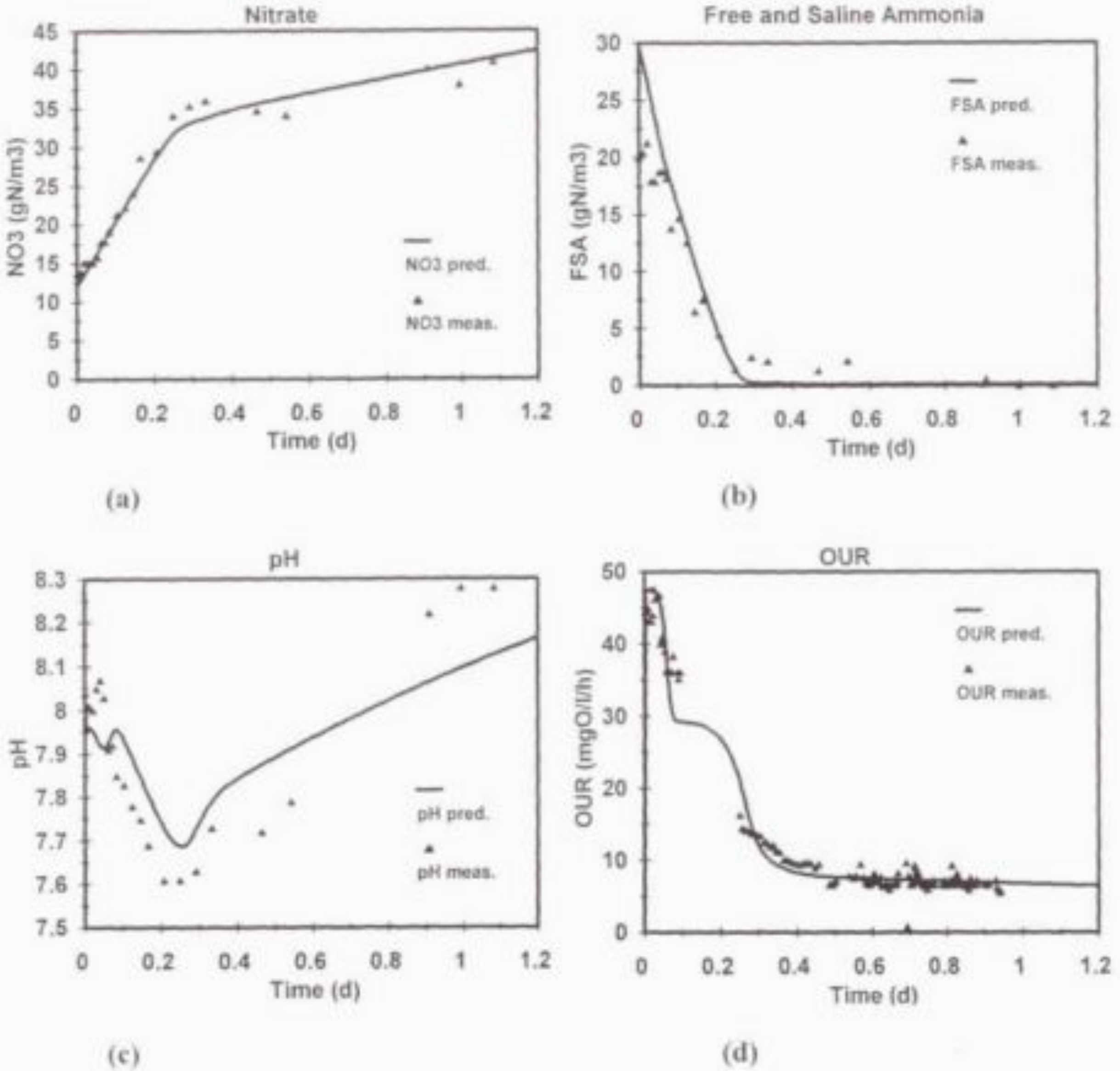
Table 4.5: Values of biological processes constants in the simulation model for aerobic batch tests with a mixture of raw sewage and WAS.

Constant	Units	Batch Test B1	Batch Test B2	Literature value
Raw sewage and WAS characteristics				
S_{ti}	gCOD/m^3	394	450	
N_{ti}	gN/m^3	40	32.4	
$f_{S,up}$		0.15	0.15	
$f_{S,us}$		0.05	0.05	
f_{bs}		0.25	0.20	
f_{sa}		0.75	0.75	
$f_{n,obs}$		0.5	0.5	
$f_{n,oup}$		0.03	0.03	
Z_{BH}	g COD/m^3	652	704	
Z_{BA}	g COD/m^3	72	35	
Kinetic Parameters at 20°C and pH = 7.2				
μ_H	/d	2.95	2.6	2.4 - 5.0
K_{SH}	g COD/m^3	5	5	5
K_H	gCOD/g cell COD.d	2.03	2.03	2.03
K_X	gCOD/g cell COD	0.027	0.027	0.027
b_H	/d	0.62	0.62	0.62
K_R	m^3/g cell COD.d	0.032	0.032	0.032
μ_A	/d	0.20	0.11	0.2 -0.75
K_{SA}	m^3/g cell COD.d	1	1	1
b_A	/d	0.04	0.04	0.04
η_b	-	0.33	0.33	0.33
η_s	-	1.00	1.00	1.00
Stoichiometric parameters				
Y_{ZH}	g cell COD/g COD utilized	0.666	0.666	0.666
Y_{ZA}	g cell COD/gN utilized	0.15	0.15	0.15
f_E		0.08	0.08	0.08
$f_{ZB,N}$	g N / g COD in active mass	0.068	0.068	0.068
$f_{ZE,N}$	g N / g COD in endogenous mass	0.068	0.068	0.068

The default values of the kinetic and stoichiometric parameters listed by Dold *et al.* (1991) were accepted as initial input to the model. The model was run and the constants adjusted where necessary to give good correlation between the theoretical model predictions and experimental values of OUR. The kinetic and stoichiometric parameters on which the batch test simulations are based, as well as the default literature values, are given in Table 4.5: Only the constants maximum specific growth rate of the heterotrophs (μ_H) and autotrophs (μ_A) required adjustment, but this is to be expected as these two constants have been shown to be system and wastewater specific (WRC, 1984; Dold *et al.*, 1991; Still *et al.*, 1996). As an example, Fig. 4.8 shows comparisons for the theoretical and measured OUR, nitrate, FSA, and pH measurements for batch test B1.

4.3.1.3 Analysis of results

A good correlation was obtained between the experimental and simulated results with the default values of the constants given in the literature. This confirmed the earlier validation of the biological processes in the kinetic model. Also, the interaction between the biological processes and the weak acid/base chemistry were correctly predicted, as evidenced by the close correlation between the measured and predicted pH; this validated this aspect of the model.



(a)

(b)

(c)

(d)

Fig 4.8: Predicted and measured (a) nitrate, (b) free and saline ammonia, FSA, (c) pH and (d) OUR for batch test B1 on a mixture of raw sewage and WAS from a laboratory-scale MLE system.

4.3.2 Batch tests on a mixture of waste activated sludge (WAS) and anaerobic digester liquor (ADL)

The waste activated sludge was obtained from the same steady state laboratory-scale MLE system described above and the ADL was obtained in the same manner as outlined in Section 4.2.1 above.

4.3.2.1 Experimental procedure

Two and a half litres of each ADL and WAS were placed in a batch reactor and an initial sample was taken for measurement of the total initial COD (except in batch test 21, where a 1:2 mixture of ADL:WAS, i.e 1.7 litres of ADS were mixed with 3.3 litres of WAS). Calcium, magnesium and phosphate concentrations of 100 mg/ℓ batch reactor each (as Ca, Mg and P) were added to the reactor. The mixture was then aerated continuously for at least 24 hours. At intervals 100 mℓ and 10 mℓ samples were drawn from the batch reactor for analysis. A few drops of mercuric chloride were immediately added to the samples to stop biological activity. The reactor pH was monitored throughout the experiment. The OUR could not be measured automatically with the OUR meter of Randall *et al.* (1991) due to the requirement of continuous aeration of the batch reactor for CO_2 stripping to raise the pH, and NH_3 stripping at higher pH. The OUR was therefore measured as follows: At intervals (about 20 minute intervals for the first 4 hours of the test and 1 hour intervals thereafter), a 250 mℓ sample was drawn from the reactor and placed in a tall stirred beaker. Immediately, a DO probe connected to the OUR meter was placed in the sample and the OUR was recorded with time as it would have been had the batch reactor had an "air off " time. The sample was returned to the reactor after OUR measurement to avoid depleting the reactor mixture before completion of the experiment.

The samples drawn from the reactor were handled in the same manner as outlined in Section 4.2.1.1 above and analysed for the same parameters, namely Ca, Mg, total phosphate species (P_T) on the acidified sample, and total carbonate species (C_T) and short chain fatty acids (SCFA) on the unacidified sample. In addition, COD and nitrate concentrations (Standard Methods, 1985) were also measured on the unacidified sample. FSA measurements were done immediately on unfiltered samples, as before.

Initial and final concentrations for three example batch tests (19 to 21) are shown in Table 4.6. More detailed results are given by Musvoto *et al.* (1998).

Table 4.6: Measured initial and final concentrations for three batch tests on a mixture of WAS and ADL.

Parameter	Batch Test 19		Batch Test 20		Batch Test 21	
	Initial	Final	Initial	Final	Initial	Final
Calcium (gCa/m^3)	107	35.2	111	45.6	135	54.6
Magnesium (gMg/m^3)	104	8.8	96.8	9	86	17
Phosphate (gP/m^3)	134	8.2	130	4.6	133	7.8
FSA (gN/m^3)	380	171	384	186	257	154
Inorganic carbon (gC/m^3)	390	79	375	64	181	48
pH	7.08	8.59	6.96	8.26	7.03	8.05
Filtered COD (mg/ℓ)	500	152	310	210	504	183
Nitrate (gN/m^3)	11.1	30.1	27	39	11	28

4.3.2.2 Model Calibration

In these experiments, physical, chemical and biological processes were expected to take place. Accordingly, the kinetic model consisted of the biological and weak acid/base processes (Table 3.4), ion pairing effects (Table 3.8b), the chemical precipitation processes (Table 3.9) and the gas exchange/stripping processes (Table 3.11), with stoichiometry and kinetics adjusted to give uniformity in units (see Musvoto *et al*., 1998). The model calibration was carried out in the same manner as outlined in Sections 4.2.3 and 4.2.42 above for physical/chemical constants and Section 4.3.1.2 for the biological constants. The ADL formed the substrate in a similar manner as the raw sewage in batch tests B1 and B2. The ADL therefore needs to be characterised into its own COD and nitrogen fractions in the same fashion as the raw sewage. However, unlike the raw sewage characteristics which are well known due to a large data base collected over the years, no such characterisation information exists for the ADL. Characterisation of the ADL was thus based on the measurements taken during the batch tests and the expected characteristics of anaerobically digested sludge liquors. Details of the characterisation of the ADS are given by Musvoto *et al*. (1998). The WAS was characterised in the same manner as outlined in Section 4.3.1 above and detailed results of the steady state periods when the batch tests were run for the MLE system are also given by Musvoto *et al*. (1998).

Experimental results were compared with model predictions for both the chemical and biological processes. As examples, Figs. 4.9 and 4.10 show comparisons between predicted and measured parameters for batch test 19. Graphs for batch tests 20 and 21 are given by Musvoto *et al*. (1998).

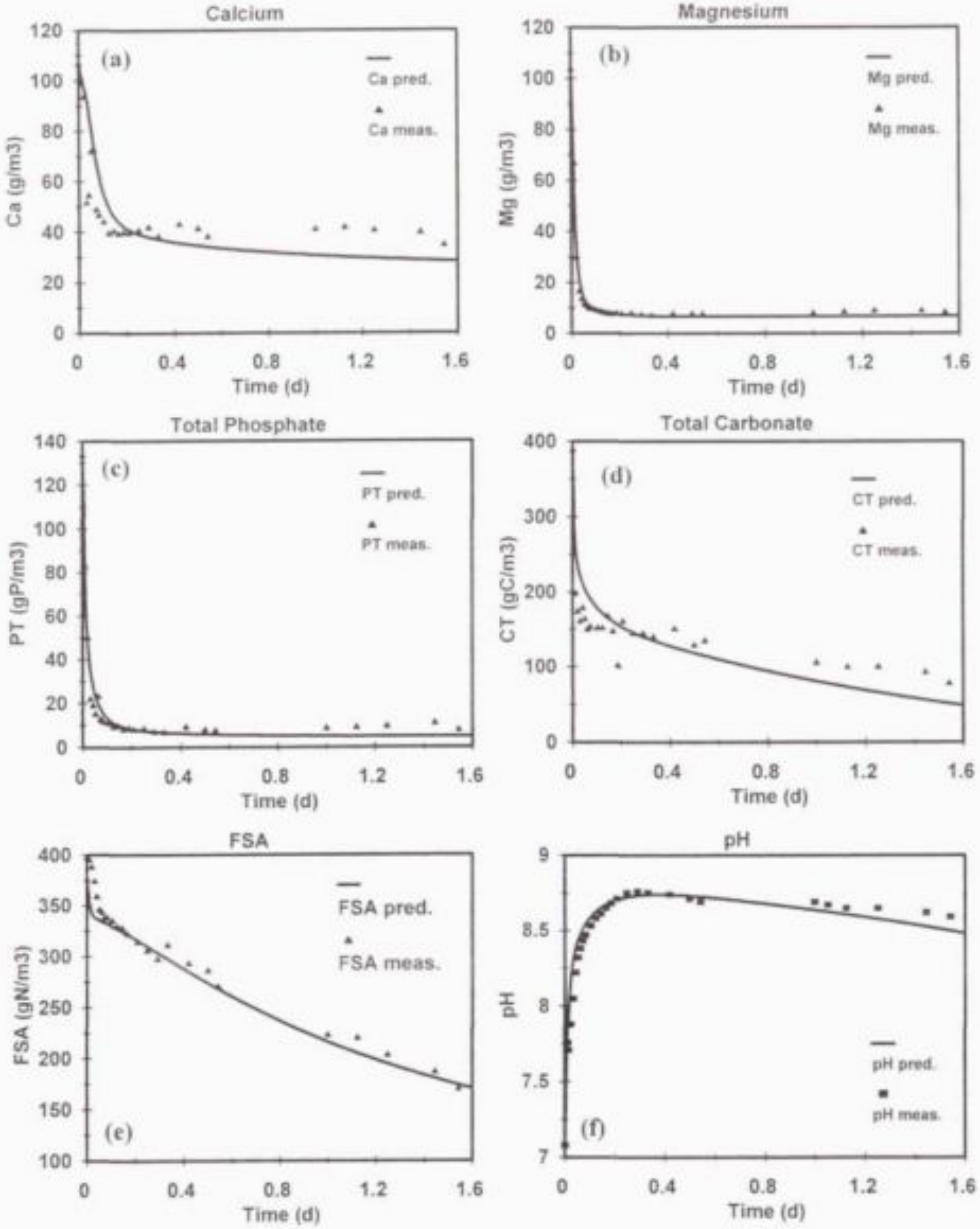


Fig 4.9: Predicted and measured soluble concentrations for (a) calcium, (b) magnesium, (c) total phosphate (P_T), (d) total carbonate (C_T), (e) free and saline ammonia (FSA) and (f) pH in aerobic batch test on a mixture of ADL and WAS from a lab-scale MLE system; Batch Test 19, Table 4.6.

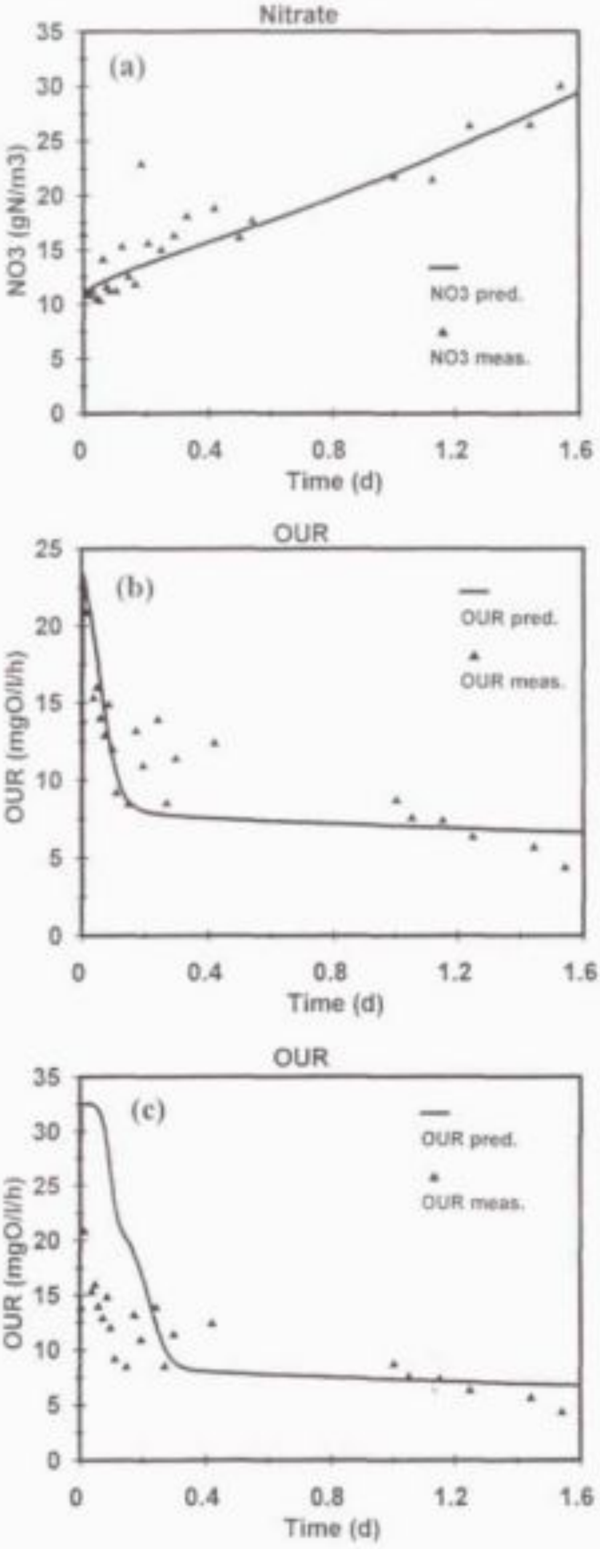


Fig 4.10: Predicted and measured soluble concentrations for (a) nitrate and (b) OUR in aerobic batch test on a mixture of ADL and WAS from a lab-scale MLE system; Batch Test 19, Table 4.6. Also shown in (c) is a comparison of the measured OUR and the OUR predicted with the default values of K_{SH} and K_X; poor correlation was obtained with these values.

4.3.2.3 Analysis of results

Physical and chemical processes

All the physical/chemical processes constants used in the model for the simulations are shown in Table 4.7. The same solids as in the ADL only batch tests were identified as the most likely to precipitate, namely struvite, ACP, newberyite, calcium and magnesium carbonate. The amounts of the different solids precipitated as predicted in the simulations are also shown in Table 4.7: In all the three batch tests, struvite formed the bulk of the precipitate, followed by ACP. In batch test 19 and 20 with a 1:1 (WAS: ADL) mixture, $CaCO_3$ and $MgCO_3$ precipitated, but in batch test 21 with a 2:1 (WAS:ADL) no $CaCO_3$ or $MgCO_3$ precipitated. In all the batch tests, newberyite did not precipitate to any significant extent, although slightly more newberyite precipitated in batch test 21. For all three batch tests a single set of solubility products and precipitation rate constants gave good correlation between experimental results and theoretical model predictions. As in the ADL only batch tests, the K_{La} values for CO_2 and NH_3 stripping differed between batch tests, due to the different airflow rates.

Biological processes

For the biological processes, all the kinetic and stoichiometric parameters input to the model are listed in Table 4.8. A good correlation between the measured and theoretically predicted OUR could not be obtained with the default values for the half saturation coefficient for heterotrophic cell synthesis on RBCOD (K_{SH}) and the half saturation coefficient for hydrolysis of enmeshed (slowly biodegradable) COD (K_X). For all three batch tests, the values for these constants had to be increased from the default values of $K_{SH} = 5$ gCOD/m^3 and $K_X = 0.027$ gCOD/gCOD to 40 gCOD/m^3 and 0.60 gCOD/gCOD respectively to obtain a good correlation. Figure 4.10 shows examples of the simulated and experimental OUR for batch test 19 with the default values and with the adjusted values of K_X and K_{SH}.

No adjustment was made to any of the other kinetic and stoichiometric parameters and the default literature values gave good correlation between experimental and simulated results (Note that, as before μ_H and μ_A were adjusted; again this is to be accepted, as these two constants are wastewater and system specific, see Section 4.3.1.2 above).

Table 4.7: Values of model constants for simulation of chemical and physical processes for aerobic batch tests on a mixture of WAS and ADL

Constant	Batch Test 19	Batch Test 20	Batch Test 21	Literature value
-Log Solubility product (pK_s)				
Struvite	13.16	13.16	13.16	9.94 - 13.16
Newberyite	5.8	5.8	5.8	5.51- 5.8
Amorphous Calcium phosphate (ACP)	25.46	25.46	25.46	24 - 32.7
$CaCO_3$	6.45	6.45	6.45	6.3 - 8.5
$MgCO_3$	7	7	7	5 - 8.2
Rate constant of precipitation (/d)				
Struvite	100	100	100	
Newberyite	0.05	0.05	0.05	
Amorphous Calcium phosphate (ACP)	350	350	350	
$CaCO_3$	50	50	50	
$MgCO_3$	50	50	50	
Rate of aeration/gas stripping (K_{LA} /d)				
O_2	600	400	450	
CO_2	545	363	409	
NH_3	3.2	5.7	4.7	
Solids precipitated (mg/l)				
Struvite	830	665	700	
Newberyite	5	3	16.5	
Amorphous Calcium phosphate (ACP)	147	140	245	
$CaCO_3$	68	60	0	
$MgCO_3$	53	70	0	

Table 4.8: Values of model constants for simulation of the biological processes for aerobic batch tests on a mixture of WAS and ADL

Constant	Units	Batch Test 19	Batch Test 20	Batch Test 21	Literature value
ADS and WAS batch test mixture characteristics					
S_t	g COD/m^3	3665	2364	3694	
N_t	g N/m^3	464	519	477	
$f_{x,sd}$		0.86	0.87	0.86	
$f_{s,us}$		0.06	0.09	0.06	
f_{ss}		0.28	0.46	0.20	
f_{ia}		0.82	0.75	0.54	
$f_{n,ubs}$		0.5	0.5	0.5	
$f_{n,usn}$		0.03	0.03	0.03	
Z_{BH}	g COD/m^3	736	664	942	
Z_{BA}	g COD/m^3	70	60	61	
Kinetic Parameters at 20^{0}C and pH = 7.2					
μ_H	/d	2.08	2.09	2.5	2.4 - 5.0
K_{SH}	g COD/m^3	40	40	40	5
K_H	gCOD/g cell COD.d	2.03	2.03	2.03	2.03
K_X	gCOD/g cell COD	0.60	0.60	0.60	0.027
b_H	/d	0.62	0.62	0.62	0.62
K_R	m^3/g cell COD.d	0.032	0.032	0.032	0.032
μ_A	/d	0.036	0.03	0.03	0.2 -0.75
K_{SA}	m^3/g cell COD.d	1	1	1	1
b_A	/d	0.04	0.04	0.04	0.04
η_h	-	0.33	0.33	0.33	0.33
η_G	-	1.00	1.00	1.00	1.00
Stoichiometric parameters					
Y_{ZH}	g cell COD/g COD utilized	0.666	0.666	0.666	0.666
Y_{ZA}	g cell COD/gN utilized	0.15	0.15	0.15	0.15
f_E		0.08	0.08	0.08	0.08
$f_{ZB,N}$	g N / g COD in active mass	0.020	0.053	0.063	0.068
$f_{ZE,N}$	g N / g COD in endogenous mass	0.068	0.068	0.068	0.068

Discussion

In order to obtain a good correlation between measured and predicted results it was possible to keep for the biological batch tests the same solids (struvite, newberyite, ACP, $MgCO_3$ and $CaCO_3$) which were identified as most likely to precipitate in ADL only batch tests (batch tests 11 to 14). Also, the same pK_s values for all the minerals were found to give a good correlation in model simulations for both sets of batch tests (see Tables 4.2 and 4.7). For the precipitation rate constants, the values for newberyite, $CaCO_3$ and $MgCO_3$ were found to be the same in both sets of tests. However, for struvite and ACP, the values were found to differ between the two sets of tests: The rate constant of precipitation for struvite of 100/d is lower in batch tests 19 to 21 with biological activity than the 300/d found in batch tests 11 to 14 on ADL only. It appears that the biological activity decreased the rate of precipitation of struvite. In contrast, a higher rate constant of precipitation for ACP of 350/d was found in batch tests 19 to 21 than in batch tests 11 to 14 with a value of 150/d. This could be due to either of two reasons:

(i) Batch tests 19 to 21 have slightly higher initial Ca than Mg concentrations, whereas in batch tests 11 to 14 the initial concentrations do not differ significantly causing the precipitation rate of ACP to be higher in the former batch tests than in the later.

(ii) The precipitation rate of ACP is not affected by biological activity whereas the rate of struvite is. In situations where struvite is inhibited, ACP would have a precipitation advantage and thus precipitates at a much faster rate.

The different quantities of solids that precipitated in batch tests 19 to 21 are listed in Table 4.7. As in batch tests 11 to 14, struvite formed the bulk of the precipitate followed by ACP, while newberyite did not precipitate in any significant amount. However, in batch tests 19 and 20 on a 1:1 mixture of ADL and WAS, $MgCO_3$ precipitated as well as $CaCO_3$; this differed from batch tests 11 to 14 where $CaCO_3$ precipitated and $MgCO_3$ did not and batch test 21 where neither $CaCO_3$ nor $MgCO_3$ precipitated. Batch tests 19 to 21 contained lower initial P concentrations because, although 100 mgP/ℓ was added to the batch reactors, the ADL contained some P which was reduced due to dilution by the WAS addition in batch tests 19 to 21, but not in batch tests 11 to 14. Thus, in batch tests 19 and 20 struvite precipitation was limited by P and there was still sufficient Mg present after struvite precipitation to exceed the solubility product of $MgCO_3$ and cause it to precipitate; in batch tests 11 to 14 struvite precipitation was limited by Mg so that after struvite precipitation inadequate Mg was left to cause $MgCO_3$ precipitation. In batch test 21 where neither $MgCO_3$ nor $CaCO_3$ precipitated, the C_T concentration was much lower due to a greater WAS dilution such that during aeration, the C_T stripped did not raise the pH high enough to cause either $MgCO_3$ or $CaCO_3$ precipitation (the pH went up to 8.78 in batch tests 19 and 20 and up to 8.24 in batch test 21).

The ADL/WAS mixture was characterised into its COD and N fractions as outlined by Musvoto *et al.* (1998). Very high values for $f_{s,up}$ of 0.86 were obtained due to the large presence of unbiodegradable solids. This is not like raw sewage with $f_{s,up}$ values of only 0.07 to 0.20. Also, all the soluble (< 0.45μm) biodegradable COD was not readily biodegradable COD (RBCOD), but was found to have a large component which the organisms treated as slowly biodegradable COD (SBCOD). Again this is not like in sewage where most biodegradable soluble (< 0.45μm) COD is normally RBCOD. The COD and N fractions obtained from the characterisation of ADL were used in the model simulation. However, in order to accurately simulate the OUR, the values of K_X and K_{SH} had to be increased from their default values of 0.027 gCOD/gCOD and 5 gCOD/m^3 respectively to 0.6 gCOD/gCOD and 40 gCOD/m^3 respectively (see Table 4.8 above). It could not be assessed whether the required decrease in the utilisation of RBCOD (achieved by increasing K_{SH} in the model) and hydrolysis of enmeshed COD (achieved by increasing K_X in the model) were due to:

1. Inaccuracy in characterising the ADL into its COD fractions and because no data exists with which the characterisation of the ADL could be compared.
2. The precipitation of minerals.
3. The increase in pH through CO_2 stripping from the ADS during aeration. The activated sludge model is valid within the pH range 7.2 - 8.2. No data exists for the behaviour of heterotrophs outside this pH range.

This cast doubt on the validity of the biological kinetics applied to ADS. It was therefore decided to repeat the batch tests for physical, chemical and biological processes eliminating these uncertainties as outlined below.

4.3.3 Batch tests on a mixture of WAS and raw sewage with addition of Ca, Mg, P and FSA

4.3.3.1 Experimental procedure

In view of the uncertainties above, batch tests were conducted on a mixture of raw sewage and WAS with addition of Ca, Mg, P and FSA. The characterisation of raw sewage into its various COD fractions is well established and accurately known thus removing uncertainty 1 above. Concentrations of ~100mg/ℓ batch reactor of Ca, Mg and P (as Ca, Mg and P from $CaC\ell_2$, $MgC\ell_2$ and K_2HPO_4 respectively) and ~500 mgN/ℓ batch reactor (from $NH_4C\ell$) of FSA were added to give conditions similar to ADS. For the first two batch tests (ART1 and ART2), the mixture was aerated as before but, because the concentration of carbonate species in raw sewage is very low, there was no increase in pH. The pH remained around 7.2 which is the region for which the activated sludge model was calibrated. This enabled the interaction of the precipitation of minerals and the biological processes to be investigated (uncertainty 2 above). In the third batch test (ART3), the pH was increased by dosing sodium hydroxide. The rate of dosing was such that the pH would increase in a similar fashion and to similar values as in the batch tests on ADS aeration. Once the pH increased to about 9, the hydroxide dose was stopped. The effect of the increase in pH on the biological processes was investigated with this batch test (uncertainty 3 above).

The same experimental procedure for batch tests 19 to 21 (section 4.3.2.1) above was followed for batch tests ART1 to ART3, except that the OUR was automatically measured with the OUR meter of Randall *et al.* (1991) because continuous aeration was not required to raise the pH. The automatic measurement of OUR allowed more OUR data points to be collected. The samples drawn from the batch reactor were analysed in the same manner as for batch tests 19 to 21. Details of the results are given by Musvoto *et al.* (1998) and the initial and final concentrations for some of the parameters are given in Table 4.9.

Table 4.9: Measured initial and final concentrations for three batch tests on a mixture of WAS and raw sewage with addition of Ca, Mg, P and FSA.

Parameter	**Batch Test ART1**		**Batch Test ART2**		**Batch Test ART3**	
	Initial	Final	Initial	Final	Initial	Final
Calcium (gCa/m^3)	137	168	127	160	153	74
Magnesium (gMg/m^3)	107	106	139	141	103	7.6
Phosphate (gP/m^3)	135	129	150	153	134	15
FSA (gN/m^3)	469	414	497	388	547	384
Inorganic carbon (gC/m^3)	60	-	75	-	80	-
pH	7.08	6.78	7.38	6.76	7.47	8.47
Filtered COD (mg/ℓ)	310	218	331	205	263	82.6
Nitrate (gN/m^3)	14.0	44.3	10.4	49.3	11.5	20.6

4.3.3.2 Model calibration

The model was calibrated in the same manner as outlined in Section 4.2.2.2 above. As examples, Figs 4.11 and 4.12 show graphs for predicted and measured parameters for batch tests ART1 and ART3 respectively.

4.3.3.3 Analysis of results

Physical and chemical processes

All the values for the constants in the model for physical and chemical processes together with the quantities of solids predicted to precipitate are listed in Table 4.10. For batch tests ART1 and ART2 where the pH was not increased, struvite was the only solid that precipitated in significant amounts. Very little newberyite precipitated. $CaCO_3$, ACP and $MgCO_3$ did not precipitate. In batch tests ART1 and ART2, the pH decreased to about 6.76 due to struvite precipitation and nitrification. At low pH, struvite becomes unstable resulting in struvite dissolution. Accordingly, for these two experiments dissolution of struvite had to be included in the model; details of the kinetics of struvite dissolution and its inclusion in the model are given by Musvoto *et al.* (1998). In batch test ART3 where the pH was artificially increased, the solids that precipitated and the amounts were similar to those in the batch tests on ADL and WAS with aeration (Section 5.3.2). Struvite formed the bulk of the precipitate as before followed by ACP. $CaCO_3$ and $MgCO_3$ also precipitated and newberyite did not precipitate significantly.

A single set of pK_s values for struvite, newberyite, ACP, $CaCO_3$ and $MgCO_3$ was found for all three batch tests, and these are the same values as found for all the previous batch tests. A single set of precipitation rate constants was also found for all three batch tests ART1 to ART3 and with the exception of struvite, these are the same values as found for the batch tests on a mixture of WAS and ADS. A more detailed comparison of the rates measured in the different batch tests is given in Section 4.4 below.

Biological processes

All the values for the biological process constants used in the model simulations are listed in Table 4.11. To obtain a good correlation between experimental and theoretical model predictions, for batch tests ART1 and ART2 the value of K_X was increased from its default of 0.027 to 0.15 gCOD/gCOD. All the other kinetic and stoichiometric constants remained at their default values for these two batch tests (except μ_H and μ_A for reasons noted above). For batch test ART3, in which the pH was artificially increased, both K_{SH} and K_X had to be increased significantly from the default values of 5 gCOD/m^3 and 0.027 gCOD/gCOD respectively; K_{SH} was increased to 40 gCOD/m^3 and K_X was varied from 0.6 initially to 1.4 gCOD/gCOD over the course of the batch test. Figure 4.13 shows a comparison of the measured and predicted OUR with the default values and adjusted values of K_{SH} and K_X respectively. No adjustment needed to be made to the other kinetic and stoichiometric parameters (except μ_H and μ_A).

