UNIVERSITY OF CAPE TOWN
Department of Civil Engineering

FINAL REPORT
to the
Water Research Commission
on the contract

CONSOLIDATION OF ACTIVATED SLUDGE AND WATER CHEMISTRY RESEARCH

(Jan 1988 – Dec 1990)

by

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SYNOPSIS

In 1988 a 3 year contract was set up between the Water Research Commission (WRC) and the University of Cape Town (UCT) to:

- provide opportunity to publish the research work undertaken so far,
- fill in the areas of research perceived to require attention in order to
  - update the activated sludge system design manual,
  - extend the general kinetic model to incorporate BEPR,
  - extend the theory on water chemistry to include mixtures of weak acid/bases,
- promote technology transfer by means of seminars, updating of design manuals and development of user–friendly computer programs.

To meet these objectives the following tasks were identified:

- Re–evaluation of the technology available on completely aerobic nitrification and on anoxic/aerobic nitrification/denitrification (ND) systems.
- Consolidation of research into nitrification/denitrification/biological excess phosphorus removal (NDBEPR) systems.
- Extention of the weak acid/base chemistry of the carbonate system in aqueous solution to include a mixture of weak acid/base systems.

During the course of the contract a further task was identified:

- Chemical phosphorus removal from municipal wastewater by the disposal of waste alum sludge to the activated sludge system.

1. NITRIFICATION AND NITRIFICATION/DENITRIFICATION SYSTEMS

From a re-evaluation of the design procedures set out in the design manual, in the light of information that has become available since the manual was published, it was concluded that the procedures are still valid for nitrification and nitrification/denitrification (ND) systems. With regard to the general ND kinetic model developed at UCT to simulate the dynamic behaviour of these systems, a user-friendly computer program for use on personal computers has been developed to make the model more widely available. The computer program will be distributed by the WRC together with a user manual.

2. NDBEPR SYSTEMS

The research on NDBEPR systems comprised the following:

- Acid fermentation of primary sludge.

- Kinetics of denitrification in NDBEPR systems.
- Modelling of biological excess phosphorus removal (BEPR).

Acid fermentation of primary sludge

Full scale studies on biological excess phosphorus removal (BEPR) plants had demonstrated that the BEPR can be increased by acid fermenting the settled sludge in the primary settling tank, and adding either the fermented sludge, or the acids elutriated from the sludge, to the influent of the BEPR removal plant (Pitman *et al.*, 1983; Pitman and Lötter, 1986). Considerable uncertainty still existed, however, as to the mass of short chain fatty acids (SCFA) that can be generated and the degree of improvement in phosphorus removal that can be expected. This study was undertaken to (1) evaluate SCFA production in laboratory scale batch, single and in-series completely mixed reactor systems, (2) develop a model for acid fermentation, and (3) theoretically estimate the effect of acid addition on BEPR.

Laboratory-scale studies of short chain fatty acid (SCFA) production by acid fermentation of primary settling tank underflow (VSS) from Mitchell's Plain, Cape Town, at 20° C showed that: Maximum SCFA (as COD) potential = 0,17.VSS (as COD); soluble non-SCFA (COD) equal to the SCFA (COD) is generated; reaction is approximately first order with K = 0,16 mgCOD/mgCOD/d; for the same total retention time up to 6 days, there is no practical difference in SCFA (COD) produced between batch, in-series, single and accumulating batch reactor systems; recommended retention time, 3d, gives ≈ 2/3 of the potential SCFA production and theoretically the P removal would be increased by about 14 percent. The effect of soluble non-SCFA (COD) on P removal was not studied, but merits future study.

Kinetics of denitrification in NDBEPR systems

The denitrification kinetics, as developed from the response of anoxic reactors in ND systems, had been incorporated unmodified in the design procedures for NDBEPR systems. However, there is an inconsistancy in this approach:

> The readily biodegradable COD (RBCOD) appears to be used twice, first in the anaerobic reactor where it is converted to short-chain fatty acids (SCFA) which are sequestered by the polyP organisms, and again in the primary anoxic reactor for denitrification. This would imply that the polyP organisms must denitrify appreciably, yet studies on enhanced cultures of polyP organisms have indicated that they do not denitrify to any significant degree.

Using plugflow anoxic reactors and batch tests, an experimental investigation was undertaken into the kinetics of denitrification in nitrification denitrification biological excess phosphorus removal (NDBEPR) systems. It was found that (1) in the primary and secondary anoxic reactors, the specific rate constant for denitrification associated with the utilization of slowly biodegradable COD (SBCOD) is respectively 2½ and 1½ times higher than in these reactors in nitrification denitrification (ND) systems and (2) in the primary anoxic reactor, the rapid rate of denitrification attributable to readily biodegradable COD is absent. The increased rate is hypothesized to be due to a stimulation in the active sludge mass of an increased rate of hydrolysis of SBCOD in the anoxic reactors of the NDBEPR system, apparently induced by the presence of the anaerobic reactor in these systems.

Modelling of BEPR

In the preceding contract, the objective was set to develop a general kinetic model that describes NDBEPR system dynamic behaviour. By the end of the preceding contract (December 1987) considerable progress had been made in achieving this objective: By using enhanced cultures of polyP organisms, the kinetic and stoichiometric characteristics of the polyP organisms had been identified and incorporated in a kinetic model describing the BEPR response of the enhanced cultures. In this contract the work on the model was continued: By accepting constant flow and load conditions, and from examination of the degree of completion of the processes (under the prevailing kinetics), many of the processes were found to be virtually complete – the kinetic relationship no longer served any function and could be replaced by stoichiometric relationships. From this simplified model, by mass balances a number of steady state equations were developed for the enhanced cultures, for polyP organism active and endogenous masses, and P release, uptake and removal due to these masses. Having developed the steady state model for the enhanced culture systems, this model was extended to a steady state model that incorporates mixed cultures of polyP and non-polyP organisms. This extention was facilitated by recognizing that the polyP and non-polyP organisms act virtually independently. However, in the model two interactions between the organism groups were identified:

(1) In the anaerobic reactor the non-polyP organisms convert RBCOD to SCFA, for sequestration by the polyP organisms.

(2) With recycling of nitrate or oxygen to the anaerobic reactor, utilization of RBCOD by the non-polyP organisms reduces the RBCOD available for conversion and thus the amount of SCFA sequestered by the polyP organisms.

Taking due cognizance of the above, the biodegradable COD was split into two fractions, one eventually to be used by the polyP organisms and the other to be used by the non-polyP organisms. Because of the independence of action of these two organism groups, it was possible to use:

(1) The simplified polyP organism enhanced culture steady state model for calculating the polyP organism active and endogenous masses formed from the sequestered substrate, and the P release, uptake and removal mediated by these masses.

(2) The steady state activated sludge model (Marais and Ekama, 1976; WRC, 1984) to calculate the non–polyP organism active and endogenous masses formed from the remaining substrate, the rate of conversion of RBCOD to SCFA in the anaerobic reactor, the inert VSS accumulated from the influent, and the P requirement of, and hence P removal associated with, the active, endogenous and inert masses.

The predictive power of the steady state mixed culture BEPR model was evaluated against observations made on 30 laboratory scale NDBEPR systems; good correlation was obtained between predicted and measured P release, P removal and VSS concentration.

The steady state mixed culture BEPR model constitutes the most recent step in modelling BEPR. In the model the nitrate recycled to the anaerobic reactor must be known: In the experimental evaluations this was available from experimental measurements; in design it has been the practice to use the denitrification theory set out in the design manual. However, as noted in the previous section, the

denitrification kinetics in NDBEPR systems are not the same as accepted in the design manual. Accordingly, in the new consolidation contract it is proposed to incorporate the denitrification aspects, as measured in NDBEPR systems, into the steady state mixed culture BEPR model, to give a steady state NDBEPR model. Having achieved this, it will be possible to integrate the kinetic and stoichiometric aspects of ND (from the investigation in the previous section) and BEPR (from the enhanced culture kinetic model) in a general dynamic NDBEPR mixed culture kinetic model.

3. WATER CHEMISTRY

The need for this task arose from the recognition that in many aqueous systems (e.g. wastewaters) mixtures of weak acid/bases are present. The water chemistry theory available when the contract commenced did not provide information on how to deal with these mixtures. To extend the water chemistry theory to include mixtures of weak acid/bases, two problems had to be resolved:

- estimation of the concentrations of the species of each of the weak acid/base subsystems, called *characterization*,
- estimation of chemicals to be added to change the pH and species concentrations of the subsystems to desired values, called *dosing estimation*.

Characterization of mixed weak acid/base systems

In characterizing a solution containing the carbonate system plus weak acid/bases, the principal difficulty arises in determining the carbonate weak acid/base total species concentration; total species concentrations of all the common weak acid/bases can be measured directly without undue difficulty, but not that of the carbonate weak acid/base. The carbonate subsystem can exist in three phases, solid, aqueous and gaseous; consequently, with the usual methods of sampling, CO_2 (a carbonate species) can be lost or gained due to differences in the partial pressure of CO_2 between the solution and the air.

For the *carbonate system only in solution*, the literature records the establishment of the mass parameter alkalinity as alternative to the total carbonate species parameter. Measurement of alkalinity plus the pH of the solution provides sufficient information to calculate the total carbonate species concentration in the system. The alkalinity parameter is defined relative to a selected reference solution state. With the carbonate system, three alkalinities can be defined, relative to the $H_2CO_3^*$, HCO_3^- and CO_3^{2-} reference solution states. The alkalinity relative to the $H_2CO_3^*$ reference solution state, termed $H_2CO_3^*$ alkalinity, has the advantage that its magnitude is not influenced by loss or gain of CO_2, which overcomes the sampling problem described earlier. With only the carbonate system present in solution, procedures to identify the $H_2CO_3^*$ solution reference state (and the HCO_3^- and CO_3^{2-} solution reference states) have been developed, some semi-empirical, some based on prior pH experimental titrations; in this way, an alkalinity relative to the solution reference state can be measured and the total carbonate species concentration determined. However, for the carbonate system only in solution, Gran (1952) had proposed an ingenious method which allows the $H_2CO_3^*$ alkalinity to be determined relative to the reference solution state without experimentally identifying the reference state.

With mixtures of weak acid/bases in solution, empirical or experimental

identification of the reference solution state is well-nigh impossible and, consequently, using the reference solution state approach provides for only an *approximate* empirically defined alkalinity measurement. It was the intention in this task to develop procedures whereby the carbonate system could be evaluated in a mixture of weak acid/bases.

To achieve this, the Gran function was extended to the carbonate subsystem in mixtures of weak acid/bases. The extention required a generalization of the concepts of alkalinity and acidity and the development of a consistant nomenclature. The extended method was tested experimentally using a number of made up mixtures of the carbonate, phosphate, acetate and ammonia subsystems and the alkalinity results were found to be within 1% of the expected values.

Dosing estimation in mixed weak acid base systems

Having characterized a solution containing a mixture of weak acid/bases, the next important aspect is that of chemical conditioning, that is, determining the chemical type and dosage to achieve a desired change in the chemical state of the solution.

It was shown that the solution alkalinity for an aqueous mixture of weak acid/bases (relative to a selected solution reference state defined by selected weak acid/base reference species) can be expressed as the sum of the subsystem alkalinities, one for each weak acid/base (relative to the same selected weak acid/base reference species) plus a water subsystem alkalinity (relative to H_2O where $[H^+] = [OH^-] = 10^{-7}$ moles/ℓ). Making use of weak acid/base subsystem and water subsystem alkalinities, relatively simple dosing estimation algorithms were developed.

5. CHEMICAL PHOSPHORUS REMOVAL FROM MUNICIPAL WASTEWATER BY THE DISPOSAL OF WASTE ALUM SLUDGE TO THE ACTIVATED SLUDGE SYSTEM

In many instances waterworks' waste alum sludge is disposed of by discharging it into a stream. In this task the disposal of alum sludge to activated sludge systems treating municipal sewage was investigated. The advantages perceived were that not only would it provide a better means of disposal of the alum sludge but it also may stimulate some phosphorus removal from the wastewater by chemical precipitation.

By monitoring P removal in laboratory scale experimental and control activated sludge systems it was found that at steady state the alum sludge stimulated a P removal of 0,18 mgP/(mg inorganic suspended solids, ISS) when the pH of the mixed liquor averaged 7,6; this is about 1/3rd of the stoichiometric removal ratio. To check this value, ancillary stirred jar batch precipitation tests were conducted for a period equal to the sludge age of the experimental system, 20 days, with both unused alum and alum sludge at different Aℓ/P ratios and pH values. It was found that the mgP removal/mg ISS added for the alum sludge, after 20 days,

- decreased from 0,54 to 0,29 as the test pH increased from 6,8 to 7,8,
- compared favourably with the unused alum values, and
- was approximately stoichiometric at pH between 6,8 and 7,3.

Analysis of the data has not been completed, so that it is not yet possible to advance an explanation for the apparent difference in P removal/ unit ISS between the batch and continuously fed systems.

Other interesting results that emerged from the work were:

- The VSS and COD of the alum sludge was not biodegradable and accumulated with the sludge in the biological reactor. Hence, the oxygen demand of the activated sludge system was not increased but the sludge production increased by the mass of alum sludge added. The filtered effluent COD and TKN (and turbidity) did not increase.

- The dewaterability of the alum sludge was rather poor. However, the dewaterability for the alum/activated sludge mixture (45% of TSS being alum sludge TSS) was the same as that of the activated sludge only, indicating that the dewaterability of the slum sludge is improved during its retention in the activated sludge plant for 20 days. This improvement is not obtained by simply mixing the two sludges – if this is done a dewaterability is obtained somewhere between the two sludges depending on their proportions in the mixture. The improvement arises from the exchange of the OH^- with PO_4^{3-} on the $A\ell^{3+}$ thereby changing the gelatinous $A\ell(OH)_3$ to an $A\ell PO_4$ precipitate.

- COD removal, nitrification and denitrification were not affected by alum sludge addition.

- Alum/activated sludge mixture settled slightly better than the activated sludge alone but still showed sporadic low F/M filamentous bulking incidents with DSVI's > 250 mℓ/g.

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- Mr A R Pitman – Johannesburg City Engineer's Department
- Dr L Lötter – Johannesburg City Health Department
- Mr P W Weideman – Water Research Commission (Committee Secretary)

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PUBLICATIONS DURING CONTRACT PERIOD (JANUARY 1988 TO DECEMBER 1990)

An important objective of this contract was the transfer of technology generated under previous contracts, and of research results obtained during the contract period. In this regard the Water Research Group participated in a number of seminars and conferences (local and international), submitted a number of papers for publication in refereed journals, and published a number of books and reports. These contributions are listed below:

A. BOOKS PUBLISHED

1. Loewenthal R E, G A Ekama and G v R Marais (1988). STASOFT : An interactive computer programme for softening and stabilization of Municipal Waters. Water Research Commission, P O Box 824, Pretoria 0001, South Africa.

2. Dold P L, M C Wentzel, A E Billing, G A Ekama and G v R Marais (1991). Activated sludge system simulation programs : Version 1.0 Nitrification and nitrification/denitrification systems. Water Research Commission, P O Box 824, Pretoria 0001, South Africa.

B. PAPERS PUBLISHED

Water chemistry and water conditioning

Papers published (refereed journals)

1. Loewenthal R E, G A Ekama and G v R Marais (1988). STASOFT : A user friendly interactive computer program for softening and stabilization of municipal waters. Water SA, 14(3), 159-162

2. Loewenthal R E, G A Ekama and G v R Marais (1989). Mixed weak acid/base systems Part I – Mixture characterization. Water SA, 15(1), 3-24

3. Loewenthal R E, M C Wentzel, G A Ekama and G v R Marais (1991). Mixed weak acid/base systems Part II – Dosing estimation, aqueous phase. Water SA, 17(2), 107–122.

