A PARAMETRIC MODEL FOR BIOLOGICAL EXCESS PHOSPHORUS REMOVAL

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Abstract

Biological excess phosphorus removal in nitrification-denitrification single sludge activated sludge processes is shown to be stimulated by having a concentration of rapidly biodegradable COD ($S_{bsa}$) ≥ 25 mg/l in the anaerobic reactor; the magnitude of the P removal is determined by a P removal propensity factor (Pf) defined by the product of ($S_{bsa}$ - 25) and the fractional mass of sludge in the anaerobic reactor. $S_{bsa}$ is rapidly depleted by nitrate entering the anaerobic reactor; in the Phoredox process treating municipal waste flows if the TKN/COD ratio of the influent is greater than about 0.08 mgN/mgCOD the process, if designed to ensure efficient nitrification, is unlikely to remove all the nitrate and nitrate is recycled to the anaerobic reactor whereupon P removal declines. A new process is proposed that protects the anaerobic reactor from the nitrate in the effluent; tests indicate that this process can give excess P removal for TKN/COD ratios up to 0.14 mgN/mgCOD.

INTRODUCTION

One of the main difficulties in devising an activated sludge process to give excess biological phosphorus (P) removal has been the lack of an acceptable mechanistic explanation of the phenomenon. Although a number of mechanisms have been advanced, process configurations and operational procedures to exploit such mechanisms have not, as yet, supported the hypothesized mechanisms unambiguously; evidently some aspects that affect the phenomena are not yet identified or correctly understood. Research into the process per se has, as a consequence, been forced to take the approach: "Let us see what happens if .....". The body of information that has been built up by this approach, although of a parametric or heuristic nature, has attained its own momentum and, in turn, provides data and situations which may be exploited by investigators focussing on the mechanistic aspects.

Since 1970 the University of Cape Town group has been engaged in intensive research into the activated sludge process. From the times Barnard in 1973 and 1975 proposed the respective explicit process configurations to remove nitrate and phosphorus biologically in the single sludge process, the group included enquiry also into these two phenomena as part of its research program. In this regard the group accepted, as a basic proposition, that nitrate and excess P removal are biologically mediated phenomena and hence should be viewed as integral parts of the general theory of the activated sludge process. In time this policy has proved to be a sound one.
because research into denitrification contributed considerably to the understanding of the aerobic process kinetics, and it was only after the establishment of the general nitrification-denitrification activated sludge model that it has become possible to make headway towards describing biological excess phosphorus removal even though the phenomenon is not yet understood.

In this paper the development of a quantitative semi-empirical parametric method for describing excess phosphorus removal will be briefly set out. A semi-historical approach is adopted as this will contribute to an overall appreciation of both the problem and the difficulties attendant in finding a solution.

EARLIER DEVELOPMENTS

With regard to excess P removal, from the reports of earlier investigators (e.g. Fuhs and Min Chen 1975, Barnard 1976) one conclusion has emerged which now appears to be generally accepted, i.e. excess removal is stimulated by stressing the organism by withholding the oxygen supply. Quantification of this stress, however, has presented major obstacles principally for two reasons, (1) the parameter in terms of which the stress is to be formulated is unknown and (2) in nitrification-denitrification systems introduction to and the presence of nitrate in the unaerated reactors are confounding factors that have complicated the problem of identification of the stress parameter. These difficulties will be evident in much of the presentation that follows.
Barnard (1974) in pilot scale studies on the Bardenpho process (Fig.1) reported that excess biological P removal is induced if at some point in the process configuration the organism mass is stressed by subjecting it to an "anaerobic" state (i.e. a state in which neither oxygen nor nitrate is present) such that phosphorus is released by the sludge mass to the bulk liquid. He proposed to produce this state efficiently by including an anaerobic reactor ahead of the primary anoxic (or pre-denitrification, pre-D) reactor in the Bardenpho process, this reactor receiving the influent flow and the underflow recycle from the secondary settling tanks, (Fig.2). This configuration has become known as the 5-stage Phoredox or simply as the Phoredox system.

For design purposes the criterion for P release did not prove helpful because it gave no guidance as to when the release could be expected. Barnard (1976) proposed that the anaerobic reactor be given a nominal retention time (mean daily flow/anaerobic volume) of one hour presumably because, from his pilot scale studies, this retention time gave rise to P release and adequate P removals.

To explain the excess removal phenomenon, Barnard in 1976 hypothesized that it is not the release per se that stimulates the excess uptake mechanism but that the release indicates that a certain low redox potential has been established, i.e. that the low redox potential triggers off the release and thereby stimulates excess P uptake. In terms of this hypothesis nitrate recycled via the underflow to the anaerobic reactor will restrain, in some degree, the level to which the redox potential can be lowered and consequently, nitrate can be expected to influence excess P uptake adversely. However, apparently he accepted that the Phoredox process can always be designed to denitrify completely in which event the recycle will contain zero nitrate, and the redox potential in consequence will attain the required low value. No measurements of the redox potential were reported.

Nicholls (1975) at full scale, and McLaren and Wood (1976) and Simpkins and McLaren (1978) at laboratory and pilot scale applied the Phoredox process at approximately 20°C to treat effluents from Johannesburg and Pretoria, and were successful in attaining excess P removal. They were also successful in obtaining excess removal in the Modified or 3-stage Phoredox (Fig.3) i.e. a Phoredox process without the post-denitrification (post-D) and reaeration reactors. Simpkins and McLaren found that (1) the anaerobic reactor was necessary for excess P removal, (2) nitrate in the recycle adversely affected P removal and (3) increasing the volume of the anaerobic reactor increased the excess P removal. These findings were in conformity with Barnard's redox potential hypothesis although again no redox potential measurements were taken.

None of the investigations above provided a reliable model to predict the magnitude of the denitrification to be expected even though it was evident from their experimental work that for design, evaluation of the nitrate in the recycle would appear to be crucial in assessing the success of a process both in stimulation of the P release and magnitude of the P uptake.

Marais and his group (Stern 1974, Martin 1975, Marsden 1976, Wilson 1976, with Marais) recognized the importance of quantization of nitrate removal. In the Bardenpho process they replaced the completely mixed pre- and post-D reactors by plug flow reactors and, by measuring the nitrate along the reactor axes under constant flow and load conditions, investigated the kinetics of denitrification. They found that:

1. In the pre-D reactor nitrate reduction took place in two consecutive linear phases; in the post-D reactor in a single linear phase. They formulated the system reduction* of nitrate concentration, ΔN, as follows:

\[
\Delta N = \frac{N_a Q (r+1)}{Q_r + rQ}
\]

*System reduction - reduction in concentration relative to the influent flow; actual reduction - reduction in actual concentration between influent and effluent of a reactor. Suppose actual reduction, ΔN, takes place in a reactor with recycle with respect to base flow of r and base flow Q, the system reduction, ΔN, is given by ΔN = N_a Q (r+1).
\[ \Delta N = K_1 X_a t + K_2 X_a (R_1-t) + K_3 X_a R_3 \]

(2) The reaction defined by \( K_1 \) persisted only for 1 to 10 minutes (i.e. \( 1 < t < 10 \) minutes) so that normally the reaction was complete well within the retention time \( R_1 \) (2-3 hours) of the plug flow reactor; also, the reduction due to the \( K_1 \) reaction was approximately proportional to the biodegradable influent COD, \( S_{bi} \), and the system removal could be expressed adequately by

\[ \Delta N = \alpha S_{bi} + K_2 X_a R_1 + K_3 X_a R_3 \]  

(1)

where

\[ R_1, R_3 \] = nominal retention time (h)  
\[ K_1, K_2, K_3 \] = denitrification rates (mg\( \text{NO}_3-N/mgX_a/h \)) 
\[ K_1 = 0.03(1,20)(T-20) \] for \( T >14^\circ C \)  
\[ K_2 = 0.0042(1.08)(T-20) \] for \( T >14^\circ C \)  
\[ K_3 = \text{for } T <14^\circ C \]  
\[ K_3 = 0.0032(1,03)(T-20) \] for \( 10^\circ C < T < 25^\circ C \)  
\[ X_a \] = active mass concentration (mg\( \text{VASS}/\ell \))  
\[ \Delta N \] = mg\( \text{NO}_3-N \) removed/\ell of influent flow  
\[ S_{bi} \] = biodegradable influent COD concentration  
\[ \alpha = 0.028 \text{ mg}\( \text{NO}_3-N/mg \text{ biodegradable COD} \) \]  
\[ t \] = duration time of \( K_1 \) reaction (h)

(3) Equation (1) was found to apply provided the nitrate was not reduced to zero in one or both of the anoxic reactors. If, in a particular reactor, nitrate was reduced to zero then by increasing the nitrate input to the reactor, (by increasing the recycle for example), the system nitrate removal increased, the zero nitrate point moved along the reactor axis towards the effluent end, until nitrate appeared in the effluent. Once this happened any further increase in the recycle had no effect on the system nitrate removal.