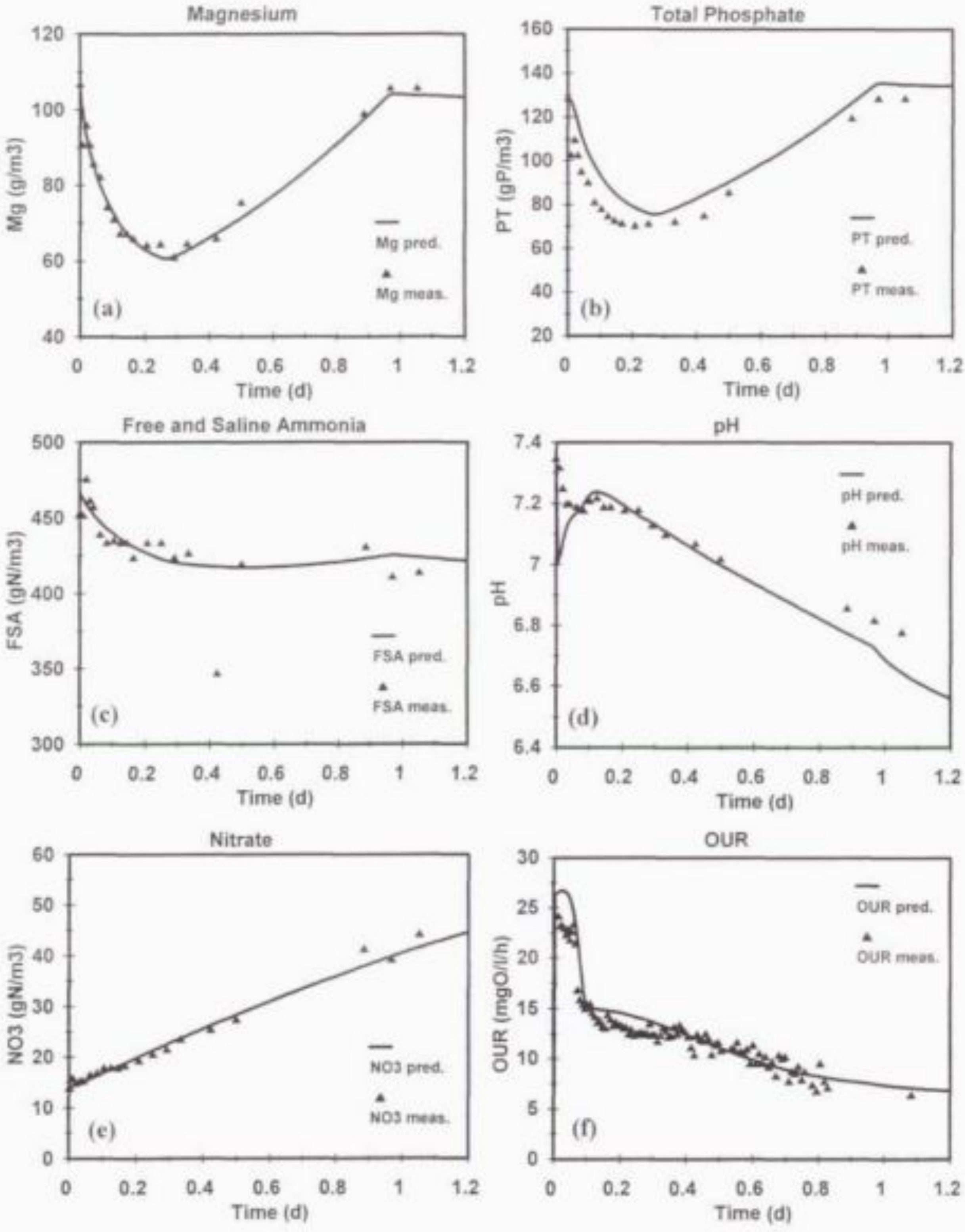


Fig 4.11: Predicted and measured soluble concentrations for (a) magnesium, (b) total phosphate (P_T), free and saline ammonia (FSA), (d) pH, (e) nitrate and (f) OUR in aerobic batch test on a mixture of raw sewage and WAS (from a lab-scale MLE system) with addition of Ca, Mg, P and FSA; Batch Test ART1, Table 4.9.

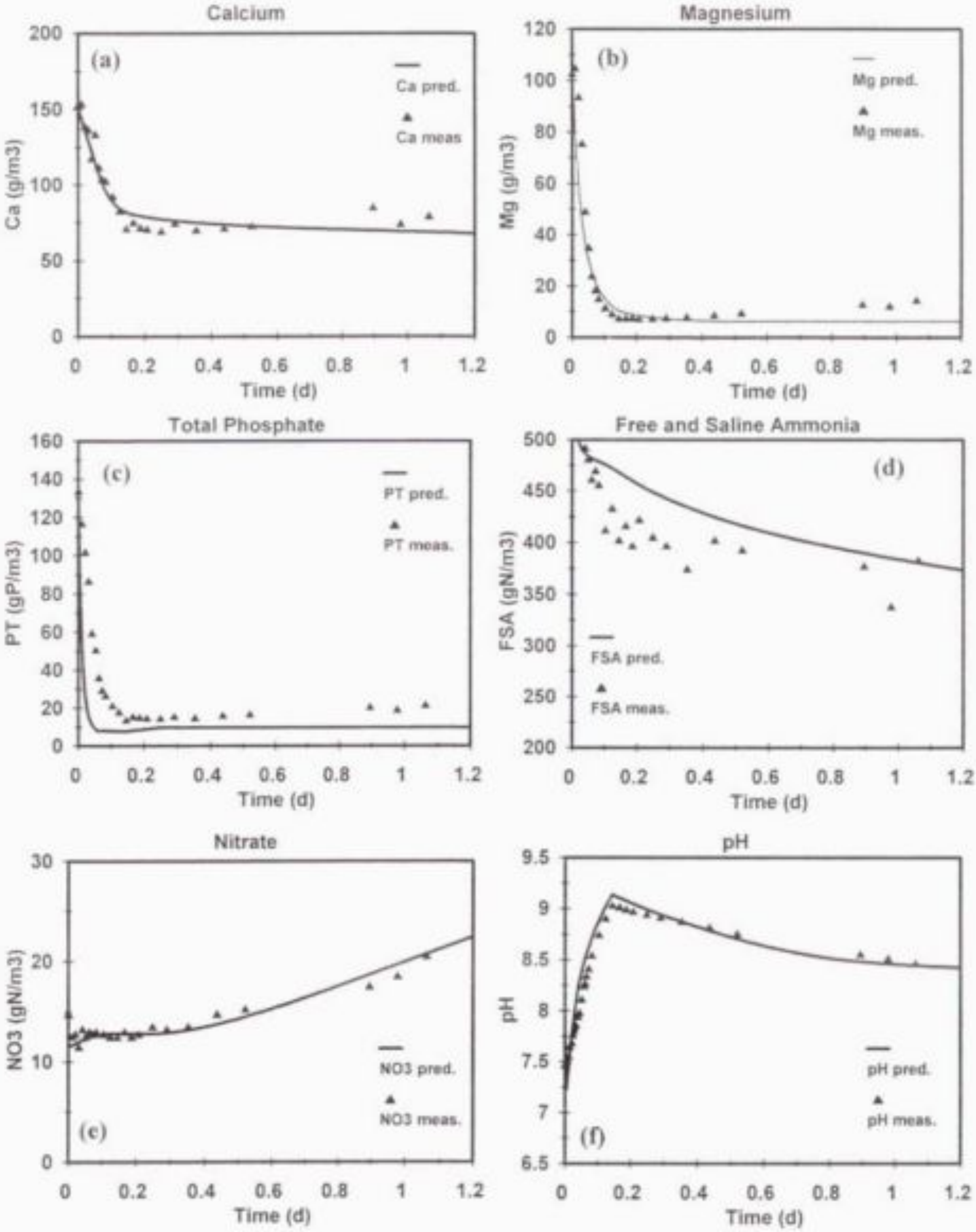


Fig 4.12: Predicted and measured (a) calcium, (b) magnesium, (c) total phosphate (P_T), (d) free and saline ammonia (FSA), (e) nitrate and (f) pH in aerobic batch test on a mixture of raw sewage and WAS (from a lab-scale MLE system) with addition of Ca, Mg, P and FSA; Batch Test ART3, Table 4.9. The pH was raised by dosing NaOH.

Table 4.10: Values of chemical and physical processes model constants in simulation of the aerobic batch tests on a mixture of WAS and raw sewage with Ca, Mg, P and FSA addition.

Constant	Batch Test ART1	Batch Test ART2	Batch Test ART3	Literature value
-Log Solubility product (pK_s)				
Struvite	13.16	13.16	13.16	9.94 - 13.16
Newberyite	5.8	5.8	5.8	5.51 - 5.8
Amorphous Calcium phosphate (ACP)	25.46	25.46	25.46	24 - 32.7
$CaCO_3$	6.45	6.45	6.45	6.3 - 8.5
$MgCO_3$	7	7	7	5 - 8.2
Rate constant of precipitation (/d)				
Struvite	30	30	30	
Newberyite	0.05	0.05	0.05	
Amorphous Calcium phosphate (ACP)	350	350	350	
$CaCO_3$	50	50	50	
$MgCO_3$	50	50	50	
Rate of aeration/gas stripping (K_{La} /d)				
O_2	150	200	350	
CO_2	136	181	317	
NH_3	2.0	2.0	1.5	
Solids precipitated (mg/l)				
Struvite	455	780	850	
Newberyite	25	30	6.2	
Amorphous Calcium phosphate (ACP)	0	0	190	
$CaCO_3$	0	0	20	
$MgCO_3$	0	0	35	

Table 4.11: Values of biological processes model constants in simulation of the aerobic batch tests on a mixture of WAS and raw sewage with Ca, Mg, P and FSA addition.

Constant	Units	Batch Test ART1	Batch Test ART2	Batch Test ART3	Literature value
Raw sewage and WAS characteristics					
S_{ti}	gCOD/m³	448	415	375	
N_{ti}	gN/m³	30	30	33.7	
$f_{S,up}$		0.15	0.15	0.15	
$f_{S,us}$		0.05	0.05	0.04	
f_{bs}		0.20	0.21	0.20	
f_{ia}		0.75	0.75	0.75	
$f_{n,ous}$		0.5	0.5	0.5	
$f_{n,ous}$		0.03	0.03	0.03	
Z_{BH}	g COD/m³	472	748	719	
Z_{BA}	g COD/m³	27	49	56	
Kinetic Parameters at 20°C and pH = 7.2					
μ_H	/d	2.50	2.1	2.1	2.4 - 5.0
K_{SH}	g COD/m³	5	5	40	5
K_H	gCOD/g cell	2.03	2.03	2.03	2.03
K_X	gCOD/g cell COD	0.15	0.15	0.6 - 1.4	0.027
b_H	/d	0.62	0.62	0.62	0.62
K_R	m³/g cell COD.d	0.032	0.032	0.032	0.032
μ_A	/d	0.15	0.11	0.04	0.2 -0.75
K_{NA}	m³/g cell COD.d	1	1	1	1
b_A	/d	0.04	0.04	0.04	0.04
η_g	-	0.33	0.33	0.33	0.33
η_h	-	1.00	1.00	1.00	1.00
Stoichiometric parameters					
Y_{ZH}	g cell COD/g COD	0.666	0.666	0.666	0.666
Y_{ZA}	g cell COD/gN	0.15	0.15	0.15	0.15
f_E		0.08	0.08	0.08	0.08
$f_{ZB,N}$	g N / g COD	0.068	0.068	0.068	0.068
$f_{ZE,N}$	g N / g COD	0.068	0.068	0.068	0.068

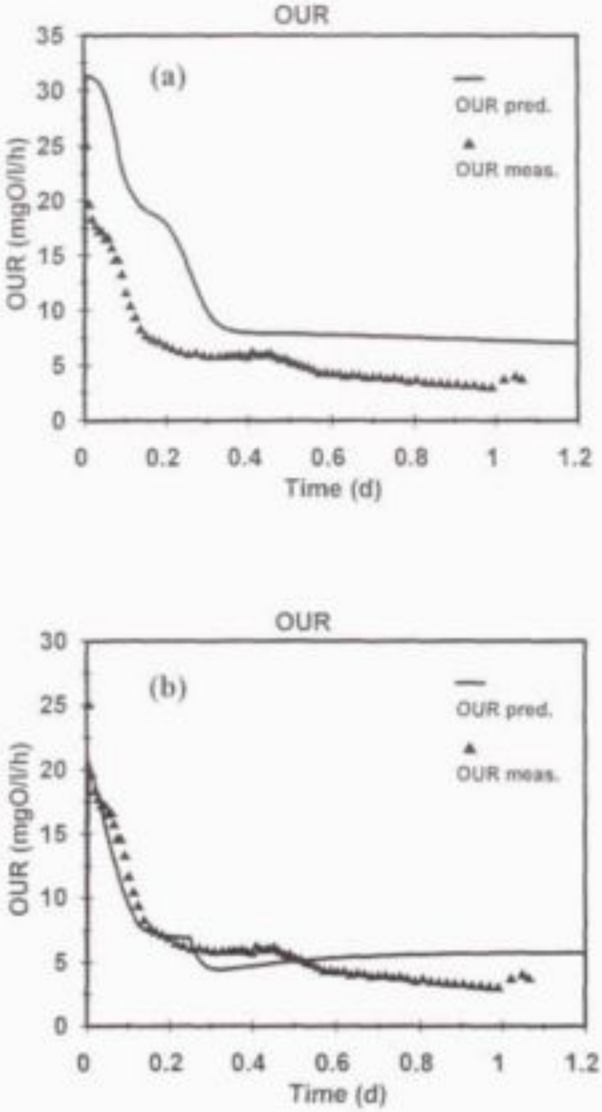


Fig 4.13: Comparison of the correlation between measured and predicted OUR for batch test ART3 with (a) default literature values of K_{SH} and K_X and (b) modified values of K_{SH} = 40gCOD/m^3 and K_X varied from 0.6 to 1.4 gCOD/gCOD obtained during model calibration. The default literature values gave poor correlation between measured and predicted OUR.

Discussion

The three batch tests ART1, ART2 and ART3 were conducted because of uncertainties that arose in the analysis of the results for batch tests 19 to 21. In batch tests 19 to 21 where the pH increased, in order to simulate the measured OUR correctly the values of K_{SH} and K_X had to be increased from the default values of 5 gCOD/m^3 and 0.027 gCOD/gCOD respectively to 40gCOD/m^3 and 0.6 gCOD/gCOD respectively. In batch tests ART1 and ART2 where the pH did not increase, the value of K_{SH} was kept at its default value of 5 gCOD/m^3 and the value of K_X was increased from the default value of 0.027 to 0.15 gCOD/gCOD. In batch test ART3 where the pH was artificially increased, to simulate the measured OUR values, K_{SH} had to be increased to 40 gCOD/m^3 (which is the same value as in batch tests 19 to 21) and K_X was increased to 0.6 gCOD/gCOD (same value for batch tests 19 to 21) for the first 10 hours of the test and then to 1.4 gCOD/gCOD thereafter. These results show that: (i) the characterisation of ADL in batch tests 19 to 21 was reasonable (ii) the increase in pH reduced both the rate of utilisation of RBCOD (increase in K_{SH}) and the rate of hydrolysis of enmeshed COD (increase in K_X) and (iii) chemical precipitation seems to affect the rate of hydrolysis of enmeshed COD to some extent, but does not seem to affect the rate of utilisation of RBCOD. The characterisation of the ADL and WAS mixture in batch tests 19 to 21 was therefore accepted as reasonable and the deviation of K_X and K_{SH} from the default values was attributed to the high pH and to a lesser extent, chemical precipitation.

4.3.4 Summary

In this section, the model has been validated for physical, chemical and biological processes. Through a sequence of batch tests, it was shown that precipitation does not affect the rate of utilisation of RBCOD. The rate of hydrolysis of enmeshed COD is however slightly decreased by precipitation. The maximum specific growth rate of heterotrophs and that of nitrifiers are decreased with precipitation and the maximum specific growth rate of nitrifiers is substantially reduced by precipitation. Increase in pH decreases the rates of utilisation of RBCOD and hydrolysis of enmeshed COD and also the maximum specific growth rate of heterotrophs to some extent. The equations proposed to model the decrease in the maximum specific growth rate of nitrifiers with increase in pH (which is an already established phenomenon) could not be validated with the results obtained in these tests.

4.4 DISCUSSION AND CONCLUSIONS

In this Chapter, an experimental investigation to calibrate and validate the three phase biological, chemical and physical model has been presented. Five groups of aerobic batch tests were carried out, the first two groups with only chemical and physical processes operating, the third group with only biological processes and the fourth and fifth groups with all three types of processes. In the batch tests with only chemical and physical processes operating (Sections 4.2.1 and 4.2.2 above), two types of batch tests were carried out, on:

Group 1: Anaerobic digester liquors (ADL) from a digester treating blended and biological excess phosphorus removal waste activated sludge (WAS) [Batch tests 11 to 14].

Group 2: Supernatant from an upflow anaerobic sludge bed (UASB) treating spent wine distillery effluent (Batch tests 16 to 18).

In the batch tests with both physical/chemical and biological processes operating (Sections 4.3.1 to 4.3.3 above), three types of batch tests were carried out, on:

Group 3: A mixture of WAS and raw sewage to calibrate the IAWQ activated sludge model No.1 for biological processes (Batch tests B1 and B2).

Group 4: A mixture of WAS and ADL to calibrate the kinetic model for physical, chemical and biological processes (Batch tests 19 to 21) and

Group 5: A mixture of WAS and raw sewage with additions of Ca, Mg, P and FSA to investigate the effect of physical and chemical processes (Batch tests ART1 and ART2) and the increase in pH (Batch test ART3) on biological activity observed in experiments under Group 4 above.

Comparing the results observed in these batch tests (Groups 1, 2, 3, 4 and 5), the following observations were made (see Table 4.12 which shows a summary of all the batch tests, Groups 1 to 5):

Table 4.12: Summary of chemical, physical and biological processes constants for all the batch tests.

Batch Test Parameter	Group 1 11 - 14				Group 2 16 - 18			Group 3 B1, B2	Group 4 19 - 21			Group 5 ART1- ART3,		
Type	ADS aeration				UASB effluent aeration			WAS and raw sewage aeration	WAS and ADS aeration			WAS and raw sewage aeration with Ca, Mg, P and FSA addition. NaOH dosing in ART3.		
No. of batch tests	4				3			2	3			3		
pH	Increasing 6.94-8.93				Increasing 6.95 to 9.53			Nearly constant 7.6 - 8.0	Increasing 6.96 to 8.8			Decreasimg slightly for ART1 and ART2 (7.38 to 6.76). Increasing for ART3 (7.47 to 9.0)		
CHEMICAL AND PHYSICAL PROCESSES CONSTANTS	No biological activity				No biological activity			With biological activity	With biological activity			With biological activity		
Initial concentrations	varied in the 4 tests				varied in the 3 tests				varied in the 3 tests			varied in the 3 tests		
	Batch Test 11	**Batch Test12**	**Batch Test 13**	**Batch Test 14**	**Batch Test 16**	**Batch Test 17**	**Batch Test 18**		**Batch Test 19**	**Batch Test 20**	**Batch Test 21**	**Batch Test ART1**	**Batch Test ART2**	**Batch Test ART3**
Calcium (g/m^3)	113	129	133	83.8	54.8	58.6	55.4		107	130	135	137	127	153
Magnesium (g/m^3)	125	116	128	128	81.8	67.6	64.6		104	96.8	86	107	139	103
Phosphate (gP/m^3)	190	152	200	177	128	106	104		134	111	133	135	150	134
FSA (gN/m^3)	714	770	812	781	128	128	127		380	384	257	469	497	547
Final concentrations	varied in the 4 tests				varied in the 3 tests				varied in the 3 tests			varied in the 3 tests		
	Batch Test 11	**Batch Test12**	**Batch Test 13**	**Batch Test 14**	**Batch Test 16**	**Batch Test 17**	**Batch Test 18**		**Batch Test 19**	**Batch Test 20**	**Batch Test 21**	**Batch Test ART1**	**Batch Test ART2**	**Batch Test ART3**
Calcium (g/m^3)	32.1	33.6	51	18.6	23.7	22.5	20.0		35.2	45.6	54.6	168	160	74
Magnesium (g/m^3)	3.7	3.5	5.4	4.6	8.6	6.4	6.1		8.8	9.0	17.0	106	141	7.6
Phosphate (gP/m^3)	15.9	14.6	13.3	13.3	28.8	19.8	17.0		8.2	4.6	7.8	129	153	15
FSA (gN/m^3)	361	490	353	386	11.5	46.8	42.0		171	186	154	414	388	384
pK$_s$	constant for all batch tests				constant for all batch tests				constant for all batch tests			constant for all batch tests		
Struvite	13.16				13.16				13.16			13.16		
Newberyite	5.8				5.8				5.8			5.8		
ACP	25.46				25.46				25.46			25.46		
$CaCO_3$	6.45				6.45				6.45			6.45		
$MgCO_3$	7				7				7			7		

Table 4.12 (continued)

Batch Test Parameter	Group 1 11 - 14				Group 2 16 - 18			Group 3 B1, B2	Group 4 19 - 21			Group 5 ART1- ART3,		
Rate constant of precipitation (/d)	constant for all batch tests				constant for all batch tests				constant for all batch tests			constant for all batch tests		
Struvite	300				3000				100			30		
Newberyite	0.05				0.05				0.05			0.05		
ACP	150				350				350			350		
$CaCO_3$	50 except for batch test 14 = 2				0.5				50			50		
$MgCO_3$	50				50				50			50		
Aeration/gas stripping (K_{LA} /d)	varied in the 4 tests due to different air flows				varied in the 3 tests due to different air flows				varied in the 3 tests due to different air flows			varied in the 3 tests due to different ai flows		
	Batch Test 11	**Batch Test 12**	**Batch Test 13**	**Batch Test 14**	**Batch Test 16**	**Batch Test 17**	**Batch Test 18**		**Batch Test 19**	**Batch Test 20**	**Batch Test 21**	**Batch Test ART1**	**Batch Test ART2**	**Batch Test ART3**
O_2	300	225	550	600	670	400	670		600	400	450	150	200	350
CO_2	273	204	500	545	609	365	609		545	363	409	136	181	317
NH_3	1.1	1.2	1.05	0.9	1.92	2.5	1.92		3.2	5.7	4.7	2.0	1.8	1.5
Solids precipitated (mg/l)	varied in the 4 tests				varied in the 3 tests				varied in the 3 tests			varied in the 3 tests		
	Batch Test 11	**Batch Test12**	**Batch Test 13**	**Batch Test 14**	**Batch Test 16**	**Batch Test 17**	**Batch Test 18**		**Batch Test 19**	**Batch Test 20**	**Batch Test 21**	**Batch Test ART1**	**Batch Test ART2**	**Batch Test ART3**
Struvite	1236	1140	1250	1270	677	532	528		830	665	700	455	780	850
Newberyite	3.8	2.8	2.8	2.6	2.1	1.2	0		5	3	17	25	30	6
ACP	140	170	160	50	91	98	92		147	140	245	0	0	190
$CaCO_3$	58	46	43	98	0	0	0		68	60	0	0	0	20
$MgCO_3$	0	0	0	0	30	30	21		53	70	0	0	0	35

Table 4.12 (continued)

Batch Test Parameter	Group 1 11 - 14	Group 2 16 - 18	Group 3 B1, B2		Group 4 19 - 21			Group 5 ART1- ART3,		
BIOLOGICAL PROCESSES CONSTANTS										
Wastewater characteristics			constant except for f_{bs}		varied except for $f_{n,obp}$ and $f_{n,ous}$			constant except for f_{bs}		
			Batch Test B1	**Batch Test B2**	**Batch Test 19**	**Batch Test 20**	**Batch Test 21**	**Batch Test ART1**	**Batch Test ART2**	**Batch Test ART3**
$f_{s,up}$			0.15	0.15	0.86	0.87	0.86	0.15	0.15	0.15
$f_{s,us}$			0.05	0.05	0.06	0.09	0.06	0.05	0.05	0.04
f_{bs}			0.25	0.20	0.28	0.46	0.20	0.20	0.21	0.20
f_{na}			0.75	0.75	0.82	0.75	0.54	0.75	0.75	0.75
$f_{n,obp}$			0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
$f_{n,ous}$			0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Kinetic and stoichiometric constants			constant except for μ_H and μ_A		varied except for K_{SH} and K_n which were constant in the three tests			μ_H and μ_A varied in the three tests others constant in ART1 and ART2 but varied in ART3		
			Batch Test B1	**Batch Test B2**	**Batch Test 19**	**Batch Test 20**	**Batch Test 21**	**Batch Test ART1**	**Batch Test ART2**	**Batch Test ART3**
μ_H			2.95	2.60	2.08	2.09	2.5	2.50	2.1	2.1
μ_A			0.20	0.11	0.036	0.03	0.03	0.15	0.11	0.04
K_{SH}			5	5	40	40	40	5	5	40
K_n			0.027	0.027	0.60	0.60	0.60	0.15	0.15	0.6 - 1.4
$f_{ZB,N}$			0.068	0.068	0.020	0.053	0.063	0.068	0.068	0.068

Note: Only the kinetic and stoichiometric constants that were affected by pH and chemical precipitation and therefore differed from the default values in Groups 4 and 5 are shown in this table. All other stoichiometric and kinetic constants at default values (see Tables 5.8, 5.11 and 5.14)

4.4.1 Chemical processes

Solids most likely to precipitate

- From the literature, for the conditions present in the batch tests, the solids struvite, ACP, newberyite, $CaCO_3$ and $MgCO_3$ were identified as the most likely to precipitate and were included in the model for simulations of the batch tests (except for Group 3 where only biological processes were present). With this set of precipitants, in all batch tests, consistency could be obtained between predicted and measured soluble concentrations of Ca, Mg, P, inorganic C, FSA and pH and this provided support for the selected set of precipitants. Initial measurements of Fe indicated this to be present in the batch tests only at very low concentrations (< 1 mg/ℓ) and accordingly precipitation of iron salts was not considered for inclusion in the model. For situations where iron or other mineral precipitants are likely to form and need to be included, the approach developed here can be followed.

- With the single set of precipitants above, varying amounts of the solids were predicted to precipitate in the different batch tests:

  - In all batch tests where chemical processes were present (Groups 1, 2, 4 and 5), irrespective of whether the pH increased (Group 1, Group 2, Group 4 and Group 5 batch test ART3) or not (Group 5, batch tests ART1 and ART2), struvite precipitated in the largest quantities. In those batch tests where the pH decreased below 7 due to nitrification (Group 5, batch tests ART1 and ART2), some redissolution of the precipitated struvite occurred.

  - In those batch tests where the pH increased (Groups 1, 2 and 4 and Group 5 batch test ART3), ACP was the second most abundant precipitant and newberyite did not precipitate significantly. In contrast, in the batch tests where the pH did not increase (Group 5 batch tests ART1 and ART2), ACP did not precipitate and newberyite was the second most abundant precipitant.

  - In those batch tests where the pH did not increase (Group 5 batch tests ART1 and ART2), $CaCO_3$ and $MgCO_3$ did not precipitate. In the batch tests where the pH did increase (Groups 1, 2 and 4 and Group 5 batch test ART3), the $CaCO_3$ and $MgCO_3$ concentrations that precipitated were variable.

  - Comparing the predicted precipitations above with established domains of precipitation for the minerals in the literature, in most cases there is close agreement. Where there are discrepancies, these arise from the relative kinetics of precipitation of the minerals; for example, where the precipitants have common species, the solid with the faster precipitation rate may reduce the common species concentration to such low values that it limits precipitation of the solid with the lower precipitation rate.

Solubility products

- For all the batch tests of Groups 4 and 5 which included high organic concentrations and biological activity, a single set of solubility product values was found for the five minerals that precipitated and these values are the same as those for Groups 1 and 2 which did not include biological activity.

- The solubility product values input for the simulations all fall within the range of values quoted in the literature. For most solids, solubility product values reported in the literature at infinite dilution differ, sometimes by a few orders of magnitude. The JESS database (Murray and May, 1996), contains values for solubility products which are based on weightings from several experimental values; this database has been found to contain the most reliable solubility product values. Values of solubility products are affected by the presence of other ions and impurities in the solution with the solubility of most solids increasing significantly: $CaCO_3$, $MgCO_3$ and ACP are reported to be most affected by the presence of impurities. pK_s values for $CaCO_3$ of 6.3, 6.4 and 6.7 have been reported for ADS, raw waste and primary and secondary effluent respectively. Also, pK_s values as low as 5 for $MgCO_3$ and 24 for ACP have been reported in anaerobically digested sludge. However, the solubility of struvite and newberyite is reported to be unaffected by the presence of impurities. (For a more detailed discussion see Musvoto *et al.*, 1998). In the model calibration, for struvite and newberyite, pK_s values from the JESS database of 13.16 and 5.8 respectively gave a good correlation with the batch test results. The value reported by Hoffmann and Marais (1977) of 25.46 for ACP precipitation in activated sludge systems gave a good correlation. The pK_s values for $MgCO_3$ (7) and $CaCO_3$ (6.45) are not from any specific database but are modifications of the values measured from pure systems. The $CaCO_3$ value is very close to those reported by Merrill and Jorden (1974) of 6.3 for ADS and 6.45 for raw waste. From the above discussion, the values found during model calibration are therefore in agreement with the literature.

Specific rate constants for precipitation

- Values for the precipitation rate constants input to the model for the simulations could not be obtained from the literature, since these are not available. Accordingly, values for the precipitation rate constants were obtained by "trial and error" curve fitting of predicted to measured results.

- Comparing the values for the precipitation rate constants found for the different batch tests with the approach above, the following observations can be made:

    - With the exception of struvite, the same set of specific rate constants for precipitation were found for Groups 4 and 5 batch tests, i.e. batch tests 19 to 21 and ART1 to ART3 respectively.

    - For struvite, the specific rate constant for precipitation is lower in Group 5 (30 /d) than in Group 4 (100 /d) batch tests. The specific rate constants for Group 4 and 5 batch tests which include biological activity also are both lower than those of Group 1 and 2 batch tests which exclude biological activity (300 and 3000 /d respectively).

    - For ACP, $CaCO_3$, $MgCO_3$ and newberyite, the specific rate constants for precipitation are the same for Group 4 and 5 batch tests (i.e. 350, 50, 50 and 0.05 /d respectively). The values for $MgCO_3$ and newberyite in Group 4 and 5 batch tests are the same as in Groups 1 and 2 (50 and 0.05 /d respectively). For ACP, the value in Group 4 and 5 batch tests is the same as in Group 2 (350 /d), but the value for these three groups differs from that in Group 1 (150 /d). Similarly for $CaCO_3$, the value in Group 4 and 5 batch tests is the same as in Group 1 (50 /d), but this value differs from that in Group 2 (0.5 /d).

- From the above, in general with the exception of struvite, there is a remarkable degree of constancy in the values found for the precipitation rate constants; only values for ACP in Group 1 and $CaCO_3$ in Group 2 differ from the "standard set" of values. For struvite, although a single precipitation rate constant was found for all the batch tests in a particular group, the values differed significantly between the groups, by up to two orders of magnitude. Although definitive reasons cannot be advanced for the variability in the struvite precipitation rate, and the deviation in ACP and $CaCO_3$ above, the literature does provide some guidance on possible causes. It can be hypothesised that:

  (i) The rates of precipitation of struvite and ACP are decreased by the presence of increasing concentrations of organic particulates.

  (ii) Biological activity decreases the rate of precipitation of struvite but not of the other minerals.

  (iii) The rate of precipitation of $CaCO_3$ is decreased by increasing concentrations of Mg and P, decreasing initial $CaCO_3$ supersaturation and possibly some other trace constituents which were not measured during the experiments.

- Since precipitation rate constants could not be obtained from the literature for the compounds considered in the model, no assessment could be made on the validity of the values used. Further, from the literature the rate of precipitation for a particular compound varies in different solution mixtures depending on the characteristics of the solution. The rates are consistent only in pure solutions and in mixed solutions, the rates deviate from the ones in pure solutions. The precipitation rates determined with the model must therefore be seen as specific for the types of wastewater tested. With different types of wastewaters, the values may vary from the values found in this investigation.

4.4.2 Physical processes

- The approach used to model the physical processes of gas stripping/exchange was successful. However, for each individual batch test different values of K_{La} for O_2/CO_2 and NH_3 were found. This is not unexpected as the aeration conditions (gas flow rates, mixing, solids, etc.) differed in each batch test.

- Comparing the K_{La} values for O_2/CO_2 with those for NH_3, the values for O_2/CO_2 are much higher, by two orders of magnitude. This is in agreement with the literature where it is evident that the volatility of NH_3 is much lower than that for O_2/CO_2. This is reflected in the value for the dimensionless Henry's constant H_c; for NH_3, $H_c = 0.011$ whereas for O_2, $H_c = 29.9$ and for CO_2, $H_c = 0.95$.

4.4.3 Biological processes

Biological activity was present only in batch test Groups 3, 4 and 5, and accordingly, only these groups are considered in this section.

Wastewater characteristics

- For batch tests with raw sewage (Group 3, B1 and B2; Group 5, ART1, ART2 and ART3), the same set of values for the wastewater characteristics was accepted in the simulations, except for the RBCOD faction (f_{bs}) which varied over a relatively small range from $f_{bs} = 0.2$ to 0.25. Further, the values found for the wastewater characteristics are typical for the Mitchell's Plain raw wastewater used in the investigation (Ubisi *et al*., 1997).

- For the batch tests with ADS (Group 4), reasonable consistency was found for the ADS characteristics between the different batch tests (19 to 21). However, very high values for the unbiodegradable particulate COD fraction ($f_{s,up} = 0.86$ to 0.87) were required to provide acceptable simulations; these high values were confirmed with 0.45 µm filtration tests which gave an 86% particulate fraction (see Appendix A). Considering that the ADS has been anaerobically digested prior to the batch tests, this result is not unexpected.

Kinetic and stoichiometric constants

- To simulate the experimental results correctly, only five constants in IAWQ Activated Sludge Model No. 1 (Henze *et al*., 1987) had to be changed from their default values, namely μ_H, μ_A, K_{SH}, K_X and $f_{ZB,N}$. The model default values for these constants are $\mu_H = 4.5$ /d, $\mu_A = 0.45$ /d, $K_{SH} = 5$ gCOD/m^3, $K_X = 0.027$ gCOD/gCOD and $f_{ZB,N} = 0.068$ gN/gCOD

- The value for the maximum specific growth rate of the heterotrophs (μ_H) for the WAS in Groups 3, 4 and 5 batch tests was established in Group 3 batch tests (B1 and B2) with the biological processes only (at neutral pH 7.0 - 8.0), at average $\mu_H = 2.78$ /d. In the batch tests where the pH increased (Group 5, ART3; Group 4, 19 and 20, but excluding 21 with a 2:1 WAS:ADS mixture), the average $\mu_H = 2.09$ /d; In those batch tests where chemical precipitation took place, but the pH did not increase (Group 5, ART1 and ART2), average $\mu_H = 2.30$ /d. Thus it appears that under the same conditions the precipitation of minerals reduces μ_H by about 17%, and an increase in pH reduces μ_H by a further 8%.

