Dynamic behavior of the activated sludge process

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The dynamic behavior of the activated sludge process is dependent on both the time-varying loading conditions and the spatial configuration of the plant. In terms of these two independent variables, it is possible to subdivide activated sludge plants into four categories of process behavior—steady state, time varying, space varying, and time and space varying. The types of loading conditions and process configuration characteristics of each category are shown in Table I.

Many mathematical models for the single reactor, completely mixed activated sludge (CMAS) process have been proposed.[1-6] All these models are formulated as sets of ordinary, nonlinear, first-order differential equations with time as the independent variable. To obtain the steady-state solution (Category 1 in Table I), the input forcing function must be time invariant, thus transforming the coefficients of the set of equations to constants. The general solution then consists of a complementary function, which defines the transient, and the particular integral, which defines the steady state. With time-invariant flow and load conditions, the transient describes the interim period between two steady states. The particular integral, which defines the steady state, is important because it forms the framework for estimating some (not all) of the kinetic constants.

Under steady-state conditions, good correlations between theoretically calculated and experimentally observed responses have been obtained even though some of the models differed fundamentally in approach to biological growth kinetics. It is when the models are applied to time-varying conditions (Category 2) and space-varying conditions (Category 3) that deficiencies in the models become apparent. To obtain good correlations between experimental data and theoretical predictions in both cases, it is necessary to adjust the constants in the models for different loading conditions[7] and for the different reactors in a series reactor plant.[8] The need for the empirical adjustment of the kinetic constants is indicative of inadequate definition of activated sludge process behavior. Consequently, the different activated sludge process versions—such as single completely mixed reactor, completely mixed reactors in series, contact stabilization, extended aeration, and aerated lagoons—tended to be considered on an *ad hoc* basis with experimentally determined constants included in the formulations of each process version such that reasonable correlations between theory and experiment are attained.

There are a number of reasons why a successful generalized model has not been developed to date.

- The pollution strength (or energy) parameter, biochemical oxygen demand (BOD), has inherent deficiencies that make it an inconsistent parameter for modeling purposes.
- All the basic mechanisms in the activated sludge process have not been delineated.
- The constitution of the wastewater is different from that implicitly accepted in all the theories.
- Some parameters, such as active, endogenous residue and inert sludge fractions, are ill-defined or ignored.

During the past decade, the activated sludge process has emerged as the principal wastewater treatment process of the future in South Africa. As a result, a comprehensive research program was initiated at the University of Cape Town to investigate the behavior of the process. The objective was to develop a generalized model that will incorporate all the aerobic activated sludge process versions; once the aerobic process kinetics are understood satisfactorily, biological denitrification and phosphorus removal will be studied. A brief review of the work on the basic aerobic kinetics is presented in this paper. Lack of space limits the presentation to the main aspects only; thus, the implications of the various find-

TABLE I. Categories of process response behavior.

Time Variable Loading Conditions	Space Variable Loading Configuration: Single Reactor	Space Variable Loading Configuration: Multi-Reactor or Plug Flow
Constant load	1[a]	3[a]
Cyclic load	2[a]	4[a]

[a] Category number.

ings to design and operating procedures are not included.

HISTORICAL BACKGROUND

Energy parameter. As yet there is no completely satisfactory energy parameter for the influent pollution strength. The two energy parameters most widely used are the 5-day BOD (BOD_5) and the chemical oxygen demand (COD) [with its variant total oxygen demand (TOD)] tests. The usefulness of these parameters depends on the degree they can be integrated into a rational kinetic theory. The BOD test is unsuitable because it gives a relative measure of the carbonaceous energy that is not proportional to the energies in the influent, effluent, or sludge mass. Besides the problem of direct proportionality, the generation of unbiodegradable volatile solids (VS) material caused by endogenous respiration makes it impossible to attempt an energy balance.

From the work of Eckenfelder and Weston,[9] which describes a relationship between VS and COD, and the work of Servizi and Bogan,[10] which relates the free energy of substrate oxidation to COD or oxygen, it is possible to do energy mass balances in terms of the oxygen used, sludge mass, and COD.

This investigation has found it is possible to obtain carbonaceous energy balances in terms of oxygen (to within 90 to 100%). These were achieved by executing the COD test exactly as set out in "Standard Methods"[11]; any

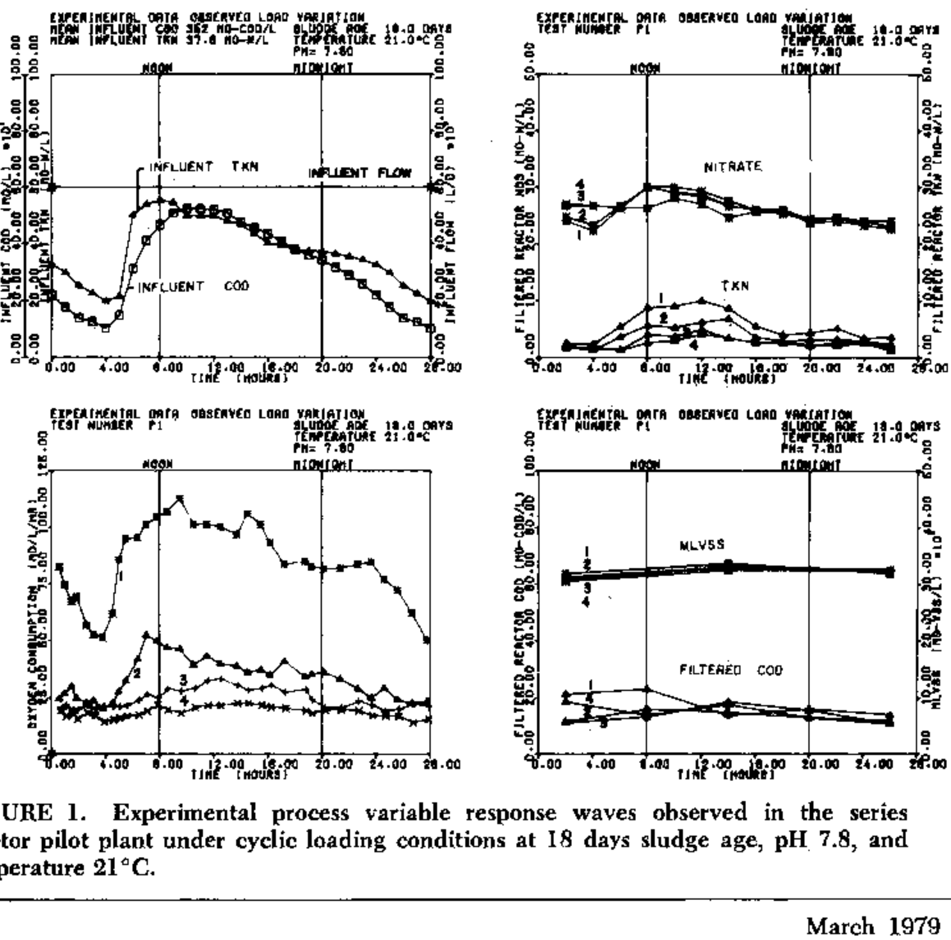

FIGURE 1. Experimental process variable response waves observed in the series reactor pilot plant under cyclic loading conditions at 18 days sludge age, pH 7.8, and temperature 21°C.