(4) The removal of nitrate could be increased by increasing the volumes of the anoxic reactors at the expense of the aerobic reactor volumes, i.e. increasing the unaerated sludge mass fraction of the system, but this fraction could not be increased \( \text{ad lib} \); if increased above some critical value nitrification ceased. The upper limit was found to be a function of the maximum specific growth rate of the nitrifiers at the process temperature, \( \mu_{\text{nmT}} \), and the sludge age, \( R_S \). It was further observed that \( \mu_{\text{nmT}} \) appeared to differ for every waste flow investigated. The \( \mu_{\text{nmT}} \) was not measured directly but the relative magnitude of \( \mu_{\text{nmT}} \) was evident by noting the maximum unaerated mass fraction that could be tolerated before nitrification ceased. For example with one waste flow, nitrification ceased at an unaerated mass fraction of 0.3 (at \( 14^\circ C \) and \( R_S = 20 \) days), whereas for another this occurred only at an unaerated mass fraction of 0.55.

(5) To ensure that efficient nitrification takes place (>95 percent conversion of available TKN) it was necessary to increase the aerobic mass fraction to a value greater than the minimum that just allows nitrification; an increase of 25 percent (\( S_F = 1.25 \)) in the aerobic sludge mass fraction calculated at the lowest process temperature expected will guarantee efficient nitrification throughout the temperature range even under cyclic flow conditions.

The denitrification formulation, Eq.(1), although without any rational link to the activated sludge theory was found to provide a close description of nitrate removal in the Bardenpho process under constant flow and load conditions. The restriction on the unaerated mass fraction, (4) and (5) above, to satisfy the requirement of efficient nitrification, may result in insufficient anoxic sludge mass to guarantee
Model for biological excess phosphorus removal

131

total nitrate removal. When total nitrate removal is not possible then, because 
$K_1 > K_3$ (for $T > 14^\circ C$) a consequence of Eq. (1) is that for maximum removal the post-
D reactor should be omitted and its volume added to the pre-D reactor - to give the 
modified Ludzack-Ettinger (MLE) configuration, Fig. 4. Under these conditions the 
MLE configuration will produce a lower nitrate effluent than the equivalent 
Bardenpho.

As part of the investigation into denitrification using the Bardenpho and MLE pro-
cesses, measurements on P release in the pre- and post-D reactors, and excess up-
take were taken. These results indicated that:

(1) A pre-D reactor, irrespective of whether it is in an "anoxic" or "anaerobic" 
state*, always stimulated some excess P removal whereas a post-D reactor 
appeared to have virtually no effect.

(2) Over periods of time excellent excess P removal was obtained with nitrate pres-
ent in the pre-D reactor, in which event the removal took place principally in 
the pre-D reactor. Over other periods P release was observed in the pre-D 
reactor with nitrate present in which event the excess uptake took place in the 
aerobic reactor.

(3) Using the MLE process with anoxic mass fractions ranging from 0.07 to 0.33, 
under a constant a-recycle of 2, to give actual anoxic retention times, (volume 
of reactor/actual flow), ranging from 15 to 90 minutes, maximum excess P removal 
was attained at an actual anoxic retention time of about 30 minutes (anoxic mass 
fraction = 0.13) when the nitrate in the effluent from the anoxic reactor was 
14 mg/l! Excess system removal achieved was 8.2 mgP/l for an influent COD of 
660 mg/l. When the anoxic mass fractions were increased above or decreased be-
low this optimal value the excess removal decreased concomitantly.

The phosphorus removal response observed above is difficult to reconcile with the 
observations of Barnard, Nicholls, Simpkins and others reported earlier - all these 
investigators found that P release under anaerobic conditions was a prerequisite to 
excess uptake. Perhaps a different mechanism operated which has not yet been 
identified.

The approach described above eventually was abandoned because (1) the process re-
response appeared to be rather unpredictable and, more important, (2) the small anoxic 
mass fractions apparently necessary to achieve high excess removal resulted in 
relatively inefficient nitrate removal. Because of the second reason principally 
the UCT group turned their attention to the P removal characteristics of the Phore-
dox process, (Rabinowitz and Marais, 1980).

The basic configuration selected was the 3-stage Phoredox; it was selected in 
preference to the 5-stage for the following reason: The sewage source did not allow 
an unaerated mass reaction of greater than 40 percent at 14°C for a sludge age ($R_s$) 
of 20 days if efficient nitrification was to be maintained; taking account of the 
fact that in the Phoredox process the anaerobic reactor cannot contribute its full 
denitrification potential for measured TKN/COD ratio of this waste flow, the 5-stage 
process could not reduce the nitrate to zero. Consequently, as discussed earlier, 
the post-D reactor volume was added to the pre-D to obtain the maximum nitrate re-

*Anoxic; anaerobic: The meaning we will attach to these two terms, in nitrifica-
tion-denitrification processes, follows that originally used by Barnard, i.e. 
Anoxic: a state in which nitrate is present but no oxygen; Anaerobic: a state in 
which neither nitrate nor oxygen is present. The inadequacies of these defini-
tions is apparent when attempting to compare the state of two reactors of the same 
size in a completely mixed and a plug flow reactor respectively. A completely 
mixed anaerobic reactor, for example, will have no nitrate in the reactor and eff-
luent; the equivalent plug flow reactor however may contain nitrate for a consid-
erable portion of the reactor length i.e. be partly "anoxic", partly "anaerobic" - 
the inadequacy arises in that no indication is given as to the intensity of the 
state.
moval and hence the minimum nitrate in the underflow recycle. The findings from this investigation can be summarized as follows:

(1) When the nitrate concentration in the effluent (and underflow recycle) was low usually P release and excess uptake were observed. In general there was a tendency for the excess uptake to decrease quite disproportionately as the nitrate in the recycle increased, a behaviour also noted by Simpkins and McLaren and Barnard.

(2) With different batches of sewage having the same nitrate concentration in the recycle, one batch may give high P release and excess removal whereas the next may give no (or little) release and little excess removal. No apparent reason for this behaviour could be discovered.

The overall P removal performance was disappointing; not only did the plant not remove P in excess over long periods of time but the removal was erratic due to the effects of (1) or (2) above, or both. Increasing the anaerobic mass fraction during periods of low P removal was found to be counter-productive as this could be done only at the expense of the anoxic mass fraction which in turn gave rise to increased nitrate in the recycle.

After a year's endeavour, by the end of 1978 it was concluded that for the waste flows from Cape Town, treatment by the Phoredox type process was not suitable for excess P removal; this did not imply that the process might not be suitable for other waste flows but the investigation did bring to light that there were constraints, not adequately recognised before, that may prevent high P removals:

(1) For any selected sludge age and minimum temperature the requirement for efficient nitrification imposes an upper limit on the unaerated mass fraction.

(2) The limitation on the unaerated mass fraction correspondingly limits the concentration of nitrate that can be removed. If the nitrate generated is higher than the denitrification achievable, nitrate will appear in the effluent and, in the Phoredox system, the P removal will be adversely affected.

**LATER DEVELOPMENTS**

**University of Cape Town Process (UCT Process)**

From the findings on the Phoredox process it was clear that irrespective of other factors that may affect the excess P uptake, a major factor influencing the uptake is the presence of nitrate in the underflow recycle. If the nitrate content in the underflow to the reactor can be eliminated or kept at very low concentration, then there is a high expectation that excess P removal will be obtained. The principal obstacle to attaining this desirable end in the Phoredox process is that the nitrate discharged to the anaerobic reactor is linked directly to its concentration in the effluent. If for any reason the nitrate concentration increases with the COD remaining constant, i.e. if the influent TKN/COD ratio increases, the process offers little option to reduce this by operational means. The only operational means available is to reduce the magnitude of the underflow recycle but this is a risky option as the settleability of the mixed liquor in the plants tends to be poorer than in pure aerobic systems. Evidently a process configuration is needed that makes the anaerobic reactor independent of the effluent nitrate concentration. Towards this end, after a series of attempts, the configuration shown in Fig.5 was devised called the University of Cape Town process (UCT process).

In the UCT process, the settling tank underflow (s) recycle as well as the mixed liquor a-recycle are discharged to the anoxic reactor and an additional mixed liquor (r) recycle from the anoxic to the anaerobic reactor is introduced. The nitrate recycled to the anoxic reactor can be controlled by appropriately adjusting the mixed liquor a-recycle such that the nitrate concentration in the outflow of the anoxic reactor remains approximately zero. In consequence the mixed liquor r-recycle from the anoxic to the anaerobic reactor will contain very little or no nitrate and the anaerobic condition in the anaerobic reactor will be optimal.
Thus, in the UCT process by application of an appropriate operational control strategy the anaerobic reactor can be maintained independent of the nitrate in the effluent even if the TKN concentration to the plant varies.