Conference papers (refereed in abstract and published in proceedings)

1. Loewenthal R E and G A Ekama (1988). Quality changes in dolomitic underground waters when brought to the surface. Presented at Workshop on dolomitic ground waters of the PWV area, Geological Society of South Africa, Pretoria, March 1988

2. Loewenthal R E (1989). Capacity parameters for solving equilibrium problems in aqueous systems. Procs. 4th International chemistry conference in Africa on 'The state of chemistry and its contribution to development in Africa', Zomba, Malawi, July 1989

Nitrification/denitrification/biological excess phosphorus removal

Papers published (refereed journals)

1. Wentzel M C, R E Loewenthal, G A Ekama and G v R Marais (1988). Enhanced polyphosphate organism cultures in activated sludge systems – Part 1: Enhanced culture development. Water SA, 14(2), 81-92

2. Wentzel M C, G A Ekama, R E Loewenthal, P L Dold and G v R Marais (1989). Enhanced polyphosphate organism cultures in activated sludge systems Part II – Experimental behaviour. Water SA, 15(2), 71-88

3. Wentzel M C, P L Dold, G A Ekama and G v R Marais (1989). Enhanced polyphosphate organism cultures in activated sludge systems Part III – Kinetic model. Water SA, 15(2), 89-102

4. Wentzel M C, G A Ekama, P L Dold and G v R Marais (1990). Biological excess phosphorus removal – steady state process design. Water SA, 16(1), 29-48

5. Wentzel M C, G A Ekama and G v R Marais (1991). Kinetics of nitrification denitrification biological excess phosphorus removal systems – a review. Presented at 15th IAWPRC biennial conference, Kyoto (1990). Wat.Sci.Tech., 23(4/6), 555-565.

6. Wentzel M C, L H Lötter, G A Ekama, R E Loewenthal and G v R Marais (1991). Evaluation of biochemical models for biological excess phosphorus removal. Presented at 15th IAWPRC biennial conference, Kyoto (1990). Wat.Sci.Tech., 23(4/6), 567-576.

7. Clayton J A, G A Ekama, M C Wentzel and G v R Marais (1991). Denitrification kinetics in biological nitrogen and phosphorus removal systems treating municipal wastewaters. Presented at 15th IAWPRC biennial conference, Kyoto (1990). Wat.Sci.Tech., 23(4/6), 1025-1035.

Conference papers (published in proceedings)

1. Marais G v R (1988). Steady state design of biological excess phosphorus removal. Presented at Technology Transfer Seminar arranged jointly by the Johannesburg City Council, Water Research Commission and University of Cape Town, October 1988, Johannesburg, Procs. 6.1-6.33

2. Wentzel M C (1988). Kinetics of biological excess phosphorus removal. Presented at Technology Transfer Seminar arranged jointly by the Johannesburg City Council, Water Research Commission and University of Cape Town, October 1988, Johannesburg, Procs. 5.1-5.46

3. Ekama G A (1988). Modelling and design of single sludge activated sludge systems for biological removal of carbon, nitrogen and phosphorus. Presented at 1988 NSC/CSIR Binational Symposium on Environmental Technology, Taipei, November 1988, Procs. 289-315

4. Burke R A, M C Wentzel, P L Dold, G A Ekama and G v R Marais (1989). Biological excess phosphorus removal in short sludge age activated sludge systems. Procs. 1st biennial WISA Conference, Cape Town, March 1989

5. Ekama G A, M C Wentzel and G v R Marais (1990). The development of nitrification denitrification biological excess phosphorus removal technology – a review. Invited plenary paper. Procs. First IAWPRC/AWWA biological nutrient removal conference, (BNR1) Bendigo, Australia

6. Wentzel M C (1990). Phosphorus removal from sewage in activated sludge systems. Invited paper, seminar of Association of Water Treatment Personnel (Western Cape Group), November 1990.

7. Wentzel M C (1991). Future of nutrient removal in South Africa. Presented at first open meeting of the WISA Nutrient Removal Technical Division, February 1991.

8. Lilley I D, M C Wentzel, R E Loewenthal, G A Ekama and G v R Marais (1991). Acid fermentation of primary sludge at 20° C. Accepted for presentation at WISA Biennial Conference, May 1991.

Research reports released

W series reports

W 59 (1988) Wentzel M C, G A Ekama, P L Dold, R E Loewenthal and G v R Marais (1988). Biological excess phosphorus removal in activated sludge systems

W 60 (1988) Wentzel M C, G A Ekama, P L Dold, R E Loewenthal and G v R Marais (1988). Biological excess phosphate removal. Final report to the Water Research Commission on a four year contract (1984-1987), WRC Report No. 148/1/88

W 63 (1989) Clayton J A, G A Ekama, M C Wentzel and G v R Marais. Denitrification kinetics in biological nitrogen and phosphorus removal activated sludge systems

W 64 (1990) Lilley I D, M C Wentzel, R E Loewenthal, G A Ekama and G v R Marais. Acid fermentation of primary sludge at 20° C

W 66 (1991) Power S P B, G A Ekama, M C Wentzel and G v R Marais. Chemical phosphorus removal in activated sludge by the addition of waste alum sludge

CHAPTER 1

INTRODUCTION

Since 1968 the Water Research Group in the Department of Civil Engineering at the University of Cape Town has conducted extensive research into

- wastewater treatment by means of the activated sludge system, and
- water chemistry.

The wastewater treatment research covered the spectrum of processes in the activated sludge system, such as organic energy (COD) removal, nitrification, denitrification and biological excess phosphorus removal (Marais and Ekama, 1976; Dold *et al.*, 1980; van Haandel *et al.*, 1981; Siebritz *et al.*, 1983). By 1984 the information gained on the activated sludge system was sufficient to enable a manual to be written, in collaboration with Johannesburg City Council and the National Institute for Water Research, for the design of aerobic (COD removal and nitrification), anoxic/aerobic (COD removal, nitrification and denitrification) and anaerobic/anoxic/aerobic (COD removal, nitrification, denitrification and biological excess phosphorus removal) systems, the last one being designated as the nutrient (nitrogen + phosphorus) removal system (WRC 1984). This design manual, disseminated by the Water Research Commission, has received a very favourable response from the research and engineering communities. In addition to the design manual, a general kinetic model describing the behaviour of aerobic and anoxic/aerobic systems had been developed (van Haandel *et al.*, 1981). This kinetic model also has been received favourably – an international task group, constituted by the International Association on Water Pollution Research and Control (IAWPRC), to enquire into the best kinetic model, accepted the UCT model with some minor modifications (IAWPRC, 1987).

The water chemistry research covered principally the behaviour of the calcium/magnesium/carbonate weak acid/base in low salinity (total dissolved solids, TDS < 1000 mg/ℓ) waters (Loewenthal and Marais, 1976; 1983). By the end of 1987 a manual had been written to assist in the chemical treatment of low salinity waters for domestic use, incorporating characterization and dosing estimation for softening, stabilization, 3-phase equilibria, etc. (Loewenthal *et al.*, 1986). This manual made extensive use of graphical procedures to reduce the labour of calculation, to such a level that routine application was achieved. To assist application even further, a user-friendly computer program was developed that replaced the graphical procedures with numerical algorithms (Loewenthal *et al.*, 1988). The design manual and the computer program (with its user manual) have been distributed through the Water Research Commission and also have been favourably received.

With regard to the activated sludge system design manual, for anaerobic/anoxic/aerobic nutrient removal systems, phosphorus removal was formulated empirically in terms of some of the system parameters such as anaerobic mass fraction, available readily biodegradable COD concentration and active mass concentration. Organisms directly implicated in biological excess phosphorus removal (BEPR) did not feature and the BEPR phenomenon was not linked to any basic biological or biochemical behaviour. As a consequence designs based on the

manual had a measure of reliability only within the range of conditions from which the empirical BEPR model in the manual had been developed; indeed there was a measure of uncertainty even with designs within this range because the basic mechanisms underlying the behaviour were not understood. Furthermore, BEPR did not feature in the general kinetic model so that no model to estimate the dynamic behaviour of BEPR was available for the purposes of design, operation and control of nutrient removal plants.

Accordingly, in 1984 a 3–year contract with the Water Research Commission (Contract No. K148) was undertaken to investigate BEPR with the principal objective to develop a microbiologically/biochemically based kinetic model for BEPR. From the research work under this contract the main development in the understanding of BEPR can be summarized as follows (Wentzel *et al.*, 1988a; 1988b):

(1) A biochemical model for BEPR was developed describing the pathways and their regulation. This model explains most of the observations relating to BEPR in the nutrient removal system.

(2) Enhanced cultures of polyP organisms were successfully developed in the Modified Bardenpho and UCT systems. By conducting batch tests on sludge harvested from the enhanced culture systems, the processes and compounds associated with BEPR could be delineated.

(3) With the processes and compounds defined, a mathematical model was developed in which the kinetics of the process rates and their stoichiometry could be quantitatively expressed. This model described the BEPR response closely, in batch tests on sludge harvested from the enhanced culture systems, and in enhanced culture systems under constant flow and load conditions.

The research tasks above in essence completed the basic enquiry into the biochemical mechanisms and kinetics of BEPR. However, by the end of the previous contract (December 1987) it was apparent that a number of tasks related to application of the basic information still had to be completed, viz. the information supplied by the enhanced culture study had not been adequately disseminated, nor had it been incorporated in the mixed culture situations present in 'real' nutrient removal systems treating domestic sewages, for the purposes of design, operation and control of such plants.

With regard to the manual and computer program on water treatment, application of these are restricted to waters containing only the calcium/magnesium/carbonate weak acid/base system in solution. In municipal wastewaters, however, in addition to the calcium/magnesium/carbonate system, the phosphate and ammonia systems are present, and in anaerobic wastewater treatment processes sulphides and short chain fatty acids (e.g. acetate and propionate) are generated. All these weak acid/base systems may be present in such large concentrations relative to the calcium/magnesium/carbonate weak acid/base system, that they exert significant influence on the pH and therefore on the treatment of the water to achieve a desired condition. No information was available on the chemistry of waters containing mixtures of weak acid/base systems and no guidelines for their treatment were available.

Accordingly, in 1988 a contract was set up between the Water Research Commission (WRC) and the University of Cape Town (UCT) to:

- provide opportunity to publish the research work undertaken so far,

- fill in the areas of research perceived to require attention in order to

  - update the activated sludge system design manual,
  - extend the general kinetic model to incorporate BEPR,
  - extend the theory on water chemistry to include mixtures of weak acid/bases,

- promote technology transfer by means of seminars, updating of design manuals and development of user-friendly computer programs.

To achieve this the following tasks were identified:

- Re-evaluation of the technology available on completely aerobic nitrification systems and on anoxic/aerobic nitrification/denitrification (ND) systems.

- Consolidation of research into nitrification/denitrification/biological excess phosphorus removal (NDBEPR) systems.

- Extension of the water chemistry theory to include mixed weak acid/base systems.

To assist the reader in obtaining an overall view of the work, a flow diagram showing the tasks and their interactions is shown in Fig 1.1. The reader will notice that the tasks relating to the design manual require input from tasks receiving attention under other contracts. Other tasks, for example mixed weak acid/base chemistry, have been developed further under other contracts and will be reported there. Also, some miscellaneous work, contiguous to the areas of interest to this contract, developed during the contract and is summarized in this final report, namely:

- Chemical phosphorus removal from municipal wastewater by the disposal of waste alum sludge to the activated sludge system.

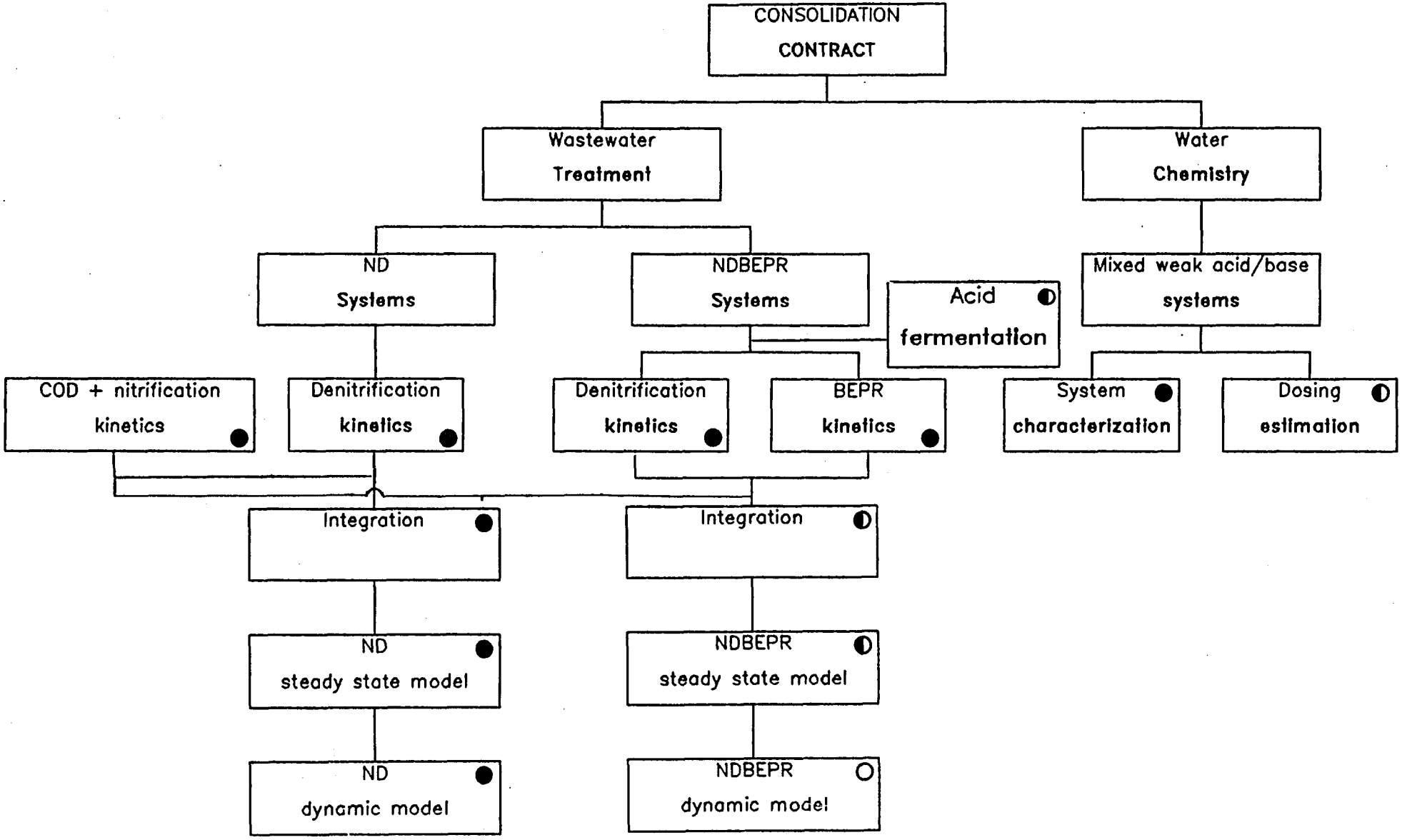

Fig 1.1: Flow diagram showing the research projects, their tasks that required completion and the interaction between these tasks.