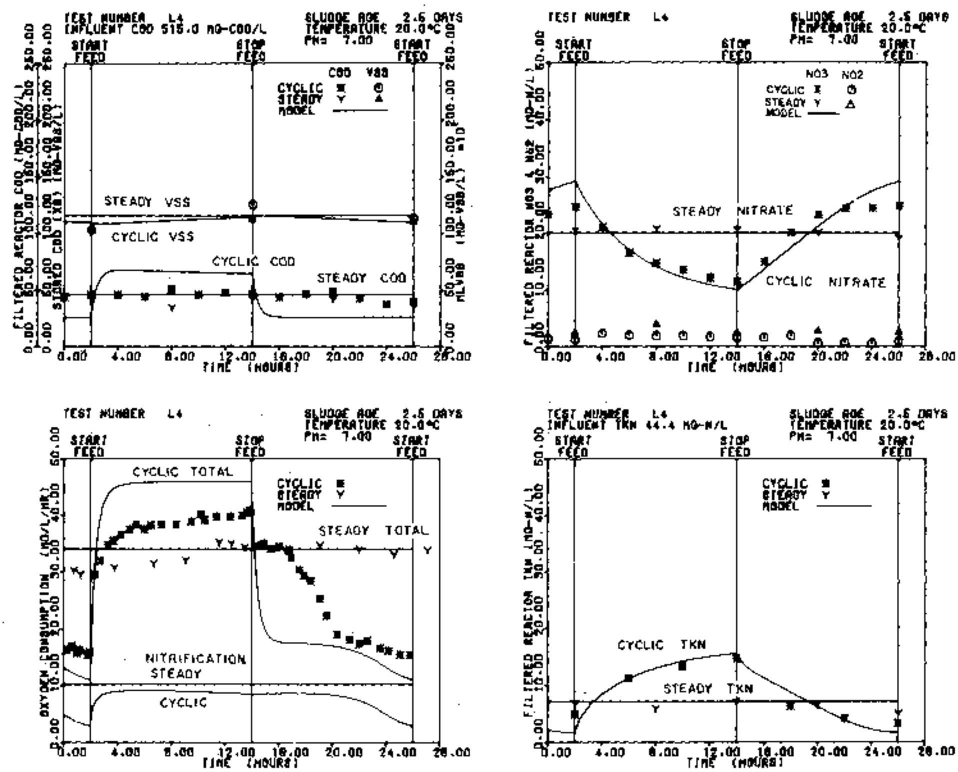

FIGURE 2. Comparison of the theoretical response waves predicted by the Marais and Ekama model with those observed experimentally for daily cyclic square wave loading conditions at 2.5 days sludge age, pH 7.0, and temperature 20°C.

deviation from this procedure resulted in poorer recoveries. Because changes in the COD test procedure give varying results, the test is not an absolute energy measurement. Because all the kinetic constants of the theory are in terms of the COD determination (as set out in "Standard Methods") and lead to good energy balances, it would seem that the parameter is acceptable from a practical point of view. In all the research reported in this paper, the standard COD test was used as the carbonaceous energy parameter.

Carbonaceous energy removal. Investigators of the mathematical models for the activated sludge process are divided into two camps regarding the formulation of the biological growth kinetics.

The first group consists of those that accept the concept of *specific* organism growth rate.[1, 3–6, 12–19]

$$\frac{1}{X_a}\frac{dX_a}{dt} = \mu_h \qquad (1)$$

where

X_a = active sludge organism concentration, mg volatile suspended solids (VSS)/l,
t = time, day, and
μ_h = heterotrophic organism *specific* growth rate, mg VSS/mg VSS·d

The form of μ_h (Equation 1) has been generally formulated as a function of the substrate concentration surrounding the organisms. The best known is the Monod[14] relationship—that is,

$$\mu_h = \mu_{hm} S_b/(K_s + S_b) \qquad (2)$$

where

μ_{hm} = maximum specific growth rate, d^{-1},
S_b = concentration of substrate surrounding the organisms, mg COD/l, and
K_s = saturation coefficient.

Under substrate limiting conditions ($K_s >>$

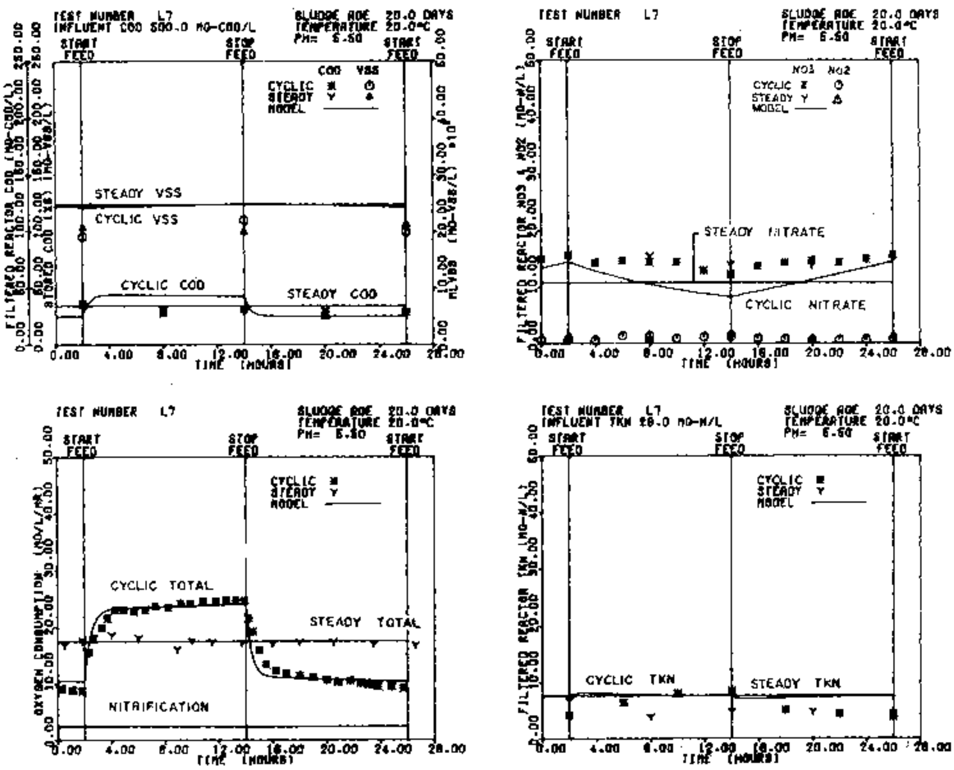

FIGURE 3. Comparison of the theoretical response waves predicted by the Marais and Ekama model with those observed experimentally for daily cyclic square wave loading conditions at 20 days sludge age, pH 5.5, and temperature 20°C.

S_b), Equation 2 reduces to

$$\mu_h = K_\mu S_b \qquad (3)$$

where

$$K_\mu = \mu_{hm}/K_s$$

For very high substrate concentrations ($S_b >> Ks$), Equation 2 reduces to

$$\mu_h = \mu_{hm} \qquad (4)$$

Equation 3 represents the usual first-order formulation for substrate utilization when modeling the CMAS process (for example, Garrett and Sawyer [1] and Eckenfelder [4]).