Laboratory scale tests on the UCT process showed immediate improvement in excess P removal in both the concentration removed and the consistency in removal over those obtained in the Phoredox process. But perhaps the most important achievement, from a research point of view, was that with the UCT process it was now possible to eliminate the confounding effect of the nitrate in the recycle flow to the anaerobic reactor on excess P removal so that other factors influencing the excess removal could be investigated with greater ease. In the experimental response data the effects of these other factors now became clearly evident:

(1) For the same influent COD, one batch of sewage gave high removals, another gave low, an observation previously surmised but not explicitly identified due to the difficulty of isolating this effect when nitrate was recycled to the anaerobic reactor.

(2) Generally as the storage time of a batch of sewage (at 5°C) increased, both the excess P removal and the nitrate removal declined. Evidently on storage a progressive change was taking place in the constitution of the sewage which acted adversely on the two phenomena; direct evidence of change was indicated by the gradual reduction of COD of the batch during storage.

Identification of the factors in the sewage that influenced P removal proved to be a long and tedious undertaking; any success eventually attained can be ascribed wholly to having available the general nitrification-denitrification kinetic activated sludge model. To describe the developments in excess P removal and inter alia to give answers to the apparently erratic behaviour mentioned above, it is necessary to review briefly those aspects in the general theory that assisted in developing a solution.

Denitrification Aspects

A general aerobic kinetic model for the activated sludge process, including nitrification, was presented by Dold, Ekama and Marais (1980). Van Haandel, Ekama and Marais (1981) extended the model to include the kinetics of denitrification. The extended model, when calibrated, was found to describe the response of the multi-reactor nitrification-denitrification activated sludge process with unexpectedly good accuracy, under any cyclic influent flow and COD and TKN load patterns, both at laboratory, (van Haandel et al., 1981) and at full scale, (Nicholls, 1982).

There are two basic aspects, inter alia, in which this model differs from previous activated sludge models, (1) the influent COD, $S_{ti}$, is divided into a number of fractions, unbiodegradable soluble, $S_{u_{si}} = f_{u_{si}}S_{ti}$, unbiodegradable particulate $S_{u_{pi}} = f_{u_{pi}}S_{ti}$ and biodegradable $S_{bi} = (1-f_{u_{pi}}-f_{u_{si}})S_{ti}$. The biodegradable fraction, $S_{bi}$, in turn is subdivided into two fractions, (i) rapidly biodegradable soluble $S_{b_{si}} = f_{b_{si}}S_{bi}$ and (ii) slowly biodegradable particulate $S_{b_{pi}} = (1-f_{b_{si}})S_{bi}$. The two biodegradable fractions are metabolised by respective mechanisms that differ substantially, the rapidly biodegradable soluble fraction being absorbed directly and the slowly biodegradable particulate requiring adsorption and extra-cellular enzymatic breakdown prior to absorption, the two mechanisms being modelled by the Monod and the Levenspiel active-site type reaction rates respectively. (2) The classical synthesis-endogenous respiration approach to modelling bacterial growth kinetics is discarded in favour of a growth-death model. In this model only growth and death is recognized, no maintenance energy per se. On death the organism lyses its energy in the form of slowly biodegradable particulate COD to the bulk liquid, to add to the energy entering the system via the influent flow. Recognition of the bi-substrate and growth-death hypotheses formed the basis for developing an integrated model to describe the process response under anaerobic, anoxic and aerobic conditions in the activated sludge process and eventually, formed the basis also for a heuristic quantitative description of the excess P removal phenomenon.
By means of the extended model, under constant flow and load conditions, the two phase behaviour of denitrification in the pre-D reactor and the single phase behaviour of denitrification in the post-D reactor could be accurately reproduced and it was demonstrated that the first phase in the pre-D reactor is due solely to the rapidly biodegradable COD, the second phase in the pre-D and the single phase in the post-D reactors due to the slowly biodegradable particulate COD. In this fashion the formerly empiric relationship for denitrification, Eq.(1), was given a fundamental basis. From the behaviour of the general model it was possible also to develop simple equations to describe the nitrification behaviour in the multi-reactor nitrification-denitrification system under constant flow and load conditions. The nitrification and denitrification behaviour as predicted by the simple equations were found to be very close to that predicted by the general model (van Haandel, Dold and Marais 1982).

Using the simple nitrification and denitrification equations described above two mass parameters were developed which assist considerably in appreciating the behaviour of nitrification-denitrification systems, i.e. (1) the nitrification capacity which is the maximum mass concentration of nitrate (with respect to the influent) the aerobic reactors can generate, and (2) the denitrification potential which is the maximum mass of nitrate (with respect to the influent) an unaerated reactor can denitrify if nitrate is always present in the reactor and in the effluent from the reactor. If insufficient nitrate is recycled to the unaerated reactor the full potential for denitrification cannot be developed and the denitrification performance or denitrification capacity is less than the potential.

The nitrification capacity and denitrification potential are dependent principally on the influent TKN and influent COD concentrations respectively. Consequently, the influent TKN/COD concentration ratio forms a rough relative measure of the ratio of the mass of nitrate produced to the mass of nitrate denitrified and its magnitude forms a useful reference parameter against which the nitrification-denitrification behaviour of the various processes can be assessed. In evaluating the Bardenpho process, van Haandel et al., (1982) developed explicit equations which, for any selected wastewater characteristics (i.e. $\bar{u}_{nm20}$, $T_{max}$ and $T_{min}$, $f_{up}$, $f_{us}$ and $f_{bs}$) and process characteristics (i.e. sludge age $R_s$, sludge underflow $s$- and mixed liquor a-recycle ratios), give the maximum TKN/COD ratio, the maximum unaerated sludge mass fraction ($f_{xm}$) and the optimal division of $f_{xm}$ into pre- and post-D sludge mass fractions ($f_{x1}$, $f_{x3}$) for complete denitrification. By performing the calculation for a range of sludge ages and noting the upper limitation on $f_{xm}$ of 0.50 (and some other minor ones), design curves can be drawn. Figure 7 gives examples of such curves for $14^\circ C$ and $20^\circ C$; raw wastewater characteristics $\bar{u}_{nm20} = 0.36(1,123)(T-20)/d$, $f_{up} = 0.13$, $f_{us} = 0.10$ and $f_{bs} = 0.24$ and process characteristics $s = 1$, $a = 2,4,6$ and 8 at $20^\circ C$ and 4 at $14^\circ C$ and the factor of safety for nitrification $S_f = 1.25$. Figure 7 clearly illustrates the effect of sludge age on (i) the maximum TKN/COD ratio with which the Bardenpho process can achieve complete denitrification at the two temperatures, (ii) the maximum allowable unaerated sludge mass fraction ($f_{xm}$), (iii) the division of $f_{xm}$ between the pre-D ($f_{x1}$) and post-D ($f_{x3}$) reactors, and (iv) the effect of different a-recycle ratios. Note that the maximum TKN/COD ratio is not increased very much by increasing the a-recycle ratio above 4.

Selection of a Bardenpho process is indicated only if a horizontal line drawn at the expected influent TKN/COD intersects the TKN/COD vs $R_s$ curve for complete denitrification, for the lowest temperature expected, in which event the intersection point defines the minimum sludge age to be used. If no intersection occurs the Bardenpho process cannot achieve complete denitrification and the MLE process should be selected. When a Bardenpho process is possible, the sludge age should be chosen longer than the indicated minimum to provide greater security in achieving complete denitrification.

The TKN/COD ratio is not calculated directly but derived by a very close approximation from the (nitrification capacity)/(biodegradable COD) ratio.
Fig. 7. Maximum influent TKN/COD ratio, maximum unaerated sludge mass fraction \( f_{xm} \), pre-D and post-D sludge mass fractions \( f_{x1}, f_{x3} \) respectively versus sludge age for the Bardenpho 4 stage nitrification-denitrification processes operating between 14°C and 20°C at mixed liquor a-recycle ratios of 2, 4, 6 and 8.

\[ \mu_{nm20} = 0.36/d, \mu_{nm14} = 0.18/d, S_f = 1.25, S_s = 1, f_{xm,\text{max}} = 0.50, \text{raw wastewater with } f_{us} = 0.10, f_{up} = 0.13 \text{ and } f_{bs} = 0.24. \]

It should be noted in Fig. 7 that there is a maximum sludge age \( R_{SO} \) beyond which the maximum TKN/COD ratio for complete denitrification does not increase, i.e. about 28 days (for the sewage characteristic, etc. in the plot) at which the maximum TKN/COD ratio is 0.10 mgN/mgCOD. This maximum occurs when \( f_{xm} \) has reached its limit of 0.50. Hence to achieve complete denitrification for TKN/COD ratios of 0.10 mgN/mgCOD requires very long sludge ages, which makes the process volume per unit COD load very large. If the sludge age is restricted to say 20 days for economic reasons, the maximum TKN/COD ratio with which complete denitrification can be achieved reduces to 0.09 mgN/mgCOD at 14°C (Fig. 7).