- The value for the maximum specific growth rate of the nitrifiers at 20°C and pH = 7.2 ($\mu_{A20,pH7.2}$) for the WAS in the Group 3, 4 and 5 batch tests was established in Group 3 batch tests (B1 and B2) with biological processes only at neutral pH, to give $\mu_{A20,pH7.2} = 0.11$ to 0.20 /d. For the batch tests in which chemical precipitation took place, but the pH did not increase (Group 5, ART1 and ART2), $\mu_{A20,pH7.2} = 0.11$ to 0.15 /d which falls within the range of values for Group 3 batch tests. For the batch tests where the pH increased (Group 4, 19 to 21; Group 5, ART3), $\mu_{A20,pH7.2} = 0.03$ to 0.04 /d which is about 5 times lower than for the batch tests where pH did not increase. In the model, the effect of pH on μ_A is taken into account [see Musvoto *et al.*, 1998]. This should enable the value of $\mu_{A20,pH7.2}$ found from the batch tests with no pH increase (Group 3; Group 5, ART1 and ART2) to be valid also for simulations of the batch tests where the pH does increase (Group 4; Group 5, ART3) because the change in μ_A with pH should be automatically adjusted in the model. However, even with the pH adjustment of μ_A the input $\mu_{A20,pH7.2}$ had to be decreased. In examining the batch test behaviour, this decrease in $\mu_{A20,pH7.2}$ could have arisen from two reasons: (i) precipitation of ACP - this is the only mineral that precipitates in all the batch tests with lower $\mu_{A20,pH7.2}$, but not in the other batch tests, or (ii) the μ_A - pH relationship proposed in Eq. (2.13) is not correct. With the data available it is not possible to assess which reason is the likely one. To establish the cause for the reduced μ_A will require further experiments where the pH is increased without ACP precipitation.

- In Group 3 batch tests (B1 and B2) with biological processes only at neutral pH (7-8) and Group 5 batch tests ART1 and ART2 with chemical precipitation also at neutral pH, the default literature value for the Monod half saturation coefficient for utilisation of RBCOD (K_{SH} = 5 gCOD/m^3) gave a good correlation between OUR experimental results and model predictions. In Group 4 batch tests (19 to 21) and Group 5 batch test (ART3) with biological activity, chemical precipitation and an increase in pH, K_{SH} had to be increased to 40 gCOD/m^3 to obtain a good correlation. Increasing the half saturation coefficient decreases the rate of utilisation of RBCOD. Thus, it appears that chemical precipitation does not affect the rate of utilisation of RBCOD, but that the rate decreases with increase in pH.

- To match measured and simulated OURs, the value for the half saturation coefficient for hydrolysis of enmeshed (slowly biodegradable) COD (K_X) had to be increased from the default literature value of 0.027 gCOD/gCOD obtained in biological activity only batch tests (Group 3 batch tests B1 and B2) to 0.15 gCOD/gCOD in Group 5 batch tests (ART1 and ART2) at low pH, but with chemical processes also. In Group 4 batch tests (19 to 21) with biological and chemical processes and an increase in pH, K_X had to be increased to 0.6 gCOD/gCOD and in Group 5 batch test ART3 with similar conditions the value was varied from 0.6 to 1.4 gCOD/gCOD. Increasing K_X decreases the rate of hydrolysis of enmeshed COD. It appears that the hydrolysis of enmeshed COD is decreased by precipitation. This decrease however becomes more substantive when precipitation is combined with an increase in pH.

4.4.4 Aeration as a treatment scheme for anaerobic supernatants

The primary objective of these batch tests was to gather data for evaluation of the combined three phase biological, chemical and physical model. In this experimental investigation a number of batch tests were conducted in which anaerobic supernatants from a municipal sewage treatment plant anaerobic digester and from a UASB reactor treating wine distillery effluent were aerated, with or without addition of waste activated sludge. However, the data from the batch tests can also be used to asses the feasibility of treating anaerobic supernatants by aeration. Anaerobic supernatants contain high nutrient concentrations (N in the form of ammonia/um, and P) but low biodegradable organic carbon concentrations. This imbalance between the nutrients and organics causes their treatment in conventional biological nutrient removal (BNR) activated sludge systems to be problematic. Also, in municipal wastewater treatment plants if the anaerobic supernatants are recycled to the head of the works (as is the usual practice), even though they only contribute a small percentage of the flow to the treatment plant, they can contribute significantly to the nutrient load to the plant. Further, in BNR systems, anaerobic supernatants also contain high Mg concentrations, which combined with the high N and P concentrations, can cause struvite precipitation which may result in operational problems, such as pipe blockages (Pitman *et al.*, 1989).

Controlled struvite precipitation has been proposed as treatment option for anaerobic sludges and supernatants and has been implemented full-scale at Goudkoppies Treatment Plant (Johannesburg, South Africa; Pitman, 1995). At Goudkoppies, WAS is thickened in a dissolved air flotation unit and primary sludge in gravity thickeners before undergoing combined anaerobic digestion. The anaerobically digested sludge is aerated to strip CO_2 (to cause pH to increase and so stimulate struvite and calcium phosphate precipitation). Lime is then added (for further precipitation) and the limed liquor is dewatered on belt presses. The liquors from the belt presses are clarified in separate thickeners and recycled to the head of the treatment works. Table 4.10 below shows results from the Goudkoppies plant as reported by Pitman (1995): After the aeration step, the pH is still low (7.7) and considerable P (170 mgP/ℓ) and ammonia (510 mgN/ℓ) remain.

Table 4.10 Average results from Goudkoppies digested sludge conditioning plant (Pitman, 1995).

Parameter	**Digested Sludge**	**Aerated Sludge**	**Lime treated sludge**	**Liquors**	**Liquor thickener overflow**
o-Phosphate (mgP/ℓ)	250	170	5.8	1.5	1.1
Ammonia (mgN/ℓ)	660	510	420	120	120
pH	7.1	7.7	9.2	8.9	8.9

The batch tests in this investigation in effect duplicate the first aeration step at Goudkoppies. Accordingly, the data from the batch tests may provide greater insight into the biological, chemical and physical processes operating in the Goudkoppies sludge and were examined with this objective:

- In batch tests with ADS (Group 1) and UASB supernatant (Group 2), aeration caused CO_2 stripping and this resulted in pH increase from ±6.95 to 8.93 and 9.53 respectively.

- The increase in pH caused precipitation of predominantly struvite and ACP, reducing concentration of both nutrients N and P to around 380 gN/m^3 and 15 gP/m^3 respectively for Group 1 and 30 gN/m^3 and 20 gP/m^3 respectively for Group 2.

- In both supernatants, the ammonia is present in excess for struvite precipitation, and so the concentrations of ammonia are still relatively high (380 gN/m^3 for Group 1 and 30 gN/m^3 for Group 2).

- Struvite precipitates very quickly within the first 20 to 45 minutes of aeration and ACP within 60 to 90 minutes of aeration.

- Ammonia is relatively non volatile so that the rate of ammonia removal via gas stripping is not a practical treatment alternative under the conditions present in the batch tests.

- Addition of waste activated sludge (WAS) to the anaerobic digester supernatant results in nitrification of the ammonia. However, this nitrification proceeds at a very slow rate ($\mu_{A20,pH7.2}$ = 0.03 to 0.04 /d). Further, addition of WAS has the undesirable effect of reducing the rate of struvite precipitation, by up to two orders of magnitude. This would imply that the aeration of anaerobic supernatants should be a two stage process: (i) aeration for CO_2 stripping and pH increase, followed by (ii) addition of WAS for nitrification. In the nitrification step, care must be taken to ensure that the pH does not decrease below 7 to cause struvite redissolution (this took place in batch tests ART1 and ART2, Group 5 when the pH decreased to 6.76).

The combined model presented in this research provides a valuable tool which can be used to provide a basic understanding of the mechanisms operating in the treatment scheme, and to theoretically refine the treatment process for practical implementation. The AQUASIM programme is flexible enough to model any combination of completely mixed or plug flow reactors with split influent flows, chemical addition, recycle flows and sedimentation tanks. It is therefore possible to simulate an ADS treatment system with the integrated chemical, physical and biological model developed in this research provided the reactor conditions such as air flow and gas transfer rates are known.

4.5 CLOSURE

The three phase systems kinetic model developed in Chapter 3 could not be validated due to lack of suitable data from the literature. In this chapter, the model has been calibrated and validated with experimental data on three types of waste, (i) ADS from a digester treating a mixture of primary sludge and waste activated sludge from a BEPR plant, (ii) effluent from a UASB digester treating spent wine and (iii) a mixture of ADS and WAS from a nitrogen removal laboratory plant. The model proved capable of simulating the experimental data accurately.

CHAPTER 5

EXPERIMENTAL INVESTIGATION: TREATMENT OF LANDFILL LEACHATES

4.1 INTRODUCTION

Parallel to the development of the integrated mathematical model (Chapter 3), experimental investigations were undertaken into the feasibility of treating selected high nutrient low organic carbon (HNLC) wastes in various treatment schemes. This Chapter reports on experimental investigations into the treatment of landfill leachates in conventional activated sludge systems receiving municipal wastewaters. In Chapter 4, experiments on treatment of waste activated sludge dewatering liquors and anaerobic digestor supernatants are reported, and in Chapter 6, a theoretical investigation into treatment of septic tank effluents.

Sanitary landfill sites are used for disposing solid refuse. In the past landfill sites were viewed only as solid waste disposal sites with little or no effort to promote the stabilization of the solids wastes. However, management and operation of landfill sites has now become a necessity due to (1) increased urban population resulting in a shortage of land for landfills and hence the need to maximise the life of a landfill, and (2) increased environmental awareness and the need to preserve the natural environment. The most serious environmental threat posed by a landfill site is the pollution of ground water caused by leachates. Leachates are formed by rain percolating through the solid waste. To avoid ground water pollution, leachate formed from sanitary landfills needs to be collected for treatment. Two types of leachates can be formed by a landfill, viz. stabilized leachate from a landfill in its methanogenic phase and acid leachate from a landfill in its acidogenic phase of decomposition. Acid leachate can be treated by discharging it onto methanogenic refuse to produce stabilized leachate (Novella, 1995). However, stabilized leachates are characterised by high organic and nitrogen contents (COD - 5 258 mg/ℓ; TKN - 440 mg/ℓ; Hansford and Ekama., 1993) and require further treatment.

Accordingly, a study was undertaken to provide additional information on the treatment of landfill leachates. In particular, the feasibility of adopting an integrated approach to municipal waste management by operating sewage treatment plants (liquid waste treatment) and sanitary landfill sites (solid waste management) in conjunction with each other was investigated. In terms of this approach, the liquid leachate stream produced in the landfill is treated in the sewage treatment plant and the waste activated sludge stream generated in the sewage treatment plant is disposed to the landfill. Two experimental studies have been completed, focussing on the treatment of the leachate in the sewage treatment plant, namely:

(1) Treatment of stabilized landfill leachate in a N removal activated sludge system.
(2) Treatment of acid leachate in a nutrient (N&P) removal activated sludge system.

Results from these studies are summarized in this Chapter; for details, see Hansford and Ekama (1993) and Sneyders *et al*. (1997).

5.2 ADDITION TO N REMOVAL ACTIVATED SLUDGE SYSTEM

In this study, the treatment of a stabilized landfill leachate in an N removal activated sludge system and its effect on the system performance were investigated. Two parallel identical N removal systems were operated, one experimental and one control. Both systems received the same municipal wastewater as influent at the same COD concentration and influent flowrate. Additionally, stabilized landfill leachate was dosed to the experimental system. By comparing the control and experimental system responses, the effect of the leachate could be determined. The investigation is summarized below (for details, see Hansford and Ekama, 1993).

5.2.1 Experimental set up and testing

To determine the effect of stabilized leachate on the nitrogen removal activated sludge system, two anoxic (4ℓ)-aerobic (8ℓ) reactor systems at 15 days sludge age were operated for 80 days at 20 °C. Both, one experimental and one control, received 15 ℓ/d real raw sewage diluted to a concentration of 600 mg COD/ℓ , but the experimental system received additionally 300 mℓ/d stabilized leachate at 5 300 mgCOD/ℓ, representing 18% of the sewage organic load. This is a leachate organic load about three times higher than would be expected on a *per capita* basis.

For 47 days, daily testing of influent, reactor and effluent COD, TKN, NH_4^+, NO_3^-, and NO_2^- concentrations were conducted on both the experimental and control systems. Also daily the VSS, TSS, sludge settleability in terms of DSVI and oxygen utilization rate were measured on the aerobic reactors of both systems.

5.2.2 Results

Analysis of the results indicated that

- The N and COD mass balances were generally good (better than 90%).
- 11.5% of leachate COD contributed to unbiodegradable soluble COD, increasing the effluent COD concentration from the experimental system by 13 mgCOD/ℓ (25%).
- 5.7% of leachate COD was unbiodegradable particulate, increasing the VSS concentration of the solids in the reactor by 75 mgVSS/ℓ (3%).
- 83% of the leachate COD was biodegradable and contributed to the biodegradable organics of the sewage.
- No noticeable difference between the effluent TKN concentration of the experimental and control systems could be detected, indicating that the leachate contains negligible soluble unbiodegradable organic N. Also nitrification was complete and all free and saline ammonia of the leachate was nitrified.
- The additional leachate biodegradable COD caused an increase in reactor VSS concentration of about 400 mgVSS/ℓ, i.e. 20% more than in the control. The biodegradable COD and TKN caused the oxygen utilization rate to increase by 5 mgO/ℓ/h

i.e. also about 20% more than in the control system. These increases seem reasonable considering the leachate increased the organic and nitrogen load by 18%.

- The effluent nitrate concentration from the experimental system was *lower* than that from the control system. This implied, and detailed comparison on the denitrification performance of the two systems confirmed this, that the leachate not only was capable of denitrifying all the nitrate that was generated from its own TKN content, but also contributed to denitrification of nitrate generated from the sewage's TKN content.
- Sludge settleability in both systems *improved* from over 150 mℓ/g at the start of the investigation to below 60 mℓ/g at the end. The filaments in the sludge were the usual AA types (i.e. *M. Parvicella*, 0092, 0041, 0675) but were only present at common level. This indicated that leachate did not stimulate poor sludge settleability in N removal systems.

5.2.3 Conclusions

Addition of stabilized leachate to an N removal activated sludge system indicates that (1) it is about 90% biodegradable and, (2) due to its high short chain fatty acid (SCFA) and readily biodegradable content it not only is able to denitrify all the nitrate that is generated from its own TKN, but also contributed significantly to the N removal of the TKN in the sewage. The high SCFA content of the leachate may also stimulate additional biological excess P removal when it is added to a nutrient removal system and this warrants investigation, see below.

5.3 ADDITION TO NUTRIENT (N&P) REMOVAL ACTIVATED SLUDGE SYSTEM

In this study, an investigation was undertaken into the treatment of an acid landfill leachate in a nutrient (N&P) removal activated sludge system. The acid landfill leachate was selected because of its high SCFA concentration, which can be expected to stimulate biological excess phosphorus removal. The approach followed is similar to that for the N removal system study: Two biological nutrient removal (BNR) activated sludge systems were operated in parallel, one receiving sewage only and the other sewage and acid leachate. The difference in response between the two systems could be ascribed to the leachate. This section summarises this research project; details are given by Sneyders *et al*. (1997).

5.3.1 Experimental setup and procedures

System setup and operation

Two identical laboratory scale systems were set up, one control and one experimental, using the UCT BNR system configuration, see Figure 5.1. The systems comprised a 6ℓ anaerobic reactor, 7ℓ anoxic reactor and a 10ℓ aerobic reactor. The anaerobic reactor received the influent as well as mixed liquor recycled from the anoxic reactor (r-recycle). The anoxic reactor received the flow from the anaerobic reactor and mixed liquor recycled from the aerobic reactor via the a-recycle. The settled sludge was also recycled back into this reactor via the s-recycle. The recycle rates (see Figure 4.1) were as follows: r-recycle = 1:1; a-recycle = 2:1; s-recycle = 1:1. Both systems were operated at a constant temperature of 20°C and sludge age of 10d.

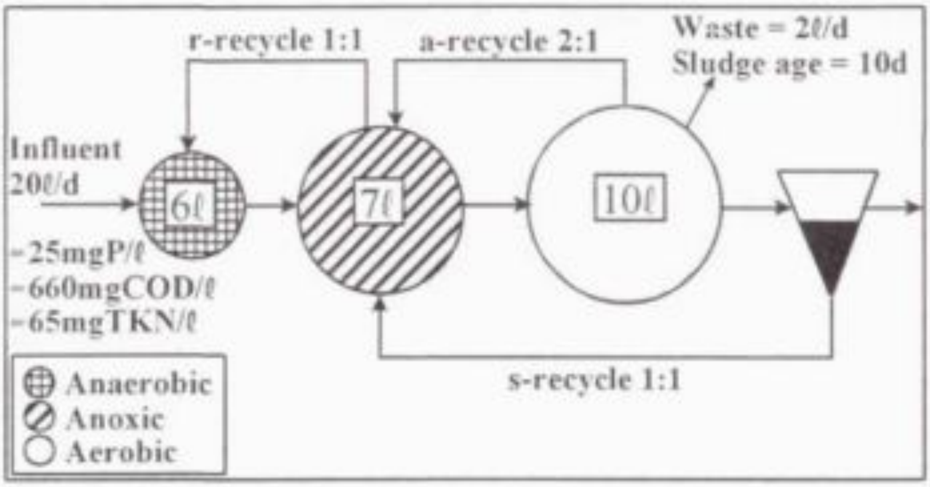


Figure 5.1: Schematic layout of UCT system configuration.

Operational procedures detailed by Burke *et al.* (1986), Pilson *et al.* (1995) and others was followed.

Source of the influent sewage

The raw sewage was collected in batches approximately every 16 days from the Mitchells Plain Sewage Works (Cape Town, South Africa), and after maceration was stored in stainless steel tanks at 4 °C. This sewage served as feed for both systems for a period of about 2 weeks, and each seawage batch was taken as a steady state period. To feed the laboratory-scale systems, a sample of sewage was drawn from the storage tanks after thorough mixing and then diluted with tap water from its raw COD of > 1 000 mgCOD/ℓ to approximately 660 mgCOD/ℓ. The diluted influent was buffered with the addition of sodium hydrogen carbonate ($NaHCO_3$) to prevent nitrification from reducing the pH of the mixed liquor. Up to 15 mgP/ℓ potassium hydrogen phosphate was dosed to the influent to ensure that the effluent total P (TP) concentration from the systems remained above 2 mgP/ℓ, and hence that the systems were not P limited. The 20ℓ diluted influent was placed in the systems' feed drums which were refrigerated at approximately 8°C and served as influent for a 24 hour period. This also provided a check that daily all the influent COD was discharged to the systems; any solids that may have accumulated in the bottom of the feed drums were collected and poured into the anaerobic reactor.

Source of leachate

The leachate was obtained from six test lysimeters, 4.5 m high with a diameter of 0.6 m, located on the UCT campus. These were originally constructed in 1989 for a previous study (Chapman and Ekama, 1991), but were still in relatively good condition to provide leachate for this study. At the start of this study, leachate samples were taken from each of the six lysimeters and their COD concentrations were measured. Of the six lysimeters, two were found to produce an acidic unstabilized leachate with an average COD concentration of 46 000 mgCOD/ℓ. The other four lysimeters produced stabilized leachate with an approximate COD concentration of 3 500 mgCOD/ℓ. The leachate from the two lysimeters in the acidic phase were used in this study, and after blending had the characteristics shown in Table 5.1.

Table 5.1: Measured leachate characteristics (Kimaru, 1996).

Parameter	Value	Units	No. of Tests
COD (unfiltered)	41 810	mgCOD/ℓ	23
COD (filtered)	39 813	mgCOD/ℓ	24
Fraction VFA (COD/COD)	0.30'		
TKN (unfiltered)	1 411	mgN/ℓ	12
TKN (unfiltered)	1 311	mgN/ℓ	13
FSA (unfiltered)	1 299	mgN/ℓ	9
FSA (filtered)	1 096*	mgN/ℓ	12
Total Phosphorous (unfiltered)	101	mgP/ℓ	10
Total Phosphorous (filtered)	90	mgP/ℓ	10

' Result obtained by Novella *et al.* (1996); *Ammonia was lost during vacuum filtration.

Sewage feed and leachate dosing

Both the experimental and control systems received 20 ℓ/d real raw sewage diluted to 660 mgCOD/ℓ and had sludge ages of 10 days. In addition to receiving the 20 ℓ/d raw sewage, 21mℓ unstabilized leachate per day was dosed to the influent to the experimental system from day number 32. The unstabilized acid leachate has an approximate COD concentration of 46 000 mgCOD/ℓ. Thus, the leachate dosing amount constituted 1/16 of the influent COD mass. The leachate dose was doubled to 42 mℓ/d on day number 57, constituting 1/8 of the influent COD mass; this was done to ensure that the effect of the leachate could be readily monitored.

Data acquisition and system performance monitoring

To monitor the effects of changes in both systems, samples were drawn virtually daily from each of the reactors of both systems for analysis, throughout the 495 day investigation. In the case of a poor quality sewage (unusually high TKN/COD ratio > 0.12 mgN/mgCOD) being fed to the systems and various other problems encountered with the operating of the systems, such as overnight pipe blockages, some daily data were rejected from the analysis. Table 5.2 illustrates the parameters measured on the samples collected from the two systems. In addition, anaerobic, anoxic and aerobic batch tests were conducted on sludge drawn from the two systems to examine the P release, denitrification and nitrification kinetics.

Table 5.2: Sampling position and parameter measurement.

Test	COD	TKN	FSA	NO_3	NO_2	Tot P	OUR	DSVI	V/TSS	pH
Influent*	✶ †	✶	✶			✶				
Anaerobic				†	†	†				✓
Anoxic				†	†	†				
Aerobic	✶	✶		†	†	†	✓	✓	✓	✓
Effluent	✶ †	✶ †		†	†	✶ †				

✓ Measurement taken (filtering not applicable). ✶ Unfiltered sample.

† Filtered through Schleicher & Schnell 0.45 µm glass fibre membrane.

* Included the leachate dose for the EXP system.

5.3.2 Results

The two systems were operated for 495 days. Averages of the daily measurements were calculated taking the duration of one sewage batch as a steady state period. Overall there were 31 steady state periods during the investigation. The experimental and control systems performance are compared below:

COD and N mass balances

To establish the accuracy of the experimental data, COD and N balances were performed on each system. In these balances, the COD and N entering the systems via the influent flow was reconciled with the COD and N leaving the systems via: (1) nitrate denitrified; (2) oxygen utilized; (3) sludge wasted and (4) the effluent flow. The nitrate and nitrite denitrified in the anoxic and anaerobic (usually zero) reactors, from which the oxygen recovered by denitrification was also calculated, was calculated from a nitrate and nitrite mass balance around these reactors. The reliability of the data is directly proportional to the mass balance deviation from the target value of 100%. i.e. the closer the mass balances were to 100 % the more reliable the data. To achieve this, the 495 day investigation was divided into a number of steady state periods. The TKN varied quite considerably between the different sewage batches and thus nearly all steady state periods started and ended with a sewage batch. Overall there were 31 steady state periods during the 495 day investigation. The data over each steady state period were averaged and the COD and N mass balance calculations were based on these averages. The steady averages were also averaged to give the overall averages.

The overall average COD balances obtained in the EXP and CTL systems were 92% and the N balances were 90% and 88% respectively. Although lower than 100 %, these are acceptable and similar to COD and N balances observed in other investigations e.g. Pilson *et al*. (1995) 84% and 97%; Clayton *et al*. (1989), 92% and 91%; Mellin *et al*. (1997) 84% and 82%, Kaschula *et al*. (1993) 84% and 89%. The only recent investigation in which COD and N balances greater than 100% were obtained was by Musvoto *et al*. (1992), 106% and 102%. Of the influent COD mass, about 7% leaves the system via the effluent, 37% in the waste sludge, 48% is passed on to electron acceptors, of which 12% is nitrate denitrified and 36% is carbonaceous oxygen utilized, and 8% is unaccounted for. Of the influent N mass, about 24% leaves the system via the waste sludge, 43% by denitrification, 22% via the effluent, of which 18% is nitrate and 4% is TKN and 11% is unaccounted for.

Since both the COD and N mass balances for the two systems are acceptable, the experimental data can be accepted as reliable.

System COD and N Removal Performance

The influent and effluent soluble COD and TKN was measured by means of the 0.45 μm glass fibre filtration method preceded by an alum flocculation-coagulation step. The biodegradable soluble COD concentration of the sewage only was determined from the difference between the CTL system influent and effluent soluble COD concentrations and was used as the input readily boidegradable (RB)COD concentration for the CTL system BEPR calculations (see below). The biodegradable soluble COD of the sewage/leachate mixture was 27.7% (i.e. 72.3% is colloidal and could be flocculated out). As 13.7% of the leachate COD was taken up for BEPR (see below), 27.7-13.7 = 14.0% of the leachate soluble biodegradable COD was not taken up in the anaerobic reactor for BEPR. A possible reason for this could be that the leachate contains slowly biodegradable soluble COD.

The 45mℓ leachate dose should have increased the COD and TKN concentration of the EXP system by 104 mgCOD/ℓ and 3.2 mgN/ℓ respectively, but the difference between the EXP and CTL system overall average influent COD and TKN concentrations were found to be 147 mgCOD/ℓ (807 vs 660) and 5.35 mgN/ℓ (72.05 vs 66.70). The measured influent COD and TKN concentrations for the EXP system were accepted for further analysis because these gave similar COD and N balances as the CTL system. The leachate therefore comprised 22.3% and 8.1% of the sewage only organic COD and TKN loads. The overall average 0.45 µm membrane filtered effluent COD and TKN concentrations from the EXP and CTL systems were 49.6 and 46.4 mgCOD/ℓ and 2.45 and 2.21 mgN/ℓ respectfully. These gave unbiodegradable soluble COD (f_{us}) and TKN (f_{nu}) fractions of $f_{us} = 0.054$ and $f_{nu} = 0.034$ for the sewage/leachate mixture and $f_{us} = 0.058$ and $f_{nu} = 0.033$ for the sewage only respectively. The difference of 3.2 mgCOD/ℓ and 0.24 mgN/ℓ represents the additional unbiodegradable soluble COD and TKN concentrations from the leachate which as a fraction of the leachate COD and TKN is 2.2% (3.2/147) and 4.5% (0.24/5.35) respectively. Therefore, because the leachate unbiodegradable particulate COD and TKN fractions were found to be zero (see below), 97.8% and 95.5% of the leachate COD and TKN were biodegraded in the system. The nitrate denitrified in the EXP and CTL systems was 31.3 and 29.7 mgN/ℓ respectively. It should be noted however, that there was no nitrate present in the anoxic reactors of both systems and so more nitrate could have been removed by increasing the mixed liquor recycle (see below).

To determine the unbiodegradable particulate COD concentration (S_{upi}) and fraction (f_{up}) (and its associated TKN $f_n/f_{cv}.f_{up} = 0.10/1.48\ f_{up} = 0.068\ f_{up}$, WRC, 1984) of the sewage fed to the CTL system, the appropriate f_{up} value was selected so that the system VSS mass calculated with the BEPR model of Wentzel *et al.* (1990) was equal to that measured using the measured influent characteristics of the sewage (f_{us}, S_{ti}, RBCOD fraction f_{bs}) and the system parameters as input. This procedure fractionates the VSS mass into its hypothetical constitutive components viz. active ordinary heterotrophic organisms (OHOs), polyphosphate accumulating organisms (PAOs), endogenous residue of OHOs and PAOs and unbiodegradable particulate COD (X_i). This fractionation also is required to determine the P removal and specific denitrification rates (see below). An average f_{up} value of 0.062 was found for the CTL system. After reconciling the calculated VSS mass in the CTL system with that measured, the calculated P removal for the standard PAO P content ($f_{xbg,p}$) of 0.38 mgP/mgPAOAVSS was lower than that measured (13.56 vs 15.24 mgP/ℓ). One of two Wentzel *et al.* (1990) model parameters could be increased to increase the calculated P removal; either (1) the conversion rate (K) of RBCOD to VFA in the anaerobic reactor, which increases the proportion of the RBCOD obtained by the PAOs and hence increases their mass in the system, or (2) the P content of the PAOs, $f_{xbg,p}$. Approach 2 does not affect the calculated VSS mass and fractionation. Approach 1 increases the calculated VSS mass and results in a lower f_{up} and OHO concentration, which in turn affects the measured batch test specific denitrification rates (see below). Because the f_{up} value was already low compared to other NDBEPR systems treating the same wastewater, it was decided to accept approach 2. This approach was also the most appropriate for design because in design situations, the active PAO mass will be calculated using the Wentzel *et al.* (1990) model from the influent RBCOD concentration with the "standard" conversion rate of K=0.06 ℓ/(mgOHOAVSS.d). A $f_{xbg,p}$ value of 0.471 mgP/mgPAOAVSS set the calculated P removal equal to that measured in the CTL system. Then the CTL system $f_{xbg,p}$ value of 0.471 mgP/mgPAOAVSS was applied to the EXP system results. Using the Wentzel *et al.* model in reverse, the RBCOD taken up in the anaerobic reactor was selected so that the calculated P removal was equal to that measured (19.57 mgP/ℓ). From this, the fraction of sewage/leachate mixture COD taken up in the anaerobic reactor was calculated (viz 17.7%). With the BEPR correctly calculated, the f_{up} value was found by adjusting the f_{up} value until the calculated VSS mass was equal to that measured. The f_{up} for the EXP system (sewage/leachate mixture) was 0.040. Because the S_{upi} of the sewage/leachate mixture was lower (0.040*807 = 32.3 mgCOD/ℓ) than that for the CTL system (0.062*660 = 40.9 mgCOD/ℓ), it was concluded that the unbiodegradable particulate COD fraction of the leachate itself was zero.

The oxygen utilization rate was 21.3% higher in the EXP system (37.8 compared with 31.2 mgO/ℓ aerobic reactor/h). This is due to the additional organic COD and TKN load from the leachate. The TSS and VSS sludge production and TSS and VSS concentrations in the EXP system (5408 mgTSS/d, 4196 mgVSS/d, 2704 mgTSS/ℓ, 2098 mgVSS/ℓ) were 25.1% and 19.7% higher compared with those in the CTL system (4321 mgTSS/d, 3507 mgVSS/d, 2161 mgTSS/ℓ, 1753 mgVSS/ℓ). The higher TSS and VSS in the EXP system is due to the leachate COD load and additional BEPR it stimulates.

Biological Excess Phosphorus Removal (BEPR) Performance

Accepting the same 31 steady state periods as for the COD and N mass balances, TP balances were calculated over each reactor in both systems from which a net P uptake or release in each reactor was determined, as well as the overall net P release, uptake and removal, see Figs. 5.2, 5.3 and 5.4. The overall average P removals in the EXP and CTL systems were 16.84 and 13.18 mgP/ℓ influent respectively (see Fig 5.4). As the leachate contributed negligibly to the TP concentration of the sewage/leachate mixture, the leachate dosing stimulated 3.7 mgP/ℓ additional P removal. However, only the average of the final 12 steady state periods (20-31) were used for detailed analysis because these results were deemed more reliable. For this period, the average P removals in the EXP and CTL systems were 19.57 and 15.24 mgP/ℓ respectively; i.e. 4.33 mgP/ℓ higher in the EXP system. The P uptake was almost completely confined to the aerobic reactor of both systems with none occurring in the anoxic reactor (see Figs. 5.2 and 5.3); indeed, in the latter part of the final 12 steady state periods, P release took place in the anoxic reactor (8.8 mgP/ℓ compared with 48.0 mgP/ℓ in the anaerobic reactor), and P uptake exclusively in the aerobic reactor.

From the calculation procedure described above, 17.7% of the biodegradable COD of the sewage/leachate mixture was taken up in the anaerobic reactor. In the CTL system this was 18.8%. Hence the leachate COD concentration taken up was 0.177(1-0.040-0.054)807 - 0.188(1-0.062-0.058)660 = 20.2 mgCOD/ℓ which is 20.2/147 = 13.7% of the leachate COD. The additional P removal (4.3 mgP/ℓ) to leachate COD added (147 mgCOD/ℓ) ratio is 0.029. Theoretically (Wentzel *et al.*, 1990), if all the influent is VFA type RBCOD, then the P removal/COD taken up ratio is 0.19 mgP/mgCOD. A leachate ratio of 0.029 therefore indicates that a proportion of 0.029/0.19 = 0.154 = 15.4% of the leachate COD was taken up in the anaerobic zone. This compares very well to the 13.7% calculated earlier.

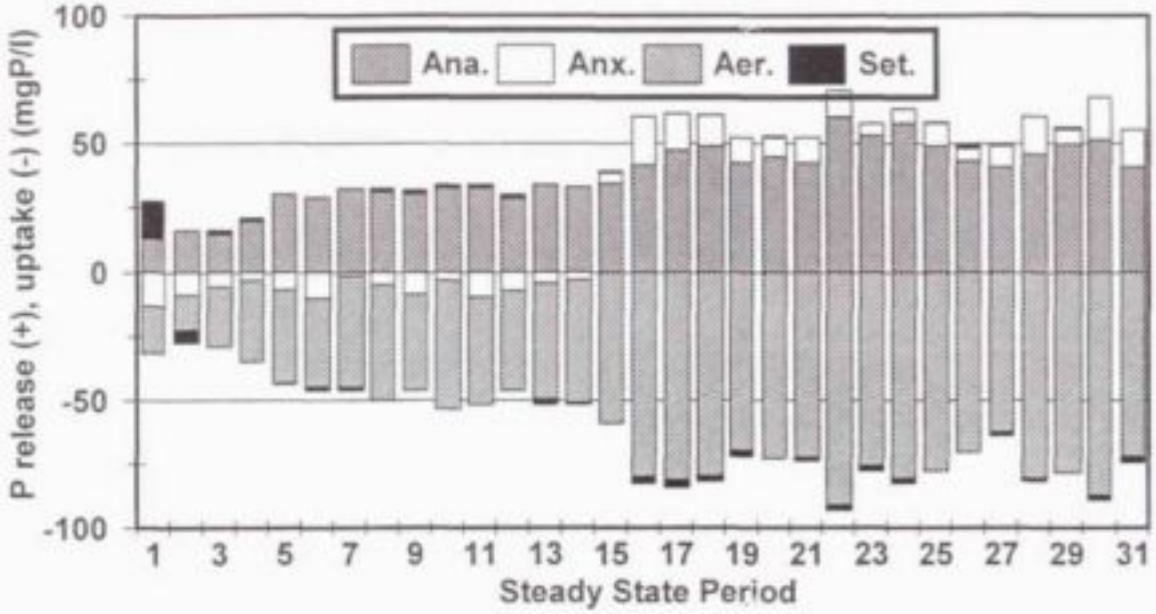


Fig 5.2: P release and uptake (mgP/ℓ influent) in the anaerobic (ana.), anoxic (anx.), aerobic (aer.) and settling tank (set.) of the leachate dosed (experimental) UCT system.