The second group consists of those that accept the concept of organism growth rate,[2, 20]

$$\frac{dX_a}{dt} = \mu'_h \qquad (5)$$

where

μ'_h = heterotrophic organism growth rate, mg vss/d.

In this approach, the organism growth rate μ'_h is related to the substrate concentration surrounding the organisms or the organism concentration, depending on the $F{:}MX_a$ ratio

$$\mu'_h = K_1 S_b \quad \text{for} \quad F{:}MX_a < 2, 1 \qquad (6)$$

$$\mu'_h = K_2 X_a \quad \text{for} \quad F{:}MX_a > 2, 1 \qquad (7)$$

where

$F{:}MX_a$ = food : microorganism ratio, and
K_1, K_2 = constants.

Substrate-limiting conditions are therefore explicitly required for the validity of Equation 6.

Attempts have been made to show the equivalence of the two approaches by comparing the steady-state solution of the equations for the CMAS process under substrate-limiting conditions.[19, 21, 22] The solutions can be shown to be identical in form in so far as the organism concentration is concerned, but to differ fundamentally insofar as the effluent quality is concerned.[19] The model of Law-

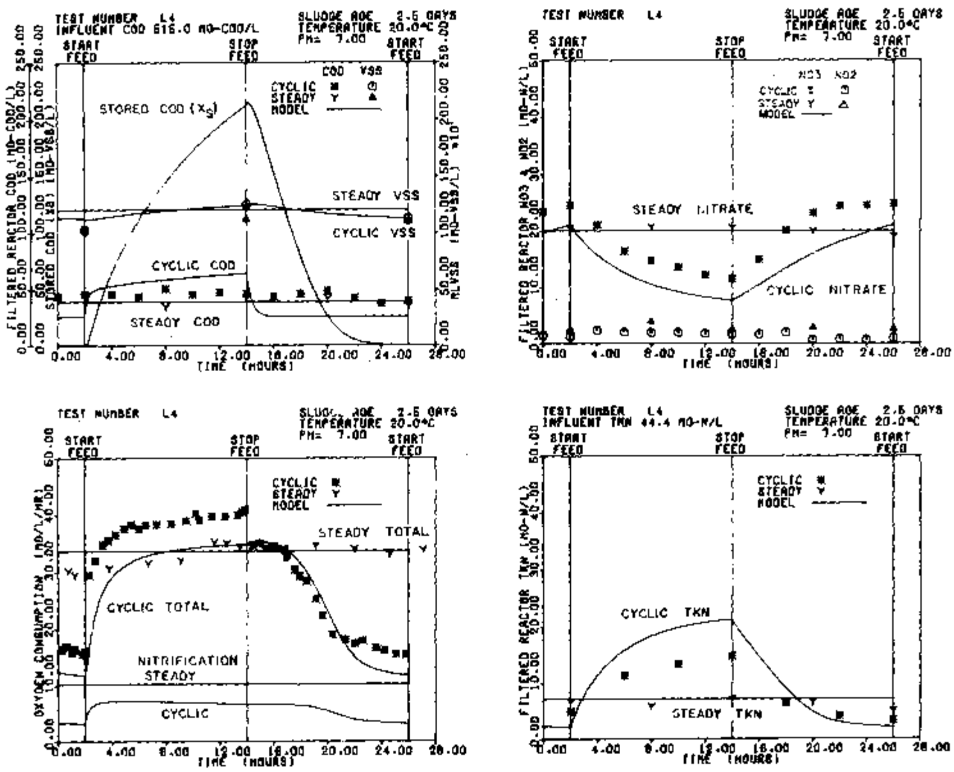

FIGURE 4. Comparison of the theoretical response waves predicted by the Marais and Ekama model incorporating storage of substrate with those observed experimentally for daily cyclic square wave loading conditions at 2.5 days sludge age, pH 7.0, and temperature 20°C.

rence and McCarty,[3] typical of the first approach, implies that the effluent quality is a function of the sludge age and independent of the hydraulic retention time. The model of McKinney,[2] typical of the second approach, implies that the effluent quality is a function of the hydraulic retention time and independent of sludge age. One would expect that such a difference in the basic behavior would make it difficult to obtain equivalent effluents. Nevertheless, the "constants" in each model eventually must be determined from experimental studies and will be assigned such values that the theoretical effluent quality reflects the experimental data. Application of the two theories to design leads to virtually identical results, if the same load factor or sludge age is specified.

The applicability of the Monod[14] function (Equation 2) to wastewater treatment processes can be criticized as having been developed for soluble nutrients. In the activated sludge process 60 to 70% of the nutrient in the wastewater is in fine particulate form.[19, 23–25] Utilization of particulate matter as an energy source by the organisms must be preceded by bioflocculation of the particulate energy onto the organisms followed by enzymatic breakdown of the particles before transfer through the cell wall. Even the soluble fraction of the nutrient contains a fraction of large complex organic molecules; diffusion rates of these molecules have been observed to be slow as a result of hydration and molecular asymmetry,[23] and they also require enzymatic breakdown prior to transfer through the cell wall. Therefore, it is likely that the fraction of energy that can be used directly by the organisms is small, much less than indicated by the 30 to 40% soluble fraction. It is probably nearer reality to accept that virtually all the energy in municipal wastewater is essentially of a particulate nature. Adsorption, therefore, is an important mechanism in biological degradation kinetics—a factor not considered in the Monod approach.

Accepting that particulate and complex soluble matter adsorbs onto the organism

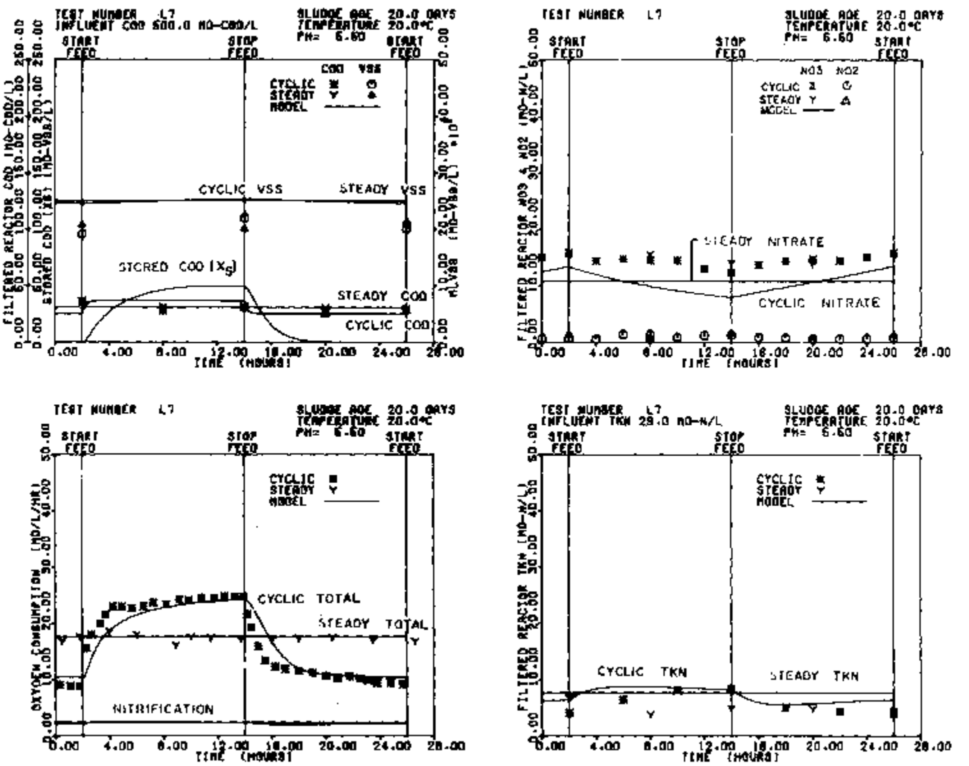

FIGURE 5. Comparison of the theoretical response waves predicted by the Marais and Ekama model incorporating storage of substrate with those observed experimentally for daily cyclic square wave loading conditions at 20 days sludge age, pH 5.5, and temperature 20°C.