CHAPTER 2

NITRIFICATION AND NITRIFICATION/DENITRIFICATION SYSTEMS

INTRODUCTION

In the early stages of deveolpment, design, operation and control of activated sludge systems were based on relatively simplistic ideas about the behaviour of the systems, and on experience acquired in running such systems. From about 1970 extensive development took place in the activated sludge method of treating wastewaters. The function of the single sludge system expanded from carbonaceous energy removal to include nitrification, denitrification and phosphorus removal, all of these mediated biologically. These extensions impacted on the system configuration in that multiple in-series reactors, some aerated and others not, with inter-reactor recycles needed to be incorporated.

Not only did the system configuration and its operation increase in complexity, but more stringent standards for effluent quality had to be satisfied. To meet these effluent standards, the design of the selected system had to be optimized and the system operated optimally. With such complexity it became no longer possible to make a reliable quantitative, or sometimes even qualitative prediction 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 of the system behaviour.

To design the system optimally and to operate it effectively, concerted efforts were made over the past 15 to 20 years to model the behaviour of these systems. This was also the case in South Africa, where development of a reliable mathematical model was given intensive attention. The result of this research endeavour was a very powerful kinetic model that gives a reliable description of the nitrification and nitrification/denitrification (ND) system response over wide ranges of system configuration (single and in-series reactor systems, aerated and non-aerated reactors, inter-reactor recycles), wastewater characteristics (COD, TKN, flow pattern) and operational parameters (sludge age, temperature, dissolved oxygen concentration) (van Haandel *et al.*, 1981).

The model had a significant impact on design and operational procedures of single sludge nitrification and ND activated sludge systems. With regard to design, the model led to the identification of procedures to estimate the optimal or near optimal design configuration, reactor sizes and operational parameters (e.g. sludge age) and to estimate the expected response (WRC, 1984). Re-evaluation of the design procedures in light of information that has become available since 1984 has indicated that the procedures set out in WRC (1984) remain valid for nitrification and ND systems.

Once the system had been designed, the time response under dynamic flow and load conditions could be estimated using the kinetic model. Thereupon the design could be modified if necessary to achieve improved performance, or, the sensitivity of the design to changes in flow and load conditions or to operational modifications could be assessed. In full-scale plant operation it also found application in assessing the

effects of changes in waste flows and loads, operational modifications (e.g. changes in recycles), and proposed modifications to plant configuration. Furthermore it proved valuable in operator training; through simulation exercises using the model the operator acquired 'instant' experience in the behaviour to be expected with changes in inputs, system configuration and operational strategies. A difficulty in making routine use of the model was that it required the availability of a main-frame computer.

To make the kinetic model more widely available at the different levels of application, in this contract it was proposed to write a computer program of the model that (1) is suitable for personal computers, (2) is 'user friendly', (3) is flexible, and (4) provides rapid solutions, numerical or graphical. This objective has been met; a computer program of the model has been written and a user manual prepared for distribution (Dold *et al.*, 1991). Details on each of these are given in the following sections.

COMPUTER PROGRAMS

The user manual entitled ***Activated Sludge System Simulation Programs Version 1.0***, includes two programs for simulation of single sludge activated sludge systems incorporating carbonaceous energy removal, nitrification and denitrification (Dold *et al.*, 1991). The two programs, **UCTOLD** and **IAWPRC** , are based on what are, arguably, the two most up to date mechanistic models of the activated sludge system. **UCTOLD** is based on the model developed by the research group at the University of Cape Town (UCT) over the past fifteen years. **IAWPRC** is based on a model proposed by a Task Group of the International Association on Water Pollution Research and Control (IAWPRC) incorporating some modifications by the UCT group. With appropriate calibration the two models give predictions that are closely equal for most situations.

Both programs presented in Version 1.0 can be applied to predict steady state and cyclic dynamic response behaviour for a range of system reactor configurations, operating conditions and waste flow and loads:

- The programs can be used to predict response of single or in-series *completely mixed* reactor systems with or without inter-reactor recycles (recycles opposite to the direction of flow through the system) over the range of temperatures from 14 to 22° C. The reactors may be aerated or unaerated and the sludge age may vary from 2 to 30 days. Waste flow and/or loads may be steady state or cyclic.

- The programs predict the response of the following compounds with their various contributory components; chemical oxygen demand (COD), oxygen, volatile suspended solids (as COD), nitrogen and alkalinity.

Application of the programs has some limitations:

- The programs cannot be used to predict the behaviour of systems in which, within a single reactor, a part is anoxic and a part aerobic.

- The programs do not provide for prediction of biological excess phosphorus (P) removal. Prediction of P removal behaviour requires a substantial increase in the number of processes and compounds to account for the response of the P removal organisms (which can constitute up to 40 percent of the organism mass in P removal systems treating municipal effluents). Despite this constraint experience has shown that the models give reasonable prediction of the sludge

masses, nitrification/denitrification, oxygen utilization and effluent COD and nitrogen of single sludge biological excess P removal systems. A separate model to include biological excess P removal is under development (Version 2.0), see Chapter 3.

- The programs have been developed from observations made on systems treating municipal waste flows at laboratory, pilot and full scale. Default values assigned to the constants in the programs, in particular to wastewater characteristics and organism growth rates, are approximate averages observed when treating South African municipal waste flows for temperatures in the range 14 to 22°C. Application of the programs to systems treating municipal waste flows in other countries may require that some of the constants have to be redetermined - the characteristics of such waste flows may consistently differ from those in South Africa, and/or temperatures may fall outside the 14 to 22°C range. In the manual the user is given some direction as to the situations under which the constants may change. Also, procedures for independent determination of some of these constants are briefly set out. (The programs have not been tested to simulate systems treating industrial waste flows).

The two programs are 'menu driven'. That is, for the most part the user selects a desired program option from a list of possible options displayed on the screen. This approach should be familiar to users of many commercial software packages and is adopted to simplify program operation, and to minimize the amount of typing by the user. A number of other features have been included in the programs in an effort to make these as 'user friendly' as possible; for example:

- The user will find that it is very difficult to upset program operation when inputting data. Protection against typing incorrect keys is built into the program wherever possible.

- A consequence of the complexity of the models is that they incorporate a large number of constants, kinetic, stoichiometric, and others. Default values for all the constants, wastewater characteristics, etc., are included. These values have been selected and calibrated for South African conditions; the default values can be updated by the user if necessary for the situation where the model is applied. In the sections of the manual dealing with kinetic and stoichiometric constants and wastewater characteristics, guidance is given as to situations in which the constants may require alteration.

- Installation of the programs is very simple. The size of memory in the computer determines the maximum number of reactors in a system that can be simulated. This is detected automatically by the program. Also, the program automatically detects the type of graphics adapter installed in the computer.

ABOUT THE USER MANUAL

The manual has been designed to give complete support to users of the two simulation programs:

Chapter 2: Models and Wastewater Characteristics presents the models and briefly highlights the key features. The division of the influent wastewater COD and TKN fractions into various sub-fractions is described; biodegradable/unbiodegradable, soluble/particulate, and so on.

Chapter 3: Installing the Programs provides instructions on how to set up working programs from the "distribution disk" accompanying the manual.

Chapter 4: Running the Programs demonstrates use of the programs in detail, and explains features of the various menus and sub-menus.

Chapter 5: Application and verification illustrates simulation of various experimental systems and includes comparison of the predicted and experimental data.

Chapter 6: Determination of model constants sets out procedures for determination of influent COD and TKN fractions and maximum specific growth rates for heterotrophs and autotrophs.

Appendix A: Retrieval of Diurnal Response Data shows how the data in a file of diurnal results may be re-arranged in a form suitable for off-line analysis. A program for making the conversion is provided; this allows the data to be imported into a spreadsheet package such as *Lotus 1-2-3* or Borland's *Quattro* should the user wish to, say, plot results in a specific format.

Appendix B: Model Representation in Matrix Format describes the matrix format used for presenting the models in Chapter 2.

Appendix C: Reactor Numbering Convention provides examples of the convention used for reactor numbering in the programs.

Appendix D: Symbols System sets out the basis for the system of symbols used in this manual.

CONCLUSIONS

For design of nitrification and nitrification/denitrification (ND) systems, the procedures set out in WRC (1984) remain valid. With regard to the kinetic model to simulate the dynamic behaviour of these systems, a user-friendly computer program of the model for use on personal computers has been developed to make the information more widely available at the different levels of application. The computer program will be distributed by the Water Research Commission together with a user manual.

CHAPTER 3

NITRIFICATION/DENITRIFICATION/BIOLOGICAL EXCESS PHOSPHORUS REMOVAL SYSTEMS

INTRODUCTION

The research on nitrification/denitrification/biological excess phosphorus removal (NDBEPR) systems comprised the following:

- Acid fermentation of primary sludge.
- Kinetics of denitrification in NDBEPR systems.
- Modelling of biological excess phosphorus removal (BEPR).

ACID FERMENTATION OF PRIMARY SLUDGE

Background

Full scale studies on biological excess phosphorus removal (BEPR) plants have demonstrated that the BEPR can be increased by acid fermenting the settled sludge in the primary settling tank, and adding either the fermented sludge, or the acids elutriated from the sludge, to the influent of the BEPR removal plant (Pitman *et al.*, 1983; Pitman and Lötter, 1986). However, when this contract commenced considerable uncertainty still existed as to the mass of short chain fatty acids (SCFA) that can be generated and the degree of improvement in phosphorus removal that can be expected. This study was undertaken to (1) evaluate SCFA production in laboratory scale batch, single and in-series completely mixed reactor systems, (2) develop a model for acid fermentation, and (3) theoretically estimate the effect of acid addition on BEPR.

Experimental investigation

The laboratory investigation comprised studies on (1) batch systems with batch retention times up to about 10 days for influent volatile solids (VSS) ranging from 11 to 42 g/ℓ, (2) 3 in-series completely mixed reactor systems with each reactor having 1 day flow through retention time for influent VSS ranging from 37 to 60 g/ℓ and, (3) single completely mixed reactor systems with flow through retention times of 1, 2, 3, 5, 6 and 9 days for influent VSS ranging from 36 to 50 g/P. All the studies were made at 20° C. For details of the experimental work see Lilley *et al.* (1990).

Results and Conclusions

From the fermentation studies the following conclusions were formed (Lilley *et al.*, 1990; 1991):

- The raw primary sludge from Mitchell's Plain, Cape Town, appears to have an acid fermentation potential for the production of SCFA, of about 17 percent of the influent sludge COD, i.e. a specific potential yield of 0,17 mgSCFA (as COD)/mg influent sludge VSS (as COD). Very likely this fraction will apply also to primary sludges at other municipal wastewater treatment plants.

- The SCFA generation potential does not appear to be influenced by the concentration of the influent primary sludge.

- The production of SCFA appears to conform to a first order reaction with a reaction specific rate constant of about 0,16 day^{-1} at 20° C, see Figs 3.1 and 3.2.

- Besides generating SCFA, acid fermentation also generates soluble (Whatman's No. 1 filtrate) non-SCFA molecules approximately equal in concentration to the concentration of SCFA, i.e. of the total soluble (Whatman's No. 1 filtrate) COD concentration generated, approximately half is SCFA (as COD) and half is non-SCFA "soluble" COD, see Fig 3.3. The production rate of the total soluble COD, (and therefore also that of the non-SCFA soluble COD) appears closely linked to the SCFA production, i.e. also approximates a first order rate not influenced by sludge concentration.

- Hydraulic retention time in an acid fermentation system should not exceed about 6 days at 20° C; at longer retention time work (elsewhere) indicates that methane fermentation can take place thereby reducing the net SCFA yield.

- The COD yield of SCFA can be estimated from the equations derived in this study; at 6 days at 20° C for Mitchell's Plain primary sludge it is approximately 60 percent of the maximum potential yield (0,17 mgSCFA as COD/mg influent sludge COD).

Applying the SCFA generation equations to evaluate the effect of using different fermentation systems, it was found that:

- For total retention times up to about 6 days the differences in the SCFA yield between a single reactor, in-series reactors and accumulating batch reactor are small. In consequence the selection of a specific system for acid fermentation will be governed by the cost of construction and the ease of operation.

Applying the SCFA generation equations developed in this study, and the steady BEPR model of Wentzel *et al.* (1990) to evaluate the effect of the fermentation systems on the BEPR system, it was found that:

- From a practical and economic point of view the most appropriate retention time in fermentation systems appears to be about 3 days: With 3 days acid fermentation retention time P removal in the BEPR plant will increase by about 14 per cent. Increasing the acid fermentation time to 6 days will improve the P removal in the BEPR plant only by a further 3 percent.

The study did not investigate experimentally, the effects of the addition of the fermented products on BEPR, denitrification and aerobic processes in the nitrification denitrification (ND) BEPR system. Such a study is important because

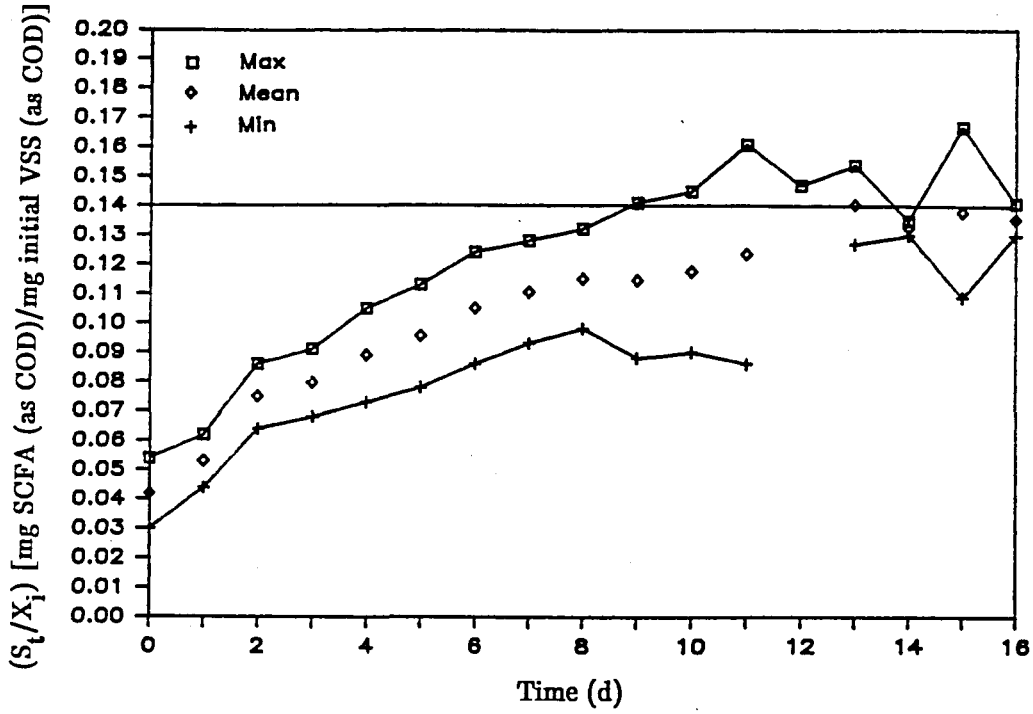

Fig 3.1: Envelope of observed maximum and minimum ratios of mgSCFA (as COD)/mg initial VSS (as COD) [i.e. (S_t/X_i)], and the calculated mean (S_t/X_i) ratio versus time for the batch system. Also shown is the estimated mean potential mgSCFA (as COD)/mg initial VSS (as COD) [i.e. (S_∞/X_i)] ratio for the batch system.