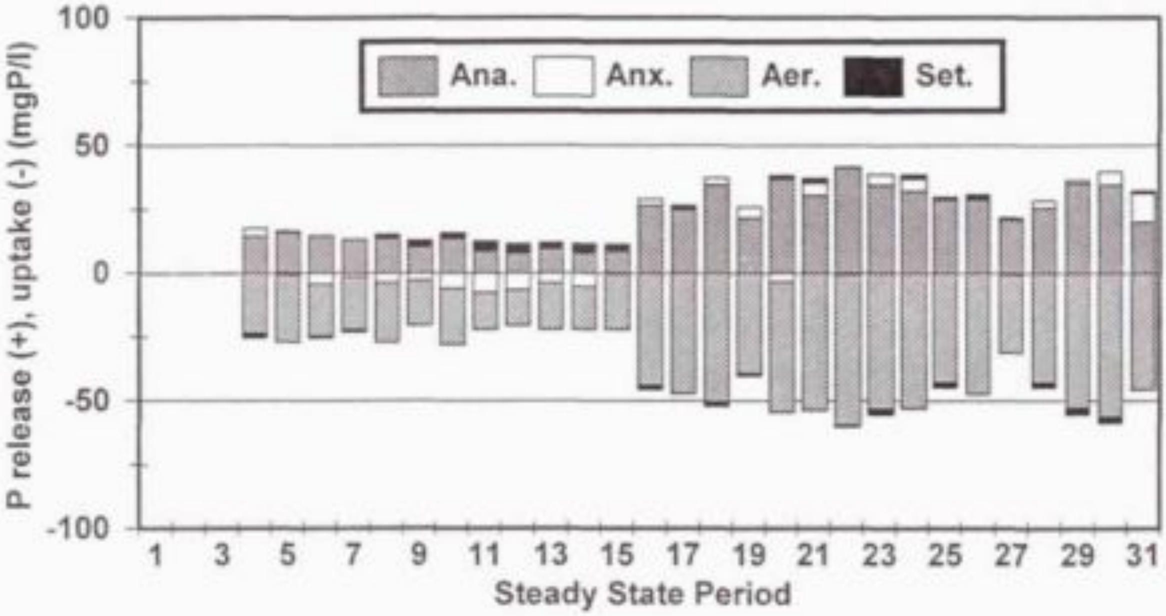


Fig 5.3: P release and uptake (mgP/ℓ influent) in the anaerobic (ana.), anoxic (anx.), aerobic (aer.) and settling tank (set.) of the non-leachate dosed (control) UCT system.

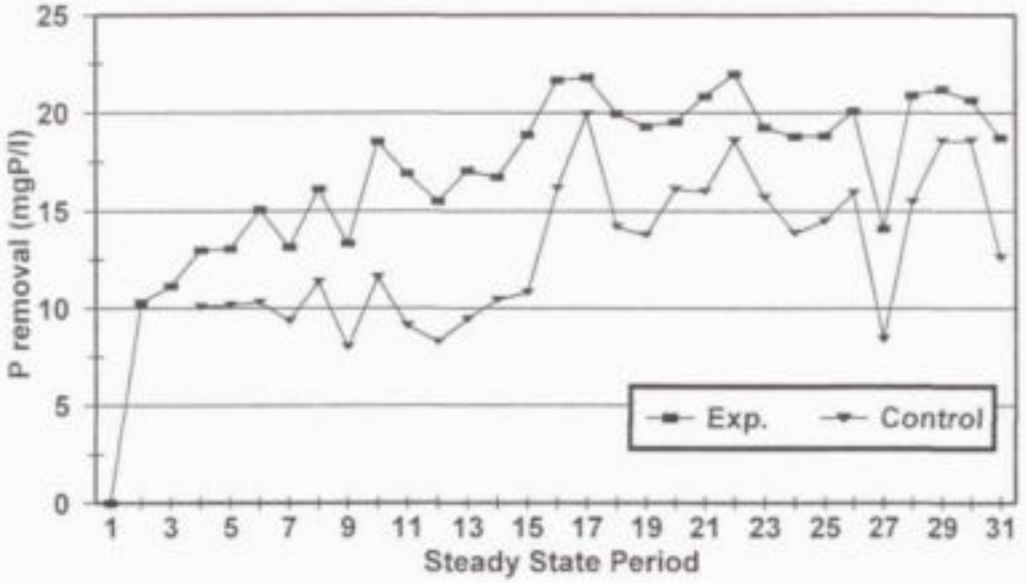


Fig 5.4: P removal in leachate dosed (experimental, exp.) and non-leachate dosed (control) UCT systems.

Six anaerobic batch tests, in which the post flocculation 0.45 μm filtration soluble COD and total P concentrations were measured over 5.5 hours, were done on sludge harvested from the anoxic reactors of the CTL and EXP systems - 2 with the sewage/leachate mixture, 3 on leachate only diluted into tap water to the same concentration as the leachate in the sewage (Kimaru, 1996), and 1 on a sewage/acetate mixture with the acetate at the same concentration as the leachate in the sewage. In all the batch tests the mass of COD added per VSS mass was the same as that in the anaerobic reactor of the parent systems. In all the batch tests, except the one on the sewage/acetate mixture, the COD taken up to P released ratio was around the expected Wentzel *et al.* (1985) value of 0.5 mgP/mgCOD; the sewage/acetate mixture yielded 0.89 mgP/mgCOD. All the batch tests showed a two phase P release behaviour, with a fast first phase and a slower second. The initial phase P release rates for the sewage/leachate and leachate only tests were 38% and 53% respectively of that for the sewage/acetate mixture. This indicated that the soluble COD in the leachate did not stimulate an acetate type P release response. In the leachate only batch tests, an average of 32.4% (47.6 out of 147 mgCOD/ℓ) was taken up. Why this was so much higher than the average 13.7% determined for the EXP syst·m, cannot be explained. However, the batch tests confirmed that the acid leachate appeared to contain an unexpectedly low concentration of organic compounds that stimulate BEPR like acetate. Clearly, the high P removal expected from the acid leachate with an anticipated (but clearly not real[1]) 30% VFA content (from Novella *et al.*, 1996) was not realized.

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[1] Novella *et al.* (1996) measured the VFA concentration in the unstabilized leachate of lysimeters 1 and 2 to be about 30 % of the leachate COD (Table 1). VFAs were not measured in the acid leachate from these two lysimeters during this investigation - six agencies with laboratories were approached to do the analysis; none were able to measure VFAs in aqueous wastewater samples. The titrametric method of Moosbrugger *et al.*, (1992) could not be used because this method gives unreliable results for samples with high VFA/carbonate species (C_T) ratios(>2:1).

Denitrification Kinetics

Twelve anoxic batch tests were carried out on sludge harvested from the EXP and CTL systems, six on each. Two batch tests were carried out simultaneously, one on each system, and the sludge was blended 1 part anaerobic to 2 parts aerobic reactor sludge in conformity with the recycles in the UCT parent systems. Nitrate in the form of sodium nitrate was added to a concentration of 30 mgN/l batch volume and at regular intervals samples were taken. The samples were immediately filtered after which some $HgCl_2$ was added to stop further biological activity. Nitrate and nitrite concentrations were measured by the AutoAnalyser method 33.69W. The denitrification rate was obtained from the nitrate concentration versus time slope. This rate was corrected for nitrite accumulation by deducting 3/5ths of the nitrite accumulation rate. In the parent systems, because P uptake was confined to the aerobic reactor, the PAOs did not participate in the denitrification. Hence, to link the nitrate reduction rate to the OHOs that perform it, the specific denitrification rate K'_2 was calculated by dividing the nitrate reduction rate by the batch test VSS concentration and the OHO active fraction of the VSS ($f_{av,OHO}$) obtained from the steady state period during which the respective batch tests were done.

No initial rapid rate of denitrification (K'_1) associated with utilization of RBCOD was noted in the tests from either system. This implies that no significant RBCOD "leaked" from the EXP system anaerobic reactor despite the low proportion of leachate COD taken up in the anaerobic reactor (13.7%). The average K'_2 rates in the EXP and CTL systems were 0.0845 and 0.0711 mgNO_3-N/(mgOHOAVSS.d) respectively. The 19% higher rate in the EXP system was not a consequence of the higher active OHO concentration in the EXP system due to the leachate addition, because this is taken into account when calculating the K_2' rates. Because so little of the leachate COD was taken up in the anaerobic reactor, it is likely that this increase in the K_2' rate is due to leakage of slowly biodegradable (soluble and colloidal) leachate COD from the anaerobic reactor, which is probably more easily degraded than the sewage particulate slowly biodegradable COD, leading to a faster rate.

In the EXP and CTL systems, the overall average nitrate denitrified in the anoxic reactors was 31.3 and 29.7 mgN/ℓ respectively. The nitrate denitrified is similar because both systems were operated at the same a-recycle ratio (2:1). This ratio was too low to load the anoxic reactors to their denitrification potential (confirmed by "zero" NO_x in the anoxic reactors). The systems were operated with this low a-recycle ratio specifically to prevent NO_X leaving the anoxic reactor, and hence to limit AA filament bulking (Casey *et al.*, 1994). Based on the batch test K'_2 rates, the denitrification potential (D_p) for the EXP and CTL systems were 23.56 and 15.53 mgNO_3-N/ℓ respectively. These potentials are lower than the nitrate denitrified in the continuous systems. The batch test K'_2 rates therefore underestimate the overall average nitrate denitrified. If the *difference* in the EXP and CTL system D_p values calculated from the batch tests is accepted (viz 23.56-15.53 = 8.03 mgN/l), then the projected nitrate concentration generated from the sewage TKN denitrified by the leachate COD would be 4.93 mgN/l (see Table 5.3). It seems therefore, that while unstabilized leachate was dosed to the EXP system because of its expected strong influence on BEPR, it actually had a greater effect on the N removal than P removal. This arises from the nature of the organics in the leachate. It was expected to have a high VFA content, but the evidence indicates it did not, and therefore did not stimulate a high additional BEPR, but rather an improved N removal.

Table 5.3: Measured and projected denitrification performance of EXP system due to leachate dosing.

Measured (concentrations in mgN/ℓ)		**Projected** (concentrations in mgN/ℓ)	
Leachate TKN added to EXP	5.35	TKN added to EXP system	5.35
N in sludge wasted due to leachate	2.01	N in sludge wasted due to leachate	2.01
Additional TKN in EXP effluent	0.24	Additional TKN in EXP effluent	0.24
Leachate TKN nitrified (5.25-2.01-	3.10	Leachate TKN nitrified (5.25-2.01-	3.10
Additional nitrate in EXP effluent	0.23	Additional denitrification potential of	8.03
Hence leachate nitrate denitrified	2.87	Leachate nitrate denitrified (all)	3.10
Leachate nitrate not denitrified	0.23	Hence sewage nitrate denitrified	4.93

Nitrification

To see the effect of the leachate on nitrification, 10 nitrification (aerobic) batch tests were carried out at 20°C; 5 on each of the EXP and CTL systems. Two batch tests, one on each system, were done in parallel. In the batch tests, sludge was harvested from the anoxic reactor, 30 mgN/l batch volume of ammonium chloride added and aeration commenced. At regular intervals samples were taken, immediately filtered, some $HgCl_2$ added to stop any further biological action and tested for nitrate and nitrite by the AutoAnalyser method 33.69W. Nitrite accumulation was very low so the nitrate generation rate was calculated from the nitrate versus time slope. The maximum specific growth rate of the nitrifiers at 20°C (μ_{nm20}) was obtained by dividing the nitrate generation rate by the concentration of nitrifiers (X_n) which was obtained from the steady state results for the period during which the batch tests were done. The average μ_{nm20} for the EXP system was 0.3005 /d, which was very similar to the 0.3002 /d rate obtained for the CTL system.

The temperature sensitivity coefficient θ of the μ_{nmT} calculated from this investigation and that of Mellin *et al.* (1997), who carried out a parallel investigation using the same sewage and identical system configuration but at 30°C, was calculated to be 1.10. This value is the same as that determined by Pilson *et al.* (1995) who carried out an investigation at 12 and 20°C. However, there was a difference between the μ_{nm20} of this investigation (0.3002 /d) and that of Pilson *et al.* (1995) (0.67 /d). This difference can be ascribed either to changes in the sewage content that was collected for the investigations or to adaptation of nitrifiers to system conditions.

Filament Identification, Bulking and Sludge Settleability

Approximately once every four weeks samples of mixed liquor were taken from each of the EXP and CTL systems and sent for microscopic analysis and filament identification. The results of 22 filament identifications on each system are summarized in Table 5.4. From Table 5.4, Anoxic-Aerobic (AA or low F/M) filaments type 0092, *M. parvicella* and type 1851 were most frequently dominant. Type 021N also occurred often in both systems but being a septic sewage filament (Jenkins *et al.*, 1984) this was probably due to aging of the sewage during storage. Apart from Type 021N, these filaments are almost always observed in full scale NDBEPR systems (Blackbeard *et al.*, 1988). It was concluded that there was nothing unusual about the filament types in the EXP system compared those in the CTL or full-scale plants.

From the results of this investigation, the overall average nitrate and nitrite concentrations leaving the anoxic reactors of both the EXP and CTL systems were found to be negligible (0.56 mgNO$_x$-N/ℓ and 0.85 mgNO$_x$-N/ℓ respectively). It can thus be concluded that complete denitrification was achieved in the anoxic reactors and therefore, according to the hypothesis of Casey *et al.* (1994), proliferation of AA (low F/M) filaments should not occur.

The mean DSVI in the EXP and CTL systems were 140 (standard deviation 35) and 153 mℓ/g (standard deviation 17) respectively i.e. 10% lower in the EXP system. Although these values are not ideal (between 80 to 100 mℓ/g), they are however below (or near to) the upper limit for a non-bulking sludge (150 mℓ/g). Comparing the DSVIs measured in this investigation with those measured by Musvoto *et al.* (1992), Clayton *et al.* (1989) and Pilson *et al.* (1995), it can be seen that although the values measured in this investigation are not ideal, they are relatively, quite good. This provides supporting evidence that the Casey *et al.* (1994) hypothesis does have value.

Table 5.4: Frequency of observation (as %) of filamentous organisms at rank dominant (Dom.), secondary (Sec.) and incidental (Icdntl.) in 22 microscopic sludge analyses from each of the Experimental and Control systems.

Filament Type	Experimental system			Control System (CTL)		
	Dom.	Sec.	Icdntl	Dom.	Sec.	Icdntl
Type 0092	45%	9%	41%	55%	18%	31%
Type 1851	23%	18%	14%	9%	41%	23%
Microthrix parvicella	18%	50%	18%	23%	36%	32%
Type 021N	9%	32%	27%	9%	18%	45%
Type 0041	5%	14%	18%	5%	5%	14%
Haliscomenobacter hydrossis	0%	0%	45%	0%	5%	36%

Metal Analysis

Over the study period, nine influent, effluent and sludge samples were analysed for their metal content. The metals that were of interest to this study were those Potentially Toxic Metals or Elements (PTMEs) specified in the Sewage Sludge Utilization and Disposal Information Document (WISA, 1994) and included Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Mercury (Hg), Molybdenum (Mo), Nickel (Ni), Lead (Pb), Zinc (Zn), Arsenic (As) and Boron (B). Due to the nature of the contents of the lysimeters, the only metal to have any significant concentration was Zn which resulted from the corrosion of the galvanized lysimeters themselves. A Zn mass balance around the EXP and CTL systems yielded a 90% and 93% recovery respectively.

The leachate in the influent of the EXP system increased the mass of Zn added to the system from 3.18 mgZn/d (CTL system) to 10.91 mgZn/d. It was found that in both systems, the bulk of the Zn left the system via the waste sludge - 85.2% in the EXP system and 82.7% in the CTL system - with only 4.9% and 10.1% leaving the EXP and CTL systems via the effluent respectively. Other metals, although at much lower concentrations, behaved similarly. For all the metals tested, except Mo and Ni, the filtered influent concentrations were significantly lower than the filtered effluent concentrations. This indicated that activated sludge not only removed the particulate/colloidal metal complexes, but also significant concentrations of soluble metal compounds. Due to the accumulation of PTMEs in the waste sludge, care should be taken in disposing of activated sludge to which leachate has been dosed, as it may contain significantly increased concentrations of PTMEs. With a large proportion of the PTMEs leaving the system via the waste sludge, leachate dosing is unlikely to result in significantly increased PTME contamination of the receiving water body.

5.3.3 Conclusions

Addition of unstabilized leachate comprising 22.3% and 8.1% of the sewage COD and TKN loads respectively, to a biological nutrient removal activated sludge system (experimental) and comparing the response to an identical system not dosed (control) indicated that:

- Good COD (both experimental and control = 92%) and N (experimental = 90%; control = 88%) mass balances were obtained, supporting the reliability of the data.
- The acid leachate dose increased both the TSS and VSS concentrations in the reactor, by about 550 mgTSS/ℓ and 350 mgVSS/ℓ respectively (25 and 20% respectively).
- The acid leachate dose increased the OUR, by about 21%.
- The acid leachate dose did not increase the effluent COD concentration significantly, i.e. the unbiodegradable soluble COD concentration in the leachate is small, 2.2% of the leachate COD.
- The unbiodegradable particulate COD fraction of the leachate was close to zero.
- From the unbiodegradable soluble and particulate COD fractions, 98.7% of the leachate COD was biodegraded in the BNR activated sludge system.
- The acid leachate dose increased the influent TKN by about 7%, but did not increase the effluent TKN or FSA significantly, i.e. nitrification was complete and the unbiodegradable soluble organic N small, at 4.5% of the leachate TKN.
- The unbiodegradable particulate TKN fraction of the leachate was close to zero.
- From the unbiodegradable soluble and particulate TKN fractions, 98.7% of the leachate TKN was biodegraded in the BNR activated sludge system.
- Only 13.7% of the leachate COD was taken up in the anaerobic reactor for BEPR, the balance contributed to additional denitrification. The leachate COD taken up in the anaerobic reactor gave an increase in P removal of 4.3 mgP/ℓ (28.9%).
- The leachate denitrified all the nitrate generated from its own TKN and had the potential to denitrify an additional 4.9 mgN/ℓ generated from the sewage TKN due to a 19% higher denitrification rate.

- Leachate dosing had no effect on the nitrifier maximum specific growth rate or the sludge settleability.

- Not only did the particulate/colloidal metal complexes from the leachate accumulate in the activated sludge, but also significant concentrations of the soluble metal compounds, leaving the effluent with lower dissolved metal concentrations than the influent.

5.4 DISCUSSION

In this task experimental investigations into the treatment of landfill leachates in activated sludge systems have been undertaken. The investigation focussed on treatment of stabilized leachate in a N removal activated sludge system and acid leachate in a BNR activated sludge. Both investigations have demonstrated that there is considerable merit in adopting an integrated approach to management and treatment of municipal wastes. In both cases, in addition to being treated, the leachate has enhanced the nutrient removal capability of the activated sludge system.

CHAPTER 6

TREATMENT OF SEPTIC TANK EFFLUENTS

6.1 INTRODUCTION

Surveys in South Africa in 1993 have indicated that nearly 50% of the population do not have adequate sanitation and nearly 30% do not have adequate water, i.e. 18.6 and 10.8 million people respectively (Palmer Development Group and University of Cape Town, 1993). In urban areas, 64% of the urban population have full waterborne sanitation and less than 5% have adequate alternative non-waterborne sanitation; more than 30% of the population in urban areas (i.e. some 7 million people) have no or inadequate sanitation. About 20% of the urban population (i.e. nearly 5 million people) do not have adequate water supply at their place of residence. Therefore, over the next decade, water supply and sanitation provision are going to be priorities in infrastructure development programs. To provide affordable and sustainable water supply and sanitation, while restricting the increased demand on limited water resources, will require far greater application of alternative (non-full waterborne) sanitation systems. The low volume flush septic tank type system (called the aquaprivy) has been identified as one such system that has considerable merit. This system is a relatively low cost, but sustainable non-full waterborne sanitation system. Also, since the system requires a small amount of water per flush (about 1 liter), it can be used for situations where communal water supplies only are available (i.e. where households are required to collect and cart water for on-site use). In the system, the waste is flushed to a digester where the particulate matter settles and remains to be digested. This results in a considerable reduction in the organic content of the waste, but little reduction in the soluble nutrients (Peters, 1993). The supernatant from the digester (effluent) requires disposal. Effluent disposal from septic tanks is usually on-site to soakaways, but can be off-site (via low flow small-bore sewer systems) depending on water quantity, soil type, plot size, etc. Currently in South Africa, most septic tank effluents are disposed of on-site in soakaways. It is therefore critical that the soakaways function effectively all the time. However, soakaway failure due to high water tables, clogging and overloading frequently occurs, especially in high-density housing areas. This has been identified to be a major cause for failure of the septic tank system (Peters, 1993). Soakaway failure has major public health implications, causing diseases, smells and unhealthy living conditions. Furthermore, the effects of septic tank effluent disposal in soakaways on soil and ground water quality are still unknown, but thought to be undesirable.

To eliminate the problems associated with soakaways, the effluents from septic tanks can be collected in small bore sewers for off-site treatment (e.g. the South African low volume flush, on-site anaerobic digester linked to a solids-free reticulation system-LOFLOS, Peters, 1993). In South Africa, this arrangement is still relatively uncommon with only a few systems installed (Palmer Development Group and University of Cape Town, 1993). However, it is expected that the merits of the system will cause it to be increasingly considered for application. Implementation of small-bore sewers may be impeded by a lack of knowledge on how to treat the collected wastewater to comply with effluent quality discharge standards. These systems characteristically produce an effluent of about 15ℓ/person/d with a COD of 4 000 - 9 000 mgCOD/ℓ and nutrient concentrations of about 1 000 - 2 000 mgTKN-N/ℓ and 100 - 180 mgTotal-P/ℓ (Peters, 1993), i.e. TKN/COD = 0.25mgN/mgCOD and TP/COD =0.03 mgP/mgCOD, compared to "normal" municipal wastewater TKN/COD = 0.1 mgN/mgCOD and TP/COD = 0.02 mgP/mgCOD. The imbalance between the organics and nutrients will cause their treatment in separate biological nutrient removal (BNR) wastewater treatment systems to be problematic. Further, should these wastewaters be discharged to conventional BNR treatment plants receiving wastewaters from full waterborne sanitation systems, they will increase the nutrient loads on these plants. The magnitude and effect of this increase are not known. This Chapter investigates this impact.

The mechanisms and technology for the treatment of wastewaters in BNR activated sludge systems are well understood and, provided the wastewater characteristics are well defined, the expected response of a system can be quantified through existing steady state design (Wentzel *et al.*, 1990) or kinetic simulation (Wentzel *et al.*, 1992, Henze *et al.*, 1995) models. Accordingly, to investigate the expected impact of septic tank effluents on existing BNR activated sludge systems, it was decided to collect information on the characteristics of septic tank effluents and to do a desk-top study on the theoretical response of BNR activated sludge systems to various septic tank effluent loads.

6.2 CHARACTERIZATION OF SEPTIC TANK EFFLUENTS

Some data on the characteristics of septic tank effluents are available in the literature, e.g. Peters (1993), Ketley (1996), Theunessin (1993). However, a particular problem with the data is that the effluents from single septic tanks have been analyzed, which raises doubts as to whether the data are representative. It would be more acceptable if the combined effluent from a number of septic tanks could be analyzed. Two sites, one in Hermanus and the other one in Sandbaai in the Western Cape were identified where ± 200 septic tanks are connected to a single sewer. Samples were taken from both of these sites over a 24-hour period at 1-hour intervals during daytime and 2 hour intervals during night time (Plaatjies, 1997). A total of 40 samples were taken over 2 days at the site in Hermanus (20 samples on each day). Twenty samples were collected at the site in Sandbaai over a 24 hour period. The samples were brought to the UCT water research laboratory and characterized by carrying out COD, TKN and total phosphorus tests (Standard Methods, 1985). Additionally, biodegradability tests were conducted to assess the unbiodegradable soluble and particulate fractions of the septic tank effluent (Plaatjies, 1997). After analysis, the average concentrations were calculated from the diurnal measurements. For the desk-top study, the septic tank effluent from Hermanus was accepted and the concentrations are shown in Table 6.1, together with the effluent characteristics.

Table 6.1: Characteristics of septic tank effluent from a site in Hermanus where ± 200 septic tanks are connected to a single sewer.

Parameter	Symbol	Unit	Value
Total influent COD	S_{ti}	mg COD/ℓ	245
Readily biodegradable COD	S_{bsi}	mg COD/ℓ	112
Filtered effluent COD	S_{use}	mg COD/ℓ	86
Total influent TKN	N_{ti}	mg N/ℓ	63
Free and Saline Ammonia	N_{ai}	mg N/ℓ	53
Fraction of total COD that is unbiodegradable particulate	$f_{S,up}$		0.04
Fraction of total COD that is unbiodegradable soluble	$f_{S,us}$		0.35
Fraction of biodegradable COD that is readily biodegradable	f_{bs}		0.75
Ammonia to TKN fraction	f_{na}		0.85
Total phosphorus	P_{ti}	mg P/ℓ	10.4

6.3 DESK-TOP STUDY ON THE EFFECT OF TREATING SEPTIC TANK EFFLUENT IN ACTIVATED SLUDGE SYSTEMS

Once the data on septic tank effluents and their characteristics were collected, a theoretical desk-top study on the effect of various septic tank effluent loads on BNR activated sludge systems was undertaken (Nongogo, 1999). For this study, the septic tank effluent was dosed into the settled wastewater serving as influent to the UCT configuration BNR activated sludge system pilot-scale plant at Mitchell's Plain (Cape Town, South Africa), and the theoretical response simulated with the UCTPHO kinetic simulation model (Wentzel *et al.*, 1992). This section provides details on these simulations.

6.3.1 Mitchell's Plain pilot plant details

The Mitchell's Plain pilot plant consists of two activated sludge system modules (A and B) operated in the UCT configuration. Module A has a volume of 1 361 m³ and consists of three zones i.e. anaerobic 227 m³, anoxic 485 m³ and aerobic 649 m³. Module B has a total volume of 2 043 m³ with anaerobic, anoxic and aerobic volumes of 342 m³, 737 m³ and 964 m³ respectively. The ultimate influent flows to Modules A and B when treating settled sewage only, whose characteristics are as in Table 6.2, at a sludge age of 20 days and bioreactor MLSS of 4 000 mg/ℓ were estimated as 1.6 and 2.4 Mℓ/d respectively (Swanepoel, 1997). Both modules are currently being run as UCT configured systems for a study on full scale demonstration of filamentous bulking control in BNR activated sludge plants (WRC contract K5/823). Module B was selected for the desk top study and the same operational parameters at pilot scale were applied in the desk top study. In the original design, the mixed liquor a-recycle was fixed at 9.6Mℓ/d (i.e. 4:1 with respect to the influent), and the return activated sludge (s-recycle) and mixed liquor r- recycle were both set at 2.4 Mℓ/d (i.e. 1:1 with respect to the influent). Fig 6.1 shows a schematic layout of the UCT system for Module B.

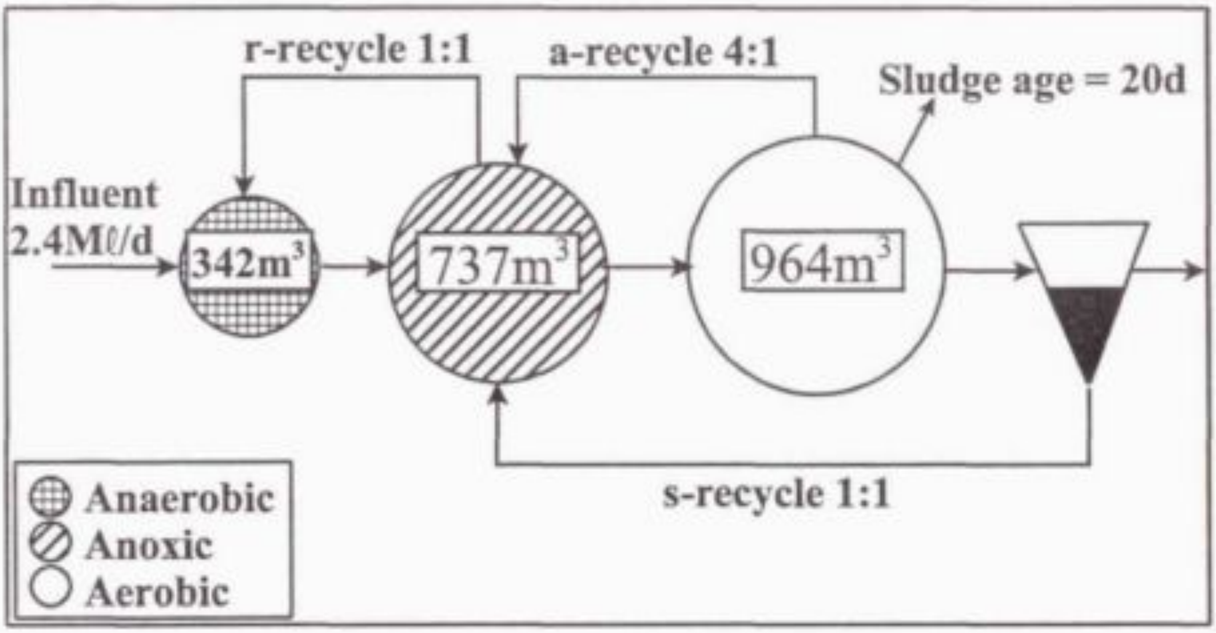

Fig 6.1: Schematic layout of Mitchell's Plain pilot plant, module B.

6.3.2 Simulation scenarios

Two main scenarios were considered:

Scenario 1: Theoretically, increasing flows of the septic tank effluent were introduced into the influent to the pilot plant and the flow of settled domestic sewage that is normally treated in the pilot plant was reduced proportionately, so that the total flow that the pilot plant was initially designed for would be maintained (i.e. 2.4Mℓ/d).

Scenario 2: The settled sewage flow was kept constant at the design value (i.e. 2.4Mℓ/d), and the septic tank effluent flow added to this flow, so that the total flow increased as the septic tank effluent dose increased. For this scenario, two alternative recycle schemes were simulated:

Scenario 2a: The recycle flow rates were kept constant at the values for **Scenario 1** above, i.e. as the total flow increased, the recycle flows remained constant and so the recycle ratios decreased.

Scenario 2b: The recycle ratios were kept constant at the values for **Scenario 1** above, i.e. as the total flow increased, the recycle ratios remained constant and so the recycle flow rates increased.

6.3.3 Mitchell's Plain settled sewage characteristics

Data from weekly composite samples on the Mitchell's Plain raw and settled sewage tested at the Mitchell's Plain Wastewater Treatment Plant (WWTP) laboratory, and results obtained from 24 hour diurnal profile tests carried out in 1992 at this WWTP (Leballo, 1992) were used to define the influent wastewater characteristics at the Mitchell's Plain WWTP. This data was applied to predict the influent settled sewage characteristics at Mitchell's Plain in mid 1997

(Swanepoel, 1997), see Table 6.2. The predicted settled sewage characteristics for 1997 were used in the desk top study.

Table 6.2: Predicted influent raw and settled sewage characteristics for Mitchell's Plain - mid 1997.

Parameter	Symbol	Unit	Raw sewage	Settled sewage
Total influent COD	S_{ti}	mg COD/ℓ	1 470	861
Readily biodegradable COD	S_{bsi}	mg COD/ℓ	329	310
Filtered effluent COD	S_{use}	mg COD/ℓ	82	82
Total influent TKN	N_{ti}	mg N/ℓ	105	96
Free and Saline Ammonia	N_{ai}	mg N/ℓ	79	79
Fraction of total COD that is unbiodegradable particulate	$f_{S,up}$		0.13	0.04
Fraction of total COD that is unbiodegradable soluble	$f_{S,us}$		0.06	0.10
Fraction of biodegradable COD that is readily biodegradable	f_{bs}		0.22	0.36
Ammonia to TKN fraction	f_{na}		0.75	0.82
Total phosphorus	P_{ti}	mg P/ℓ	19.2	12.64

6.3.4 Blended settled sewage and septic tank effluent characteristics

For **Scenario 1**, in the blend of settled sewage and septic tank effluent, the ratio of septic tank effluent flow in the total flow was increased from 0 to 100 %, while the flow of settled sewage was decreased proportionately, thereby maintaining the original maximum design flow of 2.4 Mℓ/d that can be treated in module B of the pilot plant. The characteristics of this blend at varying septic tank effluent flow as a % of total flow are given in Table 6.3.

For **Scenarios 2a** and **2b**, the settled sewage flow was kept constant and an increasing proportion of septic tank effluent dosed into this flow, thereby increasing the total flow to module B of the pilot plant. The characteristics of this blend at varying septic tank flow as a % of settled sewage flow are given in Table 6.4.

Table 6.3: Blended wastewater characteristics, Scenario 1: Constant total flow.