implies that storage of energy may also take place. Storage is substantiated from an extensive series of experiments by Porges *et al.*[26] They concluded that an appreciable mass of nutrient can be stored on the organism, that the rate of storage can exceed the rate of stored nutrient utilization by up to 2.6 times, and that the organism mass has a storage potential of up to 50% of its mass, both measured in terms of COD.

Adsorption and storage phenomena cannot be identified readily under steady-state conditions. Steady-state conditions have the inherent disadvantage that, where the process kinetics involve a series of sequentially dependent reactions having potentially different rates, the behavior of the process is characterized by an apparently single rate— that is, the rates between each reaction step are equal. Intermediate steps such as adsorption and storage of nutrient therefore cannot be observed; under steady-state conditions a particular level of stored substrate develops such that the mass of substrate adsorbed and stored is equal to the mass of stored substrate used for synthesis. Thus the adsorption and storage phases are effectively bypassed, and the use of a direct relationship between the substrate concentration in the liquid phase surrounding the organism and the organism growth rate is justified (as postulated by Monod[14] and McKinney[2]). For this reason the formulations of the two approaches to biological growth kinetics described above seem adequate for describing steady-state conditions.

In contrast, *cyclic* loading conditions result in varying levels of stored substrate. Under these conditions the stored substrate concentration changes in a manner different from the substrate concentration in the liquid and leads to a different rate of synthesis from that indicated by the substrate concentration in the liquid. This observation is substantiated by the work presented by Gaudy *et al.*[27] They provided experimental evidence that showed the Monod relationship to be invalid for a period after a step change in substrate con-

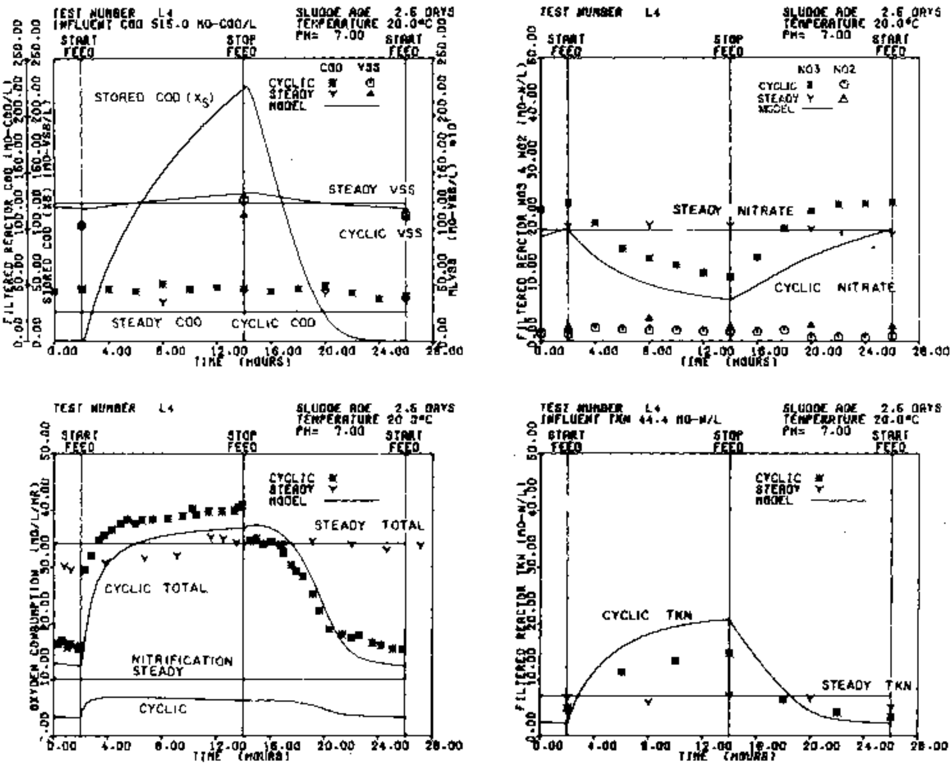

FIGURE 6. Comparison of the theoretical response waves predicted by the Marais and Ekama model incorporating storage of substrate and the recirculation of unadsorbed substrate with those observed experimentally for daily cyclic square wave loading conditions at 2.5 days sludge age, pH 7.0. and temperature 20°C.

centration. The organisms do not respond immediately to a change in substrate concentration, as expected from the Monod function; after a step increase the organisms continue to remove nutrient at the old rate and then gradually the rate increases to the new steady-state level. They ascribed this behavior to the organisms' need to develop additional adsorption sites and concluded that the Monod function is valid only under steady-state conditions.

A number of attempts have been made to determine the time-dependent behavior of the activated sludge process using the first approach to biological growth kinetics Equation 1.[7, 28-30] A review of these attempts reveals the deficiency of this approach. The following two models, one by Adams and Eckenfelder[7] and the other by Ott and Bogan,[28] illustrate this deficiency.

- Adams and Eckenfelder[7] concluded from their experimental investigation of dynamically loaded activated sludge units that the model proposed by Garrett and Sawyer[1] (similar to Equation (3) is satisfactory for describing the time-dependent behavior of the process, provided the constants are empirically adjusted for each different loading case. They speculated that this variation in the kinetic constants can be attributed to the presence of extreme amounts of substrate, particularly at the more severe cyclic loads, resulting in increased levels of adsorption and storage of substrate.
- Ott and Bogan[28] concluded from a theoretical study of activated sludge dynamics that the effluent substrate concentration is directly proportional to the instantaneous substrate loading rate; consequently, flow equalization seemed the most effective means of controlling the effluent substrate concentration. These conclusions are contrary to observations on a cyclically loaded pilot plant (see Figure 1). The data in Figure 1 show effluent COD to be virtually insensitive to the cyclic loading conditions. Such at-