**Phoredox Process Analysis**

Siebritz, Ekama and Marais (1980) extended the analysis of the Bardenpho process described above to the Phoredox process. In this process, a certain fraction \( f_{xa} \) of the total unaerated sludge mass fraction \( f_{xt} \) is "set aside" as an anaerobic reactor to establish the prerequisites for excess phosphorus removal. Only the remaining unaerated sludge mass fraction \( f_{xt} - f_{xa} \) is available as pre- and post-D reactors for nitrogen removal. If no nitrate is to be recycled to the anaerobic reactor (to ensure the most "intense" anaerobic condition) then complete denitrification must be achieved in the anoxic sludge mass fraction \( f_{xt} - f_{xa} \). The denitrification behaviour of the anoxic reactors in the Phoredox process for complete denitrification is the same as those in the Bardenpho process for complete denitrification.
fication. However for the same $f_{xt}$, the Phoredox process has less anoxic sludge mass available for denitrification than the Bardenpho process due to the presence of the anaerobic reactor. Hence, to obtain complete denitrification in the Phoredox process, the maximum TKN/COD ratio necessarily must be lower than that for complete denitrification in the Bardenpho process. By extending the example of the Bardenpho process given above (Fig.7) to the Phoredox process with $f_{xa} = 0.15$, a maximum TKN/COD ratio of 0.09 mgN/mgCOD is found for 28 days sludge age and 0.08 mgN/mgCOD for 20 days sludge age, both at 14°C. If the TKN/COD ratio of the influent to a Phoredox process exceeds these limits, complete denitrification is unlikely to be obtained, resulting in nitrate in the effluent and underflow s-recycle; nitrate discharged to the anaerobic reactor via the s-recycle will cause a decline in $P$ removal. From a design point of view, the TKN/COD ratio limits should be reduced to provide a factor of safety for denitrification, in which event the limits are probably nearer 0.07 to 0.08 mgN/mgCOD for sludge ages of 20 and 30 days at 14°C respectively.

The upper limit of the TKN/COD ratio of 0.07 to 0.08 mgN/mgCOD for successful operation of the Phoredox process severely restricts application of the process in the treatment of municipal wastewaters because the influent TKN/COD ratios of raw wastewaters range between 0.07 to 0.09 mgN/mgCOD, and of settled wastewaters generally are greater than 0.10 mgN/mgCOD.

**UCT Process Analysis**

An analysis of the UCT process showed that for this process also there is an upper limit to the TKN/COD ratio for excess $P$ removal. At a TKN/COD ratio of about 0.14 mgN/mgCOD (at 14°C and 25 days sludge age) the nitrate concentration in the effluent and hence in the underflow s-recycle ($s=1$) is so high that this recycle by itself fully loads the anoxic reactor to its denitrification potential, i.e. the mixed liquor a-recycle needs to be reduced to zero. Hence at TKN/COD ratios >0.14 mgN/mgCOD, nitrate will be present in the pre-$D$ reactor, and the discharge of nitrate to the anaerobic reactor cannot be avoided leading to a decline in excess $P$ removal. However the 0.14 mgN/mgCOD TKN/COD ratio limit for the UCT process is considerably higher than 0.08 mgN/mgCOD limit for the Phoredox process and is above that for most settled and raw municipal wastewaters which generally range between 0.07 to 0.11 mgN/mgCOD.

**Modified UCT Process**

Experience with the UCT process brought to light a different type of problem that could greatly affect the successful operation of the process. In the process, as the TKN/COD ratio increases, the a-recycle ratio needs to be reduced to avoid nitrate discharge to the anaerobic reactor. A reduction in the a-recycle ratio causes an increase in the actual anoxic retention time. It was found that for high influent COD concentrations (>500 mgCOD/l) and TKN/COD ratios >0.11 mgN/mgCOD, the actual anoxic retention time was greater than 1 hour. From experimental results, there are strong indications that when the actual anoxic retention time increases above about 1 hour, the settleability of the mixed liquor sharply declines.* One now faces a situation in which the process will operate satisfactorily with respect to $P$ removal but may fail due to settleability problems, or if the secondary settling tanks are designed to cope with the poor settling sludge, inordinately large settling tanks will be required. Consequently, in design to preserve good settleability, an upper limit of 1 hour must be imposed on the actual anoxic retention time. This limitation creates a conflict between good $P$ removal and good settleability for TKN/COD ratios >0.10 to 0.11 mgN/mgCOD (depending on the COD strength of the wastewater) because the former demands a low a-recycle ratio and the latter a high one. The problem was overcome by making a modification to the UCT process.

*For reasons not yet understood the anaerobic retention time, both nominal and actual does not appear to affect the settleability of the sludge.
In the modified UCT process (Fig 6), the anoxic is subdivided into two parts, the first having a sludge mass fraction of 0.07 to 0.10 (depending on the influent COD concentration) and the second having the balance of the anoxic sludge mass fraction available. The first anoxic reactor receives the underflow s-recycle and the r-recycle to the anaerobic reactor is taken from it. The second anoxic reactor receives the a-recycle. This process allows operation of a-recycle ratios resulting in actual anoxic retention times less than 1 hour while ensuring a nitrate free discharge to the anaerobic reactor. An added advantage of this process over the UCT process is that it obviates the need for careful control of the a-recycle ratio to ensure a nitrate free discharge to the anaerobic reactor.

Application of the modified UCT process gave the most consistent P removal and the best settleability of all the processes investigated, but the improvements are obtained at a cost: the maximum TKN/COD ratio to give a zero nitrate discharge to the anaerobic reactor is reduced from 0.14 mgN/mgCOD in the UCT process to 0.11 mgN/mgCOD in the modified UCT process. However a TKN/COD ratio of 0.11 mgN/mgCOD includes most settled and raw municipal wastewaters. Furthermore, by making provision that the r-recycle can be taken from either the first or second anoxic reactor, the process can be operated either as a modified UCT or a UCT process as may be required.

The developments that have been described so far were all guided by the hypothesis that excess P removal is stimulated, and is best achieved, by having an anaerobic reactor and that it is optimized by preventing nitrate from entering the reactor. No information has been put forward to quantify firstly, the conditions in the anaerobic reactor that cause the stimulation and, secondly, the magnitude of the excess P removal to be expected. The rest of this paper will be concerned with these two aspects.

**PREREQUISITES FOR EXCESS PHOSPHORUS REMOVAL**

The improved understanding of the nitrogen removal process behaviour led to a new approach in investigating the prerequisites in the anaerobic reactor for excess phosphorus removal. Ekama, van Haandel and Marais (1979) hypothesized that if the mass of nitrate entering an unaerated reactor is less than that reactor's denitrification potential, the difference defines an "anaerobic capacity" in the reactor. They speculated that this anaerobic capacity could substitute for the redox potential level (suggested by Barnard, 1976) as a measure for predicting when phosphorus release takes place in the anaerobic reactor. Siebritz, et al. (1980) intensively investigated this hypothesis. They plotted the P release in the anaerobic reactor, the P uptake in the aerobic reactor and the system P removal versus the anaerobic capacity ($A_C$) for data from UCT and modified Phoredox processes (Fig.8). This plot shows that (i) if $A_C < 10 \text{mgN}_3\text{N}/\ell$, no P release in the anaerobic reactor is obtained; in fact, P uptake is noted, (ii) when $A_C > 10 \text{mgN}_3\text{N}/\ell$, P release is obtained, and (iii) as $A_C$ increases above 10 mgN$3\text{N}/\ell$ the P release in the anaerobic reactor, the P uptake in the aerobic reactor and the system P removal increase.

The data in Fig.8 appeared to support the anaerobic capacity hypothesis. Consequently if the anaerobic hypothesis is correct, then provided this capacity can be induced in any system other than the UCT and Phoredox processes, P release and uptake should be observed.

To test the above conclusion experimentally, three Modified Ludzack-Ettinger (MLE) processes (Fig 4) and a modified UCT process were set up and fed from the same wastewater source. The three MLE units were given unaerated sludge mass fractions of 40, 55 and 70 percent respectively and the mixed liquor a-recycle ratios were set such that the anaerobic capacities ranged from 6 to 35 mgN$3\text{N}/\ell$ in the anoxic reactors. Over two months of operation no P release nor excess P removal were observed in any of the MLE units. In contrast, the modified UCT process with a 0.10 anaerobic sludge mass fraction, consistently gave P release and excess P removal. It was concluded from these results that the anaerobic capacity hypothesis is not
Fig. 8. P release in the anaerobic reactor, process P uptake and process P removal versus the anaerobic capacity of the anaerobic reactor ($A_C$) for the modified Phoredox and UCT processes.