Parameter	Units	Septic tank effluent (% of total flow)										
		0	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**	**100**
Sewage flow	Mℓ/d	2.4	2.16	1.92	1.68	1.44	1.2	0.96	0.72	0.48	0.24	0
STE flow	Mℓ/d	0	0.24	0.48	0.72	0.96	1.2	1.44	1.68	1.92	2.16	2.4
Total flow	Mℓ/d	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
S_{ti}	mgCOD/ℓ	861	799	738	676	615	553	491	430	368	307	245
S_{bi}	mgCOD/ℓ	745	686	626	567	507	448	388	329	269	210	150
S_{bsi}	mgCOD/ℓ	310	290	270	251	231	211	191	171	152	132	112
S_{upi}	mgCOD/ℓ	82	82	83	83	84	84	84	85	85	86	86
S_{usi}	mgCOD/ℓ	34	32	29	27	24	22	19	17	14	12	9
f_{bs}	mgCOD/mgCOD	0.42	0.42	0.43	0.44	0.46	0.47	0.49	0.52	0.56	0.63	0.75
f_{ac}	mgCOD/mgCOD	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
$f_{S,us}$	mgCOD/mgCOD	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
$f_{S,up}$	mgCOD/mgCOD	0.100	0.103	0.112	0.123	0.136	0.151	0.172	0.197	0.231	0.279	0.351
N_{ti}	mgN/ℓ	96	92.7	89.4	86.1	82.8	79.5	76.2	72.9	69.6	66.3	63
N_{ai}	mgN/ℓ	79	76.4	73.8	71.2	68.6	66	63.4	60.8	58.2	55.6	53
N_{obpi}	mgN/ℓ	5.9	5.46	5.02	4.58	4.14	3.7	3.26	2.82	2.38	1.94	1.5
N_{ousi}	mgN/ℓ	3.6	3.49	3.38	3.27	3.16	3.05	2.94	2.83	2.72	2.61	2.5
$f_{N,a}$	mgN/mgN	0.82	0.82	0.83	0.83	0.83	0.83	0.83	0.83	0.84	0.84	0.85
$f_{Nob,p}$	mgN/mgN	0.53	0.51	0.49	0.47	0.44	0.41	0.38	0.35	0.31	0.27	0.22
$f_{N,ous}$	mgN/mgN	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Total P	mgP/ℓ	12.64	12.4	12.2	12.0	11.7	11.5	11.3	11.1	10.8	10.6	10.4
$f_{Sup,P}$	mgP/mgCOD	0.014	0.014	0.014	0.014	0.014	0.014	0.014	0.014	0.014	0.014	0.014
TKN/COD	mgN/mgCOD	0.111	0.116	0.121	0.127	0.135	0.144	0.155	0.170	0.189	0.216	0.257
P/COD	mgP/mgCOD	0.015	0.016	0.017	0.018	0.019	0.021	0.023	0.026	0.029	0.035	0.042

Table 6.4: Blended wastewater characteristics, Scenarios 2a and 2b: Constant settled sewage flow, but increased septic tank effluent (STE) dose.

Parameter	Units	Septic tank effluent (% of sewage flow)										
		0	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**	**90**	**100**
Sewage flow	Mℓ/d	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
STE flow	Mℓ/d	0	0.24	0.48	0.72	0.96	1.2	1.44	1.68	1.92	2.16	2.4
Total flow	Mℓ/d	2.4	2.64	2.88	3.12	3.36	3.6	3.84	4.08	4.32	4.56	4.8
S_{ti}	mgCOD/ℓ	861	805	758	719	685	656	630	607	587	569	553
S_{bi}	mgCOD/ℓ	745	691	646	608	575	547	522	500	481	463	448
S_{bsi}	mgCOD/ℓ	310	292	277	264	253	244	236	228	222	216	211
S_{upi}	mgCOD/ℓ	82	82	83	83	83	83	84	84	84	84	84
S_{usi}	mgCOD/ℓ	34	32	30	28	27	26	25	24	23	22	22
f_{bs}	mgCOD/mgCOD	0.42	0.42	0.43	0.43	0.44	0.45	0.45	0.46	0.46	0.47	0.47
f_{ac}	mgCOD/mgCOD	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
$f_{S,us}$	mgCOD/mgCOD	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
$f_{S,up}$	mgCOD/mgCOD	0.100	0.102	0.109	0.115	0.121	0.127	0.133	0.138	0.143	0.147	0.152
N_{ti}	mgN/ℓ	96	93	90.5	88.4	86.6	85.0	83.6	82.4	81.3	80.4	79.5
N_{ai}	mgN/ℓ	79	76.6	74.7	73.0	71.6	70.3	69.3	68.3	67.4	66.7	66.0
N_{obpi}	mgN/ℓ	5.9	5.5	5.2	4.9	4.6	4.4	4.3	4.1	3.9	3.8	3.7
N_{ousi}	mgN/ℓ	3.6	3.5	3.4	3.3	3.3	3.2	3.2	3.1	3.1	3.1	3.1
$f_{N,a}$	mgN/mgN	0.82	0.82	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83	0.83
$f_{Nob,p}$	mgN/mgN	0.53	0.51	0.50	0.48	0.47	0.46	0.45	0.44	0.43	0.42	0.41
$f_{N,ous}$	mgN/mgN	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Total P	mgP/ℓ	12.64	12.4	12.3	12.1	12.0	11.9	11.8	11.7	11.6	11.6	11.5
$f_{Sup,P}$	mgP/mgCOD	0.014	0.014	0.014	0.014	0.014	0.014	0.014	0.014	0.014	0.014	0.014
TKN/COD	mgN/mgCOD	0.111	0.116	0.119	0.123	0.126	0.130	0.133	0.136	0.139	0.141	0.144
P/COD	mgP/mgCOD	0.015	0.015	0.016	0.017	0.018	0.018	0.019	0.019	0.020	0.020	0.021

6.3.5 Modelling of the treatment of septic tank effluent in the Mitchell's Plain pilot plant

To investigate the effect of treating septic tank effluent in a BNR plant, the UCTPHO model (Wentzel *et al.*, 1992) was used to simulate the treatment of a blend of various proportions of septic tank effluent from Hermanus and settled sewage from the Mitchell's Plain WWTP (Tables 6.3 and 6.4) in Module B of the pilot plant. The default kinetic and stoichiometric constants in UCTPHO were accepted for the simulation.

Scenario 1: Table 6.5 summarizes predicted reactor VSS concentrations and oxygen utilization rates (OUR) for simulations at 20 day sludge age and 20° C with the various blends of settled sewage and septic tank effluent; these data are shown plotted in Fig 6.2. Similarly, Table 6.6 summaries effluent quality and % removal for COD, N and P; Figs 6.3 and 6.4 show the predicted effluent concentrations and % removals respectively.

Scenario 2a: Table 6.7 summarizes predicted reactor VSS concentrations and oxygen utilization rates (OUR) for simulations at 20 day sludge age and 20° C with the various blends of settled sewage and septic tank effluent; these data are shown plotted in Fig 6.5. Similarly, Table 6.8 summaries effluent quality and % removal for COD, N and P; Figs 6.6 and 6.7 show the predicted effluent concentrations and % removals respectively.

Scenario 2b: Table 6.9 summarizes predicted reactor VSS concentrations and oxygen utilization rates (OUR) for simulations at 20 day sludge age and 20° C with the various blends of settled sewage and septic tank effluent; these data are shown plotted in Fig 6.8. Similarly, Table 6.10 summaries effluent quality and % removal for COD, N and P; Figs 6.9 and 6.10 show the predicted effluent concentrations and % removals respectively.

Table 6.5: **Scenario 1, constant total flow:** UCTPHO predicted reactor VSS concentration and oxygen utilization rate (OUR) when treating blended septic tank effluent and settled sewage in the Mitchell's Plain pilot plant reactor Module B.

Septic Tank Effluent (% of total flow)	Parameter			
	Reactor VSS (mg/ℓ)	OUR (mgO/ℓ/h)		
		Carbonaceous	Nitrification	Total
0	4537	35.2	33.0	68.2
10	4181	31.9	32.2	64.1
20	3810	28.5	31.4	59.9
30	3433	25.2	30.7	55.9
40	3054	22.1	29.9	52.0
50	2676	19.0	29.2	48.2
60	2299	15.9	28.4	44.3
70	1927	12.9	27.7	40.6
80	1555	9.9	26.9	36.8
90	1201	7.0	26.1	33.1
100	891	4.7	25.2	29.8

Table 6.6: **Scenario 1, constant total flow:** UCTPHO predicted effluent quality when treating blended septic tank effluent and settled sewage in the Mitchell's Plain pilot plant reactor Module B.

Septic Tank Effluent (% of total flow)	Effluent quality/removal						
	Sol COD (mg/ℓ)	COD removal (%)	FSA (mgN/ℓ)	NO3 (mgN/ℓ)	N removal (%)	Ps (mgP/ℓ)	P removal (%)
0	98.7	88.5	0.6	12.5	80.2	0.3	97.6
10	93.8	88.3	0.6	12.5	79.6	0.4	96.8
20	92.8	87.4	0.6	13.0	78.4	0.5	95.9
30	92.0	86.4	0.6	13.9	76.7	0.6	95.0
40	91.0	85.2	0.6	15.2	74.3	0.9	92.3
50	90.1	83.7	0.6	16.7	71.7	1.8	84.3
60	89.2	81.8	0.6	18.4	68.4	3.2	71.7
70	88.0	79.5	0.6	20.2	64.6	4.9	55.9
80	87.1	76.3	0.6	22.3	60.1	6.6	38.9
90	86.6	71.8	0.6	25.0	54.4	8.0	24.5
100	86.7	64.6	0.6	30.5	43.3	8.6	17.3

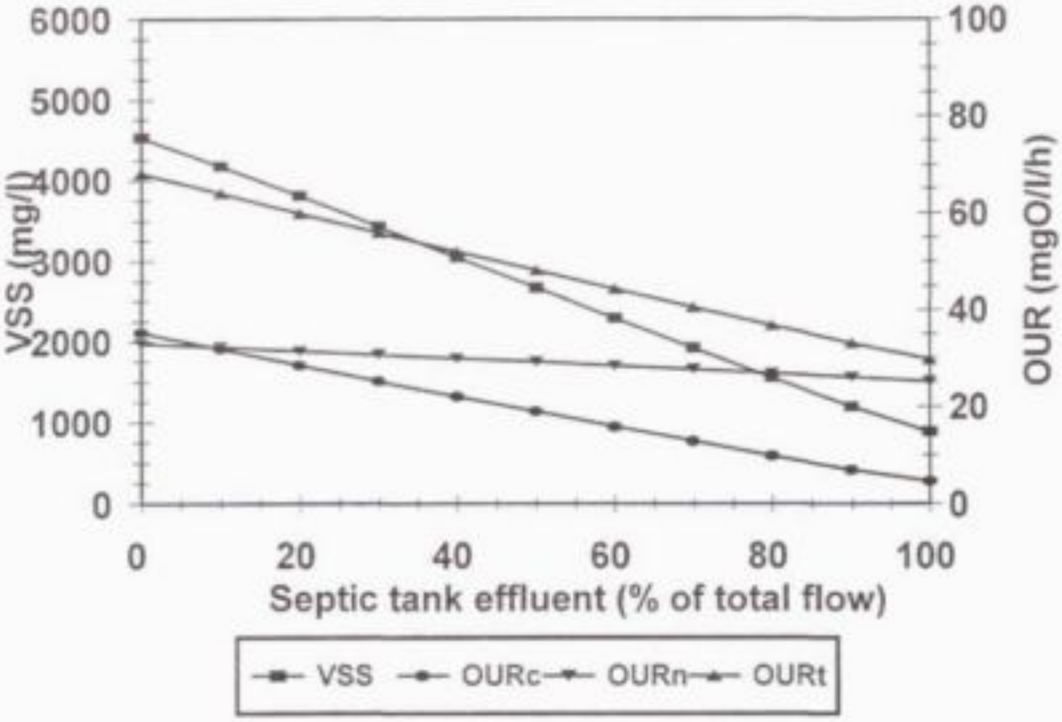

Fig 6.2: UCTPHO predicted reactor VSS concentration and oxygen utilization rate (OUR) for scenario 1; constant total flow with settled sewage flow decreased as septic tank effluent flow increases.

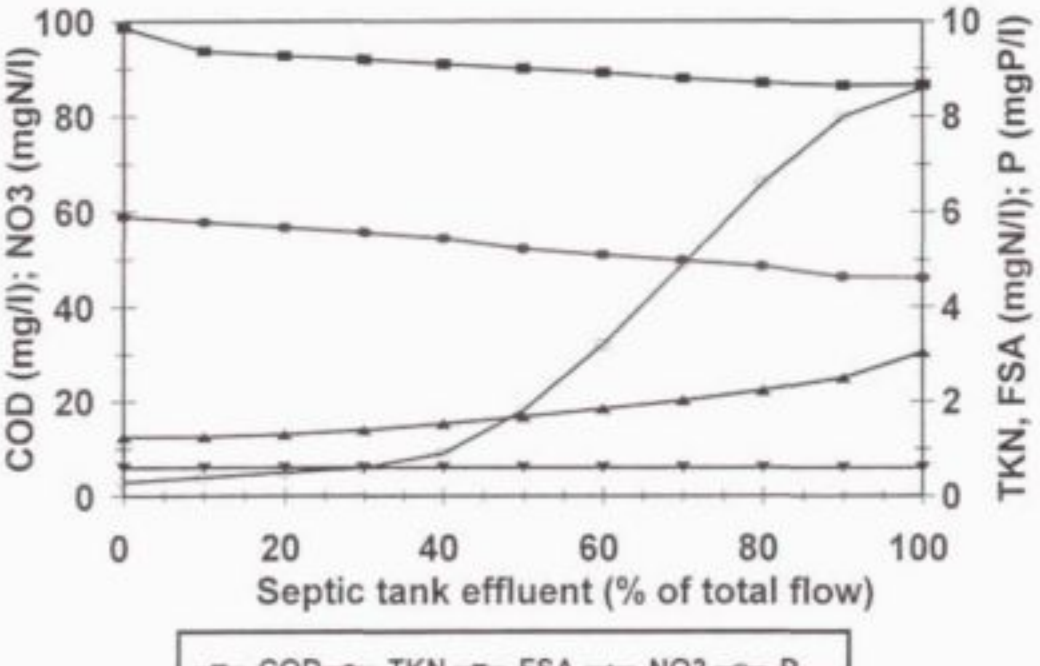

Fig 6.3: UCTPHO predicted effluent quality for scenario 1; constant total flow with settled sewage flow decreased as septic tank effluent flow increases.

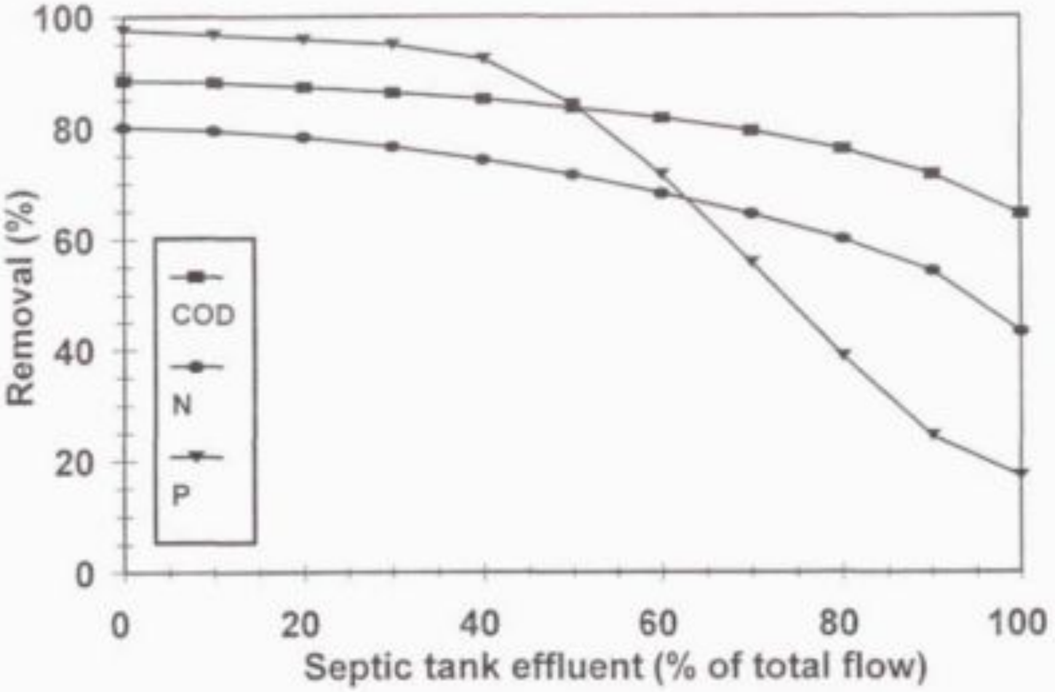

Fig 6.4: UCTPHO predicted % removals for scenario 1; constant total flow with settled sewage flow decreased as septic tank effluent flow increases.

Table 6.7: **Scenario 2a, constant sewage flow, fixed recycle flows:** UCTPHO predicted reactor VSS concentration and oxygen utilization rate (OUR) when treating blended septic tank effluent and settled sewage in the Mitchell's Plain pilot plant reactor Module B.

Septic Tank Effluent (% of settled sewage flow)	Parameter			
	Reactor VSS (mg/ℓ)	OUR (mgO/ℓ/h)		
		Carbonaceous	Nitrification	Total
0	4537	35.1	33.0	68.2
10	4659	35.7	35.5	71.2
20	4771	36.2	37.4	73.6
30	4886	36.3	40.5	76.8
40	4997	36.7	43.0	79.7
50	5105	37.1	45.5	82.6
60	5212	37.5	48.1	85.6
70	5318	38.0	50.6	88.6
80	5427	38.5	53.1	91.6
90	5541	39.1	55.6	94.7
100	5649	39.6	58.1	97.7

Table 6.8: **Scenario 2a, constant sewage flow, fixed recycle flows:** UCTPHO predicted effluent quality when treating blended septic tank effluent and settled sewage in the Mitchell's Plain pilot plant reactor Module B.

Septic Tank Effluent (% of settled sewage flow)	Effluent quality/removal						
	Sol COD (mg/ℓ)	COD removal (%)	FSA (mgN/ℓ)	NO3 (mgN/ℓ)	N removal (%)	Ps (mgP/ℓ)	P removal (%)
0	98.7	88.5	0.6	12.5	80.2	0.3	97.6
10	94.0	88.3	0.6	13.3	78.8	0.4	96.8
20	93.3	87.7	0.6	13.5	78.1	0.4	96.7
30	92.7	87.1	0.6	15.1	75.8	0.5	95.9
40	92.3	86.5	0.6	16.0	74.4	0.5	95.8
50	92.1	86.0	0.6	16.9	73.0	0.6	95.0
60	92.2	85.4	0.6	17.8	71.4	0.7	94.1
70	91.7	84.9	0.6	18.6	70.1	0.7	94.0
80	91.5	84.4	0.6	19.4	68.8	0.8	93.1
90	90.9	84.0	0.6	20.1	67.6	1.0	91.4
100	91.0	83.5	0.6	20.8	66.4	1.1	90.5

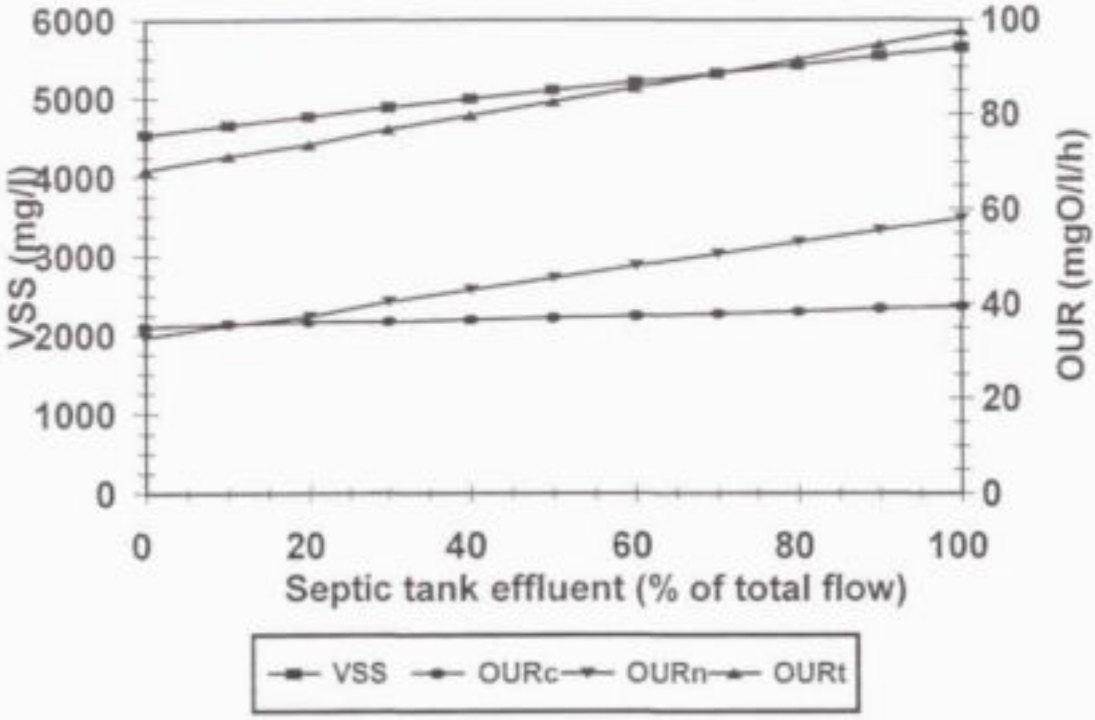

Fig 6.5: UCTPHO predicted reactor VSS concentration and oxygen utilization rate (OUR) for scenario 2a; constant settled sewage flow with increased septic tank effluent flow and recycle flow constant.

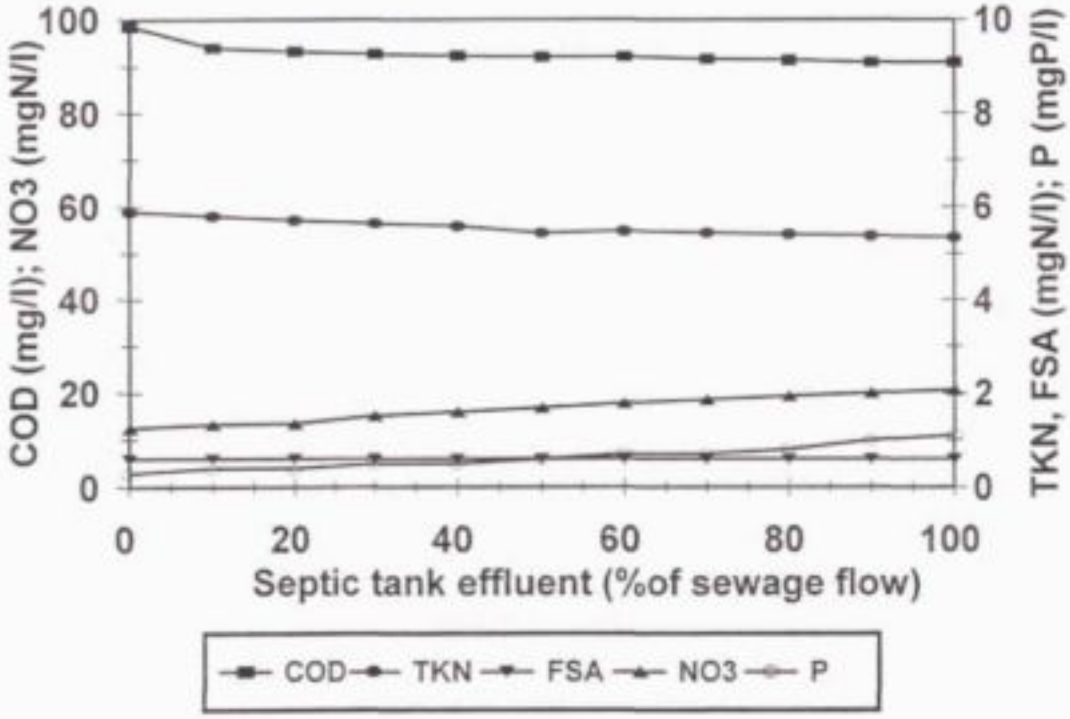

Fig 6.6: UCTPHO predicted reactor effluent quality for scenario 2a; constant settled sewage flow with increased septic tank effluent flow and recycle flow constant.

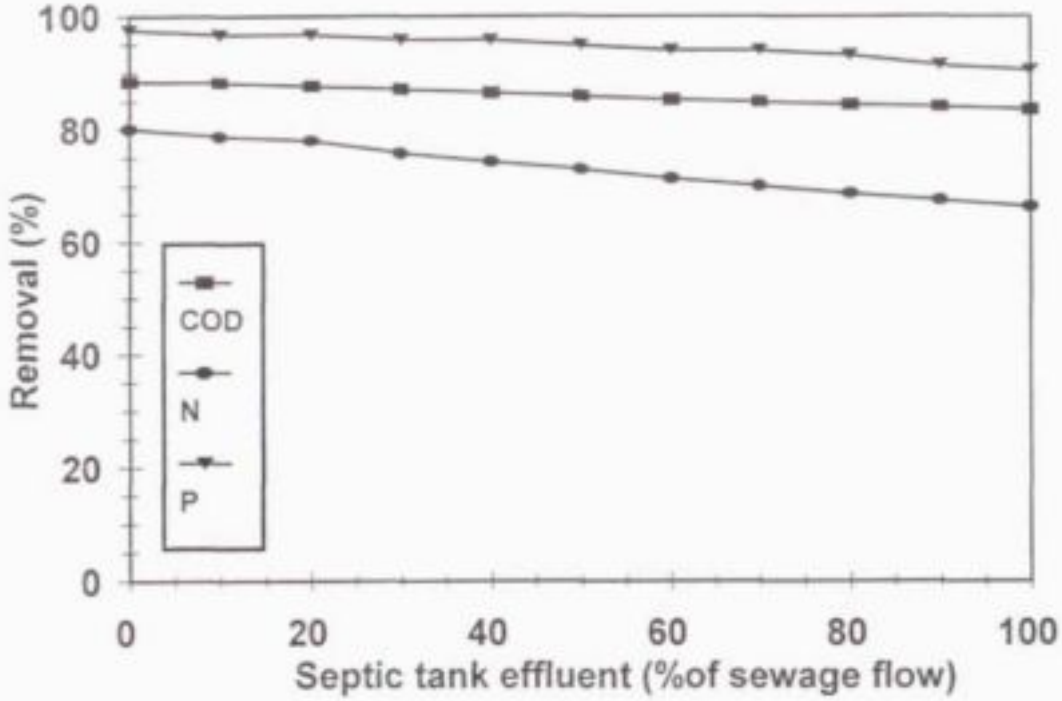

Fig 6.7: UCTPHO predicted % removals for scenario 2a; constant settled sewage flow with increased septic tank effluent flow and recycle flow constant.

Table 6.9: **Scenario 2b constant sewage flow, fixed recycle ratios:** UCTPHO predicted reactor VSS concentration and oxygen utilization rate (OUR) when treating blended septic tank effluent and settled sewage in the Mitchell's Plain pilot plant reactor Module B.

Septic Tank Effluent (% of settled sewage flow)	Parameter			
	Reactor VSS (mg/ℓ)	OUR (mgO/ℓ/h)		
		Carbonaceous	Nitrification	Total
0	4537	35.1	33.0	68.2
10	4635	35.5	35.5	71.0
20	4715	35.6	38.0	73.7
30	4798	36.0	40.6	76.6
40	4875	36.3	43.1	79.5
50	4950	36.8	45.7	82.5
60	5020	37.1	48.3	85.4
70	5092	37.6	50.8	88.4
80	5168	38.0	53.3	91.3
90	5248	38.5	55.9	94.4
100	5323	38.9	58.5	97.4

Table 6.10: **Scenario 2b constant sewage flow, fixed recycle ratios:** UCTPHO predicted effluent quality when treating blended septic tank effluent and settled sewage in the Mitchell's Plain pilot plant reactor Module B.

Septic Tank Effluent (% of settled sewage flow)	Effluent quality/removal						
	Sol COD (mg/ℓ)	COD removal (%)	FSA (mgN/ℓ)	NO3 (mgN/ℓ)	N removal (%)	Ps (mgP/ℓ)	P removal (%)
0	98.7	88.5	0.6	12.5	80.2	0.3	97.6
10	93.7	88.4	0.6	12.6	79.6	0.4	96.8
20	93.2	87.7	0.6	13.0	78.7	0.4	96.7
30	92.4	87.1	0.6	13.7	77.4	0.5	95.9
40	91.8	86.6	0.6	14.5	76.1	0.6	95.0
50	91.5	86.0	0.6	15.2	75.0	0.7	94.1
60	91.4	85.5	0.6	15.9	73.7	0.9	92.4
70	90.8	85.0	0.6	16.5	72.6	1.1	90.6
80	90.5	84.6	0.6	17.0	71.7	1.4	88.0
90	89.8	84.2	0.6	17.5	70.8	1.7	85.3
100	89.8	83.8	0.6	18.0	69.9	2.1	81.8

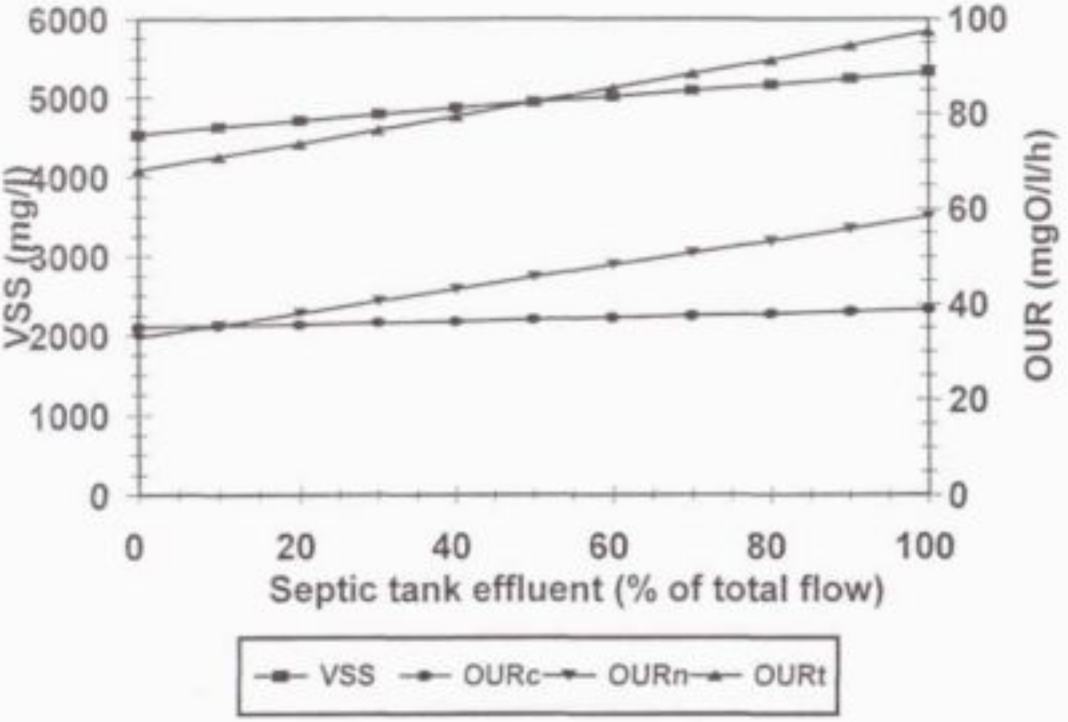

Fig 6.8: UCTPHO predicted reactor VSS concentration and oxygen utilization rate (OUR) for scenario 2b; constant settled sewage flow with increased septic tank effluent flow and recycle ratio constant.

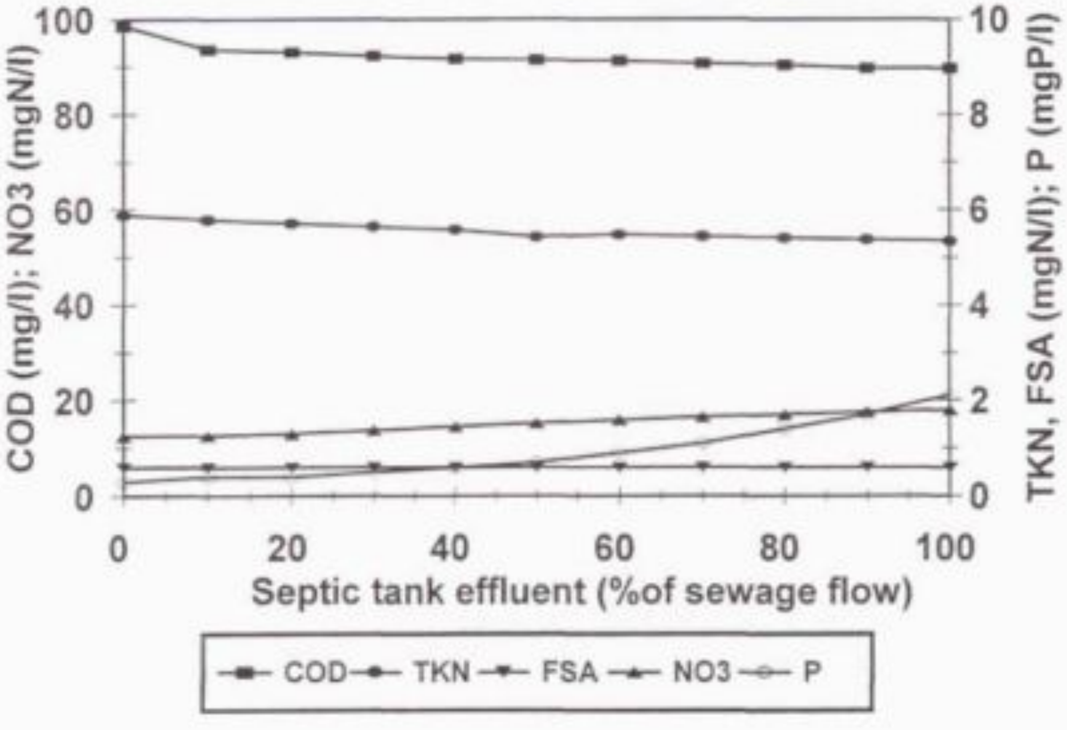

Fig 6.9: UCTPHO predicted reactor effluent quality for scenario 2b; constant settled sewage flow with increased septic tank effluent flow and recycle ratio constant.

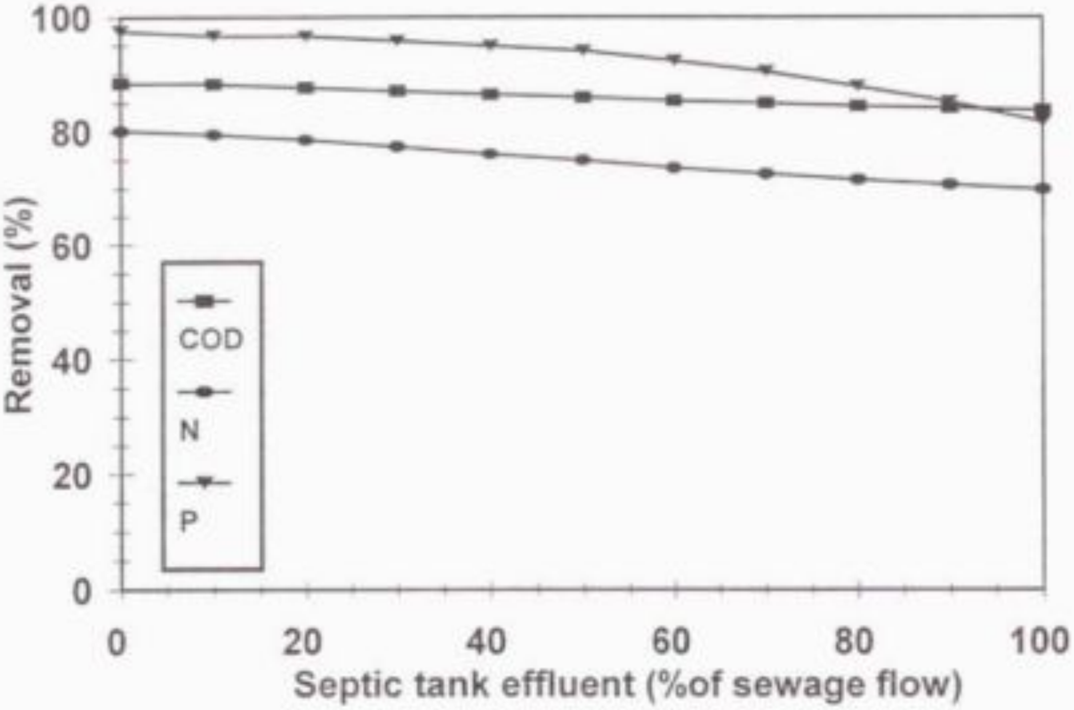

Fig 6.10: UCTPHO predicted % removals for scenario 2b; constant settled sewage flow with increased septic tank effluent flow and recycle ratio constant.