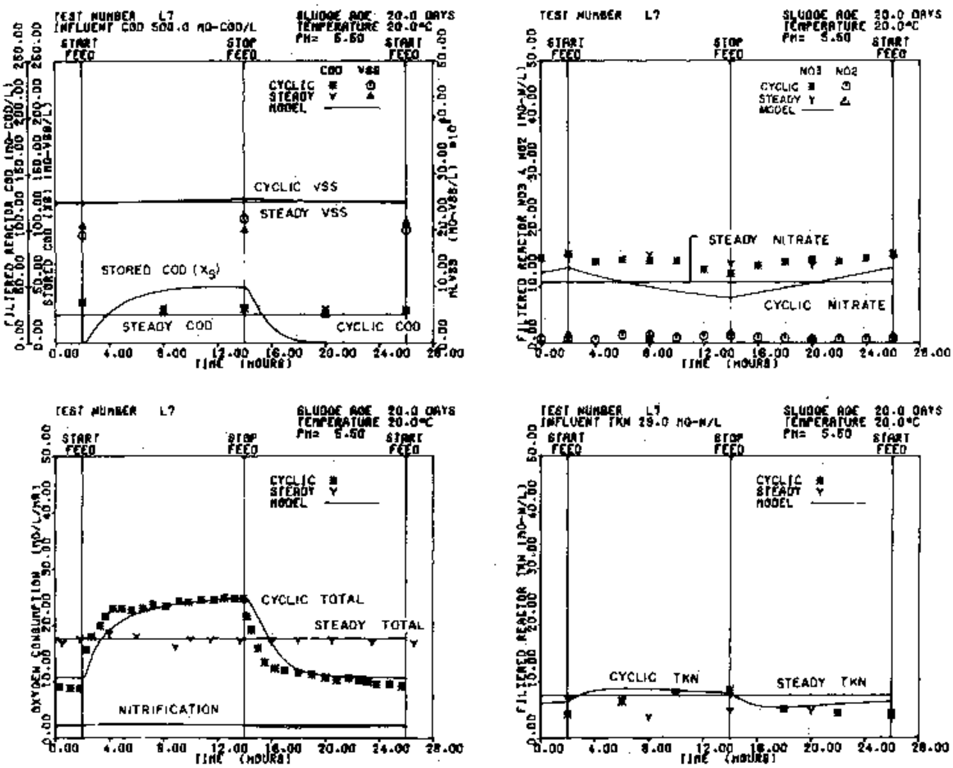

FIGURE 7. Comparison of the theoretical response waves predicted by the Marais and Ekama model incorporating storage of substrate and the recirculation of unadsorbed substrate with those observed experimentally for daily cyclic square wave loading conditions at 20 days sludge age, pH 5.5, and 20°C.

tenuation of the effluent quality is to be expected only if a considerable mass of substrate can be stored on the sludge mass. The high degree of sensitivity of the effluent quality to cyclic loading in their model is a result of the omission of storage capacity of the sludge mass, by relating the substrate in the liquid phase to the growth rate of the organisms.

Direct evidence of the adsorption and storage phenomenon is to be found in the investigations into the contact-stabilization process. The rapid removal of the substrate from the liquid in the contact reactor was described by Jones [31] as being a transfer from the liquid phase to the floc phase by means of adsorption, absorption, and physical entrapment; even though the removal is extremely rapid in the contact reactor, the organic material does not seem to be oxidized to any appreciable extent.

Quantitative expression of adsorption and storage was proposed by Katz and Rohlich.[32] They expressed adsorption as a modified Langmuir isotherm relating COD in the liquid with COD adsorbed in the sludge mass. Their investigations also provide information regarding the rates of adsorption, but it is restricted to batch conditions.

Blackwell,[33] using primarily *soluble* substrates, proposed that the rapid transfer of substrate from the liquid to the floc phase may be formulated as follows:

$$dS_b/dt = -R_k X_v (f_{mv} - X_s/X_v) \qquad (8)$$

where

S_b = substrate concentration in the liquid phase, mg COD/l,
R_k = substrate transfer rate constant, mg COD/mg VSS·d,
X_v = total volatile suspended solids, mg VSS/l,
f_{mv} = maximum fraction of substrate that can be incorporated in the sludge mass (stored), mg VSS/mg VSS, and
X_s = stored substrate concentration, mg VSS/l.

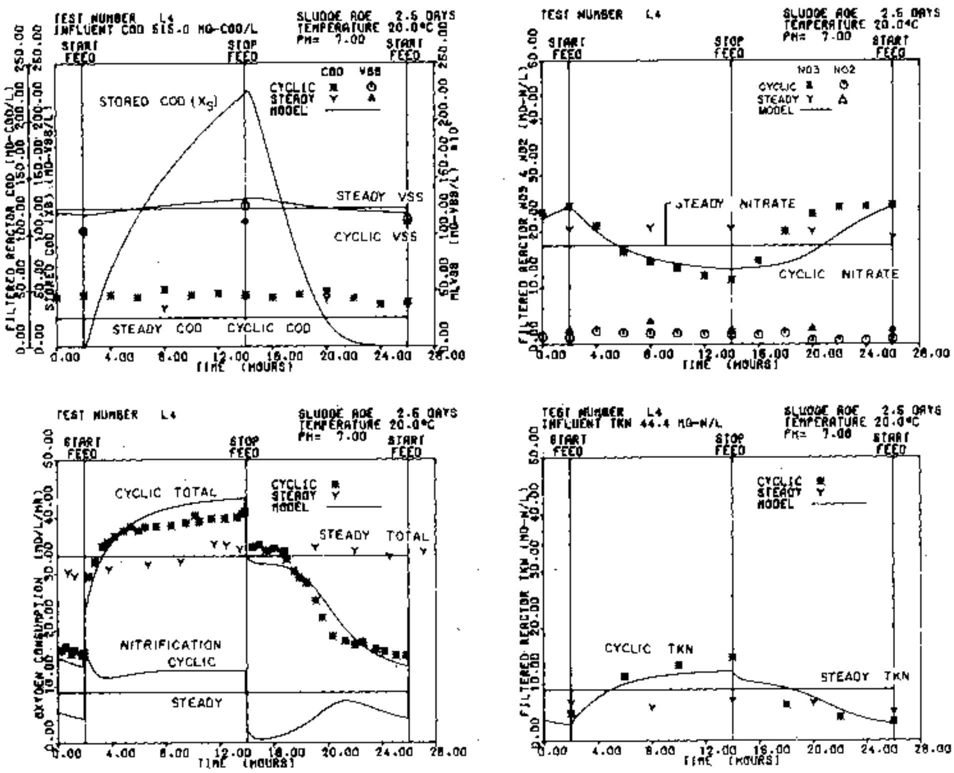

FIGURE 8. Comparison of the response waves predicted by the model proposed by Ekama and Marais, incorporating storage of substrate and the modified model for nitrification, with those observed experimentally for daily cyclic square wave loading conditions at 2.5 days sludge age, pH 7.0, and 20°C.

Equation 8 states that the rate of storage decreases as the stored mass increases, that there is an upper limit to the mass that can be stored (when this is attained the rate reduces to zero) and that the rate is independent of the substrate concentration in the liquid phase.

Blackwell[33] formulated Equation 8 from observations made by McLellan,[34] who demonstrated that there is maximum level for the stored substrate (described as an available storage potential) and that the "driving force" of substrate storage is dependent on the level of stored substrate—the lower the storage level the faster the storage rate. Other investigations provide further qualitative confirmatory evidence: Walters[35] noted that stabilized sludge removed substrate in inverse proportion to the amount of stored substrate. Morris and Stumm,[23] using primarily *suspended* substrates, noted that some initial wastewater purification can be attributed to adsorption and hypothesized that an equilibrium will be attained once the initial substrate removal satisfies an adsorption relationship. They concluded that the biological mass has a limited purification capacity that can be exhausted by prolonged contact with substrate. Blackwell[33] contended that Equation 8 holds true for the total sludge mass, including the inert volatile solids as Heukelekian[36] had observed, and that the removal of dispersed matter occurs under sterile conditions. Morris and Stumm[23] noted that flocculation caused by the tendency to decrease interfacial tension is strictly a physical phenomenon; therefore, migration of colloids in biologically active systems takes place in the same manner as in sterile systems.