In seeking an explanation for the different P release behavioural patterns in the modified UCT and MLE processes, it was noted that the only evident difference lay in the concentration of rapidly biodegradable COD surrounding the organisms in the anaerobic reactor ($S_{bsa}$). In the modified UCT process the rapidly biodegradable COD concentration in the anaerobic reactor ($S_{bsa}$) is the maximum possible as no nitrate is recycled to the anaerobic reactor; in contrast, in the MLE process sufficient nitrate is recycled to the anoxic reactor to utilize all the rapidly biodegradable COD i.e. $S_{bsa} = 0.0$. Therefore the different behavioural patterns of the processes would be consistently described if it is assumed that the concentration of rapidly biodegradable COD in the anaerobic reactor ($S_{bsa}$) surrounding the organisms is the key parameter determining whether or not P release and excess P uptake takes place.

To test the assumption above, it was necessary to develop a general equation by means of which $S_{bsa}$ can be calculated:

Consider the anaerobic reactor in the UCT process,

$$S_{bsa} = (f_{bs} S_{b1} - \Delta S_{bs})/(1+r) \text{ (mgCOD/l)} \tag{2}$$

The term $S_{bs}$ is the concentration of rapidly biodegradable COD utilized for synthesis of cell material with nitrate (introduced via the r-recycle) and dissolved oxygen (introduced via the influent) serving as terminal electron acceptors. Because 8.6 mgCOD are utilized with the removal of 1 mgNO$_3$-N (van Haandel, Ekama and Marais, 1981) and 3.0 mgCOD with 1 mgO$_2$ (Marais and Ekama, 1976), $\Delta S_{bs}$ can be expressed in terms of the nitrate in the r-recycle, $N_{nr}$, and the D.O. in the influent ($d_i$) and r-recycle ($d_r$), i.e.

$$\Delta S_{bs} = 8.6 \cdot r \cdot N_{nr} + 3.0 (d_i + r \cdot d_r) \tag{3}$$

Equations (2 and 3) can be easily adapted for the other processes by giving due consideration to the recycles and flows discharged to the anaerobic reactor.

The calculation of $S_{bsa}$ fortunately was possible because once the importance of the influent rapidly biodegradable COD fraction ($f_{bs}$) was recognized from the work on
denitrification, it became standard experimental procedure to measure or determine almost daily, $f_{bs}$, $f_{us}$, $f_{up}$, $St_{i}$, $N_{nr}$, $d_{r}$ and $d_{j}$. Consequently Eqs. (2 and 3) were applied to the data used to plot Fig.8 and replotted in Fig.9 with $S_{bsa}$ on the horizontal axis instead of the anaerobic capacity. From Fig.9 the following conclusions were drawn:

1) The minimum rapidly biodegradable COD concentration in the anaerobic reactor ($S_{bsa}$) to stimulate phosphorus release in the reactor is about 25 mgCOD/l.

2) The degree of P release appears to increase as $S_{bsa}$ increases above 25 mgCOD/l, i.e. P release increases as $(S_{bsa} - 25)$ increases.

3) Excess phosphorus uptake is obtained only when phosphorus release takes place, and tends to increase with $(S_{bsa} - 25)$.

The plots in Figs.8 and 9 show a striking similarity but on closer inspection, this similarity is more apparent than real. The similarity is there only for the UCT and Phoredox data: for these processes, the two sets of data fall in approximately the same position relative to the coordinate axes. This is so because in these processes, the principal contributor to $A_{C}$ is the rapidly biodegradable COD in the influent, $S_{bsi}$ - the contribution by the slowly biodegradable influent COD $S_{bpi}$ is very small owing to the relatively small anaerobic sludge mass fractions ($f_{XA}$) - so that $A_{C}$ and $S_{bsa}$ are essentially equivalent parameters. In contrast, in the MLE process, the influent rapidly biodegradable COD $S_{bsi}$ will have been completely utilized by the nitrate entering the anoxic reactor, i.e. $S_{bsa} = 0$. Nevertheless high $A_{C}$ values are obtained from the $S_{bpi}$ contribution because the unaerated sludge mass fractions are large. Consequently for the MLE process, there is no relationship between $S_{bsa}$ and $A_{C}$. Hence in Fig.8, the MLE data fall in the right hand side of the plot (i.e. $A_{C} > 10$ mgNO$_3$-N/l) whereas in Fig.9 they will fall in the left hand side of the plot (i.e. $S_{bsa} = 0$). Consequently, the MLE behaviour is incorrectly predicted by the $A_{C}$ hypothesis (Fig.8) but correctly predicted by the $S_{bsa}$ hypothesis (Fig.9). These results allow the following statement to be made: A prerequisite for P release in the anaerobic reactor is that the concentration of rapidly biodegradable COD surrounding the organisms in the anaerobic reactor must exceed approximately 25 mgCOD/l.

**MAGNITUDE OF EXCESS PHOSPHORUS REMOVAL**
A prerequisite for P release was stated above. However, the magnitudes of the P release and subsequent uptake and removal were not explicitly defined, once the prerequisite was satisfied. For this purpose an extensive and intensive investigation was inaugurated utilizing the UCT and modified UCT configurations. Series of tests were done under constant flow and load conditions: (1) at 14°C and 20°C, (2) using raw wastewater influents with COD's of 800, 500 and 300 mg/l, and (3) varying the r-recycle and anaerobic mass fraction. In all the investigations the influent wastewater characteristics, i.e. COD, TKN, total P and rapidly biodegradable COD fraction fbs, and filtered TKN, NH₄⁺, NO₃⁻ and total P in the process reactors were measured daily. In addition, all the normal parameters such as MLVSS, oxygen utilization rate, stirred settling velocity, pH and alkalinity were measured at regular intervals.

An analysis of these data* indicated that provided $S_{\text{BSA}} > 25$ mgCOD/l,

1) for fixed r-recycle ratio and influent COD, increasing the volume of the anaerobic reactor (at the expense of the other reactor volumes) tended to increase P release and the P removal,

2) for fixed r-recycle ratio and anaerobic reactor volume, an increase in influent COD concentration tended to increase the P release and the P removal.

Although the trends stated above were evident it was not possible to identify a consistent behavioural pattern and it was concluded that the basic parameters had not been properly identified or isolated. In part, this was due to the interactive effects between the different parameters, for example, increasing the r-recycle ratio, (i) increases the mass of sludge passing through the anaerobic reactor, (ii) decreases the time the sludge is retained in the anaerobic reactor, (iii) increases the concentration of sludge in the reactor, and (iv) decreases the concentration of $S_{\text{BSA}}$ in the anaerobic reactor (even if no nitrate is present in the r-recycle). With so many associated changes it was difficult to see directly which parameters are the significant ones. It was decided, therefore, to investigate the system theoretically on the basis of the perceived and hypothesized behaviour.

Consideration of the P release in the anaerobic reactor indicated that the magnitude of the release was not a consistent parameter; experimental P release data showed that the release at any particular time depended on the P removal performance prior to the time the test was taken. If, for example, the prior removal was low the P release observed also was low; as the removal increased so in time the release did likewise and vice versa. For this reason the P release per se, was not incorporated in the analysis and attention was focussed on the excess P removal; here the following behavioural pattern was hypothesized based on the observed behaviour,

1) Excess P removal is obtained only when $S_{\text{BSA}} > 25$ mgCOD/l.
2) As $S_{\text{BSA}}$ increases above 25 mgCOD/l, so the P removal increases.
3) The longer the actual anaerobic retention ($R_{\text{AN}}$), the higher the P removal.
4) The larger the mass of sludge recycled through the anaerobic reactor, the higher the P removal.

Scrutiny of (4) above showed that it could be transformed to a more useful equivalent,

4) The greater the mass of sludge recycled through the anaerobic reactor each day expressed as a fraction of the mass of sludge in the process, n, the higher the P removal.

The statements (2) and (4) above do not give an explicit quantitative expression of

*Detailed description of the experimental investigation will be published in a later publication.
the expected behaviour. To obtain such an expression an hypothesis on the expected behavioural pattern of (2) to (4) has to be made. An hypothesis consistent with the observations is:

"When any one of the factors \((S_{bsa-25}), R_{an}, \text{ or } n\), is zero, excess phosphorus removal will be zero."

From this hypothesis, the simplest form of an equation expressing the tendency of a process to achieve excess P removal is

\[
P_f = (S_{bsa-25}).R_{an}.n
\]

where

\(P_f\) = excess phosphorus removal propensity factor.