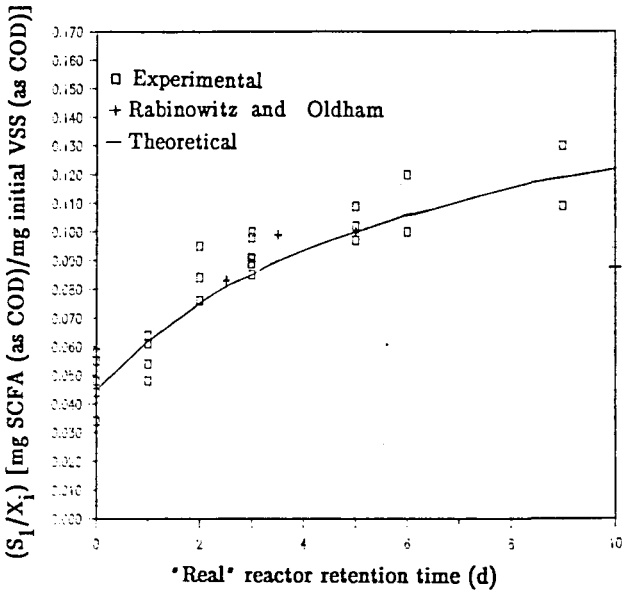

Fig 3.2: Predicted and observed mgSCFA (as COD)/mg initial VSS (as COD) [i.e. (S_1/X_i)] values for a single completely mixed reactor versus 'real' reactor retention time.

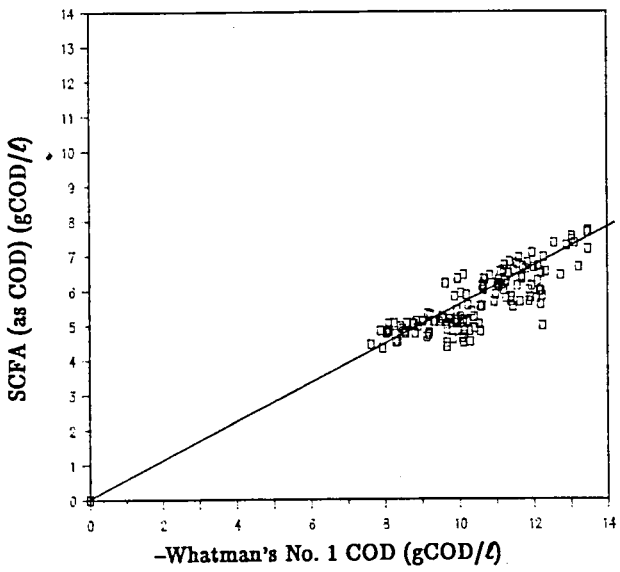

Fig 3.3: Correlation plot of average SCFA COD concentrations versus average –Whatman's No. 1 COD concentrations in a single, completely mixed reactor system of 2, 3, 5, 6 and 9 d retention time, for all batches of sludge.

it would give an indication what proportion of the non-SCFA soluble COD (Whatman's No. 1 filtrate COD minus SCFA COD) generated, is RBCOD which in turn can be converted to SCFA in the anaerobic reactor. The increases in P removal cited above are those due only to SCFA generation and ignore the possible additional P removal due to a RBCOD component in the non-SCFA soluble COD fraction.

KINETICS OF DENITRIFICATION IN NDBEPR SYSTEMS

Background

In single sludge nitrification/denitrification (ND) systems the kinetics of biological denitrification have been extensively investigated and a general kinetic model has been developed (van Haandel *et al.*, 1981, see Chapter 2). From this model, with steady state operation the denitrification kinetics can be approximated very closely by using the formulation $dNO_3/dt = -KX_a$. Three values of K are defined: In the primary anoxic or predenitrification reactor, K_1 related to the reduction of readily biodegradable COD (RBCOD) and K_2 related to the reduction of slowly biodegradable COD (SBCOD); in the secondary anoxic or postdenitrification reactor, K_3 related to the reduction of SBCOD. Even though K_2 and K_3 both relate to the utilization of SBCOD, they have different values; in terms of the general kinetic model, the adsorbed externally stored SBCOD to active organism mass ratio (i.e. occupancy of adsorption sites) differs between the primary and secondary anoxic reactors, the occupancy of stored SBCOD mass being higher in the primary than in the secondary anoxic reactor.

In the development of nitrification/denitrification/biological excess phosphorus removal (NDBEPR) systems, Siebritz *et al.* (1983) have shown that it is essential to reduce nitrate discharge to the anaerobic reactor to zero, in order to ensure maximum phosphorus (P) removal. For design, this requires that the denitrification potentials of the anoxic reactors have to be determined accurately. Application of the simplified denitrification equations (as developed for denitrification reactors of ND systems) to the primary and secondary anoxic reactors of NDBEPR systems has given predictions that are close to those observed experimentally. Accordingly, the simplified denitrification model has been incorporated unmodified in the design procedures for the UCT and Modified Bardenpho NDBEPR systems (WRC, 1984). Although apparently satisfactory, the use of the simplified denitrification model in NDBEPR design procedures has been criticized, the arguments being as follows:

> The RBCOD appears to be used twice, first in the anaerobic reactor where it is sequestered by the polyP organisms, and again in the primary anoxic reactor for denitrification; this would be possible only if, in NDBEPR systems, the polyP organisms totally utilize the stored RBCOD in the primary anoxic reactor with nitrate as electron acceptor (for growth and polyP accumulation) in the same fashion as RBCOD is totally utilized by non-polyP organisms in the primary anoxic reactor of ND systems. In this event the major portion of the P uptake should take place in the primary anoxic zone. However, P uptake and polyP storage has been observed to take place principally in the aerobic zone. Furthermore, investigations of NDBEPR systems with enhanced cultures of polyP organisms have shown that polyP organisms do not denitrify to any significant degree (Wentzel *et al.*, 1989a).

These observations suggested that the denitrification response in NDBEPR systems is not consistent with the response predicted by the denitrification model, and that

the good predictions that have been obtained are fortuitous. Accordingly, in this contract an experimental investigation into the denitrification kinetics of NDBEPR systems was initiated.

Experimental investigation

A laboratory-scale UCT/modified UCT system was set up and operated for 570d. The primary anoxic reactor was changed from a completely mixed to a plugflow mixing regime. The response of the system was monitored daily and profiles on the plugflow primary anoxic reactor measured periodically. In addition, a variety of anoxic batch tests were conducted using mixed liquor harvested from the MUCT/UCT system. (For details of the experimental investigation see Clayton *et al.*, 1989; 1991).

Results

Typical profiles for the plugflow primary anoxic reactor are shown in Fig 3.4 (a,b and c). The batch tests showed similar denitrification behaviour to that in Fig 3.4 (b and c). Analysis of the data indicated the following:

- The initial fast denitrification rate observed in plugflow primary anoxic reactors of ND systems is either non-existent or continues for a much shorter time-span in NDBEPR systems.

- The specific denitrification rate constants for the NDBEPR system compared to those measured for ND systems (in Table 3.1) shows that in NDBEPR systems, the specific rate constant for denitrification associated with the utilization of slowly biodegradable COD (SBCOD) is 2½ times higher in the primary anoxic reactor (K_2') and 1½ times higher in the secondary anoxic reactor (K_3') than in the corresponding reactors in ND systems.

Causes for increased primary anoxic denitrification rate K_2'

Three hypotheses were advanced as possible explanations for the increased denitrification rate constant K_2' observed in the primary anoxic zone of NDBEPR systems:

(1) PolyP organisms can denitrify utilizing the intracellular PHB acquired in the anaerobic zone.

(2) PolyP organisms cannot denitrify; the SBCOD is modified in the anaerobic zone to a more readily hydrolyzable form thereby inducing a faster rate of denitrification by the non-polyP organisms.

(3) PolyP organisms cannot denitrify and the SBCOD is not modified in the anaerobic zone; a higher rate of SBCOD hydrolysis/utilization is stimulated in NDBEPR systems by anaerobic/anoxic/aerobic sequencing.

Hypothesis (1) – Denitrification due to polyP organisms
If it is accepted that the polyP organisms can denitrify, then the stored PHB will be significantly reduced under anoxic conditions. Accordingly,

(i) PHB concentrations were measured in anaerobic, anoxic and aerobic zones of the MUCT system,

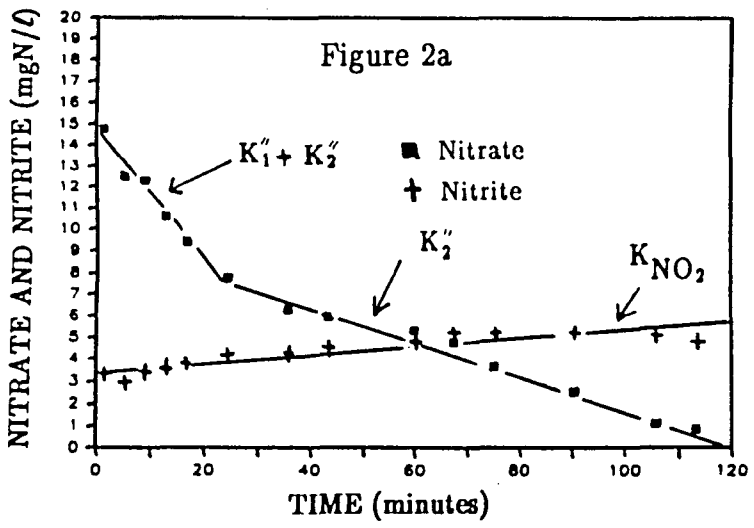

Fig 3.4a: Typical example of the two phase nitrate and nitrite concentration–time profiles observed in the plugflow primary anoxic reactor

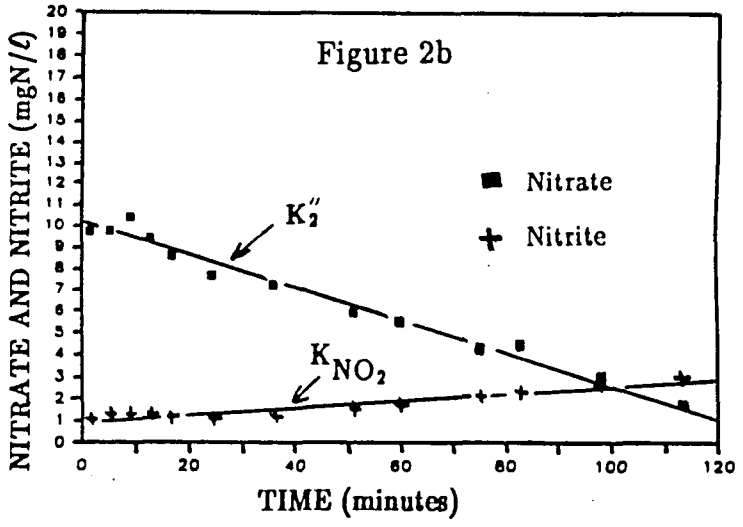

Fig 3.4b: Typical example of the single phase nitrate and nitrite concentration–time profiles observed in the plugflow primary anoxic reactor

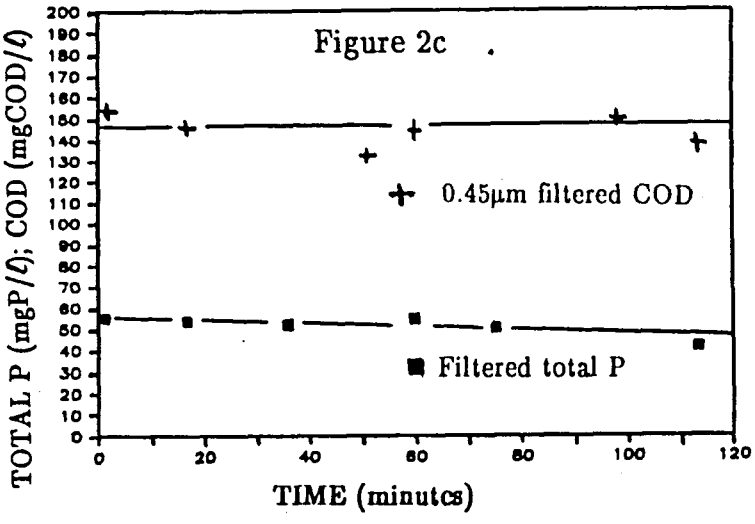

Fig 3.4c: Typical phosphorus (filtered total P) and soluble COD (<0,45µm filtered) concentration–time profiles observed under single and two phase denitrification conditions in the plugflow primary anoxic reactor.

Table 3.1: Comparison between the denitrification rates in systems with anaerobic and anoxic reactors (NDBEPR) and with only anoxic reactors (ND).

MUCT/UCT system (NDBEPR)	ND system
Predenitrification One phase	Primary anoxic Two phases
$K_2' = 0.224$*	$K_1 = 0.720$* $K_2 = 0.101$*
Postdenitrification ** One phase	Secondary anoxic One phase
$K_3' = 0.100$*	$K_3 = 0.072$*

* Units $mgNO_3$–N/(mgAVSS.d).
** UCT/MUCT system does not have secondary anoxic reactor. K_3' was measured on sludge harvested from aerobic reactor of system.

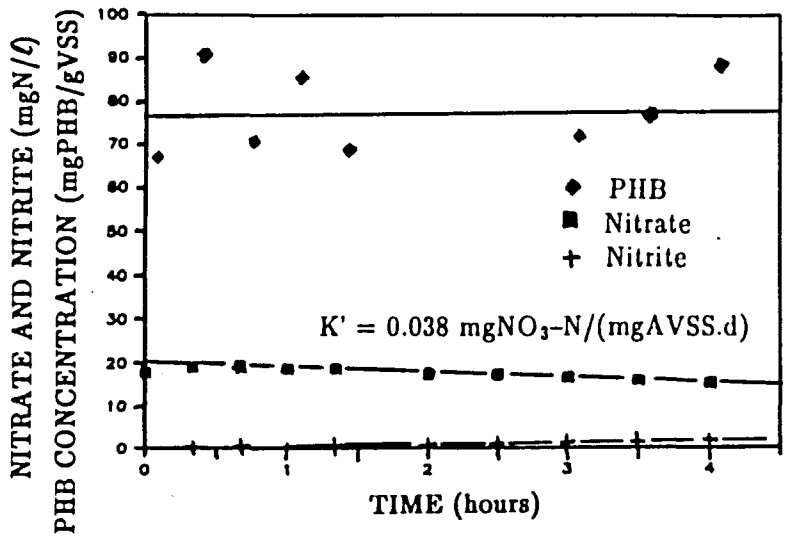

Fig 3.5a: Nitrate, nitrite and PHB concentration–time profiles in an anoxic batch test on sludge harvested from the enhanced polyP organism culture system. Note there is virtually no denitrification nor reduction in PHB concentration.

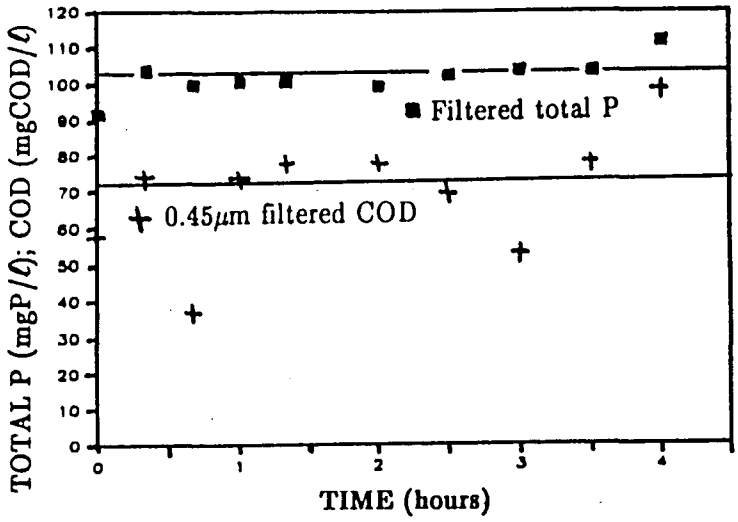

Fig 3.5b: Filtered total P and COD (<0.45μm filtered) concentration–time profiles in an anoxic batch test on sludge harvested from the enhanced polyP organism culture system. Note there is virtually no P uptake.