6.4 DISCUSSION

6.4.1 Scenario 1, constant total flow

In this scenario, the total flow was kept constant at 2.4Mℓ/d; as the septic tank flow was increased, the settled sewage flow was correspondingly decreased.

Reactor VSS concentration and OUR

From Table 6.5 and Fig. 6.2, as the relative contribution of the septic tank effluent increases, the reactor VSS concentration and OUR both decrease. This arises because the septic tank effluent COD and TKN concentrations are lower than the Mitchell's Plain settled sewage (Table 6.3). Thus, keeping the total flow rate constant (at 2.4Mℓ/d) and increasing the proportion of the septic tank effluent in the total (Table 6.3) causes the COD and TKN loads to the plant to decrease. The decrease in COD load causes a corresponding decrease in both reactor VSS concentration and carbonaceous OUR (Table 6.5 and Fig. 6.2), while the decrease in TKN load causes a corresponding decrease in nitrification OUR. The nitrification OUR does not decrease as rapidly as the carbonaceous OUR with increase in septic tank effluent proportion (Fig. 6.2), since the septic tank effluent and settled sewage TKN (96 and 63 mgN/ℓ respectively) are closer than the respective COD concentrations (861 and 245 mgCOD/ℓ) (Table 6.3).

COD removal

As the ratio of septic tank effluent increases, the effluent COD concentration decreases (Table 6.6 and Fig. 6.3). This is because the total COD of the septic tank effluent is much lower than that of the settled sewage and as the % of septic tank effluent in the blend increases, this concentration decreases. However, the % COD removal decreases from 88.5% when treating settled sewage only to 64.6% when treating septic tank effluent only (Table 6.6 and Fig. 6.4). This is because the septic tank effluent unbiodegradable soluble COD fraction of 0.35 (Table 6.1) is much higher than that for settled sewage which is 0.095 (Table 6.2). Thus, as the % of septic tank effluent increases in the blend, a greater proportion of the blended COD is in the form of unbiodegradable soluble COD (Table 6.3), which is unaffected by the treatment process and leaves with the effluent. However, the decrease in % COD removal only becomes significant when the septic tank effluent flow exceeds ~50% of the total, an unlikely scenario in practice.

Nutrient removal

Both denitrification and phosphorus removal decrease with increased septic tank effluent flows (Table 6.6 and Figs. 6.3 and 6.4). The % nitrogen removal decreases from 80.2% when treating settled sewage only to 43.3% when treating septic tank effluent only, while the % P removal decreases from 97.6% when treating settled sewage only to 17.3% when treating septic tank effluent only. The decrease in nutrient removal when treating blends with higher ratios of septic tank effluent is due to the high N and P ratios in the septic tank effluent as compared to the COD concentrations. The TKN/COD and P/COD ratios increase from 0.11 and 0.015 respectively for settled sewage to 0.26 and 0.042 respectively for septic tank effluent. The higher TKN/COD ratio causes that less organic material is available for denitrification per unit influent N, and hence % N removal decreases. This causes an increase in the effluent nitrate concentration (Fig. 6.3), resulting in increased nitrate recycled to the anoxic reactor to exceed the denitrification potential of this reactor, causing nitrate to be recycled to the anaerobic reactor which reduces P removal.

Again, it should be noted that the % N and P removal only decrease significantly when the septic tank effluent flow exceeds ~50% of the total, an unlikely scenario in practice.

6.4.2 Scenario 2a, constant sewage flow, fixed recycle flows

In this scenario, the settled sewage flow was kept constant at 2.4Mℓ/d and the septic tank flow increased; the recycle flow rates were kept constant at the values for settled sewage only, i.e. recycle ratios decreased as septic tank effluent flow increased.

Reactor VSS concentration and OUR

From Table 6.7 and Fig. 6.5, as the septic tank effluent flow increases, the reactor VSS concentration and OUR both increase. This arises because the COD and TKN loads to the plant both increase (Table 6.4). The increase in COD load causes a corresponding increase in both reactor VSS concentration and carbonaceous OUR (Table 6.7 and Fig. 6.5), while the increase in TKN load causes a corresponding increase in nitrification OUR. The nitrification OUR increases more rapidly than the carbonaceous OUR with increase in septic tank effluent proportion (Fig. 6.5), since the septic tank effluent and settled sewage TKN (96 and 63 mgN/ℓ respectively) are closer than the respective COD concentrations (861 and 245 mgCOD/ℓ) (Table 6.4).

COD removal

As the septic tank effluent flow increases, the effluent COD concentration decreases (Table 6.8 and Fig. 6.6). This is because the unbiodegradable soluble COD concentration (which appears as the effluent COD) of the septic tank effluent is lower than that of the settled sewage and hence in effect dilutes the unbiodegradable soluble COD concentration of the blend. The % COD removal decreases only slightly when adding septic tank effluent, from 88.5% when treating settled sewage only to 83.5% when treating equal quantities of settled sewage and septic tank effluent (Table 6.8 and Fig. 6.7). This is because the septic tank effluent unbiodegradable soluble COD fraction of 0.35 (Table 6.1) is much higher than that for settled sewage which is 0.095 (Table 6.2). Thus, as the % of septic tank effluent increases in the blend, a greater proportion of the blended COD is in the form of unbiodegradable soluble COD (Table 6.4), which is unaffected by the treatment process and leaves with the effluent. However, as noted above the decrease in % COD removal is not significant.

Nutrient removal

Both denitrification and phosphorus removal decrease with increased septic tank effluent flows (Table 6.8 and Figs. 6.6 and 6.7). The % nitrogen removal decreases from 80.2% when treating settled sewage only to 66.4% when treating equal quantities of settled sewage and septic tank effluent, while the % P removal correspondingly decreases from 97.6% to 90.5%. The decrease in nutrient removal when treating blends with higher ratios of septic tank effluent is due to the high N and P ratios in the septic tank effluent as compared to the COD concentrations. The TKN/COD and P/COD ratios increase from 0.11 and 0.015 respectively for settled sewage to

0.144 and 0.021 respectively for the equal blend of settled sewage and septic tank effluent (note that these ratios are lower than for scenario 1 above). The higher TKN/COD ratio causes that less organic material is available for denitrification per unit influent N, and hence % N removal decreases. This causes an increase in the effluent nitrate concentration (Fig. 6.6). Since the recycle ratio to the anoxic zone is not correspondingly increased, the nitrate recycled to the anoxic zone does not increase as significantly as in scenario 1 above; the excess nitrate is allowed to leave with the effluent. Thus, in this scenario the denitrification potential of this reactor is not significantly exceeded and significant nitrate is not recycled to the anaerobic reactor and hence P removal does not decrease significantly (Figs. 6.6 and 6.7).

6.4.3 Scenario 2b, constant sewage flow, fixed recycle ratios

In this scenario, the settled sewage flow was kept constant at 2.4Mℓ/d and the septic tank flow increased; the recycle flow ratios were kept constant at the values for settled sewage only, i.e. recycle flow rates increased as septic tank effluent flow increased.

Reactor VSS concentration and OUR

From Table 6.9 and Fig. 6.8, as the septic tank effluent flow increases, the reactor VSS concentration and OUR both increase. This is identical to scenario 2a above, since the change in recycle flow rates do not significantly influence these parameters.

COD removal

As the septic tank effluent flow increases, the effluent COD concentration decreases (Table 6.10 and Fig. 6.9), for reasons set out for scenario 2a above. The % COD removal decreases only slightly when adding septic tank effluent, from 88.5% when treating settled sewage only to 83.8% when treating equal quantities of settled sewage and septic tank effluent (Table 6.10 and Fig. 6.10), for reasons set out for scenario 2a above. Again, as noted above the decrease in % COD removal is not significant.

Nutrient removal

Both denitrification and phosphorus removal decrease with increased septic tank effluent flows (Table 6.10 and Figs. 6.9 and 6.10). The decreases are similar to those for scenario 2a above, but the decrease in P removal is more significant; the % P removal correspondingly decreases from 97.6% to 81.8%. This larger decrease in P removal is due to more nitrate being recycled to the anoxic reactor with the higher recycle flow rates, which exceeds the denitrification potential of this reactor and so nitrate is recycled to the anaerobic reactor decreasing P removal.

6.5 CONCLUSIONS

From the UCTPHO simulation results when modeling treatment of a blend of settled sewage from Mitchell's Plain Treatment Plant (Cape Town, South Africa) and septic tank effluent from Hermanus, the following conclusions can be drawn on the treatability of the septic tank effluent in BNR activated sludge plants:

- In all three scenarios considered, septic tank effluents do not impact significantly on COD removal and nitrification. The effluent COD concentrations decreased slightly and effluent TKN and FSA remained essentially constant with increased flows of septic tank effluents.

- Depending on the scenario considered, the reactor VSS concentrations and oxygen utilization rates (OUR) either decreased (scenario 1, settled sewage flow decreased in proportion to septic tank effluent flow), or increased (scenario 2, settled sewage flow kept constant and septic tank effluent flow increased). In practice, it is likely that scenario 2 will apply, and hence provision will have to be made to accommodate the increased VSS concentrations and OURs with increased septic tank flow.

- Both denitrification and biological excess P removal decrease as the septic tank effluent flow increases. However, these decreases are only significant when proportionally large quantities of septic tank effluent are treated. The lowest impact of septic tank effluent on nutrient removal performance are for scenario 2.

- When septic tank effluent is treated by itself (scenario 1, 100% septic tank effluent), poor nutrient removal performance is achieved. This confirms that treatment of septic tank effluents in dedicated BNR plants is not a viable option.

- In practice if an activated sludge plant were to treat a blend of settled sewage and septic tank effluent the blend ratio can be selected depending on the standard of effluent that the plant is expected to meet in terms of legal requirements laid down by the Department of Water Affairs and Forestry.

- In this study, the septic tank effluent from a number of septic tanks sited at Hermanus was selected. From the characterization of this effluent it would appear that the concentrations (COD, N and P) are considerably lower (245 mgCOD/ℓ, 63 mgN/ℓ and 10.4 mgP/ℓ respectively) than those obtained elsewhere (typically > 4 000mgCOD/ℓ, > 1 000 mgN/ℓ and > 100 mgP/ℓ, see Section 6.1). This probably arises because the septic tanks at Hermanus have full water flush (10 - 15 ℓ/flush) while those in the quoted studies have restricted water flush (1ℓ/flush). This would imply that with low volume flush septic tanks deterioration in BNR nutrient removal performance would be experienced at much lower septic tank effluent flow rates than obtained in this study. This aspect requires further investigation.

CHAPTER 7

HETEROTROPHIC ACTIVE BIOMASS COMPONENT OF ACTIVATED SLUDGE MIXED LIQUOR

7.1 INTRODUCTION

To comply with more stringent effluent quality legislations, over the past 20 years there have been extensive developments in the activated sludge method for treating wastewater. The functions of the single sludge system have expanded from carbonaceous energy removal to include progressively nitrification, denitrification and phosphorus removal, all mediated biologically. These extensions have increased considerably the complexity of the system configuration and its operation. Concomitantly, the number of biological processes influencing the effluent quality and the number of compounds involved in these processes have increased. With such complexity, design procedures based on experience and semi-empirical methods no longer will give optimal performance; design procedures based on more fundamental behavioural patterns are required. Furthermore, it is no longer possible to make reliable quantitative predictions as to the effluent quality to be expected from a design, or to assess the effect of a system or operational modification, without some model that simulates the system behaviour accurately. To meet these requirements, increasingly sophisticated, fundamentally based steady state design procedures (e.g. Marais and Ekama, 1976; WRC, 1984) and dynamic kinetic simulation models (e.g. Dold *et al.*, 1980, 1991; Henze *et al.*, 1987, 1995; Wentzel *et al.*, 1992) have been developed. Through their successful use and application, this group of models have achieved widespread acceptance and have had a significant impact on the approach to design, operation and control of the activated sludge system, and on the research into its' behaviour.

This group of models is based, to a large degree, on a common simplified conceptualization of the mechanisms operating in the activated sludge system, which has developed particularly from an understanding of the interactions between the components making up the mixed liquor in the bioreactor of the activated sludge system, and the influent wastewater.

In terms of the conceptual framework of the models, in the bioreactor of the non-nitrifying aerobic activated sludge system the mixed liquor organic suspended solids is made up of three components; (1) heterotrophic active biomass, (2) endogenous residue and (3) inert material. In the nitrifying aerobic and anoxic/aerobic activated sludge systems, a fourth mixed liquor organic suspended solids component is included; (4) autotrophic active biomass. The heterotrophic active biomass arises from synthesis of living heterotrophic organisms on biodegradable organic substrates and is "lost" via endogenous respiration/death processes; in the activated sludge system this mixed liquor component performs the biodegradation processes of COD removal and denitrification. The autotrophic active biomass arises from synthesis of autotrophic organisms in the nitrification of ammonia to nitrate under aerobic conditions and is "lost" via endogenous respiration/death processes. The endogenous residue is generated from the unbiodegradable portion of the heterotrophic and autotrophic active biomasses that are lost in the endogenous respiration/death processes. The inert material arises from the influent wastewater unbiodegradable particulate organics which, on entry into the bioreactor, are enmeshed in the mixed liquor organic suspended solids. All four mixed liquor organic suspended solid components settle out in the secondary settling tank and are returned to the bioreactor via the underflow recycle; these components leave the activated sludge system via the waste flow.

If an anaerobic reactor is included in the system to stimulate biological excess phosphorus removal (BEPR), additionally (5) the organisms mediating the BEPR [variously termed polyP organisms (Wentzel *et al*., 1986), bio P organisms (Comeau *et al*., 1986), phosphate accumulating organisms (PAO, Henze *et al*., 1995)] and (6) their endogenous residue will contribute to the mixed liquor organic suspended solids - to avoid this complication, only the aerobic and anoxic/aerobic systems will be considered in this research project.

Historically, the mixed liquor organic suspended solids have been measured as a lumped parameter, via the volatile suspended solids test (Standard Methods, 1985), or, more recently, the COD test. Specific rates for the biological processes (e.g. denitrification, oxygen utilization) often were, and still are, expressed in terms of this lumped parameter. However, from the description above, in the bioreactor of the aerobic and anoxic/aerobic activated sludge systems only a part of the mixed liquor organic suspended solids is heterotrophic active biomass, the active fraction, and only this part mediates the biological processes of COD removal and denitrification. Accordingly, the specific rates for these (and associated) processes should be expressed in terms of the heterotrophic active biomass to allow a meaningful comparison of the rates measured in different systems. More recently, with the proliferation of kinetic simulation computer programmes that invariably include heterotrophic active biomass as a parameter, this parameter and the use of specific rates in terms of it seem to have become almost universally accepted. However, it must be remembered that this parameter exists only hypothetically within the structure of the design procedures and kinetic models: Although indirect evidence provides support for this parameter (by consistency between observations and predictions over a wide range of conditions, e.g. Dold *et al*., 1980, 1991; Van Haandel *et al*., 1981; Warner *et al*., 1986), it has not been directly measured experimentally and compared to the theoretical values. This deficiency must cast a measure of uncertainty on the entire framework within which the steady state design and kinetic simulation models have been developed. The problem in measurement of the heterotrophic active biomass parameter has been the lack of suitable experimental techniques: In the literature, principally microbiological techniques have been proposed; for example, (i) pour plate or other culturing techniques (e.g. Gaudy and Gaudy, 1980), (ii) adenosine triphosphate (ATP) analysis (Nelson and Lawrence, 1980), (iii) deoxyribonucleic acid (DNA) analysis (Liebeskind and Dohmann, 1994), and (iv) florescent probes for ribosomal RNA (Wagner *et al*., 1994). However, these microbiological techniques have not yet been adequately integrated with the design and kinetic modelling theory. Furthermore, the culturing techniques [(i) above] have been widely criticized for their unreliability (e.g. Cloete and Steyn, 1988), the DNA methods [(iii) above] requires reliable quantitative DNA extraction which appears problematic (Liebeskind and Dohmann, 1994), the florescent probes are still in their infancy, and, the last three methods [(ii), (iii) and (iv) above] require very sophisticated equipment and experimental techniques that are not widely available.

In contrast, recently a simple batch test procedure has been developed to quantify heterotrophic active biomass (Kappeler and Gujer, 1992; Wentzel *et al*., 1995; Mbewe *et al*., 1995). In this project, this batch test method will be modified and adapted to quantify the heterotrophic active biomass of activated sludge system mixed liquor. The modified method will be evaluated by applying the test to mixed liquor samples drawn from a well defined laboratory-scale activated sludge system and comparing these measured values to those calculated theoretically with the models: If agreement between measured and predicted heterotrophic active biomass can be obtained, this will provide powerful evidence validating both the models and the experimental method. This research is summarized in this Chapter; for details the reader is referred to Ubisi *et al.* (1997a,b).

7.2 EXPERIMENTAL METHODS

7.2.1 Experimental approach

A well-defined and controlled parent laboratory-scale anoxic/aerobic nitrification/ denitrification system was operated and monitored. Mixed liquor samples were harvested from the parent system and various quantities combined with unsettled municipal wastewater in batch reactors under aerobic conditions. The OUR response in the batch tests was monitored with time and used to derive estimates for heterotrophic active biomass. Parallel batch tests were run without addition of mixed liquor to quantify the heterotrophic active biomass present in the wastewater. The difference in heterotrophic active biomass between the batch tests with and without mixed liquor addition gives the heterotrophic active biomass due to the mixed liquor addition. This will be compared to the theoretically calculated values for the parent laboratory-scale system.

7.2.2 Parent laboratory-scale system

System layout and feed preparation

A laboratory-scale completely mixed aerobic single reactor activated sludge system was set up, as in Fig 7.1(a). The wastewater source for the laboratory-scale activated sludge unit was raw (unsettled) sewage from Mitchell's Plain Treatment Plant (Cape Town, South Africa). This wastewater is primarily of domestic origin with a small (<25%) industrial component.

A batch of wastewater was collected from the head of the works, after the course screens, but before the grit removal and primary sedimentation tanks. Each batch served as feed for the system for 10 to 14 days, mainly to overcome organism acclimatization problems and to ensure that steady state was maintained. The sewage batches were stored in 400ℓ stainless steel vessels in a cold room at 4°C; this was done to minimize the utilization of readily biodegradable COD (RBCOD). The total COD concentration for the feed to the parent system was kept constant at ± 500mgCOD/ℓ. Daily, the wastewater in the storage vessel was thoroughly mixed and a volume of sewage drawn from the tanks and diluted with tap water to achieve the required COD concentration for the feed. The diluted wastewater was poured into the daily feed bucket which was kept at 8°C. The influent feed in the feed bucket was stirred slowly, in order to keep the particulate material in suspension, but to limit Dissolved Oxygen (DO) entrainment. The system was run following the procedures set out in detail by Burke *et al.* (1986); Clayton *et al.* (1989) and others.

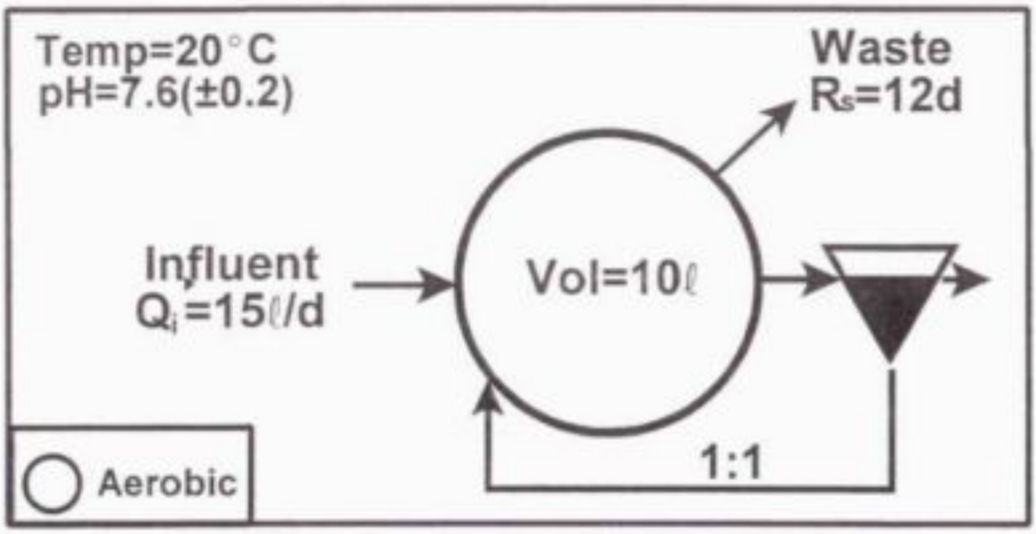

Fig 7.1(a): Schematic layout and operational data for parent laboratory-scale completely aerobic activated sludge system.

The completely aerobic system was run for three sewage batches whereafter severe bulking problems started (DSVI > 150mℓ/gMLSS), due to the filament *Sphaerotilus natans*. Several methods recommended by Gabb *et al*. (1989) to remedy bulking by *S. natans* were tried:

- The reactor and all feeding and recycling tubes were cleaned using hypochlorite and the reactor constantly aerated for 3 days,
- the aeration in the reactor was switched off for 4 successive days, and
- two sets of influent feed tubes were set up; one set was used for feeding and the spare set was kept in hypochlorite diluted with water; daily fresh hypochlorite solution was made up and the two sets of tubes swopped - this practice avoids the growth of the *S. natans* in the feed pipes and seeding of the organism into the bioreactor.

However, none of the actions above could successfully remedy the bulking by *S. natans*. An alternative method to control their growth is to include unaerated zones in the system layout (Gabb *et al*., 1989). This approach was then tried. An unaerated independently stirred pre-denitrification reactor was included in the system, that is, the system layout was changed to that of a Modified Ludzack-Ettinger (MLE) configuration, see Fig 7.1(b). This system has resolved the bulking problem (DSVI<150mℓ/gMLSS), and was used for the experimental investigation.

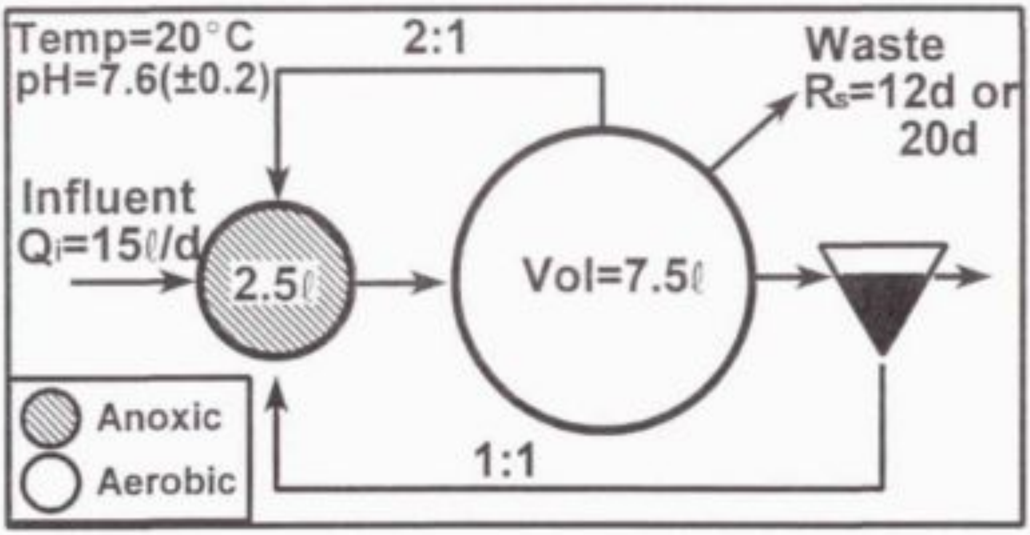

Fig 7.1(b): Schematic layout and operational data for parent laboratory-scale Modified Ludzack Ettinger (MLE) activated sludge system.

System sampling and measurements

Daily, before the influent was poured in the feed bucket, the feed was thoroughly mixed and a sample taken and stored at 4°C for analysis the following day. Daily, three 50mℓ mixed liquor samples were drawn from the bioreactor whilst the system was still feeding with the previous day's feed. Daily, from the effluent bucket, after mixing a sample was drawn. The following tests (Standard Methods, 1985) were performed on the samples daily:

1. COD and TKN on influent sample.
2. COD and TKN on unfiltered effluent sample.
3. COD and TKN on filtered effluent sample (sample filtered through a 0.45μm filter paper).
4. COD and TKN on aerobic reactor mixed liquor.
5. Oxygen utilization rate (OUR) in aerobic reactor.
6. pH of aerobic reactor.
7. Nitrate and nitrite concentration (Technicon Auto Analyser) on effluent, aerobic and anoxic reactors, all samples filtered through a 0.45μm filter paper.
8. Total suspended solids (TSS), organic/volatile suspended solids (VSS) and inorganic suspended solids (ISS) on aerobic reactor mixed liquor.

7.2.3 Batch tests

Two types of batch tests were run (Ubisi *et al.*, 1997a,b). In one type, only unsettled municipal wastewater was added, and in the second a mixture of wastewater and mixed liquor. For both types of batch tests, wastewater was drawn from the storage tanks after thorough mixing and diluted to approximately the same COD concentration as that fed to the parent system (~ 500 mg COD/ℓ). For the wastewater only batch tests, 3ℓ of the diluted wastewater was preheated to 20°C and then placed in a continually stirred batch reactor, at a constant temperature of 20°C. A sample was drawn to obtain initial total COD concentration. In operating the batch test, the surface of the wastewater was covered with small plastic balls to limit surface exchange of oxygen. The OUR was monitored continually using an automated technique (Randall *et al.*, 1991). The pH was controlled to 7.5 ($\pm$ 0.2). Because of the low OUR values, the walls of the reactor were thoroughly brushed (regularly during an aeration cycle) to prevent particulate matter adhering to them. At intervals, samples were drawn from the reactor, filtered (0.45μm) and analysed for nitrate + nitrite and nitrite (for the purpose of the batch test, nitrite concentrations were found to be negligible compared to nitrate concentrations, <1%). The batch tests were conducted for approximately 24h. At the end of the batch tests the contents of the batch reactor were homogenised, a sample drawn and total COD concentration measured.

For the mixture of wastewater and mixed liquor, a sample of mixed liquor was harvested from the aerobic reactor of the parent system and a defined volume (100 to 400 mℓ) placed in the batch reactor. The batch reactor volume was made up to 3ℓ with the same diluted unsettled municipal wastewater used in the wastewater only batch tests, also preheated to 20°C (see above). The batch test procedure detailed above was then followed.

Details on the development of the batch test procedure and data analysis procedures are given in Ubisi *et al.* (1997a,b).

7.2.4 Parent system operational parameters and dates of tests

The parent system operational parameters that were changed were aerobic and anoxic/aerobic configuration (changed to control bulking, see above), system sludge age 12 and 20d (changed to vary the mixed liquor production and composition) and sewage batch (batches used to ensure steady state conditions, but changed every ± 2 weeks to prevent degradation under storage). In total 28 batches of sewage were fed to the parent system over 450 days. With the parent system at a sludge age of 12d, batch tests were conducted during 7 sewage batches, and at a sludge age of 20d, batch tests were conducted during 5 sewage batches; the sewage batches during which batch tests were conducted are set out in Table 7.1

Table 7.1: Parent system sludge age, sewage batch number and the dates it was used as feed, and the number of batch tests with wastewater (WW) only and wastewater + mixed liquor (WW+ML) for the particular sewage batch.

Parent System Sludge Age (d)	Sewage Batch No.	Dates	Number of Batch Tests	
			WW only	WW+ML
12	12	17 Oct - 31 Oct	4	8
	13	1 Nov - 17 Nov	1	4
	17	12 Jan - 25 Jan	11	11
	18	26 Jan - 7 Feb	11	11
	19	8 Feb - 21 Feb	12	12
	20	22 Feb - 5 Mar	8	13
	21	6 Mar - 19 Mar	4	7
20	22	4 Apr - 12 Apr	6	6
	23	13 Apr - 23 Apr	8	8
	24	24 Apr - 8 May	6	11
	26	20 May - 31 May	10	10
	27	1 Jun - 14 Jun	8	14
TOTAL			89	115

7.3 RESULTS

7.3.1 Parent system

For each of the batches of wastewater fed to the parent system (28 batches), the daily results were averaged, see Table 7.2. Batch tests were conducted during 7 wastewater batches with the parent system at 12d sludge age, and during 5 wastewater batches at 20d, Table 7.1. Following Ekama *et al.* (1986) the following were determined: The influent wastewater unbiodegradable soluble and particulate COD fractions ($f_{S,us}$ and $f_{S,up}$ respectively); system COD and N mass balances; the COD and TKN to VSS ratios of the mixed liquor (f_{CV} and f_N respectively), see Table 7.3. Referring to Table 7.3, two wastewater batches (13 and 21) had N mass balances outside the acceptable range 90-110%; these data were rejected for further analysis. COD mass balances for the remaining batches ranged from 80-96%. The COD mass balance contains 5 elements - COD of the influent and effluent, OUR for carbonaceous material (i.e. measured OUR - nitrification OUR), COD consumed in denitrification, and sludge production. The COD measurements were checked with standard potassium phthalate (Standard Methods, 1985) and found to be accurate. The acceptable N mass balances indicated that the cause for the low COD mass balances did not lie in nitrate measurements - to improve the COD mass balance, the nitrate generated had to be reduced which reduced the N mass balance unacceptably. The cause appeared to lie in the measurement of the carbonaceous OUR or the MLOSS. Of particular importance to this investigation is the measurement of MLOSS; this was used to estimate the theoretical heterotrophic active biomass (X_H) active fraction (see later). Three independent measurements were made on the MLOSS; VSS, COD and TKN. For all 28 batches of wastewater tested, mean COD/VSS (f_{CV}) = 1.49 mgCOD/mgVSS [sample standard deviation (SSD) = 0.08] and TKN/VSS (f_N) = 0.106mgN/mgCOD (SSD = 0.011). These values compare very favourably with the accepted standard values of COD/VSS = 1.48mgCOD/mgVSS and TKN/VSS = 0.10mgN/mgVSS (WRC, 1984). Accordingly, it could be accepted that the reasons for the low COD mass balances did not lie in the measurement of the MLOSS, and thus no wastewater batches were rejected on the basis of the COD mass balance.

Table 7.2: Steady state results for parent anoxic/aerobic activated sludge system receiving sewage batches during which batch tests were conducted. For each sewage batch (sew btch) tested, the daily results have been averaged and the averages are listed with standard deviations in brackets.

ANOXIC/AEROBIC STEADY STATE SYSTEM												
Sew Btch	No. tests	COD (mg/ℓ)		TKN (mg/ℓ)		Nitrate+Nitrite(mgN/ℓ)			OUR mgO/ℓ.h	Mixed liquor (mg/ℓ)		
		Inf	Eff	Inf	Eff	Anoxic	Aerobic	Eff		VSS	COD	TKN
12	15	517 (30)	49 (15)	41 (3)	3.6 (0.6)	0.4 (0.1)	5.3 (0.6)	4.9 (0.7)	24.6 (1.7)	2293 (149)	3433 (341)	255 (13)
13	15	492 (30)	46 (10)	47 (3)	3.5 (0.4)	1.7 (0.7)	10.9 (1.2)	10.4 (0.7)	23.7 (0.6)	1684 (118)	2833 (301)	210 (16)
17	14	481 (30)	44 (10)	48 (1)	3.7 (0.3)	1.6 (0.9)	8.7 (1.0)	8.8 (1.0)	25.8 (0.6)	2033 (78)	2839 (185)	222 (11)
18	12	450 (31)	72 (9)	37 (1)	3.5 (0.6)	0.6 (0.4)	5.3 (0.3)	5.4 (0.3)	22.7 (1.6)	1709 (85)	2513 (144)	193 (15)
19	13	492 (27)	59 (8)	45 (2)	3.2 (0.4)	0.5 (0.5)	5.9 (0.3)	6.3 (0.3)	23.5 (0.5)	1775 (28)	2640 (153)	222 (9)
20	13	500 (21)	48 (10)	49 (1)	3.4 (0.3)	6.0 (0.7)	13.1 (1.2)	13.5 (1.1)	24.3 (0.9)	2052 (118)	2958 (286)	221 (20)
21	14	503 (34)	49 (10)	52 (4)	3.8 (0.5)	1.6 (1.0)	7.9 (0.6)	8.2 (0.8)	25.9 (1.1)	2116 (112)	3477 (185)	258 (21)
22	9	476 (16)	38 (5)	58 (1)	3.0 (0.4)	9.6 (0.7)	19.7 (0.5)	19.8 (0.4)	27.4 (0.3)	2729 (108)	4284 (151)	294 (11)
23	11	493 (39)	33 (8)	57 (4)	3.2 (0.5)	6.8 (1.4)	16.0 (1.1)	16.5 (1.1)	27.6 (0.6)	2668 (51)	4236 (246)	314 (24)
24	14	489 (19)	43 (7)	53 (2)	3.1 (0.4)	3.2 (2.5)	13.0 (2.7)	12.9 (2.5)	29.3 (0.3)	2557 (66)	3659 (236)	284 (24)
26	11	458 (23)	51 (9)	58 (3)	3.1 (0.6)	12.8 (1.2)	23.4 (1.4)	23.4 (1.6)	27.9 (0.5)	2861 (51)	4297 (227)	303 (14)
27	13	479 (39)	46 (8)	47 (4)	3.0 (0.5)	2.8 (1.1)	9.8 (2.4)	10.7 (2.0)	23.9 (1.3)	3185 (101)	4873 (266)	333 (15)

Table 7.3: Steady state COD and N mass balances, wastewater fractions and mixed liquor parameters for parent anoxic/aerobic activated sludge system. Data calculated from Table 7.2, either directly or using the steady state (SS) design (WRC, 1984) or kinetic simulation (sim.) models (Dold *et al.*, 1991).