If \(P_f\) as defined above describes the observed behaviour of the three parameters, then the P removal due to excess uptake \((\Delta P_u)\) should be a function of \(P_f\), i.e.

\[
\Delta P_u = f(P_f)
\]

Equation (4) can be expressed in terms of the process configuration and operational parameters. This is demonstrated below for the UCT process.

\[
R_{an} = V_{an}/(Q(1+r))
\]

\[
n = (rQ.X_{ax})/(V_tX)
\]

From a sludge mass balance around the anaerobic reactor it follows that

\[
X_{ax} = (\frac{1+r}{r})X_{an}
\]

The anaerobic sludge mass fraction, \(f_{xa}\), is given by

\[
f_{xa} = (X_{an}.V_t)/(X.V)
\]

\[
= (X_{an}.f_{xav})/\bar{X}
\]

where

\(\bar{X}\) = mean sludge concentration in process

\[
= (X_{an}.V_t + X_{ax}.V_{ax} + X_{ae}.V_{ae})/V_t
\]

i.e. \(X_{an} = \bar{X}.(f_{xa}/f_{xav})\)

Substituting Eq. 10 into Eq.8 and Eq.8 into Eq.7;

\[
n = (rQ.(\frac{1+r}{r}).f_{xa}/f_{xav}).X/(V_t\bar{X}) = (Q(r+1))f_{xa}/f_{xav})/(V_t\bar{X})
\]

Multiplying Eq.11 by LHS and RHS of Eq.6

\[
nR_{an} = (Q(r+1))f_{xa}/f_{xav} = \frac{V_{an}}{V_tQ(r+1)} = f_{xa}
\]

Substituting \(f_{xa}\) for \(nR_{an}\) in Eq.4

\[
P_f = (S_{bsa-25})f_{xa}(\text{mgCOD}/\ell)
\]

Hence the propensity to give excess phosphorus removal appears to be a function only of the magnitude of \(S_{bsa}\) above 25 mgCOD/\ell and the magnitude of the anaerobic sludge mass fraction.

Equation 12 can be shown to hold also for the Phoredox type processes.
I. P. SIEBRITZ et al.

Fig. 10. Coefficient of excess P removal ($\gamma$) versus P removal propensity factor ($P_f$) observed in the modified Phoredox, UCT and modified UCT processes at different anaerobic sludge mass fractions ($f_{xa}$), influent COD concentrations and temperatures.

**QUANTITATIVE MODEL OF EXCESS PHOSPHORUS REMOVAL**

As excess P removal is accepted to be a biological activity, it can be assumed that, (i) only the active fraction of the sludge can take up phosphorus in excess, (ii) the phosphorus removal will increase as the proportion of phosphorus in the active mass increases, and (iii) the proportion of phosphorus in the inert fractions of the sludge will remain unchanged. Accepting these assumptions, Martin and Marais (1975) developed the following equation for phosphorus removal based on the steady state activated sludge process model presented by Marais and Ekama (1976):

$$\Delta P_s = S_{ti} \left\{ \frac{(1-f_s - f_{us}) P_{up} h_{RS}}{(1+b_{hi} R_s)} \left( \gamma f + b_{hi} R_s \right) + \frac{f f_{up} P_{up}}{P_{v}} \right\}$$

With the aid of Eqs. 2 and 3, 13 and 14, the coefficient of excess phosphorus removal and the propensity factor $P_f$ were calculated for daily sets of experimental data measured over a period of 18 months. In calculating the daily $\gamma$ and $P_f$ data pairs, those data for which there were known causes that may have adversely or favourably influenced the process behaviour were discarded.* The remaining daily $\gamma$ and $P_f$ data pairs are shown plotted in Fig. 10.

The data in Fig. 10 shows considerable scatter although a definite trend is discernible. The scatter is due mainly to the selection of the data values in the

---

* The rapidly biodegradable COD fraction $f_{bs}$ in the influent was measured in accordance with the procedure developed by Ekama and Marais (1978) as follows: A single completely mixed aerobic activated sludge unit is operated at 2.5 days sludge age. The wastewater is fed in a daily cyclic square wave loading pattern (12 hours on, 12 hours off). By measuring the precipitous decrease in oxygen consumption rate over the period of feed termination, the $f_{bs}$ fraction can be readily ascertained.

** It was found that after a disruption of the process due to a mechanical breakdown, or a change in influent sewage characteristics or process parameter, the process required approximately 2 to 3 days to restabilize.
calculation of $P_f$: The $f_{bs}$, nitrate and $P$ removal values used in the calculations were all measured on the same day, i.e. the assumption was made that the response of $\gamma$ to $P_f$ is instantaneous. This, in fact, is not so; due to the long hold up time in the system it was repeatedly observed that the $P$ removal response is out of phase with the input by some fraction of a day. (This is apparent in Fig.12 which records the observed and predicted $P$ removal in one set of experiments).

Accepting the inevitable large scatter, the form of the relationship and the constraints on the $\gamma$-$P_f$ relationship were derived as follows: From Fig.9 apparently

i) there is an upper limit to $\gamma$, of about 0.35 at very high propensity factors,

ii) there is a lower limit to $\gamma$ of about 0.06 at a propensity factor of zero,

iii) for propensity factors ranging from infinity to zero the maximum change in is $(0.35-0.06) = 0.29$ and the decrease in $\gamma$ with decrease in $P_f$ appears to be of an exponential form.

On the basis of the above the following expression was chosen to represent the trend in the plotted data

$$\gamma = 0.35 - 0.29 \exp(-C.P_f)$$ (15)

Fig 11. Left, daily experimental data of influent COD, TKN and rapidly biodegradable COD concentrations and nitrate concentrations in the effluent and the recycle to the anaerobic reactor and right the measured and predicted phosphorus removal for a modified UCT process with the following sludge mass fractions: anaerobic 0.10, first anoxic 0.08, second anoxic 0.22, aerobic 0.60.
Fig. 12. Response of a laboratory scale UCT process at 14°C, Anaerobic mass fraction = 0.15, Anoxic mass fraction 0.30. Aerobic mass fraction 0.55, Sludge age 20 days, treating unsettled flow from Mitchell's Plain.
The value of C was found by a least square analysis of the differences between the measured and predicted phosphorus removals and found to be equal to $-0.242$, i.e.

$$\gamma = 0.35 - 0.29 \exp(-0.242 \, P_f) \quad \text{(mgP/mgVASS)}$$

To check the predictive capacity of Eq.16, it was applied to the daily $P_f$ data in all the five sets of experiments on the modified UCT, UCT and Phoredox processes in which $S_{bsi}$ and the nitrate in the recycles were measured. (As stated above these sets of data covered influent COD values from 300 to 800 mg/l at 14° and 20°C under a variety of TKN/COD ratios, anaerobic mass fractions from 0.10 to 0.20 and sludge ages 4 to 20 days. As an illustration two sets of data are shown in Figs. 11 and 12 together with the predicted P removal values. Evidently the model gives a good prediction of the observed P removal. In Fig.11, the pronounced favourable effect of an increase in the rapidly biodegradable COD concentration ($S_{bsi}$) on the P removal, and in Fig.12 the depressing effect of nitrate in the recycle to the anaerobic reactor, is clearly illustrated.

The theory was tested additionally by feeding extra rapidly biodegradable COD to the anaerobic reactor, acetate and glucose. Taking due account of the increased COD, again the predictions of P removal were in satisfactory correlation with those observed.

While doing a biodegradability investigation of the waste flow from the town of Caledon in South Africa, unexpected verification of the theory was obtained. The process configuration was a Modified Ludzack-Ettinger process (Fig.4) with an anoxic sludge mass fraction of 0.30 operated at 20 days sludge age, at 20°C, and with a mixed liquor (a) and an underflow (s) recycle ratio of 4:1 and 1:1 respectively. The wasteflow contained an industrial fraction (from a malting factory) constituting approximately 2/3 of the total COD load. The influent COD and TKN strengths were 1300 mg/l and 70 mgN/l respectively. It was found that the malting waste was virtually completely rapidly biodegradable resulting in a very high rapidly biodegradable COD fraction ($f_{bsi}$) and concentration ($S_{bsi}$), 0.70 and 980 mgCOD/l respectively. Taking due account of the diluting effect of the total recycle flow of 5 and the reduction of the rapidly biodegradable COD in the "anoxic" reactor by the nitrate discharged in the recycle flows (nitrification was complete, effluent TKN = 4 mgN/l) the rapidly biodegradable COD concentration in the "anoxic" reactor ($S_{bsa}$) was estimated at 101 mgCOD/l, the propensity factor ($P_f$) at 22.9 (Eq.13), the $\gamma$ coefficient at 0.35 (Eq.15) to give an estimated P removal of 31 mgP/l influent (Eq.14 with $f_{us} = 0.05$ and $f_{up} = 0.06$). The observed P removal was 29 mgP/l. The results of this experiment should be contrasted with those discussed earlier on the Modified Ludzack-Ettinger processes. In these processes, no excess P removal was observed or predicted, even though the anoxic mass fraction was as high as 0.70, principally because the rapidly biodegradable COD concentration in the influent ($S_{bsi}$) was low and completely utilized in the anoxic reactor by the nitrate recycled to this reactor. Clearly if sufficient $S_{bsi}$ is available and the TKN not excessive, it is possible to obtain high P removals even though the nitrate recycled to the anaerobic reactor is high, without having to resort to Phoredox or UCT configurations, provided the conditions for P release are satisfied as set out in this paper.