(ii) PHB concentration-time behaviour was monitored in anoxic batch tests on mixed liquor harvested from the anaerobic zone of the MUCT system, and

(iii) PHB concentration-time behaviour was monitored in anoxic batch tests on mixed liquor harvested from the anaerobic zone of an enhanced polyP organism culture (Wentzel *et al.*, 1988a; 1989a), see Fig 3.5 (a and b).

These three test series demonstrated that PHB does not serve as a substrate source for denitrification, i.e. the polyP organisms do not contribute in any significant manner to the K_2' denitrification rate in the primary anoxic reactor – hypothesis (1) was rejected.

Hypothesis (2) – SBCOD is modified in the anaerobic zone
If the anaerobic reactor does modify the influent SBCOD to a readily utilizable form, there should be a difference in the K_2' denitrification rates when an activated sludge is fed influent sewage that has not passed through an anaerobic reactor, and when it is fed influent sewage that has passed through the anaerobic reactor.

From the experimental investigation it was found that the same high K_2' denitrification rate was obtained with NDBEPR sludges irrespective of whether the sewage SBCOD had passed through an anaerobic reactor or not. This forced the conclusion that the high rate is not due to modification of the SBCOD in the anaerobic reactor – hypothesis (2) was rejected.

Hypothesis (3) – Stimulation of higher SBCOD hydrolysis/utilization rate in the sludge
For the present this null hypothesis must be accepted by default – no experimental means could be devised to test the hypothesis. It does however provide a consistent explanation for the observations. Thus, the increased specific denitrification rate in NDBEPR systems is hypothesized to be due to an increased SBCOD hydrolysis/utilization rate by non-polyP organisms apparently induced by anaerobic/anoxic/aerobic sequencing in these systems. Whether this increase in rate is due to stimulation of enzyme activity in non-polyP organisms already present in the system, or due to selection of non-polyP organisms with such higher enzyme activity, is not clear.

Conclusions

In an appropriately designed NDBEPR system, the RBCOD leaking through the anaerobic reactor will be minimal and have little or no influence on the denitrification in the primary anoxic reactor. The dominant electron donor source in this reactor therefore is the SBCOD. Thus, the specific rate of hydrolysis/utilization of this material fixes the rate of denitrification. In this study, apparently the rate of denitrification is increased significantly in the NDBEPR system compared to the ND system. Applying the increased specific rate constant (K_2') in the NDBEPR system design procedure and accepting that no RBCOD is available for denitrification, the denitrification obtained is approximately equal to that obtained using the ND rate constants (K_1 and K_2) and accepting that the RBCOD is totally utilized in the primary anoxic reactor. Thus, in the usual long sludge age NDBEPR systems the denitrification in the primary anoxic reactor can be estimated with reasonable accuracy utilizing the denitrification equations valid for ND systems. However, this equality is fortuitous and cannot be expected to apply if the mass fraction for the primary anoxic reactor deviates considerably from that usually employed.

The K' values determined in this study were calculated assuming that the active mass was made up totally of non-polyP organisms. Based on the steady state model of Wentzel *et al.* (1990) (see later), the fraction of the active mass consisting of polyP organisms in a NDBEPR system treating municipal wastewater (at 20d sludge age), will be approximately 1/3; that is, the specific rate of hydrolysis/utilization of adsorbed SBCOD by the non-polyP organism mass is nearer 0,23/(2/3) = 0,35 mgNO_3-N/(mg non-polyP active mass.d). This implies that the presence of an anaerobic reactor increases the specific rate of hydrolysis of adsorbed SBCOD by approximately 0,35/0,101 = 3,5 times, giving rise to an associated K_2" for the non-polyP heterotrophic active mass. A more accurate estimate of K_2" cannot be made at present; it will have to wait until a general NDBEPR kinetic model is developed (see later). The interactions between the bulk liquid SBCOD concentration, the (adsorbed SBCOD)/(non-polyP heterotrophic organism) concentration ratio, and the hydrolysis rate under anoxic conditions and denitrification are complex; only by having a general kinetic model, with formulations which describe these reactions with sufficient accuracy, can the observed specific denitrification rates K_2" and K_3" observed in the primary and secondary anoxic reactors of NDBEPR systems, be interpreted adequately (Wentzel *et al.*, 1991a).

For constant flow and load conditions, the simplified design equations as set out in WRC (1984) can be fairly readily modified to reflect the constant flow and load denitrification behaviour of NDBEPR systems. These modifications will be incorporated in the updating of the design manual (as required in the new consolidation contract). For the present, the existing design procedure set out in WRC (1984) can be used with confidence to determine the denitrification that can be achieved in NDBEPR systems.

MODELLING OF BEPR

Background

In the preceding contract which terminated at the end of 1987, an extensive investigation into the phenomenon of BEPR was undertaken (Wentzel *et al.*, 1988a; 1988b). The objective set was to develop a general kinetic model that describes NDBEPR system dynamic behaviour. The progress achieved during the period of the previous contract (Jan. 1984 - Dec. 1987), in meeting this objective, is summarized below:

It was assumed that in a NDBEPR system treating municipal wastewaters, a mixed culture would develop which could be categorized into three groups of organisms (1) heterotrophic organisms able to accumulate polyP, termed polyP organisms, (2) heterotrophic organisms unable to accumulate polyP, termed non-polyP organisms, and (3) autotrophic organisms mediating nitrification, termed autotrophs. That is, development of an activated sludge kinetic model describing the behaviour of NDBEPR systems would require inclusion of all three organism groups, and their interactions. With regard to the non-polyP and autotrophic organisms, a general kinetic model was already in existence that describes their behaviour in activated sludge systems containing aerobic and anoxic zones, (Dold *et al.*, 1980; van Haandel *et al.*, 1981; Henze *et al.*, 1987; Dold *et al.*, 1991), see Chapter 2. What was required was to extend this model to include polyP organism behaviour in order to develop a model that would describe the response of NDBEPR systems. To achieve this, the kinetic and stoichiometric characteristics of the polyP ***in the activated sludge environment***

needed to be established. From attempts to obtain information on the characteristics of the polyP organisms using mixed liquor from NDBEPR systems treating municipal wastewaters, it was concluded that, in these mixed culture systems, the non–polyP organism behaviour tends to dominate and mask the polyP organism behaviour. Accordingly, it was endeavoured to isolate the polyP organism characteristics, by developing enhanced cultures of these organisms in activated sludge systems. To develop enhanced cultures of polyP organisms, the microbiology and biochemistry of these organisms were investigated. This resulted in the development of a biochemical model for polyP organism behaviour (Wentzel *et al.*, 1986; 1991b). From the biochemical model, conditions to be imposed in a NDBEPR activated sludge system to produce an enhanced culture were identified – anaerobic/aerobic sequence with adequate anaerobic mass fraction; influent fed to the anaerobic reactor with acetate as substrate and with adequate macro– and micronutrients, in particular Mg^{2+}, K^{+} and to a lesser degree Ca^{2+} and; pH control in the aerobic reactor (Wentzel *et al.*, 1988c). Using the UCT and 3–stage Modified Bardenpho systems, with system sludge ages ranging from 7,5 – 20d, enhanced cultures of the polyP organism *Acinetobacter* spp. were developed – >90% of the organisms cultured aerobically were identified to be *Acinetobacter* spp. using the Analytical Profile Index (API) 20E procedure.

From experimental observations made on the enhanced culture systems, and on batch tests in which mixed liquors drawn from the systems were subjected to a wide variety of conditions, the characteristics and the kinetic response of the polyP organism mass were elucidated (Wentzel *et al.*, 1989a).

A conceptual model was developed incorporating these characteristics and, from the experimental investigation, the processes and compounds of importance were identified. The process rates and their stoichiometric interactions with the compounds were formulated mathematically, to develop a kinetic model for the enhanced cultures of polyP organisms (Wentzel *et al.*, 1989b). Using the enhanced cultures, the kinetic and stoichiometric constants in the kinetic model were quantified by a variety of procedures (Wentzel *et al.*, 1989b). With these constants, application of the kinetic model to the various test responses for the enhanced culture systems gave good correlation between observations and simulations (see Figs 3.6 to 3.9). The kinetic model then was applied to simulate the steady state behaviour of the enhanced culture UCT and 3–stage Modified Bardenpho systems; again good correlation was obtained.

The review above represents the state of knowledge at the end of the previous contract (December 1987). From the review it is apparent that the principal objective set for the previous contract, to develop a general kinetic model that describes NDBEPR system behaviour, had not been achieved. Accordingly, research on this aspect was continued in the Consolidation contract which started in January 1988. The approach adopted to continuing the development of a general kinetic NDBEPR model, was to divide the development into four stages:

(1) Develop a steady state model (as against a kinetic model operating under constant flow and load) for the enhanced polyP organism cultures.

(2) Extend the enhanced culture steady state model to a steady state model for mixed cultures.

(3) Incorporate the denitrification aspects from the previous section into (2) above, to give a steady state NDBEPR mixed culture model.

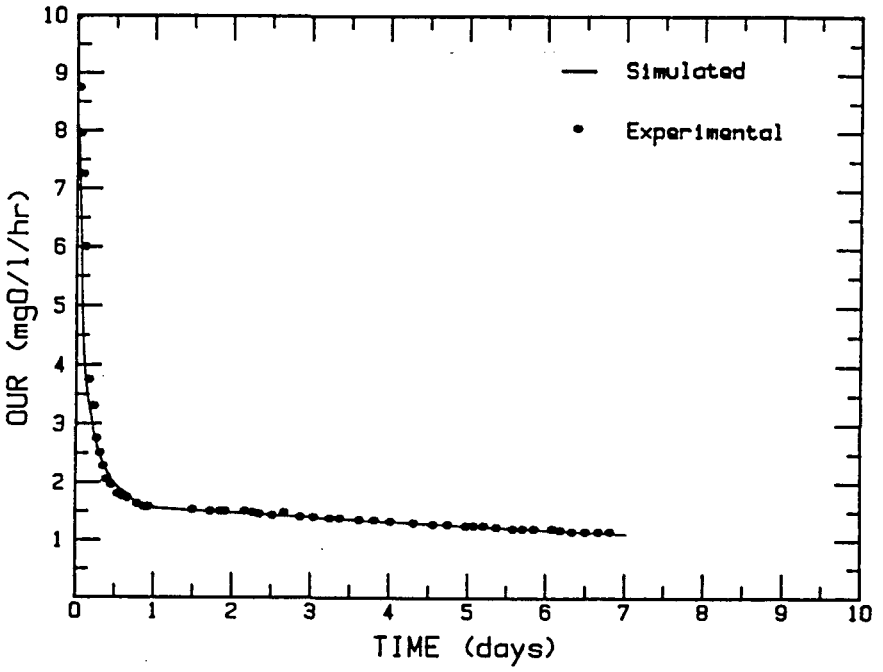

Fig 3.6a: Experimentally observed and simulated oxygen utilization rate (OUR) response with time in a batch aerobic digestion of mixed liquor from the enhanced culture system (Wentzel *et al.*, 1989b).

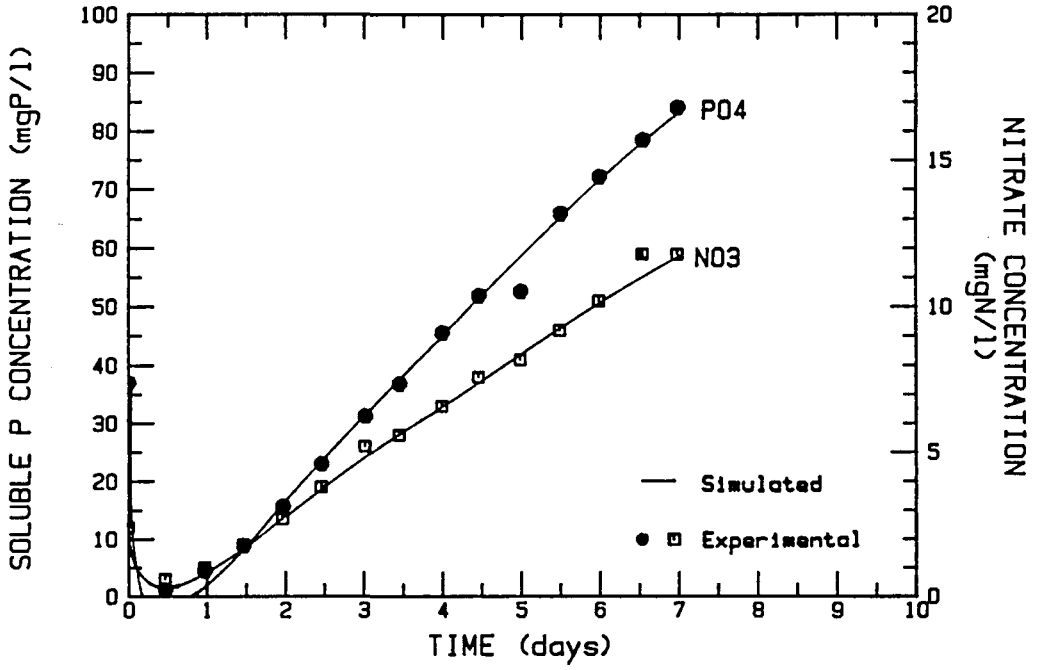

Fig 3.6b: Experimentally observed and simulated total soluble phosphate (PO_4) and nitrate (NO_3) concentration–time profiles for the batch aerobic digestion in Fig 3.6a.

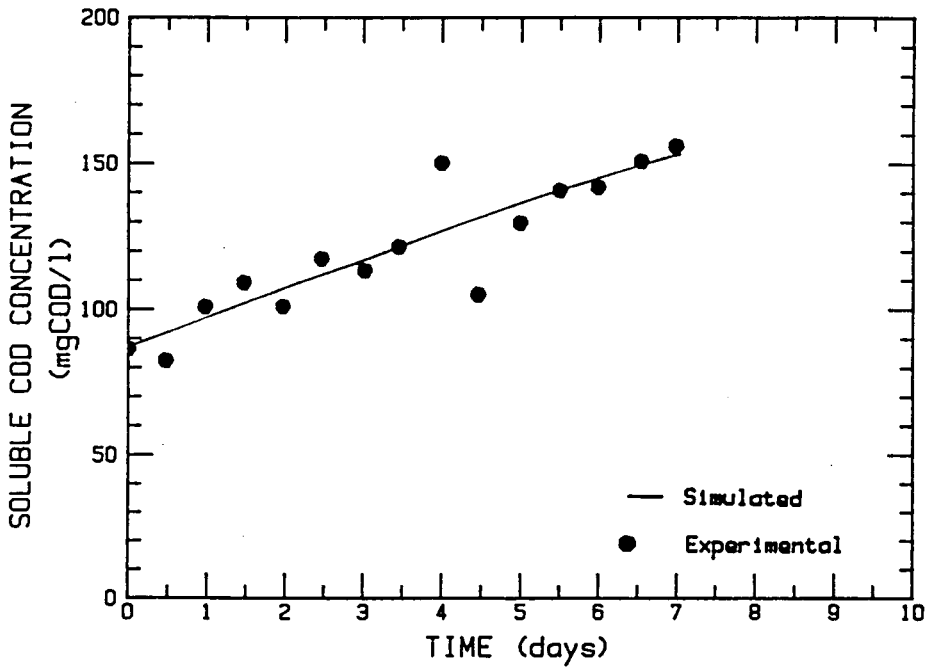

Fig 3.6c: Experimentally observed and simulated filtered COD concentration–time profiles for the batch aerobic digestion in Fig 3.6a.