ANOXIC/AEROBIC STEADY STATE SYSTEM									
Sew Batch	Mass Balance (%)		Wastewater COD fractions			Mixed liquor			
	COD	N	Unbiod. Soluble ($f_{S,us}$)	Unbio. Particulate ($f_{S,up}$)		COD/VSS ratio (mgCOD/ mgVSS) (f_{cv})	TKN/VSS ratio (mgN/mgVSS) (f_N)	Active Fraction (f_{av})	
				SS Design	Kinetic Sim.			SS Design	Kinetic Sim.
12	94	95	0.095	0.167	0.154	1.50	0.111	0.348	0.349
13*	79	111	0.093	-	-	1.68	0.125	-	-
17	91	93	0.091	0.129	0.093	1.40	0.109	0.385	0.426
18	96	96	0.160	0.116	0.099	1.47	0.113	0.398	0.408
19	88	91	0.120	0.081	0.061	1.49	0.125	0.462	0.474
20	83	92	0.096	0.123	0.097	1.44	0.108	0.397	0.420
21*	97	84	0.097	-	-	1.64	0.122	-	-
22	81	92	0.080	0.106	0.100	1.57	0.107	0.331	0.316
23	80	90	0.067	0.081	0.080	1.59	0.118	0.367	0.343
24	84	98	0.088	0.065	0.038	1.43	0.111	0.377	0.404
26	85	96	0.111	0.142	0.125	1.50	0.106	0.278	0.283
27	87	93	0.096	0.168	0.159	1.53	0.105	0.258	0.253

* Batches rejected due to poor N mass balances.

From the steady state data, the theoretical X_H of the mixed liquor drawn from the parent system and added to the batch tests needs to be calculated (Ubisi *et al.*, 1997a,b). To do this two approaches were followed - the steady state design and the kinetic simulation models were used: For the steady state design models, from WRC (1984) and the data in Table 7.3, the X_H as fractions of the MLOSS (f_{av}) were calculated and are listed in Table 7.3. For the kinetic simulation models, using UCTOLD (Dold *et al.*, 1991) values for f_{av} were determined from simulations of the steady state periods - for each period the values for the influent wastewater $f_{S,up}$ were adjusted until the simulated and measured reactor MLOSS concentrations (COD units) were nearly equal and the f_{av} calculated from the simulated results, Table 7.3. Comparing the values for f_{av} from the steady state design and kinetic simulation models, reasonably close agreement was obtained for the wastewater batches tested (average difference = 4.4%) . The differences arise principally because (i) with the steady state design models the $f_{S,up}$ and f_{av} were determined from the measured MLOSS VSS concentration whereas with the kinetic simulation models these were determined from the measured MLOSS COD concentration, and (ii) the kinetic simulation models include autotrophic active biomass and non-utilised slowly biodegradable COD in the MLOSS whereas these are ignored in the steady state design models. Due to their near equality, the f_{av} from either the steady state design or kinetic simulation models could be used, but because of the simpler more direct analytical calculation procedure, the f_{av} from the steady state design model were used. Now, knowing f_{av}, the concentration of the mixed liquor VSS or COD drawn from the parent system (Table 7.2), and the volume of mixed liquor added to the batch tests, the *theoretical heterotrophic active biomass concentration in the batch reactor* due to the added mixed liquor could be readily calculated (Ubisi *et al.* 1997a,b).

7.3.2 Batch tests

Batch tests with wastewater only

For each wastewater batch, on average 7 batch tests on wastewater only were conducted (89 in total, see Table 6.1). As an example, the OUR vs. time for one batch test is plotted in Fig. 7.2(a). No nitrate or nitrite was detected in this series of batch tests indicating the absence of nitrification, that is, no autotrophic biomass was present in the wastewater. (Should nitrification take place, it can be readily taken into account, Ubisi *et al.*, 1997a,b). Referring to Fig. 7.2(a), the OUR profile conforms to that described by Wentzel *et al.* (1995): During the first period (<8.5h) the OUR exhibits an exponential increase due to X_H growth. After ± 8.5h, the OUR drops precipitously due to depletion of the wastewater readily biodegradable COD. For the remainder of the batch test, the OUR exhibits an inverted S pattern typical of saturation kinetics, due to slowly biodegradable COD utilisation.

Following Wentzel *et al.* (1995) and Mbewe *et al.* (1995), the batch tests were analysed to determine COD recovery (%) and wastewater heterotrophic active biomass (X_H). A probability plot of %COD recovery for the different batch tests with wastewater only is shown in Fig. 7.3; %COD recoveries ranged from 90 to 106%, with mean 96% and sample standard deviation (SSD) 4%. The good mass balances provide support for the reliability of the measurements.

To determine X_H at the start of the batch test ($X_{H(0)}$), the OUR values up to the precipitous drop in OUR were plotted ℓn OUR vs. time (for example, the OUR data in Fig. 7.2(a) are plotted in Fig. 7.2(b)), and linear regression applied to determine the y-intercept, slope and correlation coefficient (R^2). Batch tests with R^2 <0.9 were rejected for further analysis (1 out of 89). From the slopes and y-intercepts, $X_{H(0)}$ were calculated (Wentzel *et al.*, 1995). These values represent the *heterotrophic active biomass concentration in the batch reactor due to the wastewater only*, $X_{H(0)}$(WW). For each wastewater batch, the $X_{H(0)}$(WW) values were averaged: As reported by Mbewe *et al.* (1995) and Wentzel *et al.*, (1995), for Mitchells Plain wastewater, heterotrophic active biomass was found to be present at relatively low concentrations, 2 to 7% of total COD.

Batch tests with wastewater + mixed liquor

One hundred and fifteen batch tests were conducted on mixtures of various quantities of mixed liquor and wastewater. As an example, the OUR vs. time response with 100 mℓ mixed liquor from the parent system at 12d sludge age (Table 7.2, WW Batch 12) added to 2.9 ℓ diluted wastewater is shown plotted in Fig. 7.2(a): The general shape of the OUR time profile is the same as that for wastewater only. However, due to the larger concentration of X_H present (added with the mixed liquor) the OURs are higher and the time to the precipitous drop in OUR shorter. Further, since the mixed liquor was drawn from a nitrifying activated sludge system, nitrification was observed, see Fig. 7.2(a). The OUR due to this nitrification ($OUR_{N(t)}$) had to be taken into account in deriving estimates for % COD recovery and $X_{H(0)}$, since both parameters are determined from the OUR for heterotrophs only ($OUR_{H(t)}$) . The $OUR_{N(t)}$ was determined from the nitrate concentration time profile (e.g. Fig. 7.2(a)); for details see Ubisi *et al.* (1997a,b). Then, from each measured OUR value ($OUR_{M(t)}$), the nitrification OUR ($OUR_{N(t)}$) was subtracted to give the OUR due to the heterotrophs only ($OUR_{H(t)}$), i.e. $OUR_{H(t)} = OUR_{M(t)} - OUR_{N(t)}$.

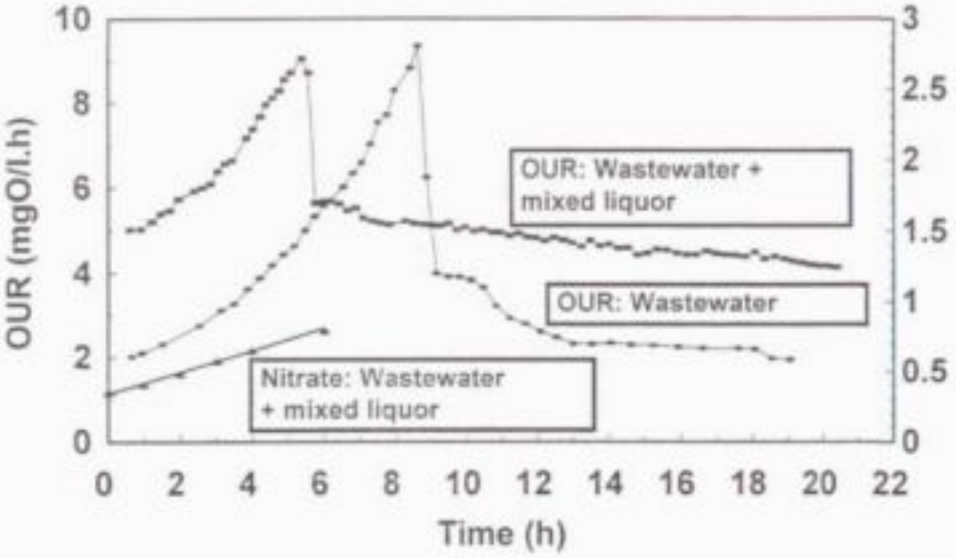

Fig 7.2(a): OUR and nitrate time responses for aerobic batch tests on raw municipal wastewater from Mitchells Plain (Cape Town, South Africa) and on a mixture of this raw municipal wastewater (2.9ℓ) with mixed liquor (0.1ℓ) drawn from the aerobic reactor of the parent system. (For wastewater batch test, nitrate = 0).

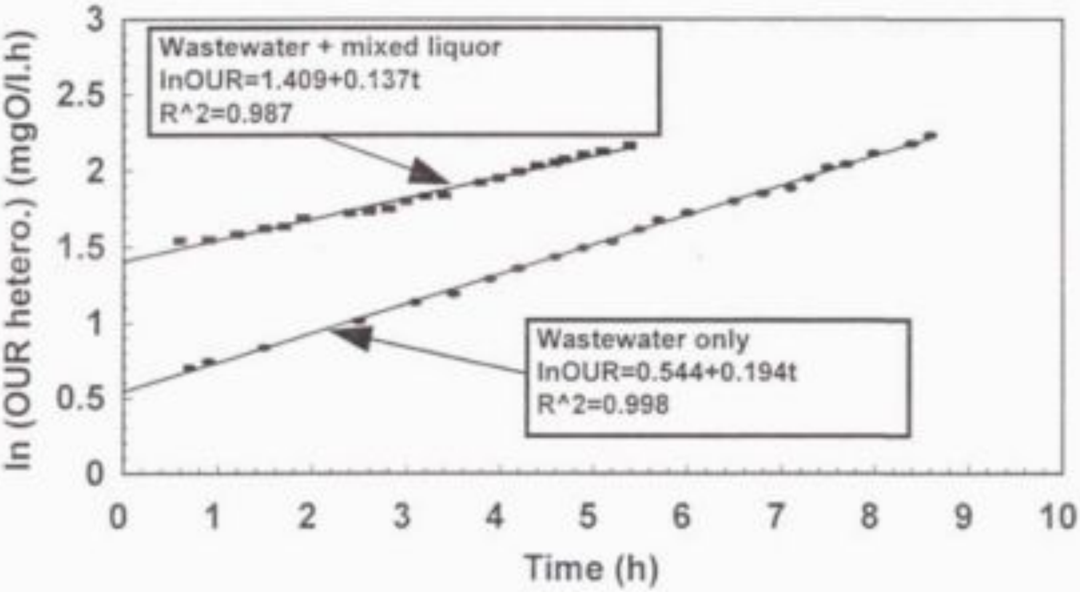

Fig 7.2(b): ℓn OUR due to heterotrophic active biomass vs. time for the OUR data in Fig. 7.2(a) up to the precipitous drop in OUR [i.e. OUR due to nitrification subtracted from measured OUR data and then plotted].

Having determined the $OUR_{H(t)}$, the % COD recoveries were calculated (Ubisi *et al.*, 1997a,b). The %COD recoveries ranged from 74 to 120%. From a statistical analysis, batch tests with %COD recoveries <90% or >110% were rejected as outliers (9 tests). The remaining %COD recoveries are plotted in Fig. 7.3; mean = 102% and SSD = 5%. Again, the good COD recoveries provide support for the reliability of the measurements. To determine X_H present at the start of the batch tests, $X_{H(0)}$, the $OUR_{H(t)}$ up to the precipitous drop in OUR were plotted (ln $OUR_{H(t)}$ vs. time, for example see Fig. 7.2(b). Linear regression was used to determine the y-intercept, slope and correlation coefficients (R^2). Batch tests with $R^2 < 0.9$ were rejected for further analysis (11 batch tests). From the y-intercept and slope, values for $X_{H(0)}$ were calculated (Wentzel *et al.*, 1995; Ubisi *et al.*, 1997a,b). These values represent the *heterotrophic active biomass concentrations in the batch test due to that added with the mixed liquor and that present in the original wastewater*, i.e. $X_{H(0)}$ (WW+ML).

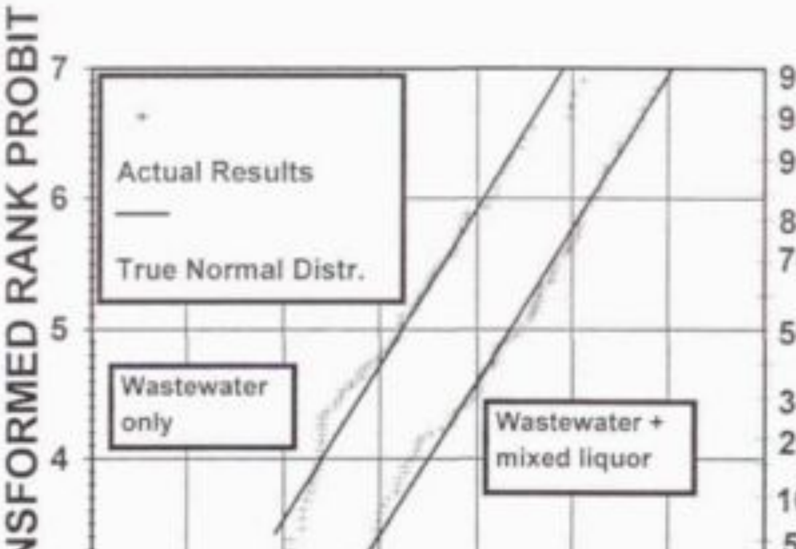

Fig 7.3: Probability plot of %COD recovery for the batch tests on raw municipal wastewater from Mitchells Plain (Cape Town, South Africa) and on mixtures of this raw municipal wastewater with mixed liquor drawn from the aerobic reactor of the parent system (Fig. 7.1(b)).

7.3.3 Comparison between theoretical and measured heterotrophic active biomass

In the batch tests with both wastewater and mixed liquor present, to determine $X_{H(0)}$ due to the mixed liquor only [$X_{H(0)}$ (ML)], the $X_{H(0)}$ due to the wastewater [$X_{H(0)}$ (WW)] must be subtracted from $X_{H(0)}$ (WW+ML). To determine $X_{H(0)}$ (WW), the 4 to11 wastewater only batch tests on each wastewater batch were averaged. Then, the dilution in $X_{H(0)}$ (WW) caused by the addition of mixed liquor to the batch tests with wastewater and mixed liquor was taken into account (Ubisi *et al.*, 1997a,b) and values for $X_{H(0)}$ (ML) calculated; these values represent the *measured mixed liquor heterotrophic active biomass concentration in the total batch test volume*. The measured and theoretical $X_{H(0)}$ (ML) are plotted against each other in Figs. 7.4 (a and b) for the parent system at sludge ages 12d and 20d respectively. For sludge age 12d, with the exception of wastewater batch 19 the measured and theoretical $X_{H(0)}$ (ML) correspond remarkably closely. However, for sludge age 20d the measured $X_{H(0)}$ (ML) are consistently lower, only about half the theoretical values.

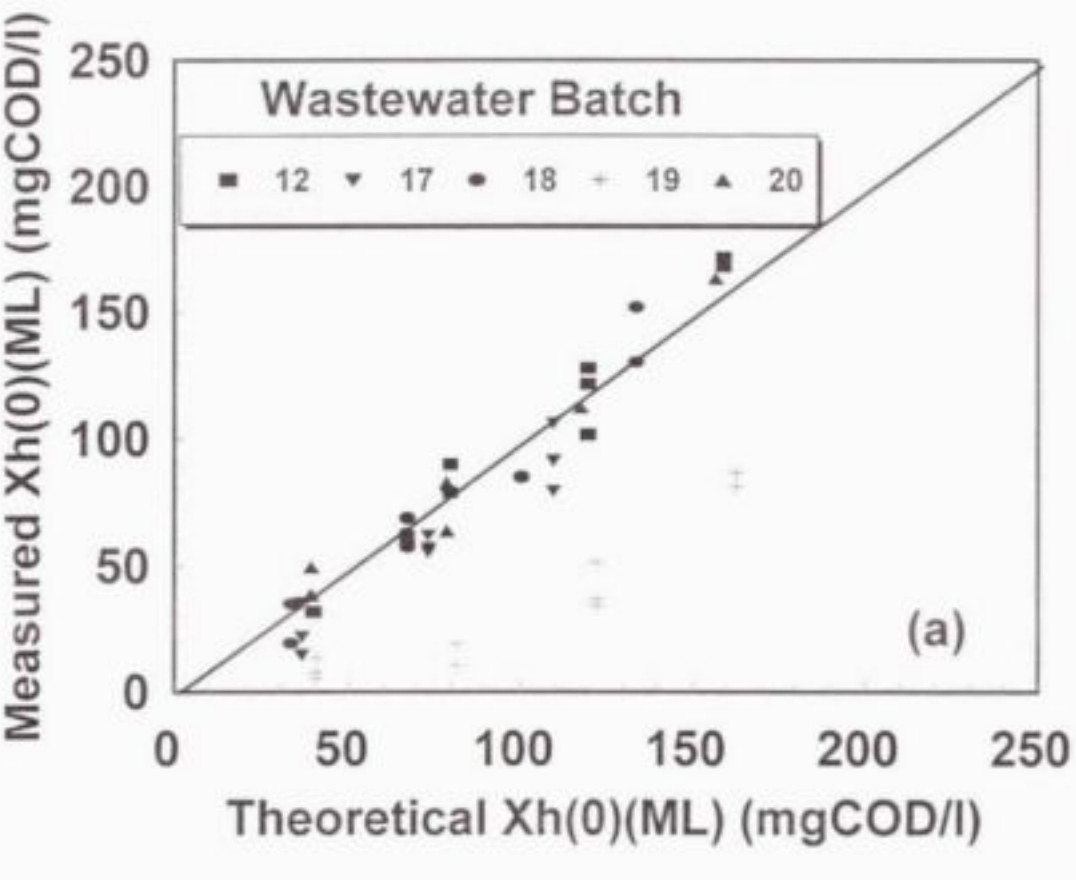

Fig 7.4(a): Measured versus theoretical heterotrophic active biomass concentration [$X_{H(0)}$(ML)] in the batch test due to addition of mixed liquor drawn from the parent system [Fig 7.1(b)] at 12d sludge age.

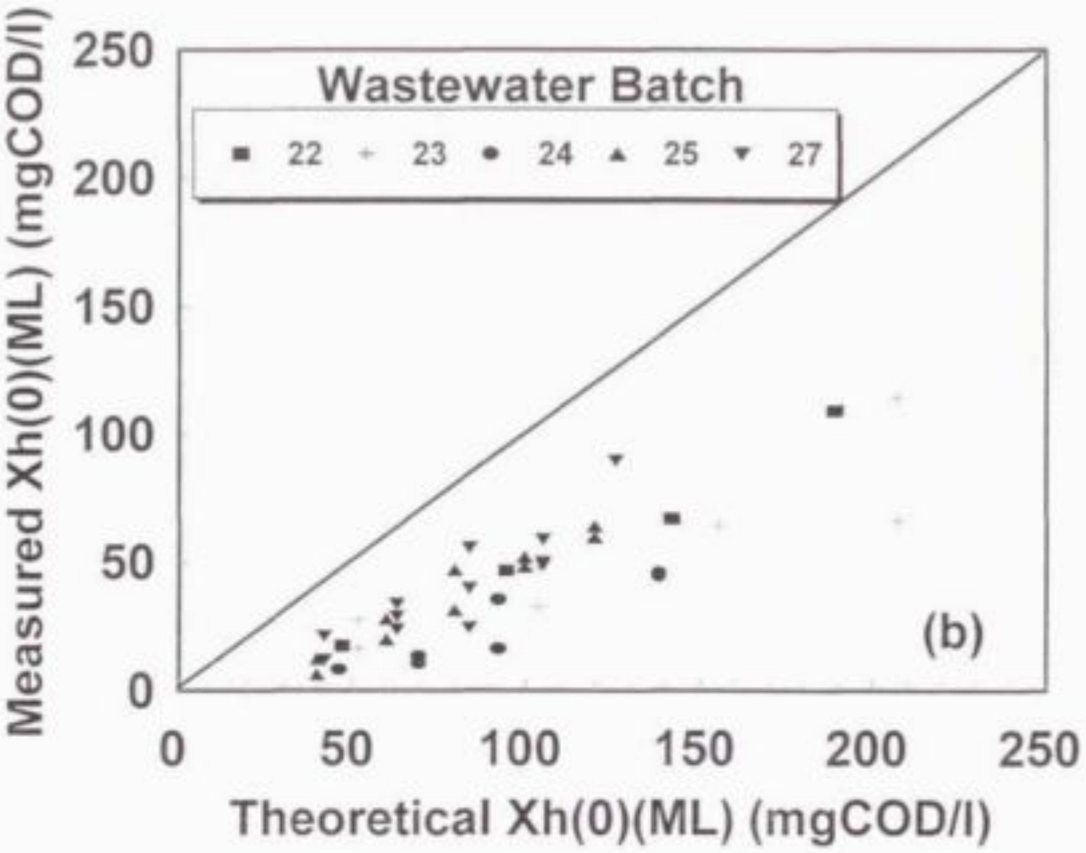

Fig 7.4(b): Measured versus theoretical heterotrophic active biomass concentration [$X_{H(0)}$(ML)] in the batch test due to addition of mixed liquor drawn from the parent system [Fig 7.1(b)] at 20d sludge age.

7.4 DISCUSSION

Fundamental to the current steady state design and kinetic simulation models for activated sludge systems is the parameter heterotrophic active biomass (X_H). This mixed liquor organic suspended solids component mediates the biodegradation processes of COD removal and denitrification (and associated processes), and, in the models all relevant specific rates are expressed in terms it. Although recently X_H has gained more acceptance than in the past, it would seem that this is due to the convenience of computer programmes based on the models, rather than substantive proof of its validity so that the parameter remains hypothetical within the structure of the models. Thus, to promote confidence in application of the models for design, operation and control of activated sludge systems, and indeed in the models themselves, it is essential that X_H is validated by experimental measurement. In this Chapter a simple batch test procedure has been used to quantify the heterotrophic active biomass concentration of mixed liquor drawn from a well-defined parent anoxic/aerobic activated sludge system. The results obtained are both encouraging and perplexing. With the parent system at 12d sludge age, the agreement between measured and theoretical values is remarkably good. However, with the parent system at 20d sludge age the agreement is poor, with the theoretical values being about 2 times those measured. No explanation could be found for this inconsistency, and this requires investigation. The results do indicate that the batch test method may prove to be a valuable tool that can be used to provide greater insight into the behaviour of the aerobic and anoxic/aerobic activated sludge systems. However, in systems that include biological phosphorus removal the method will not be of use. In these systems the heterotrophic organisms mediating the phosphorus removal are present also and the batch test will not be able to distinguish between the two groups of heterotrophic organisms. Furthermore, experimental evidence from such systems indicates that there are behaviours in these systems that are not recognized in the models (Ekama and Wentzel , 1997). For example, for the same wastewater there is an inconsistency in the sludge production between aerobic and anoxic/aerobic systems on one hand and anaerobic/anoxic/aerobic systems on the other; also, the sludge production in anaerobic/anoxic/aerobic systems has been found to be linked to filamentous bulking. In the current models both these observations have to be taken into account by using different influent unbiodegradable particulate COD fractions (a wastewater characteristic) which markedly affects the X_H as a fraction of the mixed liquor organic solids (active fraction, f_{av}) , clearly an unacceptable solution.

In this investigation, data on the inorganic materials in influent, effluent and mixed liquor of the parent system has also been collected. This data has been analyzed to provide information on the incorporation of inorganics into the activated sludge mixed liquor, see Ubisi *et al*. (1997b).

CHAPTER 8

DISCUSSION/FUTURE WORK

For the research contract "The treatment of wastewaters with high nutrients (N & P) but low organic carbon (COD) contents" (K5/692), the principle aim was:

- To evaluate, investigate, develop and refine chemical, physical and biological processes and technologies to treat wastewaters with high nutrient (N & P) but low organic contents

In terms of this aim, four main tasks were identified:

- Develop a fundamentally based mathematical model which will integrate the biological, physical and chemical processes that are operative in systems treating high nutrient low organic wastes.
- Review the literature to, (i) identify the origin and nature of these wastes, (ii) identify technologies currently used for the treatment of these wastes, (iii) identify new technologies that hold potential for the treatment of these wastes, and (iv) provide experimental data for calibration, testing and refinement of the mathematical model.
- Collect experimental data on the wastes and various treatment schemes. This will provide information on the feasibility of the schemes, and for the development, calibration and validation of the mathematical model.
- Evaluate and develop existing/new processes and technologies.

Each of these tasks is described below.

8.1 Task 1: Model Development

The objective of this task was to develop a fundamentally based mathematical model which integrates physical, chemical and biological processes. This task was prioritised since it was recognised that such a model would be particularly useful for application to the treatment of wastewaters where physical, chemical and biological processes play a significant role, such as the high nutrient low organic carbon (HNLC) wastewaters considered in the research project.

Fundamental to the devlopment of an integrated physical, chemical and biological processes model is to incorporate weak acid/base chemistry and pH as a parameter/compound. In evaluating the conventional equilibrium approach to modelling weak acid/base chemistry and pH, it was realised that this approach was not suitable for the kinetic model developed here. Accordingly, a kinetic approach to including pH was developed which formulates the weak acid/base equilibria in terms of the kinetics of the forward and reverse reactions for dissociation. This enabled the parameter (H^+) and all the individual species of the various weak acid/base systems to be explicitly included in the model so that pH is calculated directly from $pH = -\log(H^+)$. The advantages of the kinetic approach over the equilibrium-based approach are (i) kinetics are used throughout and this expedites integration of weak acid/base processes with existing biological kinetic models and (ii) the approach is general and can be applied to include any weak acid/bases of interest.

Having developed an appropriate method to incorporate pH in the model, the model was developed in stages namely, (i) single phase aqueous systems, (ii) two phase solid-aqueous systems, (iii) two phase gaseous-aqueous systems and (iv) three phase solid-aqueous-gaseous systems which is a combination of the first three. Where possible, each section of the model was validated with data from the literature; close correlation between literature data and predictions was obtained. However, not all sections of the model could be validated with data from the literature requiring an experimental investigation to collect suitable data for model validation.

During model development, the three phase systems model with weak acid/base systems reactions, biological processes, precipitation reactions of all solids and the processes of gas stripping could not be validated with data from the literature. This prompted an experimental investigation at 20°C to collect suitable data to validate most of the processes in the integrated model. Experiments in the form of aerated batch tests were carried out on four types of waste; (a) anaerobic digester liquor (ADL) from a biological nutrient removal (BNR) plant, (b) ADL from an upflow anaerobic sludge bed (UASB) reactor treating spent wine (c) a mixture of municipal raw sewage and waste activated sludge (WAS) from a nitrogen removal plant with and without chemical (Ca, Mg, P, and free and saline ammonia) addition and (d) a mixture of ADL from a BNR plant and WAS from a nitrogen removal plant. This enabled the model to be calibrated and validated by comparing model predictions with experimental results for physical and chemical processes only (with the first two wastes), biological processes only (with the third waste) and physical, chemical and biological processes of carbon and nitrogen removal, with the third and last type of waste.

In simulating the experimental results with the three phase kinetic model, a good correlation was obtained between model predictions and experimental results for all batch tests. The good correlation between predicted and measured results enabled the kinetic model to be used to gain greater insight into the behaviour in the experiments, e.g. which minerals dominate in the precipitation and what masses precipitate, what stimulates precipitation of the different minerals.

The kinetic based model developed in this research project constitutes a significant advance over the existing equilibrium chemistry based models for chemical processes, and the kinetic based models for biological processes. This kinetic model and the approach on which it is based can form a starting point for the development of a host of new models, for a variety of treatment systems in which pH and/or chemical and physical processes are of importance.

8.2 Task 2: Review of literature

A review of the literature has been undertaken to identify technologies that are in use, or have potential for use in the treatment of the HNLC group of wastewaters. This review has indicated that a number of different treatment methods have been developed, which include biological, chemical and physical processes, usually separately:

- Precipitation methods usually aided by cation supplementation are in use in South Africa at Goudkoppies and Northern Works to remove nutrients from anaerobic digester liquors and activated sludge dewatering liquor respectively. This removes the phosphorus to relatively low values, but the ammonia concentrations in the anaerobic digester liquors may still be high (120mgN/ℓ), requiring further treatment.

- A number of treatment systems have been developed overseas that are not in use in South Africa. While each of these systems has its own particular advantages and disadvantages, in general the systems have been developed for the removal of N and not P. Only the CAFR system has the immediate potential for both N and P removal; however, evaluation in the Netherlands indicates that most likely the CAFR system will not be economically feasible.
- In this category of wastes, the imbalance between the nutrients (N & P) and organic carbon would suggest that treatment using combined biological, chemical and physical processes may be the best option for the removal of both N and P. Combined biological, chemical and physical processes are not well understood. In particular the interaction between the processes are poorly defined. It was considered therefore imperative that a model incorporating the biological, chemical and physical processes be developed to give a better understanding of the processes, to form a basis for design of treatment plants (see Task 1 above).
- Specific experimental investigations to be undertaken were identified, namely, treatment of:
  - (i) Waste activated sludge dewatering liquors and anaerobic digestor supernatants, by combined chemical/physical and chemical/biological/physical methods.
  - (ii) Landfill leachates in activated sludge systems receiving municipal wastewaters.
  - (iii) Septic tank effluents in conventional BNR removal activated sludge systems.

  Research on these has been undertaken, and is reported in Task 3 below.

8.3 Task 3: Experimental investigation of treatment schemes

Parallel to the development of the mathematical model, the feasibility of treating selected HNLC wastes was investigated. In terms of the contract proposals the wastes investigated were:

- Waste activated sludge dewatering liquors and anaerobic digestor liquors, by combined chemical/physical and chemical/biological/physical methods.
- Landfill leachates in activated sludge systems receiving municipal wastewaters.
- Septic tank effluents in conventional BNR removal activated sludge systems.

8.3.1 Waste activated sludge dewatering liquors and anaerobic digestor liquors

This experimental investigation was undertaken in conjunction with the development of the mathematical model, see **Task 1** above.

8.3.2 Landfill leachates in activated sludge systems receiving municipal wastewaters

Two experimental studies have been undertaken:

(1) Treatment of stabilized landfill leachate in an N removal system.
(2) Treatment of an acid leachate in a nutrient (N&P) removal system.

With regard to treatment of stabilized landfill leachate in an N removal system, the results indicated that:

- The N and COD mass balances were generally good (better than 90%).
- 11.5% of leachate COD contributed to unbiodegradable soluble COD, increasing the effluent COD concentration from the experimental system by 13 mgCOD/ℓ (25%).
- 5.7% of leachate COD was unbiodegradable particulate, increasing the VSS concentration of the solids in the reactor by 75 mgVSS/ℓ (3%).
- 83% of the leachate COD was biodegradable and contributed to the biodegradable organics of the sewage.
- No noticeable difference between the effluent TKN concentration of the experimental and control systems could be detected, indicating that the leachate contains negligible soluble unbiodegradable organic N. Also nitrification was complete and all free and saline ammonia of the leachate was nitrified.
- The additional leachate biodegradable COD caused an increase in reactor VSS concentration of about 400 mgVSS/ℓ, i.e. 20% more than in the control. The biodegradable COD and TKN caused the oxygen utilization rate to increase by 5 mgO/ℓ/h i.e. also about 20% more than in the control system. These increases seem reasonable considering the leachate increased the organic and nitrogen load by 18%.
- The effluent nitrate concentration from the experimental system was *lower* than that from the control system. This implied, and detailed comparison on the denitrification performance of the two systems confirmed this, that the leachate not only was capable of denitrifying all the nitrate that was generated from its own TKN content, but also contributed to denitrification of nitrate generated from the sewage's TKN content.
- Sludge settleability in both systems *improved* from over 150 mℓ/g at the start of the investigation to below 60 mℓ/g at the end. The filaments in the sludge were the usual AA types (i.e. *M. Parvicella*, 0092, 0041, 0675) but were only present at common level. This indicated that leachate did not stimulate poor sludge settleability in N removal systems.

Addition of unstabilized (acid) leachate comprising 22.3% and 8.1% of the sewage COD and TKN loads respectively, to a biological nutrient removal activated sludge system (experimental) and comparing the response to an identical system not dosed (control) indicated that:

- Good COD (both experimental and control = 92%) and N (experimental = 90%; control = 88%) mass balances were obtained, supporting the reliability of the data.
- The acid leachate dose increased both the TSS and VSS concentrations in the reactor, by about 550 mgTSS/ℓ and 350 mgVSS/ℓ respectively (25 and 20% respectively).
- The acid leachate dose increased the OUR, by about 21%.
- The acid leachate dose did not increase the effluent COD concentration significantly, i.e. the unbiodegradable soluble COD concentration in the leachate is small, 2.2% of the leachate COD.
- The unbiodegradable particulate COD fraction of the leachate was close to zero.
- From the unbiodegradable soluble and particulate COD fractions, 98.7% of the leachate COD was biodegraded in the BNR activated sludge system.
- The acid leachate dose increased the influent TKN by about 7%, but did not increase the effluent TKN or FSA significantly, i.e. nitrification was complete and the unbiodegradable soluble organic N small, at 4.5% of the leachate TKN.
- The unbiodegradable particulate TKN fraction of the leachate was close to zero.
- From the unbiodegradable soluble and particulate TKN fractions, 98.7% of the leachate TKN was biodegraded in the BNR activated sludge system.
- Only 13.7% of the leachate COD was taken up in the anaerobic reactor for BEPR, the

balance contributed to additional denitrification. The leachate COD taken up in the anaerobic reactor gave an increase in P removal of 4.3 mgP/ℓ (28.9%).