Blackwell[33] further developed Equation 8 by incorporating a switching mechanism that, depending on substrate storage levels, allows substrate to be stored or channeled directly to synthesis pathways. He found the incorporation of the switching mechanism was necessary to fit the model to experimental data obtained by pulse and step feed patterns using primarily *soluble* substrates. Jacquart *et al.*,[37] in an attempt to fit Equation 8 to experimental data, concluded that the rate of substrate storage depends on the nature of the substrate. Consequently, they used separate transfer mechanisms for the storage of particulate and soluble substrates.

Andrews and Busby[38] hypothesized that the Blackwell formula (Equation 8) was defective in that it did not consider the effect of the substrate concentration in the liquid phase. They suggested a modification as follows:

$$\frac{dS_b}{dt} = -R_k X_v \left[f_{mv} \left(\frac{S_b}{K_{ss} + S_b} \right) - \frac{X_s}{X_v} \right] \quad (9)$$

where

K_{ss} = saturation coefficient for the storage of substrate, mg COD/l.

They substantiated this modification by noting the observations of Morris and Stumm,[23] who found that the adsorption of substrates was dependent on the substrate concentration in the liquid phase. However, it is doubtful whether Equation 9 achieves this objective as the modification merely introduces a variable upper limit to the storage potential.

Andrews and Busby[38] specifically exclude the switching mechanism of substrate storage or direct utilization for synthesis suggested by Blackwell and the separate transfer mechanism for soluble and particulate substrate suggested by Jacquart *et al.*[37] The substrate transfer mechanism (Equation 9) implies, therefore, that no distinction is made between soluble and particulate fractions of the substrate and that all the substrate must pass through the storage phase. These assumptions seem reasonable when one notes that the substrate in municipal wastewater is essentially of a particulate nature and, as a result, must all pass through the storage phase prior to utilization.[23, 24, 39, 40]

The Monod relationship adequately describes the utilization of stored substrate for synthesis. The models incorporating storage of substrate[33, 37, 39] prior to utilization for synthesis all use the Monod function to de-

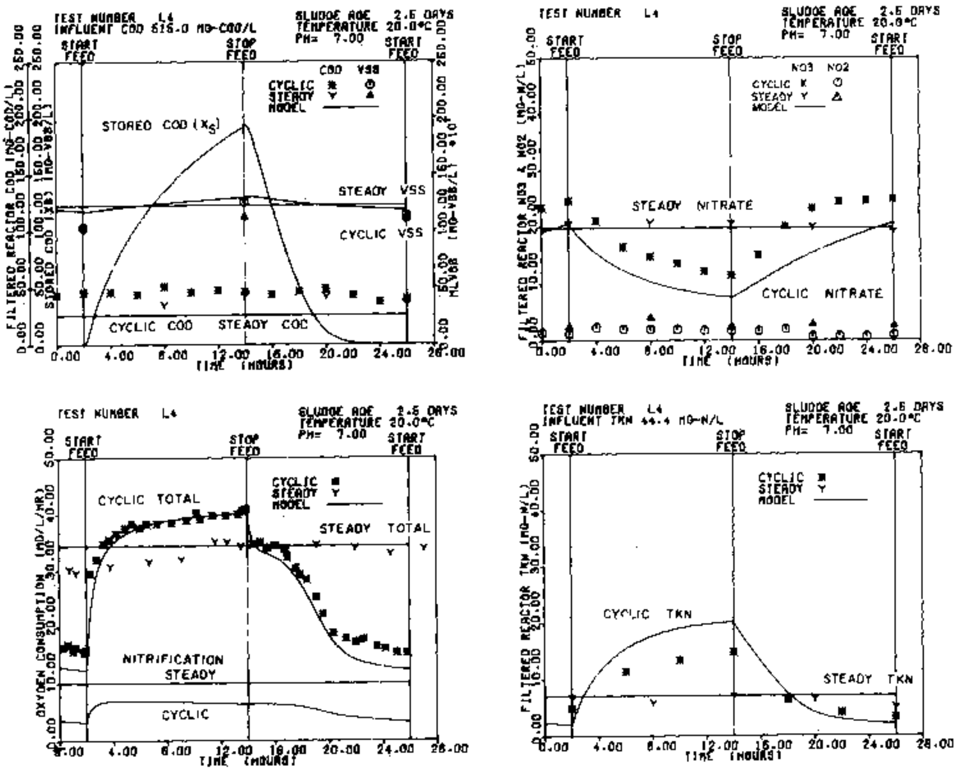

FIGURE 9. Comparison of the response waves calculated by the theoretical model, incorporating adsorption and storage of substrate and the Monod kinetics for nitrification, with those observed experimentally for 2.5 days sludge age, pH 7.0, and 20°C.

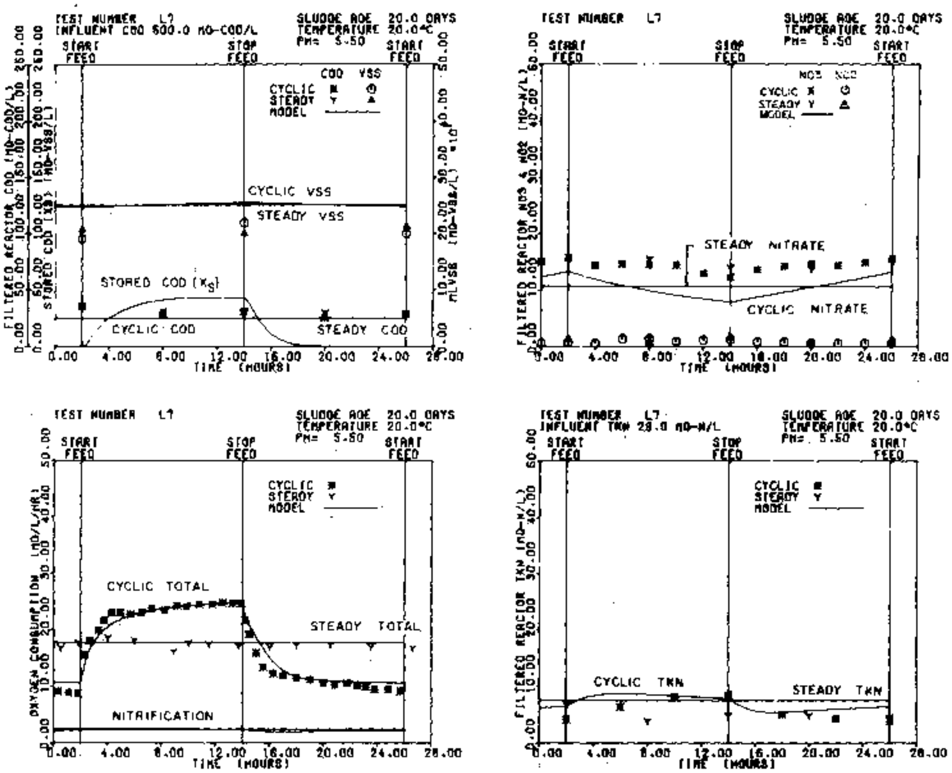

FIGURE 10. Comparison of the response waves calculated by the theoretical model, incorporating adsorption and storage of substrate and the Monod kinetics for nitrification, with those observed experimenally for 20 days sludge age, pH 5.5, and 20°C.