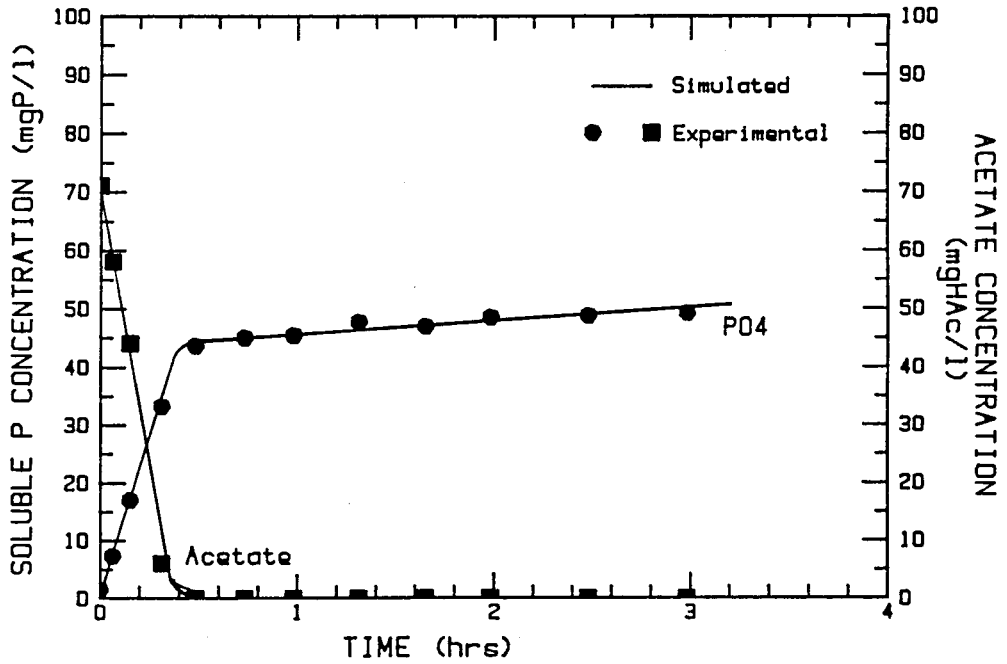

Fig 3.7: Experimentally observed and simulated total soluble phosphate (PO_4) and acetate concentration–time profiles with anaerobic addition of 0,11 mgCOD acetate/mgVSS to a mixed liquor batch from the enhanced culture system (Wentzel *et al.*, 1989b).

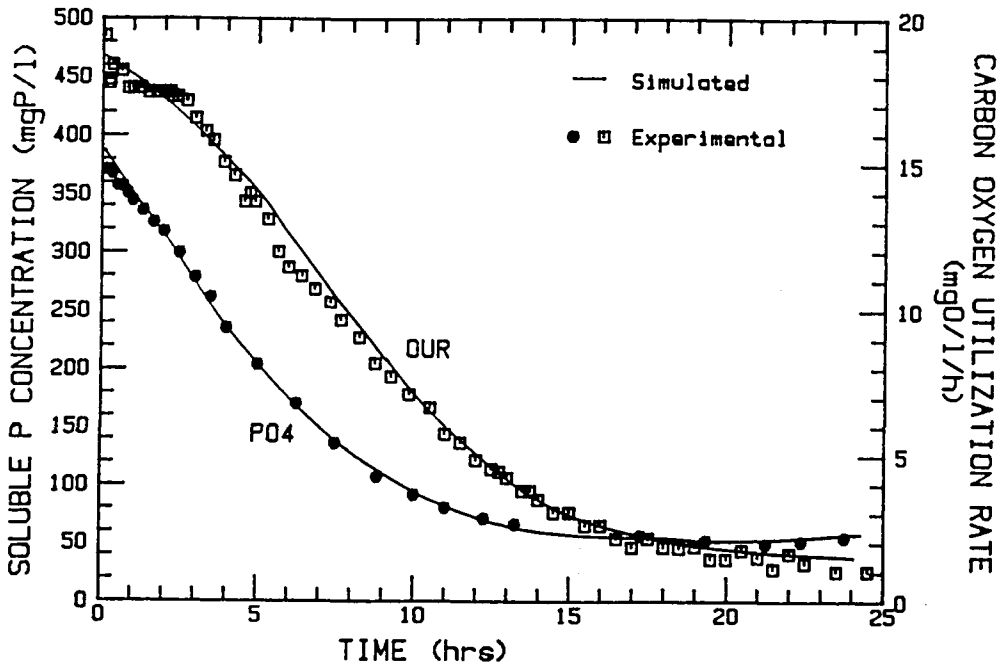

Fig 3.8: Experimentally observed and simulated total soluble phosphate concentrations (PO_4) and carbonaceous oxygen utilization rate (OUR) on aeration following anaerobic acetate addition of 0,363 mgCOD acetate/mgVSS to a mixed liquor batch from the enhanced culture system (Wentzel *et al.*, 1989b).

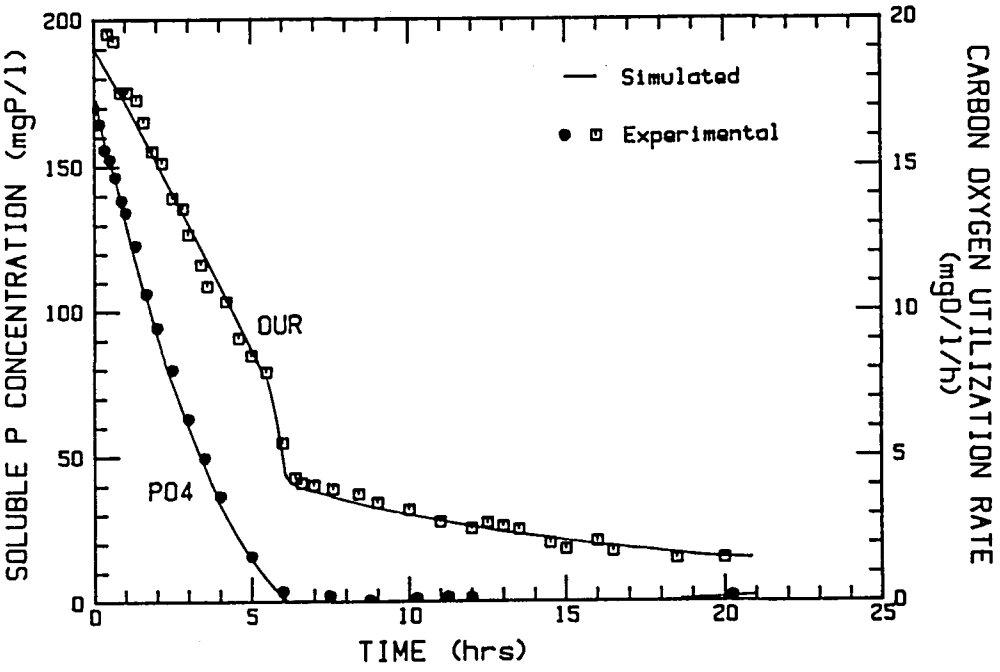

Fig 3.9: Experimentally observed and simulated total soluble phosphate concentrations (PO_4) and carbonaceous oxygen utilization rate (OUR) on aeration following anaerobic acetate addition of 0,22 mgCOD acetate/mgVSS to a mixed liquor batch from the enhanced culture system. The PO_4 concentration falls to zero during the course of this test (Wentzel *et al.*, 1989b).

(4) Having established (3), integrate the kinetic and stoichiometric aspects of ND (from the previous section) and BEPR (from the enhanced culture kinetic model) in a general NDBEPR mixed culture kinetic model.

Progress achieved on these tasks is reported below.

Simplified enhanced culture steady state model

To develop a steady state model for the enhanced culture systems under constant flow and load conditions the enhanced culture kinetic model was greatly simplified (Wentzel *et al.*, 1990): Under steady state conditions some of the processes included in the enhanced culture kinetic model have relatively minor influence on the eventual mass of P removal; accordingly, these processes were neglected in developing the steady state model. Further, two assumptions were made which simplified development of the steady state model:

(1) P release for anaerobic maintenance energy requirements is always small compared to P release for sequestration energy requirements, i.e. the kinetics of P release for anaerobic maintenance energy need not be incorporated. The implication of this is that under steady state the polyP content of the polyP organisms in the activated sludge wasted per day, remained constant.

(2) All the substrate sequestered in the anaerobic zone and stored as PHB is utilized completely in the subsequent aerobic zone, i.e. the kinetics of PHB substrate utilization need not be incorporated.

Taking due account of these assumptions, and the observation that the anaerobic mass fractions provided in the enhanced cultures were sufficient to ensure that all the acetate substrate was sequestered in the anaerobic zone (i.e. kinetics of acetate sequestration need not be incorporated in the model), by mass balances a number of steady state equations were developed for the enhanced cultures, for, polyP organism active and endogenous masses, and P release, uptake and removal due to these masses. Using the experimental results from the enhanced culture UCT and 3-stage Modified Bardenpho systems, the steady state model provided the structure whereby it was possible to quantify one parameter that could not be measured experimentally, the P content of the polyP organism ***active*** mass.

Mixed culture steady state model

Having developed the steady state model for enhanced culture systems, this model was extended to a steady state model that incorporated mixed cultures of polyP and non-polyP organisms present in NDBEPR systems receiving domestic wastewater as influent. In extending the steady state model one aspect that emerged was the difference in the endogenous mass loss rate between polyP organism enhanced culture sludges and the "normal" aerobic non-polyP organism activated sludge. The high specific endogenous mass loss rate with non-polyP organism systems had been attributed to a high rate of predation and regrowth, formulated as death-regeneration in the general activated sludge model by Dold *et al.* (1980). The low specific endogenous mass loss rate observed with polyP organisms in the enhanced cultures systems had led Wentzel *et al.* (1989a) to conclude that the polyP organisms are not predated to the same degree as non-polyP organisms. [From simulations subsequently with the steady state mixed culture model, it was found that, if the polyP organisms were subjected to a high predation rate, then significant BEPR in the mixed culture NDBEPR system would not be possible – the rate of death of the polyP organisms would be so high that no significant mass of these organisms could accumulate in the system, and BEPR would be near zero.]

Taking due cognizance of the above, Wentzel *et al.* (1989b) had concluded that the low predation rate on the polyP organisms, and the fact that the polyP and non-polyP organisms essentially do not compete for the same substrate, implied that polyP and non-polyP organism populations act virtually independently of each other in 'normal' mixed culture NDBEPR systems. In developing the steady state model for mixed culture NDBEPR systems, this conclusion was accepted and it was noted that this implies that analysis of the two population groups can be largely separated. However, two significant interactions were identified for inclusion in the mixed culture NDBEPR steady state model, both in the anaerobic reactor, as follows:

(1) In many 'normal' municipal wastewaters the acetate (or other SCFA) content is small or not present (Wentzel *et al.*, 1988a). Wentzel *et al.* (1985) had shown that in the anaerobic reactor the RBCOD component of the influent is converted to SCFA by the non-polyP organisms, thereby making SCFA available to the polyP organism mass for sequestration. The rate of conversion is much slower than the rate of sequestration, so that the rate of conversion controls the rate of sequestration. Hence, the mass of SCFA substrate that becomes available in the anaerobic reactor to the polyP organisms is governed by the kinetics of conversion mediated by the non-polyP organisms. [The work of Meganck *et al.* (1985) and Brodisch (1985) supports this conversion hypothesis; they had shown that anaerobic/aerobic systems develop organisms which convert sugars, and similar compounds, to SCFA in the anaerobic reactor.]

(2) If nitrate (or oxygen) is recycled to the anaerobic reactor, RBCOD is utilized by the non-polyP organisms with nitrate (or oxygen) as external electron acceptor thereby reducing the mass of RBCOD converted to SCFA.

Wentzel *et al.* (1985) had recognized (1) and (2) above, and formulated a kinetic model for conversion of RBCOD to SCFA, and hence for sequestration of these SCFA's. This conversion model was accepted, but provision was made to include situations where SCFA's are present in the influent by noting that the rate of SCFA sequestration is so rapid that ***all influent SCFA's*** will be sequestered by the polyP organisms in the anaerobic reactor for anaerobic mass fractions >10% and sludge ages >10d (this can be verified from the kinetics of sequestration). This theory provided the means for calculating the mass of SCFA substrate (from the influent and from conversion of RBCOD) sequestered by the polyP organisms in the anaerobic reactor. Knowing the mass of substrate sequestered by the polyP organisms, the mass of substrate remaining, available to the non-polyP organisms, could be calculated. In effect the biodegradable influent COD was split into two fractions, one eventually to be utilized by the polyP organisms and the other to be utilized by the non-polyP organisms. Because of the independence of action of these two groups of organisms, it was possible to use:

(1) The simplified polyP organism enhanced culture steady state model for calculating the polyP organism active and endogenous masses formed from the sequestered substrate, and the P release, uptake and removal mediated by these masses.

(2) The steady state activated sludge model (Marais and Ekama, 1976; WRC, 1984) to calculate the non-polyP organism active and endogenous masses formed from the remaining substrate, the rate of conversion of RBCOD to SCFA in the anaerobic reactor, the inert VSS accumulated from the influent, and the P requirement of, and hence P removal associated with, the active, endogenous and inert masses.

The total P removal for the system was calculated by summation of the individual P removals.

The predictive power of the steady state mixed culture BEPR model was evaluated against observations made on 30 laboratory scale NDBEPR systems over a six year period; system configurations were Phoredox, 3-stage Modified Bardenpho, UCT, MUCT and Johannesburg (for details on development of Johannesburg system, see Nicholls *et al.*, 1987) with system sludge ages ranging from 3 to 28 days. For this purpose the measured nitrate in the recycle to the anaerobic zone was used to estimate the RBCOD removal in the anaerobic zone by the non-polyP organisms using nitrate as external electron acceptor. The RBCOD remaining was available for conversion in the anaerobic reactor to SCFA, for sequestration by the polyP organisms. Plots of the predicted versus measured P release, P removal and VSS concentration are shown in Figs 3.10 to 3.12; good correlations between predicted and observed results were obtained.

This steady state mixed culture BEPR model represents the most recent development in modelling of BEPR. A number of tasks still require attention to achieve the final objective of developing a general kinetic NDBEPR model; these aspects will be considered in the new consolidation contract and are discussed briefly below.

Incorporation of denitrification aspects in steady state mixed culture model

In the steady state phosphorus evaluations using the mixed culture model (Figs 3.10 to 3.12), necessarily the nitrate recycled to the anaerobic reactor needed to be known, and this was available from experimental observations on the NDBEPR systems. Clearly for completeness denitrification needs to be incorporated into the steady state mixed culture model, an aspect omitted up to this stage. One possibility to accomplish this is to estimate the nitrate in the recycle to the anaerobic reactor from the denitrification theory for the ND steady state model (WRC, 1984). However, experimental data indicates that the ND steady state model predicts the denitrification in NDBEPR systems only approximately. Furthermore, with the development of the BEPR theory, in applying the ND steady state model to NDBEPR systems an inconsistency in the approach became evident:

> The enhanced culture studies have indicated that polyP organisms do not denitrify. This implies that the RBCOD, converted to SCFA by the non-polyP organisms and sequestered by the polyP organisms in the anaerobic reactor, no longer is available for denitrification in the primary anoxic reactor of a NDBEPR system. This in turn would imply that the magnitude of the denitrification in the primary anoxic reactor of the NDBEPR system should be significantly smaller than that in the primary anoxic reactor of the ND system. However, experimental observations on NDBEPR systems indicate that this is not so, that approximately the same magnitude of denitrification is achieved. The implications are that the denitrification kinetics for ND systems need to be adapted, or modified, for application in NDBEPR systems.