- The leachate denitrified all the nitrate generated from its own TKN and had the potential to denitrify an additional 4.9 mgN/ℓ generated from the sewage TKN due to a 19% higher denitrification rate.
- Leachate dosing had no effect on the nitrifier maximum specific growth rate or the sludge settleability.
- Not only did the particulate/colloidal metal complexes from the leachate accumulate in the activated sludge, but also significant concentrations of the soluble metal compounds, leaving the effluent with lower dissolved metal concentrations than the influent.

Thus, both investigations have demonstrated that, in addition to being treated, the leachate enhanced the nutrient removal capability of the activated sludge system. This would indicate that there is considerable merit in adopting an integrated approach to the management and treatment of municipal wastes, with soluble wastes generated in a landfill being treated in the municipal wastewater treatment plant (MWWTP), and the solid waste generated in the MWWTP being treated in the landfill.

8.3.3 Septic tank effluents in conventional BNR activated sludge systems

To investigate the expected impact of septic tank effluents on existing BNR activated sludge systems, it was decided to collect information on the characteristics of septic tank effluents and to do a desk-top study on the response of BNR activated sludge systems to various septic tank effluent loads. Some data on the characteristics of septic tank effluents are available in the literature, e.g. Peters (1993), Ketley (1996), Theunessin (1993). However, a particular problem with the data is that the effluents from single septic tanks have been analysed, which raises doubts as to whether the data are representative. It would be more acceptable if the combined effluent from a number of septic tanks could be analysed. A site in Hermanus was identified where ±200 septic tanks are connected to a single sewer. Samples from this sewer were obtained and analysed using chemical and biological tests to characterise the septic tank effluent. Having derived data on septic tank effluents and their characteristics, a theoretical desk top study was undertaken on the effect of various septic tank effluent loads on BNR activated sludge systems. For this study, the septic tank effluent was dosed into the settled wastewater serving as influent to the UCT configuration BNR activated sludge system pilot-scale plant at Mitchell's Plain (Cape Town, South Africa), and the theoretical response simulated with the UCTPHO kinetic simulation model (Wentzel *et al*., 1992). Two main scenarios were considered:

Scenario 1: Theoretically, increasing flows of the septic tank effluent were introduced into the influent to the pilot plant and the flow of settled domestic sewage that is normally treated in the pilot plant was reduced proportionately, so that the total flow that the pilot plant was initially designed for would be maintained (i.e. 2.4Mℓ/d).

Scenario 2: The settled sewage flow was kept constant at the design value (i.e. 2.4Mℓ/d), and the septic tank effluent flow added to this flow, so that the total flow increased as the septic tank effluent dose increased. For this scenario, two alternative recycle schemes were simulated:

Scenario 2a: The recycle flow rates were kept constant at the values for

Scenario 1 above, i.e. as the total flow increased, the recycle flows remained constant and so the recycle ratios decreased.
Scenario 2b: The recycle ratios were kept constant at the values for **Scenario 1** above, i.e. as the total flow increased, the recycle ratios remained constant and so the recycle flow rates increased.

Results from these simulation studies indicated that:

- In all three scenarios considered, septic tank effluents do not impact significantly on COD removal and nitrification. The effluent COD concentrations decreased slightly and effluent TKN and FSA remained essentially constant with increased flows of septic tank effluents.
- Depending on the scenario considered, the reactor VSS concentrations and oxygen utilization rates (OUR) either decreased (scenario 1, settled sewage flow decreased in proportion to septic tank effluent flow), or increased (scenario 2, settled sewage flow kept constant and septic tank effluent flow increased). In practice, it is likely that scenario 2 will apply, and hence provision will have to be made to accommodate the increased VSS concentrations and OURs with increased septic tank flow.
- Both denitrification and biological excess P removal decrease as the septic tank effluent flow increases. However, these decreases are only significant when proportionally large quantities of septic tank effluent are treated. The lowest impact of septic tank effluent on nutrient removal performance are for scenario 2.
- When septic tank effluent is treated by itself (scenario 1, 100% septic tank effluent), poor nutrient removal performance is achieved. This confirms that treatment of septic tank effluents in dedicated BNR plants is not a viable option.
- In practice if an activated sludge plant were to treat a blend of settled sewage and septic tank effluent the blend ratio can be selected depending on the standard of effluent that the plant is expected to meet in terms of legal requirements laid down by the Department of Water Affairs and Forestry.
- In this study, the septic tank effluent from a number of septic tanks sited at Hermanus was selected. From the characterization of this effluent it would appear that the concentrations (COD, N and P) are considerably lower (245 mgCOD/ℓ, 63 mgN/ℓ and 10.4 mgP/ℓ respectively) than those obtained elsewhere (typically > 4 000mgCOD/ℓ, > 1 000 mgN/ℓ and > 100 mgP/ℓ, see Section 6.1). This probably arises because the septic tanks at Hermanus have full water flush (10 - 15 ℓ/flush) while those in the quoted studies have restricted water flush (1ℓ/flush). This would imply that with low volume flush septic tanks deterioration in BNR nutrient removal performance would be experienced at much lower septic tank effluent flow rates than obtained in this study. This aspect requires further investigation.

8.4 <u>Task 4: Evaluate/develop existing/new technologies</u>

In Task 2 above, the literature was reviewed to identify promising new technologies for treatment of HNLC wastewaters. This review indicated that the majority of technologies developed overseas have as their principle objective the removal of nitrogen. This causes that these technologies will have limited application in South Africa to HNLC wastewaters, where the removal of phosphorus also is of fundamental importance. In South Africa, aeration stimulated precipitation methods usually aided by cation supplementation are in use at Goudkoppies and

Northern Works to remove nutrients from anaerobic digester liquors and activated sludge dewatering liquor respectively. It would appear that this technology has considerable potential for more widespread application. Accordingly, the kinetic model developed in Task 1 above was applied to examine aeration as a treatment scheme for anaerobic liquors.

The batch tests in the model validation investigation (Task 1 above) were critically examined with the objective to provide greater insight into the biological, chemical and physical processes operating in plants treating anaerobic liquors by aeration. The example case selected for study was Goudkoppies Treatment plant (Johannesburg, South Africa) where anaerobically digested sludge is first aerated to strip CO_2 (to cause pH to increase and so stimulate struvite and calcium phosphate precipitation) and lime is added for further precipitation. The batch tests in the model validation investigation in effect duplicate the first aeration step at Goudkoppies. The data from these batch tests were examined in detail and the following was concluded:

- In batch tests with anaerobic digester and UASB liquors, aeration caused CO_2 stripping and this resulted in pH increase from ±6.95 to 8.93 and 9.53 respectively.
- The increase in pH caused precipitation of predominantly struvite and ACP, reducing concentration of both nutrients N and P to around 380 gN/m^3 and 15 gP/m^3 respectively for anaerobic digester liquor and 30 gN/m^3 and 20 gP/m^3 respectively for UASB liquor.
- In both liquors, the ammonia was present in excess for struvite precipitation, and so the concentrations of ammonia were still relatively high (380 gN/m^3 for anaerobic digester liquor and 30 gN/m^3 for UASB liquor).
- Struvite precipitated very quickly within the first 20 to 45 minutes of aeration and ACP within 60 to 90 minutes of aeration.
- Ammonia is relatively non volatile so that the rate of ammonia removal via gas stripping is not a practical treatment alternative under the conditions present in the batch tests.
- Addition of WAS to the anaerobic digester liquor resulted in nitrification of the ammonia. However, this nitrification proceeded at a very slow rate (maximum specific growth rate of the nitrifiers, $\mu_{A20,pH7.2} = 0.03$ to 0.04 /d). Further, addition of WAS had the undesirable effect of reducing the rate of struvite precipitation, by up to two orders of magnitude.

The results above would indicate that the aeration of anaerobic liquors for nutrient removal should be a two stage process: (i) aeration for CO_2 stripping and pH increase, followed by (ii) addition of WAS for nitrification. In the nitrification step, care must be taken to ensure that the pH does not decrease below 7 to cause struvite redissolution.

8.5 Closure

The imbalance between the nutrients and the organic carbon in the high nutrient low organic carbon category of wastewaters considered in this project causes that treatment of these wastewaters in conventional BNR activated sludge systems is not a viable option. This is clearly demonstrated in the theoretical desk top study on the treatment of septic tank effluents. For the treatment of these wastewaters, unit processes that incorporate combined chemical, physical and biological processes would seem essential. In this project a mathematical kinetic model has been developed that simulates the behaviour of such systems. From the simulations it is evident that the kinetic model offers considerable advantages over equilibrium based models. Not only can it predict time dependent data, but also it can predict the final equilibrium state for situations with precipitation of multiple minerals which compete for the same species - equilibrium models are not capable of predicting either situation. Further, the kinetic modelling approach also allows the determination of the specific precipitation rates for a number of minerals simultaneously in an integrated manner from a single batch test. Also, the kinetic model provides greater insight into the processes operative in the system, and their interactions.

The three phase kinetic based weak acid/base chemistry model, and the approach on which it is based, is proving to be a useful tool for research into and design of wastewater treatment systems in which several weak acid/bases influence the behaviour and various combinations of biological, physical and chemical processes are operative. For research, the model helps to focus attention on issues not obvious from direct experiment and also allows determination of mineral precipitation rates for a particular wastewater from a single batch test. Once calibrated with the precipitation (and gas stripping if included) rates, this kind of model can be used to predict the performance of different treatment systems to identify for investigation those that appear technically and economically viable. For design, the model can be used to identify the critical design parameters and hence to optimize the design.

In conclusion, the kinetic based model developed in this research project constitutes a significant advance over the existing equilibrium chemistry based models for chemical processes, and the kinetic based models for biological processes. This kinetic model and the approach on which it is based can form a starting point for the development of a host of new models, for a variety of treatment systems in which pH and/or chemical and physical processes are of importance.

8.6 Recommendations

With regard to the mathematical model:

1. Although a remarkable degree of constancy was found for precipitation rate constants of the minerals in each type of waste, definitive reasons could not be advanced for the variability in the struvite precipitation rate constant and deviation in the rate constants of ACP and $CaCO_3$. Further experimental work needs to be done to obtain more data on the precipitation rate constants of these minerals in different wastes and establish the factors that affect the precipitation rate constants of these minerals.

2. For practical application of the model to a treatment scheme, the air flow rates and gas transfer rate coefficients (K_{La}) should be measured through the established methods and then applied to the model.

3. Further experimental work needs to be done to investigate (i) the validity of the μ_A-pH relationship for the maximum specific growth rate of nitrifiers proposed in the model and (ii) the effect of increased pH above the optimum range for biological activated sludge systems on the rates of utilisation of RBCOD and hydrolysis of enmeshed COD and come up with formulations similar to the ones for the effect of pH on the maximum specific growth rate of nitrifiers.

4. Since the approach for including weak acid/base dissociation reactions is general, it can be applied to model development in other areas of wastewater treatment and

biotechnology research.

5. The combined model presented in this research can be used to provide a basic understanding of the mechanisms operating in treatment schemes, and to theoretically refine the treatment process for practical implementation. The AQUASIM programme is flexible enough to model any combination of completely mixed or plug flow reactors with split influent flows, chemical addition, recycle flows and sedimentation tanks. It is therefore possible to simulate an anaerobic digester supernatant treatment system with the integrated chemical, physical and biological model developed in this research provided the reactor conditions such as air flow and gas transfer rates are known.

With regard to the treatment of septic tank effluents:

6. In this study, the septic tank effluent from a number of septic tanks sited at Hermanus was selected. From the characterization of this effluent it would appear that the concentrations (COD, N and P) are considerably lower (245 mgCOD/ℓ, 63 mgN/ℓ and 10.4 mgP/ℓ respectively) than those obtained elsewhere (typically > 4 000mgCOD/ℓ, > 1 000 mgN/ℓ and > 100 mgP/ℓ, see Section 6.1). This probably arises because the septic tanks at Hermanus have full water flush (10 - 15 ℓ/flush) while those in the quoted studies have restricted water flush (1ℓ/flush). This would imply that with low volume flush septic tanks deterioration in BNR nutrient removal performance would be experienced at much lower septic tank effluent flow rates than obtained in this study. This aspect requires further investigation.

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APPENDIX A

IDENTIFICATION OF MINERAL PRECIPITANTS TO BE INCLUDED IN THE KINETIC MODEL

A.1 INTRODUCTION

High nutrient low organic carbon (HNLC) wastewaters, such as liquors from anaerobic digesters, typically contain Mg, Ca, free and saline ammonia (FSA), and phosphate and carbonate system species, in various combinations. Under the conditions of treatment of these wastewaters, for example aeration of anaerobic digestor liquors (ADL), the solids most likely to precipitate are various magnesium and calcium carbonates and phosphates, as set out in Table A.1. Domains for precipitation of the various forms of these minerals have been delineated in the literature, and are reviewed briefly below to identify the precipitation processes to be included in the model (for a detailed review, see Musvoto et al., 1998).

A.2 MAGNESIUM PHOSPHATES

From the literature, four possible magnesium phosphate species can crystallize from solutions containing Mg, ammonia and phosphate system species (Table A.1): Magnesium ammonium phosphate or struvite ($MgNH_4PO_4 \cdot 6H_2O$), magnesium hydrogen phosphate trihydrate or newberyite ($MgHPO_4 \cdot 3H_2O$) and trimagnesium phosphate in two states of hydration, $Mg_3(PO_4)_2 \cdot 8H_2O$ (bobierrite) and $Mg_3(PO_4)_2 \cdot 22H_2O$. Studies have identified the regions for precipitation of these minerals (e.g. Abbona et al., 1982, 1986, 1988): Struvite precipitates at neutral and higher pH and at Mg/Ca molar ratios > 0.6; newberyite precipitates significantly only at lower pH (< 6.0) and at high concentrations of Mg and P_T; trimagnesium phosphate, which is reported to have a low precipitation rate (Mamais et al., 1994), has never been observed in the pH range expected in treatment of HNLC wastewaters ($6 < pH < 9$). Accordingly, precipitation of struvite and newberyite were included in the model, using the general kinetic rate formulation of Koutsoukos et al. (1980), see Eq. 3.6, with the order of reaction n=3 for struvite (Gunn, 1976) and the default n=2 for newberyite. This formulation applies only to precipitation and not to dissolution; in the model the equation is valid only if the ionic product is greater than the solubility product - this condition must be checked (Musvoto et al., 1998). ***This restriction applies to all precipitation processes.***

A.3 CALCIUM PHOSPHATES

Five calcium phosphate crystalline species can precipitate from solutions containing Ca and P; in order of decreasing solubility these are (Table A.1): Hydroxyapatite [HAP, $Ca_5(PO_4)_3OH$], tricalcium phosphate (whitlockite) [TCP, $Ca_3(PO_4)_2$], octacalcium phosphate [OCP, $Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$], monenite (DCP, $CaHPO_4$) and dicalcium phosphate dihydrate (brushite) (DCPD, $CaHPO_4 \cdot 2H_2O$). Thermodynamically HAP is the most stable phase and could be expected to precipitate. However, it has been established that a number of species act as precursors to the precipitation of HAP, such as amorphous calcium phosphate (ACP, with approximate formulation $Ca_3(PO_4)_2 \cdot xH_2O$, similar to TCP, but with no structured crystalline order, Blumenthal et al., 1977; Betts et al., 1981), OCP and DCPD. With time these species may transform to HAP. The precursor species which first precipitate and their transformation are significantly affected by the interaction between pH, Ca and Mg concentrations in the wastewater, as well as the alkalinity and organic material present. From experimental investigations of these processes, it can be concluded that in highly supersaturated solutions containing Ca, Mg and P, DCPD and ACP are the phases that precipitate first, with DCDP precipitating at low pH (<7.0) and ACP at higher pH (Abbona et al., 1986, 1988). Precipitation follows Oswald's rule of stages (when a number of similar solids are highly supersaturated, the least stable solid will precipitate) with the initially formed metastable precursor species ACP and DCPD converting with time to the more thermodynamically stable species of DCP, HAP or TCP. The conversion from the initial to final species takes place via a solution mediated species transition with the initial species dissolving first and the new species growing. Whereas the formation of the first species is a relatively fast process, the growth of the second species is very slow such that the conversion takes a long time (from a minimum of one month to a number of years). The presence of Mg in solution strongly affects the conversion process (Arvin, 1983). Conversion of ACP to the thermodynamically stable species HAP does not take place in solutions with high Mg/Ca molar ratios > 4.0. Other factors such as high pH, high ionic strength, high HCO_3^-/PO_4^{3-} molar ratio, presence of pyrophosphates as well as certain proteins, and lack of HAP seed material also stabilize ACP. Therefore, ACP can be expected to precipitate in HNLC wastewaters such as sewage effluents, ADL and sludge dewatering liquors which have characteristics that suppress precipitation of HAP, but promote and stabilize the formation of ACP. Furthermore, in such wastewaters the transformation of ACP to HAP will be retarded so that within the timescale of typical treatment systems (~60h), significant HAP is unlikely. For these reasons, ACP was included in the model as the calcium phosphate mineral most likely to precipitate. The general kinetic rate formulation of Koutsoukos et al. (1980) given by Eq 3.6 was followed for ACP precipitation, with the default order of reaction n=2.

A.4 CALCIUM CARBONATES

Three crystalline structure varieties of $CaCO_3$ can precipitate, namely calcite, aragonite and vaterite (Table A.1). The species that precipitate have been shown to depend on the temperature, degree of supersaturation, presence of foreign ions as well as the nucleation and crystal growth rates. From the literature, calcite is the thermodynamically stable form at ambient temperature and atmospheric pressure (Roques and Girou, 1974), and will precipitate under the conditions present on treatment of HNLC wastewaters. Accordingly, precipitation of the $CaCO_3$ mineral calcite was included in the model. The rate of precipitation of $CaCO_3$ is heavily influenced by the presence of Mg, Fe, phosphate system species as well as dissolved organics, which decrease the rate and increase the solubility. These factors were recognized in the determination of the $CaCO_3$ precipitation rate, see Chapter 3.

A.5 OTHER MINERALS

Other minerals which may precipitate in HNLC wastewaters are magnesium carbonates and calcium magnesium carbonates. Two forms of magnesium carbonates are possible (Table A.1), magnesite ($MgCO_3$) and nesquehonite ($MgCO_3 \cdot 3H_2O$). Of the two, $MgCO_3$ is stable below pH ≈10.7 and $MgCO_3 \cdot 3H_2O$ is not; accordingly, $MgCO_3$ precipitation was included in the model, using the Koutsoukos et al. (1980) kinetic rate formulation given by Eq. 3.6, with the default order of reaction n=2. Two mixed carbonates of Ca and Mg occur in nature, dolomite

[$CaMg(CO_3)_2$] and huntite [$CaMg(CO_3)_4$] (Table A.1). However, the conditions under which these precipitate are not well understood, and attempts to precipitate dolomite under atmospheric conditions have not been successful (Mamais et al., 1994). Accordingly these minerals were not considered for inclusion in the model. Also not included in the model are $Ca(OH)_2$ and $Mg(OH)_2$ (Brucite) (Table A.1). These minerals precipitate only at high pH (>10), and in the presence of the other precipitating minerals incorporating Ca and Mg discussed above, the ionic products of the hydroxide and Ca and Mg species at pH < 9.5 would not exceed the solubility products of $Mg(OH)_2$ and $Ca(OH)_2$.

A.6 SOLUBILITY PRODUCTS

Solubility products in the literature for the five minerals identified above as likely to precipitate in HNLC wastewater treatment (calcite, struvite, newberyite, ACP and magnesite) are listed in Table A.1. These solubility products are at 25°C and infinite dilution, i.e. for ideal solutions unless otherwise indicated. To account for the effect of ionic strength in non-ideal solutions, in application of the kinetic model the solubility products were adjusted following the Debye-Hückel theory for low and medium salinity waters (Loewenthal et al., 1989; Musvoto et al., 1998). The solubility products could not be adjusted for temperature, since no information in the literature is available on this. The solubility products were regarded as model constants in that once the appropriate values were selected from the literature, they were not changed except for the ionic strength adjustments above. The values at 25°C and infinite dilution included in the model for the five minerals are given in Table 3.16.

Table A.1: Minerals that could possibly precipitate on aeration of ADS; values of solubility products at 25 °C and infinite dilution obtained from databases in the literature. The five compounds marked with an * were included in the kinetic model.

Solubility equilibria		pK_{sp} at 25°C			
Mineral	**Reaction**	**Stumm and Morgan (1981)**	**Nordstrom *et al.* (1990)**	**JESS (Murray and May, 1996)**	**Other sources**
*Calcite/Aragonite/Vaterite	$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$	8.42; 8.22	8.48; 8.34	8.5; 8.22	8.3[e] ; 7.8[f] ; 6.7[h]
*Magnesite	$MgCO_3 \rightleftharpoons Mg^{2+} + CO_3^{2-}$	7.46; 8.2		7.46; 8.2	5.9[e] ; 7.9[f]
Nesquehonite	$MgCO_3.3H_2O \rightleftharpoons Mg^{2+} + CO_3^{2-} + 3H_2O$	5.19		4.67; 5.19	
Dolomite (disordered)	$CaMg(CO_3)_2 \rightleftharpoons Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	16.7	16.54	16.5	
Dolomite (ordered)	$CaMg(CO_3)_2 \rightleftharpoons Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$		17.09	16.98	17[f]
Huntite	$CaMg(CO_3)_4 \rightleftharpoons Ca^{2+} + Mg^{2+} + 4CO_3^{2-}$				N/A
Calcium hydroxide	$Ca(OH)_2(s) \rightleftharpoons Ca^{2+} + 2OH^-$	5.2	5.2		
Brucite	$Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + 2OH^-$	11.16	11.16		10.7[e]
HAP	$Ca_{10}(PO_4)_6(OH)_2(s) \rightleftharpoons 10Ca^{2+} + 6PO_4^{3-} + 2OH^-$	114		57.5; 48.6	57.8[f]
TCP	$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$			32.63; 32.7	
OCP	$Ca_8(HPO_4)_2(PO_4)_4.5H_2O \rightleftharpoons 8Ca^{2+} + 2HPO_4^{2-} + 4PO_4^{3-} + 5H_2O$				94.16[i]; 72.53[i]
DCP	$CaHPO_4(s) \rightleftharpoons Ca^{2+} + HPO_4^{2-}$	6.6		6.6; 6.5	
DCPD	$CaHPO_4.2H_2O \rightleftharpoons Ca^{2+} + HPO_4^{2-} + 2H_2O$	6.6		6.6	
*ACP	$Ca_3(PO_4)_2.xH_2O \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-} + xH_2O$	31.45			26.0[a];; 25.2[b], 24[e];25.46[g]
*Struvite	$MgNH_4PO_4.6H_2O(s) \rightleftharpoons Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O$	12.6		13.16	12.6[a]; 12.72[c]; 13.15[d], 13[e]
*Newberyite	$MgHPO_4.3H_2O(s) \rightleftharpoons Mg^{2+} + HPO_4^{2-} + 3H_2O$			5.8	5.51[c] ; 5.8[d]
Bobierrite	$Mg_3(PO_4)_2.8H_2O(s) \rightleftharpoons 3Mg^{2+} + 2PO_4^{3-} + 8H_2O$			25.2	25.2[d]
Trimagnesium phosphate	$Mg_3(PO_4)_2.22H_2O(s) \rightleftharpoons 3Mg^{2+} + 2PO_4^{3-} + 22H_2O$				23.1[d]

Notes: 1. Temperature dependency of solubility products for some of the reactions has been given by Stumm and Morgan (1981) and Nordstrom *et al.* (1990).

2. Lettered references apply to the following: [a]Butler (1964); [b]Meyer and Eanes (1978) cited by Moutin *et al.* (1992); [c] Abbona *et al.* (1982); [d] Taylor *et al.* (1963) cited by Scott *et al.* (1991); [e] Mamais *et al.* (1994); [f]Ferguson and McCarty (1971). [g]Hoffmann and Marais (1977) - value from Butler (1964) corrected for ionic strength. [h]Wiechers et al. (1980); [i]Verbeeck and Devenyns (1992).

APPENDIX B

STRIPPING OF GASES

Stripping of CO_2 and NH_3 gasses is being widely used in commercial processes (e.g. packed bed towers), such as for the treatment of anaerobic digester supernatants and sludge dewatering liquors. Stripping of CO_2 has the advantage of raising the pH to ranges (>8) where precipitation of phosphates is likely to occur. The raising of pH through stripping reduces the amount of chemicals which are normally added to raise the pH to sufficiently high levels for phosphate precipitation. At high pH, NH_3 ammonia stripping occurs, which removes the nitrogen from the wastewater. The stripping methods applied in commercial processes are usually very expensive (e.g. the elevation of temperature to about 70 °C or the creation of a vacuum to break the carbonate buffers and evolve CO_2). In the model developed for this research, it was decided to strip the gases using normal aeration as in the activated sludge process. The gas stripping kinetics were modelled on this basis, and this is summarised below (for details see Musvoto *et al*., 1998).

B.1 RATE EQUATIONS

B.1.1 Carbon dioxide exchange

In solution the carbonate weak acid/base consists of four species, viz. CO_2 dissolved; carbonic acid (H_2CO_3); bicarbonate (HCO_3^-); and carbonate (CO_3^{2-}). The ratio CO_2 dissolved: H_2CO_3 is fixed and equal to 99.76 : 0.24 at 25°C and is independent of pH and ionic strength. Accordingly, these two species are dealt with as a single combined species, $H_2CO_3^*$ (Stumm and Morgan, 1970), i.e.:

$$[H_2CO_3^*] = [CO_2\ \text{dissolved}] + [H_2CO_3] \qquad (B.1)$$

The CO_2 dissolved, and hence $H_2CO_3^*$, tends to equilibrium with the partial pressure of CO_2 (gas) outside the liquid, i.e.:

$$CO_2\ (g) \rightleftharpoons CO_2\ \text{dissolved} \qquad (B.2a)$$

or equivalently:

$$CO_2\ (g) \rightleftharpoons H_2CO_3^* \qquad (B.2b)$$

This gives rise to CO_2 exchange at the liquid/gas interface, resulting in loss or gain of $H_2CO_3^*$ in the solution, and accordingly in total carbonate species concentration. Thus, CO_2 loss or gain would need to be included in the model. This can be done by following the same approach used for the weak acid/base dissociation reactions, i.e. by modelling separately the rate of the forward and reverse reactions in Eq. (B.2b). For the forward reaction:

$$r_f = K'_{fCO2}\,[\,CO_2\,(g)\,] \tag{B.3}$$

where:

r_f = rate of forward reaction, Eq. (B.2b)
K'_{fCO2} = apparent specific rate constant for forward reaction.

Similarly, for the reverse reaction:

$$r_r = K'_{rCO2}\,[H_2CO_3^*\,] \tag{B.4}$$

where:

r_r = rate of reverse reaction, Eq. (B.2b)
K'_{rCO2} = apparent specific rate constant for reverse reaction.

The approach of modelling the forward and reverse reactions separately has been used to include CO_2 exchange in the model. Note that in the model the concentration of $CO_2(g)$ is kept constant; the $CO_2(g)$ is included as a compound in the model only for continuity. The constant concentration of $CO_2(g)$ can be calculated from the partial pressure of CO_2 using Daltons' law of partial pressure (Stumm and Morgan, 1970):

$$[\,CO_2\,(g)\,] = \rho CO_2/RT \tag{B.5}$$

where:

ρCO_2 = partial pressure of CO_2 (atm)
R = universal gas constant
= $8.20575 \cdot 10^{-2}$ (ℓ atm/K/mol)
T = temperature in Kelvin

In Eqs. (B.3) and (B.4) values are required for the apparent specific rate constants for the forward (K'_{fCO2}) and reverse (K'_{rCO2}) reactions respectively. When considering the equilibrium condition, exact values for the specific rate constants are not required. However, the relative values for K'_{fCO2} and K'_{rCO2} are important since the relative values will establish the equilibrium concentration of $H_2CO_3^*$. At equilibrium:

$$r_f = r_r \tag{B.6}$$

Substituting Eqs. (B.3) and (B.4) into Eq. (B.6) and rearranging gives:

$$\frac{K'_{fCO2}}{K'_{rCO2}} = \frac{[H_2CO_3^*]}{[CO_2(g)]} = K'_{eqCO2} \tag{B.7a}$$

where:

K'_{eqCO2} = apparent equilibrium constant for CO_2 exchange

From Eq. (B.7a):

$$K'_{fCO2} = K'_{eqCO2} \cdot K'_{rCO2} \tag{B.7b}$$

Thus, if K'_{eqCO2} is known, by selecting a value for K'_{rCO2} the relative value for K'_{fCO2} can be calculated and the correct equilibrium condition will be established giving the correct equilibrium concentration of $[H_2CO_3^*]$. What is required is to determine a value for K'_{eqCO2}. This can be done by noting that at equilibrium (Stumm and Morgan, 1970):

$$K'_{H,CO2} = K'_{eqCO2} / RT \tag{B.7c}$$

where:

$K'_{H,CO2}$ = Henry's law constant for CO_2 (mol/ℓ/atm)
K'_{eqCO2} = $K'_{D,CO2}$
$K'_{D,CO2}$ = distribution (mass law) constant

Values for the variation in Henry's law constant for CO_2 ($K'_{H,CO2}$) with temperature are available in the literature (Friend and Loewenthal, 1992). From $K'_{H,CO2}$, the equilibrium constant (K'_{eqCO2}) can be calculated using Eq. (B.7c), and for a selected value for K'_{rCO2}, K'_{fCO2} can be calculated using Eq. (B.7b). To select a value for K'_{rCO2}, if only the equilibrium condition is considered then an exact value is not required; the only requirement is that equilibrium must be reached by the end of the simulation. If, however, the time dependent response is to be determined, then the value for K'_{rCO2} will have to be determined by calibration for the specific situation, because the rate of CO_2 exchange will depend on site specific conditions (such as aeration rates, mixing, solids, etc.). This can be done directly, or by relating the rate of CO_2 exchange to oxygen (see below).

A near identical formulation for CO_2 exchange can be derived from the theories of interphase mass transfer; here the rate of change in the bulk liquid concentration is considered to be proportional to the product of a mass transfer rate constant times a concentration driving force:

$$\frac{dC_L}{dt} = K_{LA}(C_e - C_L) \tag{B.8}$$

where:

K_{LA} = overall liquid phase mass transfer rate coefficient (d^{-1})
C_e = equilibrium concentration in the bulk liquid
C_L = actual concentration in the bulk liquid

With exchange to the atmosphere, from Daltons' and Henry's laws (Stumm and Morgan, 1970), the dissolved CO_2 equilibrium concentration (C_{eCO2}) is given by:

$$C_{eCO2} = K'_{H,CO2} \, \rho CO_2 \tag{B.9}$$

Substituting the equilibrium CO_2 concentration from Eq. (B.9) into Eq. (B.8) and accepting that $C_L = [H_2CO_3^*]$, the rate of exchange of CO_2 is:

$$\frac{dH_2CO_3^*}{dt} = K_{LA,CO2}(\,K_{H,CO2}\cdot\rho CO_2 - [H_2CO_3^*]) \qquad (B.10)$$

This equation is identical to the ***sum*** of the forward and reverse reaction rates used in the model, substituting for $[CO_2(g)]$ from Eq. (B.5) and accepting from Eqs. (B.7b) and (B.7c) that $K'_{fCO2} = K'_{H,CO2}\cdot RT\cdot K'_{rCO2}$ and that $K'_{rCO2} = K'_{LA,CO2}$.

B.1.2 Ammonia exchange

When stripping to the atmosphere, for ammonia (NH_3) it can be assumed that the atmosphere acts as an infinite sink. Accordingly, there is no dissolution of NH_3 into solution, only loss from solution. The loss of ammonia can be modelled as:

$$\frac{dNH_3}{dt} = K_{LA,NH3}[NH_3] \qquad (B.11)$$

Again, this expression can be derived from the theories of interphase transfer, accepting the equilibrium concentration in the bulk liquid as zero.

B.2 USE OF OXYGEN AS A REFERENCE COMPOUND

In order to model the rate of transfer of a gas, the mass transfer coefficient K_{LA} needs to be measured/calibrated. In work involving the stripping of organic compounds from water, several authors (Rsathburn and Tai, 1981; Smith *et al.*, 1980,1981; Roberts and Dändliker, 1983; Roberts *et al.*, 1984) proposed the use of a tracer or reference compound to predict the extent of mass transfer of organic compounds at gas-liquid interfaces. This is convenient because only the mass transfer coefficient for the reference compound needs to be measured and since the geometric characteristics and the hydrodynamic conditions in a given reactor do not change, the mass transfer coefficients for the other compound will be calculated from the reference compound. The rate of mass transfer of a compound I is thus related to the rate of mass transfer of the reference compound r by the proportionality factor ψ (Munz and Roberts,1989):

$$\frac{\psi_i = \dfrac{K_{L,i}}{K_{L,r}} = \left(\dfrac{D_{L,i}}{D_{L,r}}\right)^n = K_{L,i}}{K_{L,r}} \qquad (B.12)$$

Munz and Roberts (1989) also reviewed the basic underlying concepts of mass transfer across air-water interfaces. From this review they defined the proportionality factor ψ such that it becomes applicable for all compounds independently of their volatility and oxygen was found to be the most suitable reference compound. Thus

$$\psi = \left|\frac{D_{L,i}}{D_{L,O_2}}\right|^{n}\left[1 + \frac{1}{(k_G/k_L)H_{c,i}}\right]^{-1} = \frac{K_{L,i}}{K_{L,O_2}} \qquad \text{(B.13)}$$

Hence, the rate of stripping of a gas in a given situation can be calculated from the rate of stripping or absorption of oxygen. Oxygen was used as the reference compound because mass transfer data are ample, measurements can easily be made and oxygen transfer is usually the main objective in certain treatment processes, such as the activated sludge process. Munz and Roberts (1989) carried experimental work to verify this approach and concluded that values of $k_G/k_L = 40$ are used for surface aeration and that oxygen can be used as a reference compound if the solute has a value for the dimensionless Henry's law (H_c) constant ≥ 0.55.

In the AQUASIM model, the reference compound approach was used to calculate the mass transfer coefficient for CO_2 ($H_c = 1.39$ at 20^0C), but could not be applied for NH_3 ($H_c = 5.68x10^{-4}$) which is less volatile; the mass transfer coefficient for ammonia had to be measured during the experimental work. However, even though the mass transfer coefficient for CO_2 was determined from the reference species oxygen, in application of the model the value for oxygen was selected such that the CO_2 exchange was correctly predicted, i.e. in effect the mass transfer coefficient for CO_2 was calibrated. This was because oxygen transfer data were not measured. Despite this, the general approach to modelling gas exchange was retained in the model for future applications where oxygen transfer data are measured.