termine the rate of synthesis. Instead of relating the substrate concentration in the liquid phase to the specific growth rate of the organisms, the substrate concentration stored on the organism is related to the specific growth rate—that is

$$\frac{1}{X_a}\frac{dX_a}{dt} = Y_h\left(\frac{K_m X_s P}{K_s + X_s P}\right) \qquad (10)$$

where

Y_h = growth yield coefficient in terms of stored substrate as mg COD/l, mg VSS/mg COD,
K_m = maximum specific growth rate constant, mg VSS/mg COD·d,
X_s = stored substrate concentration, mg COD/l,
P = COD:VSS ratio, and
K_s = saturation coefficient, mg COD/l.

It is important to note that the Monod relationship is not invalidated by the adsorption and storage phenomenon, but that it is assigned to its "appropriate" place of operation in the biological growth kinetic theory.

The models reviewed above all assume that adsorption and storage occur as a single mechanism. This is a simplistic description of the adsorption and storage phenomenon for, though they may be directly related, they are distinctly separate phenomena. Adsorption may be energy-demanding reaction. Because free energy for the organism can only be obtained by redox reactions, identification of the adsorption reaction and its related storage phenomenon may be obtained in the activated sludge process by measuring oxygen consumption rates. Surprisingly, not one of the investigators studying the adsorption and storage mechanism measured oxygen consumption rates to check this behavior.

The possibility of an energy requirement for adsorption of substrate was suggested by Stern and Marais[41] from observations of biological denitrification in the activated sludge process. They concluded that biological denitrification in the primary anoxic reactor, using wastewater as the influent energy source, takes place in two sequential phases. The first phase seems to be linked to a phase of rapid substrate removal and the second phase to the synthesis of substrate. They speculated that the rapid substrate removal during the first phase may be a result of some form of biological sorption. Subsequently, from a detailed study of the initial phase of biological denitrification, Wilson and Marais [25] concluded that this phase of denitrification and the phase of rapid substrate removal are linked through a biological adsorption mechanism—that the nitrate serves as the electron acceptor to make energy available for adsorption. They analyzed their experimental data, together with that of others [41] in terms of the Katz and Rohlich [32] adsorption isotherm for activated sludge, and found that the initial denitrification phase is consistent with biological adsorption.

Although the conclusions of Wilson and Marais were drawn from the observation of activated sludge in an anoxic environment, a similar behavior can be expected under aerobic conditions. Under aerobic conditions, a corresponding *oxygen* requirement for the adsorption of substrate would be needed. This phenomenon should threfore be amenable to observation by monitoring the oxygen consumption rates in the activated sludge process operated under cyclic loading conditions.

NITRIFICATION

Downing *et al.*[42] presented one of the first nitrification models for the activated sludge process. They successfully used the Monod formula for estimating the rate of growth of the nitrifying bacteria. The model of Downing *et al.*[42] has, over the years, found wide application and it has become established as *the* nitrification model for the activated sludge process.

Only steady-state verification of the model was undertaken by Downing *et al.* Subsequent investigations,[43–45] all using the Monod relationship relating the substrate concentration in the liquid phase to the rate of growth of the organisms, including some minor modifications, established that the

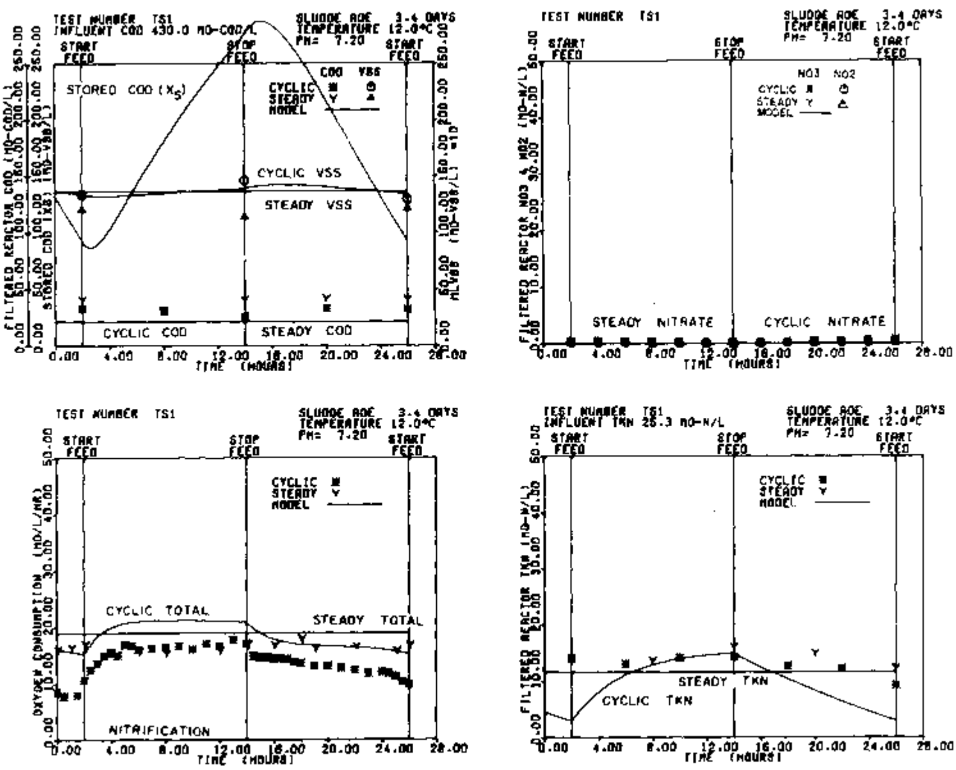

FIGURE 11. Comparison of the response waves predicted by the theoretical model with those observed experimentally under daily cyclic square wave loading conditions at 3.3 days sludge age, pH 7.2, and 12°C.

TABLE II. Values of kinetic and other constants used in the model for the activated sludge (see appendix for nomenclature).