As reported in the previous section (**KINETICS OF DENITRIFICATION IN NDBEPR SYSTEMS**), experimental investigations have been conducted into the kinetics of denitrification in NDBEPR systems (Clayton *et al.*, 1989; 1991) to clear up this inconsistency. These have indicated that the specific denitrification rate in the primary anoxic reactor associated with adsorbed SBCOD is up to 2½ times higher than in ND systems; this explains the apparent equality in the denitrification achieved in NDBEPR and ND systems. It seems that the inclusion of an anaerobic zone in the NDBEPR system increases the specific hydrolysis rate of the SBCOD,

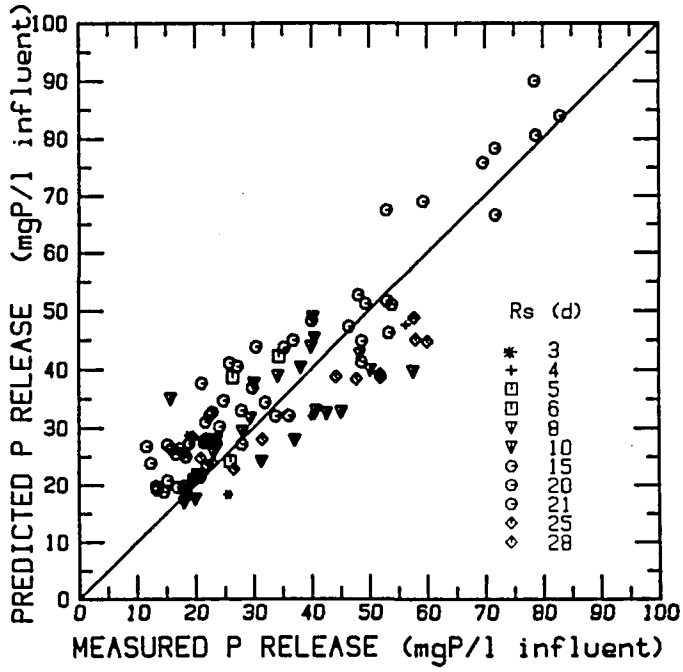

Fig 3.10: Predicted versus measured P release; predictions using the mixed culture steady state model, data from laboratory scale systems (Wentzel *et al.*, 1990).

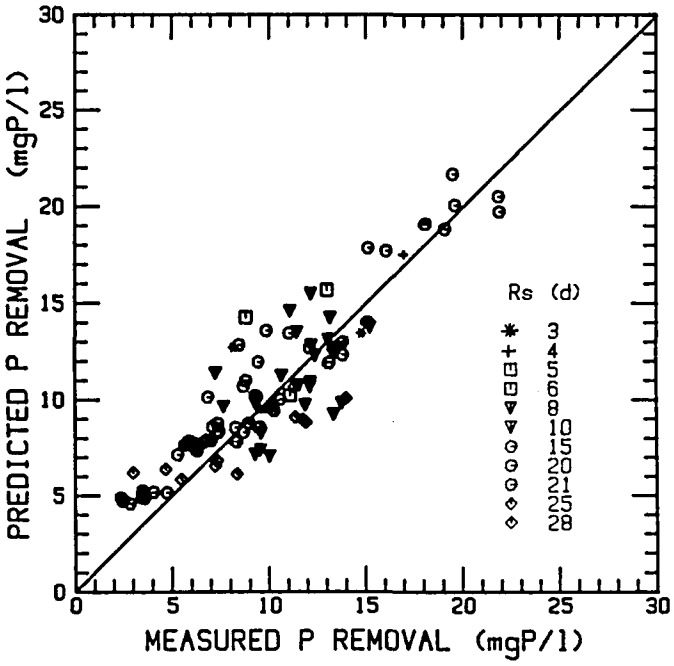

Fig 3.11: Predicted versus measured P removal; predictions using the mixed culture steady state model, data from laboratory scale systems (Wentzel *et al.*, 1990).

and the associated denitrification rate. It is the intention in the new consolidation contract to incorporate the denitrification aspects, as interpreted from the denitrification studies on NDBEPR systems, into the NDBEPR steady state model and evaluate its predictions against the observations available from 30 laboratory-scale NDBEPR systems over a six year period.

NDBEPR kinetic model

The steady state mixed culture BEPR model, described above, is restricted to constant flow and load conditions. It has been shown earlier in this section that this restriction makes it possible to accept certain behavioural patterns which largely eliminate the need for complete kinetic descriptions of the processes. For example, acceptance that PHB is completely utilized in the aerobic reactor eliminates the need for a description of the kinetics of PHB utilization. To develop a model that will describe system behaviour under cyclic flow and load conditions, such simplifications no longer can be accepted – this will require the integration of the enhanced culture BEPR ***kinetic*** model with the general activated sludge ND ***kinetic*** model (see Chapter 2), to give a general activated sludge NDBEPR ***kinetic*** model (Ekama *et al.*, 1990). This model will incorporate a large number of compounds and processes, in excess of 18 and 25 respectively and, to become manageable, some assumptions may still be necessary. For example, the assumption in the steady state mixed culture NDBEPR model, that the actions of the polyP and non-polyP organisms are relatively independent, may form a useful starting point. Also the development of this model will have to take cognizance of the hypothesized increased rate of hydrolysis of adsorbed SBCOD, and its implications on denitrification and other processes.

CONCLUSIONS

Between the objectives set for this task - development of an NDBEPR kinetic model - and its attainment, the review above has shown that quite a number of difficulties had to be overcome, difficulties that were not even conceived of at the the commencement of the task 3 years ago. We believe, however, that a firm base has been laid on which a general NDBEPR kinetic model can be built, as required in the new Consolidation contract.

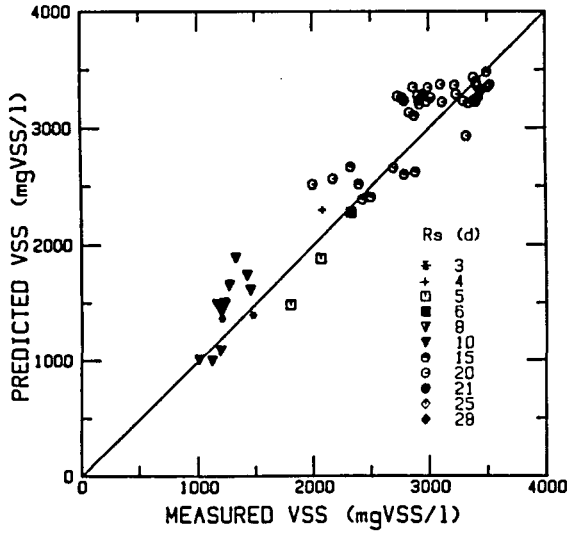

Fig 3.12: Predicted versus measured VSS concentrations; predictions using the mixed culture steady state model, data from laboratory scale systems (Wentzel *et al.*, 1990).

CHAPTER 4

WATER CHEMISTRY

INTRODUCTION

In the aqueous environment, weak acids and bases play an important role in establishing the pH and damping pH changes. In terrestrial waters the carbonate system is the dominant one, to such a degree that other weak acid/base systems usually are neglected. In municipal wastewaters, however, in addition to the carbonate system the phosphate and ammonia systems are present, and in anaerobic wastewater treatment processes sulphides and short-chain fatty acids (e.g. acetate and propionate) are generated. All these weak acid/base systems may be present in such large concentrations relative to the carbonate weak acid/base system, that they exert significant influence on the pH established.

For waters with only the carbonate system present in solution, the chemistry has been well established (Loewenthal and Marais, 1976) and incorporated in a design manual (Loewenthal *et al.*, 1986) to provide guidelines for the treatment of such waters. For waters that contain in addition to the carbonate weak acid/base other weak acid/bases in solution, little information has been available on the chemistry of these waters and no guidance could be given on the treatment of these waters to obtain a desired final state. The objective in this research project was to investigate the chemistry of mixtures of weak acid/bases in solution with a view to applying the chemistry to wastewater treatment systems (e.g. activated sludge, anaerobic digestion), and to other situations where mixtures of weak acid/bases are present in solution.

In working with mixtures of weak acid/bases one is confronted with two problems, viz.

- estimation of the concentrations of the species of each of the weak acid/base subsystems, called *characterization*,
- estimation of chemicals to be added to change the pH and species concentrations of the subsystems to desired values, called *dosing estimation.*

CHARACTERIZATION OF MIXED WEAK ACID/BASE SYSTEMS

Background

A weak acid/base dissociates in solution; the degree of dissociation depends on the pH, dissociation constant(s), the total species concentration of the weak acid/base subsystem and the ionic strength of the solution. If the total species concentration of each subsystem in a mixture of weak acid/base subsystems is known, then for any selected pH, the concentration of each of the dissociated and undissociated species can be calculated theoretically via the dissociation and mass balance equations governing each subsystem, i.e. the solution can be characterized completely. However, in practice the problem is that it is not always possible to determine

directly by chemical or chemical based procedures the total species concentration of each of the weak acid/bases in solution. This applies particularly to solutions containing the carbonate subsystem.

In characterizing a solution containing the carbonate subsystem plus other weak acid/bases, the principal difficulty arises in determining the carbonate weak acid/base total species concentration; total species concentrations of all the common weak acid/bases can be measured directly without undue difficulty, but not that of the carbonate weak acid/base. The carbonate subsystem can exist in three phases, solid, aqueous and gaseous. Consequently, it is difficult to sample aqueous solutions which contain the carbonate subsystem – with the usual methods of sampling CO_2 can be lost or gained due to differences in the partial pressure of CO_2 between the solution and the air.

For the *carbonate subsystem only in solution*, the literature records the establishment of the mass parameter alkalinity as alternative to the total carbonate species parameter. Measurement of alkalinity plus the pH of the solution provides sufficient information to calculate the total carbonate species concentration in the system. The alkalinity parameter is defined relative to a selected reference solution state. With the carbonate subsystem, three alkalinities can be defined, relative to the $H_2CO_3^*$, HCO_3^- and CO_3^{2-} reference solution states. The alkalinity relative to the $H_2CO_3^*$ reference solution state, termed $H_2CO_3^*$ alkalinity, has the advantage that its magnitude is not influenced by loss or gain of CO_2, which overcomes the sampling problem described earlier. With only the carbonate subsystem present in solution, procedures to identify the $H_2CO_3^*$ solution reference state (and the HCO_3^- and CO_3^{2-} solution reference states) have been developed, some semi-empirical, some based on prior pH experimental titrations; in this way, an alkalinity relative to the solution reference state can be measured and the total carbonate species concentration determined. However, for the carbonate subsystem only in solution, Gran (1952) had proposed an ingenious method which allows the $H_2CO_3^*$ alkalinity to be determined relative to the reference solution state without experimentally identifying the reference state.

With mixtures of weak acid/bases in solution, empirical or experimental identification of the reference solution state is well-nigh impossible and, consequently, using the reference solution state approach provides for only an *approximate* empirically defined alkalinity measurement. It was the intention in this task to develop procedures whereby the carbonate subsystem could be evaluated in a mixture of weak acid/bases.

<u>Extension of Gran function method to assess $H_2CO_3^*$ alkalinity in mixtures of weak acid/bases</u>

In reviewing the procedures available to determine the alkalinity for a solution containing only the carbonate subsystem, the method developed by Gran (1952) was the only one that did not require knowledge of the reference solution state. Accordingly, this method was selected for extension to mixtures of weak acid/base systems that include the carbonate subsystem. This extension required a generalization of the concepts of alkalinity and acidity and the development of a consistent nomenclature for naming these (Loewenthal *et al.*, 1989), as follows:

- Alkalinity (acidity) is defined as the proton (i.e. hydrogen ion) accepting (donating) capacity of the solution of mixed acid/base subsystems in water relative to some reference solution state.

- The reference state, also called the equivalent solution state, is defined in terms of a selected set of reference species, one species from each of the weak acid/base subsystems (in water) making up the mixture.

- The alkalinity (or acidity) is named after the particular set of reference species selected e.g. the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity (acidity) is the alkalinity (acidity) associated with $H_2CO_3^*$, $H_2PO_4^-$, HAc and NH_4^+ reference species of the carbonate, phosphate, acetate and ammonium subsystems respectively in a mixture of these four weak acid/base subsystems.

- Theoretically there is complete freedom in selecting the set of reference species, but practically a particular set will be superior to other sets because it leads to more accurate measurement of the associated alkalinity (acidity).

- For the same mixture of weak acid/base subsystems, alkalinity (acidity) with respect to one set of reference species is related to the alkalinity (acidity) with respect to another set of reference species via the total species concentrations of the weak acid/base systems making up the mixture, i.e. an alkalinity or acidity with respect to one set can be converted to an alkalinity or acidity with respect to another set (In the next section, this conversion will be shown to be of crucial importance in solving dosing problems).

- To characterize a mixture of weak acid/base subsystems, the number of measurements to be made are one for the water, which is the pH, and one for each of the weak acid/base subsystems which usually is the total species concentration, except for the carbonate subsystem. For the carbonate subsystem the total carbonate species concentration measurement is replaced by an alkalinity measurement associated with a particular set of reference species.

- The set of reference species that provides the most accurate alkalinity measurement of a mixture of carbonate, phosphate, acetate and ammonium subsystems, and hence the most accurate for characterization of the mixture, is the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity.

Taking note of the considerations above, the Gran function was extended to include mixtures of weak acid/bases in solution in which the carbonate subsystem is present. In this regard:

- The $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity is quantified by means of a Gran titration in which the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity equivalent solution pH (i.e. end point pH) is not required to be known; pH values versus acid added are recorded in the pH range 3 to 4 and the $H_2CO_3^*/H_2PO_4^-/HAc/NH_4^+$ alkalinity is calculated by means of the extended Gran function from the pH versus acid added data.

- For calculating the alkalinity from the Gran function for the carbonate subsystem alone, only pH readings versus acid added in the pH range 3 to 4 are required to be known. For calculating the alkalinity from the *extended* Gran function to *mixtures* of weak acid/base subsystems, the total species concentrations of those subsystems which exert buffer capacity in the pH range 3 to 4 and the activity of the hydrogen ion are also required to be known: For example, to calculate the alkalinity of a mixture of carbonate, phosphate, acetate and ammonium systems, the total phosphate and acetate species concentrations need to be known because these subsystems exert buffer capacity in the pH range 3 to 4; the total ammonium species concentration does not need to be known because this subsystem does not exert buffer capacity in this pH range. The

activity of H^+ can be estimated from the Davies equation provided the TDS < 2 500 mg/ℓ.

- For characterization, *all* the total species concentrations of the weak acid/base subsystems of interest need to be known.

- The sulphate-bisulphate system influences the Gran titration results but not the alkalinity value that is calculated from these results.

- Using a number of made-up mixtures of carbonate, phosphate, acetate and ammonium subsystems, the extended Gran titration method was tested and found to give alkalinity values within 1% of the expected values, and total carbonate species concentrations within 2% of the expected values.

- The characterisation procedure gives the total carbonate species concentration at the time the pH of the sample is taken. Consequently, in this procedure, like that for the carbonate subsystem only, care must be exercised that CO_2 evolution/dissolution and/or $CaCO_3$ precipitation/dissolution does not take place between the time the sample is taken and the pH is measured. Once the pH has been measured, the CO_2 exchange no longer affects the results because the reference species for the carbonate system for determining the alkalinity are the $H_2CO_3^*$ species. Neither will $CaCO_3$ precipitation, provided the full sample is titrated in the sample container.