At full scale Nicholls (1982) tested the predictive power of the general nitrification-denitrification model on the Goudkopies 5-stage Phoredox plant receiving an effluent that had passed through primary settling and then through an equalization tank. The P removal behaviour of the plant was also monitored by measuring P conditions in the anaerobic and aerobic reactors and in the effluent. To evaluate both the model and P removal theory, inter alia the rapidly biodegradable COD in the influent discharged to the process ($S_{bsi}$) was measured, as described by Dold, Ekama and Marais (1980). The $S_{bsi}$ was found to be very low due to its utilization by an anaerobic sludge layer that formed on the bottom of the unstirred equalization tank. In terms of the theory set out here the $S_{bsi}$ was so low that with the 1:1 underflow recycle from the secondary settling tank to the anaerobic reactor, even
if no nitrate was present in the recycle, $S_{BSA}$ would be less than 25 mg/l and consequently no excess P removal was to be expected, and, virtually no excess removal was observed for the plant. Measurements of $S_{BSI}$ on the influent to the equalization tank however indicated that the $S_{BSI}$ was sufficiently high that, if the equalization tank was bypassed, excess P removal was theoretically possible provided the nitrate in the underflow recycle to the anaerobic reactor could be maintained at less than 5 mgN/l. Now at this point a computer-based equalization control strategy was implemented on the equalization tank (Dold, Buhr and Marais, 1982) and operated in such a fashion that any settled material was flushed daily from the tank. The flushing action prevented build-up of a sludge layer and effectively eliminated the loss of $S_{BSI}$ in the tank. The process recycles in the plant were changed in accordance with those predicted by the general model to achieve maximum nitrate removal. As this removal was still insufficient to reduce the nitrate in the underflow recycle to less than 5 mgN/l, the aeration next to the discharge points from the primary anoxic reactor were switched off, thereby effectively increasing the anoxic zone and further reducing the nitrate in the effluent. (Sufficient aerator capacity was available in the rest of the aeration basin not to affect the nitrification efficiency). In this fashion the nitrate was kept between 3 and 5 mgN/l in the effluent and the underflow recycle. Under these conditions the predicted P removal was 4 to 5 mgP/l influent; observed mean removal was 5 mgP/l. The results from this investigation are particularly instructive because they verified that no P removal is achievable if $S_{BSI}$ is too low, or, where $S_{BSI}$ is sufficiently high although the potential for removal is there, it will not be possible to realise this potential if nitrate in the anaerobic recycle is so high that it reduces the $S_{BSA}$ concentration to below the critical level.

When investigating P removal behaviour in laboratory scale processes, batches of sewage usually are obtained from the outfall sewer and stored at 5°C for subsequent feed to the laboratory process units. Often it will be noticed that with time the magnitudes of denitrification and P removal decline while feeding from the same raw sewage batch. Measurement of the rapidly biodegradable COD fraction of the daily feed taken from the cold storage batch has indicated that normally there is a slow continuous loss of this fraction. Theoretically the model accounts for the reduction in denitrification and P removal observed. Hence, batches should not be stored longer than about one to one and a half weeks and the $S_{BSI}$ in the feed should be measured daily. Furthermore, by monitoring the $S_{BSI}$ on a routine basis, changes in $S_{BSI}$ between batches are picked up that explain the "erratic" P removal behaviour noted earlier between different batches of wastewater. Also, it is vitally important that the tanker transporting the batch to the laboratory and the cold storage tank are thoroughly cleaned between batches otherwise hydrogen sulfide generation and rapid loss of $S_{BSI}$ will be encountered. High hydrogen sulfide concentration in the feed to a process can have severe adverse effects on the process response.

Reviewing the model in its entirety, it would appear that the P removal model gives predictions very consistent with those observed. This does not imply in any manner that the model has achieved finality; findings on the biochemical mechanism discussed by Marais et al. (1982) provide new directions for research and these may significantly modify the parametric model proposed here.

**IMPLICATIONS OF THE PHOSPHORUS REMOVAL THEORY**

Lack of space limits detailed discussion of all the aspects and implications of the P removal theory developed above. However brief mention of the following is merited:

1. The magnitude of P removal per unit influent COD declines as the influent COD decreases. The main reason for this is that the concentration of rapidly biodegradable COD concentration, $S_{BSI}$, decreased concomitantly with decrease in total influent COD concentration. For raw municipal wastewater the fraction
of rapidly biodegradable COD ($S_{bsi}$) with respect to the total COD ($S_{ti}$) is about 0.2; consequently, when $S_{ti}$ decreases to about 250 mg/l, $S_{bsi}$ decreases to 50 mg/l so that for $r = 1$, even if no nitrate is recycled to the anaerobic reactor, $S_{bsa} = 25$ mg/l, hence, $(S_{bsa} - 25)\geq 0$, and no excess removal can be expected ($\gamma \geq 0.06$). Generally (for $S_{ti} > 250$) as $S_{ti}$ increases so the $P$ removal per unit influent COD increases and the removal becomes less sensitive to external factors. Because $P_{f}$ (and hence $\gamma$) is dependent on both $(S_{bsa} - 25)$ and $f_{xa}$, $P$ removal for any particular $(S_{bsa} - 25)$ can be improved by increasing the anaerobic sludge mass fraction $f_{xa}$. This often is necessary for low $S_{ti}$. Values of $f_{xa}$ up to 0.2 have been tested. However as $f_{xa}$ increases so nitrate removal reduces unit per influent COD. The reason for this is that the total unaerated mass fraction ($f_{xti}$) is limited to 0.5 so that an increase in $f_{xa}$ necessarily must reduce the anoxic mass fraction.

(2) Any practice that reduces $S_{bsi}$ should be avoided. For example, recycling of excess underflow liquor to a point prior to the primary settling tank, to improve settleability, is to be avoided as any oxygen present in the influent, introduced by say archimedian screw pumps, will cause that the $S_{bsi}$ be reduced by an amount equal to 3 times the oxygen introduced (see Eq.3). Conversely, any practice that increases $S_{bsi}$ will improve $P$ removal. For example, the Johannesburg City Council has augmented $S_{bsi}$ as follows: the primary settling tank underflow is digested at very short sludge ages to produce fatty acids, the digested mixed liquor is settled and the fatty acid rich supernatant is fed to the $P$ removal plant. The principal fatty acid produced is acetic acid – which is a most rapidly biodegradable COD source; this raises the $S_{bsi}$ value of the influent and consequently will raise the magnitude of excess $P$ removal. This innovation holds promise by providing a means to extend the $P$ removal control over the plant, particularly where high $P$ removal per unit influent COD is needed and when this removal is not attainable using the raw influent sewage as the only source of rapidly biodegradable COD.

(3) Cyclic flow and load conditions do not appear to affect the mean daily excess $P$ removal, in fact, the removal often is improved, particularly under low average influent COD conditions. The reason for this improvement is that under the cyclic conditions (with constant recycle flows) during the peak periods the peak COD is higher than the daily mean causing a higher $(S_{bsa} - 25)$ condition and hence higher $P$ removals during the associated high flow period. However, under cyclic flow conditions the oxygen concentration in the aerobic reactor must be closely controlled; too high D.O. concentration reduces the nitrate removal whereas too low concentration may inhibit nitrification and adversely affect settling. The practical difficulties associated with oxygen control are such that serious consideration should be given to equalization tanks operated under a control strategy that equalizes both flow and load. Such a strategy is now available (Dold, Buhr and Marais, 1982).

With regard to design, the following important considerations deserve mention:

(1) For design of nutrient removal plants the influent wastewater characteristics (or their ranges) need to be known with much greater surety than for conventional activated sludge plants otherwise a design may be produced that fails totally in its $P$ removal objectives. Vital influent characteristics are (i) $S_{ti}$, TKN/COD, P/COD, $S_{bi}$, $S_{bsi}$, $\mu_{ann20}$, $T_{max}$ and $T_{min}$. Useful data are the Total Alkalinity and the unbiodegradable COD fractions $f_{ub}$ and $f_{up}$. In the event that these characteristics are known only approximately, values should be selected that lead to conservative designs, usually at the cost of reduced N and P removal.