DOSING ESTIMATION IN MIXED WEAK ACID/BASE SYSTEMS

Background

Having characterized a solution containing one or more weak acid/bases, the next important aspect is that of chemical conditioning of a solution, that is, determining the chemical type and dosage to achieve a desired change in the chemical state of the solution.

Chemical conditioning is necessary in a wide spectrum of weak acid/base problems. Examples of such problems, categorized according to the phases in which the chemical reactions take place (aqueous, solid or gaseous) are as follows:

(1) *Single phase aqueous problems.* pH/alkalinity/acidity adjustment of solutions by addition of weak or strong acids and bases, or salts of these (e.g. carbonate system in stabilization of water supplies); assessment of transient solution states during which precipitation/dissolution or gas exchange takes place (e.g. kinetics of solid $CaCO_3$ precipitation, or dissolution of solid $CaCO_3$).

(2) *Two phase aqueous-gas equilibrium problems.* Equilibrium between dissolved carbonate species, gaseous CO_2 and pH (e.g. in anaerobic digesters the effect due to changes in pH caused by changes in short chain fatty acid concentration).

(3) *Two phase aqueous-solid equilibrium problems.* Incongruent precipitation/ dissolution (e.g. in chemical removal of SO_4^{2-}, aqueous-solid equilibrium of $BaCO_3$, $BaSO_4$ and $CaCO_3$); precipitation of $CaCO_3$ and $Mg(OH)_2$ (e.g. water softening); precipitation with changes in CO_2 (e.g. struvite precipitation in anaerobic digesters).

(4) *Three phase aqueous-solid-gas equilibrium problems.* CO_2 stripping (e.g. CO_2 from dolomitic ground water with concomitant $CaCO_3$ precipitation); dissolution potential of solid $CaCO_3$ (e.g. redissolution of $CaCO_3$ after overdosing an anaerobic digester with lime and consequential precipitation of $CaCO_3$).

In the past equilibrium chemical dosing estimation procedures have been developed for solutions containing only the carbonate subsystem (Loewenthal and Marais, 1976; Loewenthal *et al.*, 1986; 1988). In this task it was proposed to develop dosing estimation procedures for solutions containing mixtures of acid/bases which may or may not include the carbonate subsystem. In this development, the procedures were to be restricted to single phase aqueous problems; two and three phase problems could be addressed in future contracts. Furthermore, taking due cognizance of the complexity of mixed weak acid/base systems, it was decided to focus attention almost exclusively on developing numerical procedures (algorithms) for dosing estimation; due to the increased availability of personal computers, for complex systems numerical type procedures are rapidly superseding graphical type procedures.

Solution and subsystem alkalinity

When it was attempted to apply the classical alkalinity/acidity/pH approach (used in solving dosing problems with the carbonate system only present in solution, Loewenthal *et al.*, 1986; 1988) to situations where more than one weak acid/base was present, the solution procedures became specific to each mixture and were very cumbersome. It became apparent that the difficulty in this approach arose from viewing the solution state *in toto* and developing equations for this solution. Accordingly, the focus of interest was shifted from the solution itself to the weak acid/base *subsystems* making up the solution. With this approach the solution alkalinity could be redefined in terms of the subsystem alkalinities and water subsystem alkalinity as follows:

Alkalinity of a solution (system) is the sum of the alkalinities due to the individual weak acid/bases (subsystems) in the solution relative to their respective selected reference species, plus the water subsystem alkalinity.

Expressing this definition mathematically,

$$\text{Solution alkalinity} = \sum_{j=1}^{n} \text{Alk}_j + \text{Alk } H_2O$$

where Alk_j = subsystem alkalinity for the "jth" weak acid/base subsystem relative to its selected reference species in a mixture of "n" weak acid/bases.

For example, for the weak acid/base subsystems carbonate, phosphate, ammonia and water with reference species $H_2CO_3^*$, H_3PO_4, NH_4^+ and H_2O respectively, one can write

$$H_2CO_3^*/H_3PO_4^-/NH_4^+ \text{ alkalinity} = \text{Alk } H_2CO_3^* + \text{Alk } H_3PO_4 + \text{Alk } NH_4^+ + \text{Alk } H_2O$$

Note that the set of reference species for the weak acid/base subsystems are the reference species for the solution.

or, if Y moles of HCO_3^- are added to this solution:

$$\Delta H_2CO_3^*/H_3PO_4/NH_4^+ \text{ alkalinity} = (2\text{–}1)\cdot Y = Y \text{ mol}$$

Dosing estimation algorithms

Algorithms for resolving chemical conditioning problems were developed from two basic tenets:

(1) Solution alkalinity equals the sum of the subsystem alkalinities plus the water subsystem alkalinity.

(2) Solution alkalinities either remain constant or change in a simple stoichiometric fashion with chemical dosing. (Note that subsystem alkalinities do not change in a stoichiometric fashion with chemical dosing).

Taking note of the above, dosing estimation algorithms were developed to resolve two types of dosing problems:

- Chemical dose for specified chemical dosage type and specified initial and final solution states.
- Final state for a specified initial state and specified chemical dosage and dosage type.

These dosing algorithms are relatively simple and are general, applying to any single or mixture of weak acid/bases in solution. The algorithms also lend themselves very readily to computerized solution procedures. These algorithms are set out in detail by Loewenthal *et al.* (1991).

DISCUSSION

In developing the dosing algorithms it became evident that the use of the terms alkalinity *and* acidity as explicit descriptive parameters was unnecessary and a cause for confusion, because for the same reference solution state the acidity was equal to the alkalinity, but of opposite sign. Since an alkalinity measurement is a 'normal' one whenever the carbonate subsystem is present, the alkalinity term was retained as a capacity parameter; the acidity term accordingly was discarded.

The terms alkalinity and acidity developed from very practical considerations. Even though they have been defined quantitatively in terms of a reference solution state, there still exists confusion in the minds of many users as to what the terms actually mean, illustrated by, for example, a definition for alkalinity relative to $H_2CO_3^*$ reference solution state and one for acidity relative to CO_3^{2-} reference solution state.

In this task we emphasized the inseparability of alkalinity and acidity with respect to the same reference solution state and hence discarded the acidity term. However, even retaining only the alkalinity term creates a restricted image in the mind of the user. It would be most desirable to separate out the true concept of alkalinity from that conjured up in the mind of the user. For this reason, the Authors suggest that in future development, instead of the term alkalinity, the term *proton accepting capacity* (defined relative to some proton reference state) be used. The proton donating capacity will be simply the negative of the proton accepting capacity

Following the approach described above, capacity parameter equations could be developed for subsystem alkalinities in terms of pH and subsystem total species concentrations, with the solution capacity parameters equal to the sum of the subsystem capacity parameters of the individual weak acid/base subsystems.

Changes in capacity parameters with dosing

To develop dosing estimation procedures, the change in capacity parameters with dosing must be determined.

In determining the change in the capacity parameters with dosing (in alkalinities and total species concentration), clear distinction must be made between the *subsystem* parameters and *solution* parameters as these change very differently with dosing.

Subsystem parameters
For the subsystem parameters, the following generalizations could be identified:

(1) Subsystem alkalinities change in a complex fashion with dosing (due to change in pH).

(2) Total species concentrations for all subsystems except that including the dosing type remain constant with dosing.

(3) Total species concentration for the subsystem including the dosing type increases by the amount of dosage chemical added.

Solution parameters
For the solution parameters the following generalizations could be identified:

(1) Solution alkalinities that *include* the dosage type as a reference species do not change with dosing. For example, $H_2CO_3^*/H_3PO_4/NH_4^+$ alkalinity does not change for addition of $CO_2(H_2CO_3^*)$, H_3PO_4 or NH_4^+.

(2) Solution alkalinities that *do not include* the dosage type as a reference species change in a simple stoichiometric fashion with dosing, given by

$$\Delta \text{ Solution alkalinity} = (\text{number of protons for reference species of the subsystem including dosing type} - \text{number of protons for dosing type}) \cdot \text{mass of dose added}$$

For example, if X moles of $CO_2(H_2CO_3^*)$ are added to a solution with reference species CO_3^{2-}, H_3PO_4 and NH_4^+, then:

$$\Delta CO_3^{2-}/H_3PO_4/NH_4^+ \text{ alkalinity} = (0-2) \cdot X$$

$$= -2X \text{ mol}$$

If X moles of CO_3^{2-} are added to a solution with reference species $H_2CO_3^*$, H_3PO_4 and NH_4^+, then:

$$\Delta H_2CO_3^*/H_3PO_4/NH_4^+ \text{ alkalinity} = (2-0) \cdot X$$
$$= 2X \text{ mol}$$

CHAPTER 5

CHEMICAL PHOSPHORUS REMOVAL FROM MUNICIPAL WASTEWATER BY THE DISPOSAL OF WASTE ALUM SLUDGE TO THE ACTIVATED SLUDGE SYSTEM

INTRODUCTION

In many instances waterworks waste alum sludge is disposed of by discharging it into a stream. In this investigation the disposal of alum sludge to activated sludge systems treating municipal sewage was investigated. The advantages perceived were that not only would it provide a better means of disposal of the alum sludge but it also may stimulate some phosphorus removal from the wastewater by chemical precipitation.

EXPERIMENTAL INVESTIGATION

Two long sludge age (20 days) Modified Ludzack Ettinger (MLE) predenitrification systems receiving unsettled municipal wastewater at a controlled concentration of 500mg COD/ℓ as influent were operated for a period of 310 days, one as an experimental and the other as a control unit. The anoxic mass fraction in each unit was large (70%), to mimic many long sludge age nitrification denitrification systems in operation in South Africa, and nitrate was dosed into the anoxic reactors to maintain anoxic conditions so that biological excess phosphorus removal would not take place to interfere with the chemical removal results.

Alum sludge was dosed into the anoxic reactor of the experimental system on a once daily batch basis at a controlled rate varying between 173 mg inorganic suspended solids (ISS/d) to 491 mg ISS/d which is equivalent to 17,3 to 49,1 mg ISS/ℓ. The alum sludge was derived for Kloofnek and Steenbras water treatments works which treat the brown waters of the Western Cape. The total suspended solids (TSS) of these sludges averaged 61% organic (volatile), 39% inorganic (ash), 0,005 mgN/mgTSS and 0,61 mgCOD/mgTSS. Accepting that the ash content is entirely $A\ell_2O_3$, a reasonable assumption for the soft waters of the Western Cape and confirmed with unused alum, the Aℓ content of alum sludge is 0,53 mg Aℓ/mgISS or 0,20 mg Aℓ/mgTSS.

RESULTS AND DISCUSSION

By monitoring the P removal in the experimental and control systems it was found that at steady state the alum sludge stimulated a P removal of 0,18 mgP/mgISS added when the pH of the mixed liquor averaged 7,6. On the basis of the removal ratios given above, this was about 1/3rd of the stoichiometric removal ratio. To

relative to the same proton reference state. This approach will remove completely a confusion often encountered, that the term alkalinity is associated with an alkaline state and the term acidity with an acidic state. The work in this task has shown that one may have a proton accepting or proton donating capacity in the alkaline or acidic region depending only on the selection of the reference solution state.

The work on mixtures of weak acid/bases in aqueous solutions has been developed even further in another contract between the WRC and UCT [pelletization in upflow anaerobic sludge bed (UASB) systems]. This work provides for the determination of H_2CO_3* alkalinity and short-chain fatty acid (SCFA) concentrations in solutions containing these two weak acid/bases as unknowns, and concentrations of phosphate, ammonium and other weak acid/bases as knowns. The H_2CO_3* alkalinity and SCFA are estimated from a single acid 5 pH point titration, a procedure requiring considerably less effort than the extended Gran function method.

CHAPTER 6

CLOSURE

One of the principal objectives of this contract was to update the manual for the design of nutrient removal plants published in 1984. Such an update, to be of substantive value, should provide, with credible expectation, improved guidelines for the design of nutrient removal plants, that would substantially increase their performance and would resolve problems that have become apparent in the operation of existing plants.

A nutrient removal plant is a complex system in which the different system elements, processes and compounds often exhibit interaction in a complex manner; resolution of one problem may bring into focus, or create, another problem – it is most unlikely that a "final" solution ever will be attained.

The design manual of 1984 provided credible guidelines and recommendations for carbonaceous material degradation, nitrification and denitrification aspects based on sound microbiological/biochemical and kinetic behavioural patterns. Design guidelines for biological excess phosphorus removal (BEPR), however, still contained an appreciable empirical content.

Research at the University of Cape Town under this contract, together with research by the Johannesburg City Council, has significantly broadened understanding of BEPR, and of its microbiology/biochemistry and kinetics. At the present moment, BEPR can be judged to have attained the same level as the nitrification and denitrification aspects; it awaits only integration with the nitrification/denitrification to give a general nitrification/denitrification/biological excess phosphorus removal (NDBEPR) kinetic model. Once this integration has been achieved, it should greatly assist in identifying soundly based guidelines for design of NDBEPR systems.

In nutrient removal plants the one important problem still unresolved is the cause(s) for the bulking sludges, which are so common in these plants. However, even in this aspect research over the past 6 years (under a separate contract between the WRC and UCT) has led to significant advances in understanding, particularly so over the past year. There is now a reasonable expectation that soon will be available that will guide the designer as to the intensity of bulking to be expected in a particular nutrient removal plant.

We can conclude that within the near future, sufficient information will be available to enable the design manual to be updated. The updated design manual will assist in a substantial manner in the design of nutrient removal plants to attain improved and more dependable nutrient removal performance and optimal sludge settling characteristics. Work on this aspect will be continued in the new consolidation contract.

check this value, ancillary stirred jar batch precipitation tests were conducted for a period equal to the sludge age of the experimental system, 20 days, with both unused alum and alum sludge at different Aℓ/P ratios and pH values. It was found that the mgP removal/mg ISS added for the alum sludge, after 20 days, (1) decreased from 0,54 to 0,29 as the test pH increased from 6,8 to 7,8, (2) compared favourably with the unused alum values, and (3) was approximately stoichiometric at pH between 6,8 and 7,3. A thorough analysis of the data has not been completed, so that it is not yet possible to advance an explanation for the apparent difference in P removal/unit ISS between the batch and continuously fed experimental systems.

Other interesting results that emerged from the work were:

(1) The VSS and COD of the alum sludge was not biodegradable and accumulated with the sludge in the biological reactor. The filtered effluent COD and TKN (and turbidity) did not increase probably as a result of the low soluble COD in the alum sludge. Hence the oxygen demand of the activated sludge system was not increased but the sludge production increased by the mass of alum sludge added.

(2) The dewaterability of the alum sludge was rather poor yielding SRF and CST values of 70.10^{12} m/kg and 25 sec respectively. However, the values for the alum/activated sludge mixture (45% of TSS being alum sludge TSS) was the same as that of the activated sludge only, i.e. 20.10^{12} m/kg, indicating that the dewaterability of the alum sludge is improved during its retention in the activated sludge plant for 20 days. This improvement is not obtained by simply mixing the two sludges – if this is done a dewaterability is obtained somewhere between the two sludges depending on their proportions in the mixture. The improvement arises from the exchange of the OH^- with PO_4^{3-} on the $A\ell^{3+}$ thereby changing the gelatinous $A\ell(OH)_3$ to an $A\ell PO_4$ precipitate.

(3) COD removal, nitrification and denitrification were not affected by alum sludge addition.

(4) Alum/activated sludge mixture settled slightly better than the activated sludge alone but still showed sporadic low F/M filamentous bulking incidents with DSVI's > 250 mℓ/g.

Details of this research task are given by Power *et al.* (1991).

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