(2) The selected process must have factors of safety built into it or have flexibility in operation, so that if the influent characteristics are more adverse than accepted for design, it will be possible to accommodate them. For example, if a Phoredox process is selected it is recommended that normally the
maximum TKN/COD ratio should not exceed 0,07 mgN/mgCOD, and the process should have a built-in safety factor by designing it for 0,08 mgN/mgCOD. For TKN/COD ratios > 0,07 mgN/mgCOD, the modified UCT/UCT* process should be selected; with this process combination, by appropriate regulation of the a-recycle ratio, excess P removal always can be induced (subject to \( S_{d2} \)) at the cost of a reduced nitrogen removal. Theoretically, at low TKN/COD ratios (<0,08), the Phoredox process will be the optimal one, but practically its inflexibility to accommodate TKN/COD ratio variations, makes its selection a risky one.

(3) The selected process should require the least amount of decision making from the operator to obtain consistent results. In this regard the modified UCT process appears to lend itself most readily to setting operational procedures to absorb adverse conditions when these arise. Also operational adjustment to mitigate the regular changes in wastewater flow and characteristics observed over different days of the week can be preprogrammed.

**GENERAL CONCLUSIONS**

This paper presented evidence that

(1) A prerequisite for P release under anaerobic conditions is that the concentration of rapidly biodegradable COD (similar to glucose or acetate) surrounding the organisms must exceed some minimum critical concentration (±25 mg/l). P release appears to serve as an indicator that the organism mass has been conditioned to take up the released and additional P when subsequently aerated. Particulate slowly biodegradable COD does not appear to influence the release or excess uptake other than it contributes to active mass production which performs the P release and uptake.

(2) The magnitude of the excess biological P removal per unit of active mass of sludge (as VASS) under constant flow and load conditions is determined by (i) the actual mean retention time of the organisms in the anaerobic reactor, (ii) the fraction of the sludge mass in the system recycled through the anaerobic reactor each day, and (iii) the concentration of rapidly biodegradable COD in excess of 25 mgCOD/l.

(3) The mass of P removed per day per unit COD load by a process is dependent on the mass of excess active sludge produced per day times the magnitude of the excess removal coefficient induced by (2) above. Consequently, the shorter the sludge age, the greater the removal of P per unit COD load.

(4) The source of the rapidly biodegradable COD is the influent wastewater and consists of about 20 percent of the influent COD in unsettled municipal wasteflows. The concentration of rapidly biodegradable COD in the anaerobic reactor is reduced by any nitrate recycled to this reactor (1 mg(NO₃-N) removes 8,6 mgCOD) and thereby reduces the excess P removal, to zero if the nitrate discharged is high enough.

(5) Analysis of the Phoredox process with respect to its nitrification and denitrification capacities and excess P removal, indicates that complete denitrification normally cannot be guaranteed if the influent TKN/COD ratio is greater than about 0,08 (for temperatures not falling below 12 to 14°C). At higher TKN/COD ratios nitrate will be present in the effluent and hence in the underflow recycle to the anaerobic reactor in which event excess P removal will decline or cease.

(6) To protect the anaerobic reactor from nitrate in the effluent and underflow recycle, a new process (the UCT process) is proposed in which the underflow (s) recycle as well as the mixed liquor (a) recycle discharge to the anoxic reactor

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*One may ask why not make provision for a Phoredox/UCT/modified UCT process combination by installing the extra recycles. This of course is possible but in converting a Phoredox to a UCT type process, the anaerobic sludge mass fraction immediately is nearly halved (for r=1) and the P removal reduced accordingly."
and an extra (r) recycle is introduced from the anoxic to the anaerobic reactors. By controlling the a-recycle ratio the nitrate concentration in the anoxic reactor can be maintained at near zero so that the r-recycle will contain little or zero nitrate and the rapidly biodegradable COD concentration in the anaerobic reactor is at a maximum level possible. This can be maintained in the process up to influent TKN/COD ratios of about 0,14 mgN/mgCOD (at 12°C to 14°C).

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LIST OF SYMBOLS

- \( A_c \): anaerobic capacity (mgN/ℓ influent) i.e. difference between an unaerated reactor's denitrification potential (\( D_p \)) and the nitrate entering it.
- \( a \): mixed liquor recycle ratio from the aerobic to the anoxic reactors. Subscript 0 denotes optimum.
- \( b_{hT} \): endogenous mass loss rate for heterotrophic organisms at \( T \) °C (/d).
  \[ b_{hT} = b_{h20}(1,029)(T-20) \]
- \( b_{h20} \): the rate at 20°C = 0,24/d.
- \( D_p \): denitrification potential (mgN/ℓ influent). Maximum concentration of nitrate an unaerated reactor can remove by denitrification provided sufficient nitrate is available.
- \( d \): dissolved oxygen concentration (mgO/ℓ). Subscripts a, r, s and i refer respectively to the concentrations in the a, r and s-recycles and influent.
- \( f \): unbiodegradable fraction of active mass
  \[ f = 0,20 \text{ mgVSS/mgVSS.} \]
- \( f_{bs} \): fraction of biodegradable influent COD which is rapidly biodegradable.
- \( f_p \): phosphorus fraction of the inert MLVSS
  \[ f_p = 0,015 \text{ mgP/mgVSS.} \]
- \( f_u \): unbiodegradable COD fractions of the influent COD. Subscripts p and s refer to particulate and soluble fractions respectively.
- \( f_x \): unaerated sludge mass fraction. Subscripts a, 1, 3, t and m refer respectively to the anaerobic, primary anoxic, secondary anoxic, total and maximum allowed. Additional subscript v refers to process volume fractions.
- \( K \): general parameter for denitrification rate (mgNO_3-N/mgVASS/d). Subscripts 1 and 2 refer respectively to the 1st and 2nd rates in the primary anoxic, and 3 to the rate in the secondary anoxic. Additional subscripts T and 20 refer to T°C and 20°C respectively.
- \( N_n \): nitrate concentration (mgN/ℓ). Subscripts e, r and s refer respectively to the concentrations in the effluent and r and s-recycles.
- \( n \): fraction of total mass of sludge in process passing through the anaerobic reactor per day.
- \( \Delta N \): system reduction of nitrate (mgNO_3-N/ℓ influent).
- \( P_f \): excess phosphorus removal propensity factor (mgCOD/ℓ).
\( P_S \) = process phosphorus removed in daily sludge wastage (mgP/ℓ influent).
\( P_V \) = COD/VSS ratio of the volatile sludge mass
\( = 1,48 \) mgCOD/mgVSS.
\( \Delta P_u \) = Phosphorus removal due to excess uptake (mgP/ℓ influent).
\( Q \) = influent flow rate (ℓ/ℓ).
\( r \) = mixed liquor recycle ratio from the anoxic to the anaerobic reactors.
\( R_s \) = sludge age (d).
\( R_{so} \) = maximum sludge age beyond which maximum influent TKN/COD ratio for complete denitrification does not increase.
\( R_{an} \) = actual anaerobic retention time (d).
\( R \) = nominal retention time (d). Subscripts 1 and 3 refer to primary and secondary anoxic reactors respectively.
\( S_f \) = factor of safety for nitrification.
\( S_{ei} \) = total influent COD (mgCOD/ℓ).
\( S_{bi} \) = biodegradable influent COD (mgCOD/ℓ).
\( S_{ui} \) = unbiodegradable influent COD (mgCOD/ℓ).
\( S_{bsi} \) = rapidly biodegradable soluble influent COD.
\( S_{mpi} \) = slowly biodegradable particulate influent COD.
\( S_{upi} \) = particulate unbiodegradable influent COD.
\( S_{usi} \) = soluble unbiodegradable influent COD.
\( S_{bsa} \) = concentration of rapidly biodegradable COD In the anaerobic reactor (mgCOD/ℓ).
\( \Delta S_{bs} \) = rapidly biodegradable COD utilized in the anaerobic reactor due to dissolved oxygen and nitrate discharged to it.
\( t \) = duration of first denitrification rate in the primary anoxic reactor (h).
\( T \) = temperature. Subscripts max. and mIn. refer respectively to maximum and minimum.
\( V \) = volume (ℓ). Subscripts an, ax, ae and t refer respectively to the anaerobic, anoxic and aerobic reactors and the process total.
\( X \) = volatile sludge concentration (mgVSS/ℓ). Subscripts an, ax, ae refer to the anaerobic, anoxic and aerobic reactors.
\( \bar{X} \) = weighted average volatile sludge concentration in the process (mgVSS/ℓ).
\( X_a \) = active mass concentration (mgVASS/ℓ).
\( Y_h \) = growth yield coefficient = 0,45 mgVSS/mgCOD.
\( \alpha \) = denitrification attributable to the rapidly biodegradable COD (mgNO3-N/mg biodegradable influent COD).
\( \gamma \) = coefficient of excess phosphorus removal (mgP/mgBASS) i.e. the proportion of phosphorus in the active mass.
\( \mu_{nm} \) = maximum specific growth rate of the nitrifiers. Subscripts T and 20 refer respectively to T°C and 20°C.
REFERENCES