Symbol	Value	Units	Symbol	Value	Units
			Carbonaceous material degradation kinetics		
$K_{a20}{}^{b}$	0.135	l/mg VSS·d	f_{ma}	1.000	mg VSS/mg VSS
$K_{m20}{}^{b}$	3.00	mg COD/mg VSS·d	f_{ca}	0.078	mg COD/mg COD
K_{s20}	100.0	mg COD/l	$K_{r20}{}^{b}$	0.015	l/mg VSS·d
b_{h20}	0.24	d^{-1}	$\theta_{ha}{}^{b}$	1.200	
$Y_h{}^{1}$	0.45	mg VSS/mg COD	$\theta_{hs}{}^{b}$	1.100	
f	0.20	mg VSS/mg VSS	$\theta_{he}{}^{b}$	1.029	
f_n	0.10	mg N/mg VSS	ϕ_{ha}	1.000	
P	1.48	mg COD/mg VSS	ϕ_{hs}	1.000	
$f_{ae}{}^{b}$	0.00	mg N/mg VSS	ϕ_{he}	1.000	
$f_{as}{}^{b}$	1.00	mg N/mg VSS			
			Nitrification kinetics		
$\mu_{nm}{}^{c}$	0.65 0.21	d^{-1}	b_{n20}	0.04	d^{-1}
K_{n20}	1.00	mg N/l	Y_n	0.10	mg VSS/mg N
θ_{ns}	1.123		ϕ_{ns}	2.350	
θ_{ne}	1.029		ϕ_{ne}	1.000	
			Influent wastewater fractions[b]		
$f_{us}{}^{a}$	0.033 0.050	mg COD/mg COD	$f_{un}{}^{a}$	0.00 0.00	mg N/mg N
$f_{up}{}^{a}$	0.025 0.090	mg VSS/mg COD	$f_{sn}{}^{a}$	0.84 0.75	mg N/mg N

[a] Upper value refers to unsettled wastewater; lower value to settled wastewater.
[b] Values determined by simulation.
[c] Lower value includes a certain degree of inhibition.

model is also valid under time- and space-varying conditions. The reasons for the successful application of the Monod relationship to nitrification kinetics can perhaps be attributed to the fact that the nitrifiers are a specific organism type using *specific soluble* substrates that are readily assimilable. The nitrifiers do not seem to adsorb and store their substrate prior to metabolism, possibly because the transfer of ammonia through the cell wall is diffusion-controlled.

In the application of Monod's formula to nitrification in the activated sludge process, the fate of organic nitrogen does not seem to have been considered. When modeling nitrification in the process treating municipal wastewater, in which 20% of the total nitrogen is in the organic nitrogen form, it was necessary to incorporate the biodegradation of organic nitrogen to obtain an adequate description of the nitrification aspect in the process. The organic nitrogen seems to be slowly biodegraded by heterotrophic organisms.

EVOLUTION OF GENERAL MODEL

The evolution of the general model was based on an extensive experimental investigation into the time-dependent behavior (Category 2) of the activated sludge process, including nitrification. An attempt was made to simulate the process behavior by using one of the conventional models of Approach I (Equation 1). This model was then sequentially modified to incorporate storage of substrate and other effects as these became apparent, until finally a model was developed that gave a reasonable correlation under steady-state, time-varying, and space-varying conditions. The modifications will only be described on a qualitative basis.

In the experimental investigation using raw wastewater, daily cyclic square wave loading conditions were imposed on laboratory scale activated sludge units at 2.5 and 20 days sludge age at 20°C at Cape Town. The process response to these conditions was observed over a number of 24-hour cycles during which the process variables [such as mixed

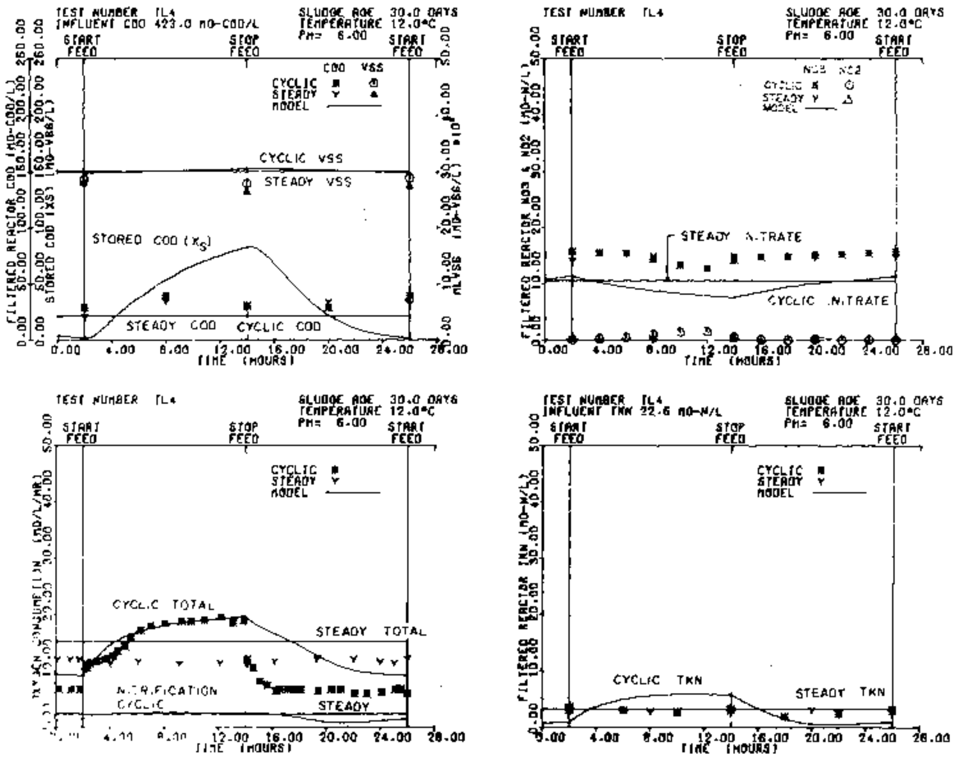

FIGURE 12. Comparison of the response waves predicted by the theoretical model with those observed experimentally under daily cyclic square wave loading conditions at 30 days sludge age, pH 6.0, and 12°C.

liquor volatile suspended solids (MLVSS), COD, total Kjeldahl nitrogen (TKN), and nitrate concentrations, and the oxygen consumption rate in the reactor] were observed at regular intervals. As a basis for initiating the simulation program, the model of Marais and Ekama [19] was used. This model is an extension of the model of Lawrence and McCarty [3] and (*a*) incorporates nitrification based on the Monod function relating the specific growth rate of *nitrosomonas* to the ammonia concentration in the liquid phase; (*b*) separates active, endogenous, and inert fractions of the sludge; (*c*) provides a rational link between the carbonaceous oxygen consumption rate and heterotrophic cell synthesis and endogenous respiration; and (*d*) is readily modified to include general conditions of substrate concentration by retaining the full Monod [13] relationship relating the specific growth rate of the heterotrophic organisms to the substrate concentration (COD) in the liquid phase (the simplification of the Monod function in the Marais and Ekama model is only valid under substrate-limiting conditions). The experimental work by Marais and Ekama was done on raw and settled wastewater at steady-state conditions only. By using a method of analysis directly based on their theory, they provided new estimates of the yield coefficient Y'_h and the endogenous respiration rate b_h under steady-state conditions. These values differ significantly from those generally reported. They showed that (*a*) the load factor is *not* linearly related to the inverse of sludge age, (*b*) the linear relationship significantly underestimates the endogenous respiration rate, and (*c*) Y'_h and b_h are interrelated in such a fashion that it is not possible to determine them simultaneously —that is, that one of them, b_h, must be determined independently for an accurate estimate of the other.

Marais and Ekama also found that the influent COD can be divided into three fractions—biodegradable (which includes soluble and particulate fractions), unbiodegradable soluble, and unbiodegradable particulate. It was found convenient to express these fractions in terms of the total influent COD. The

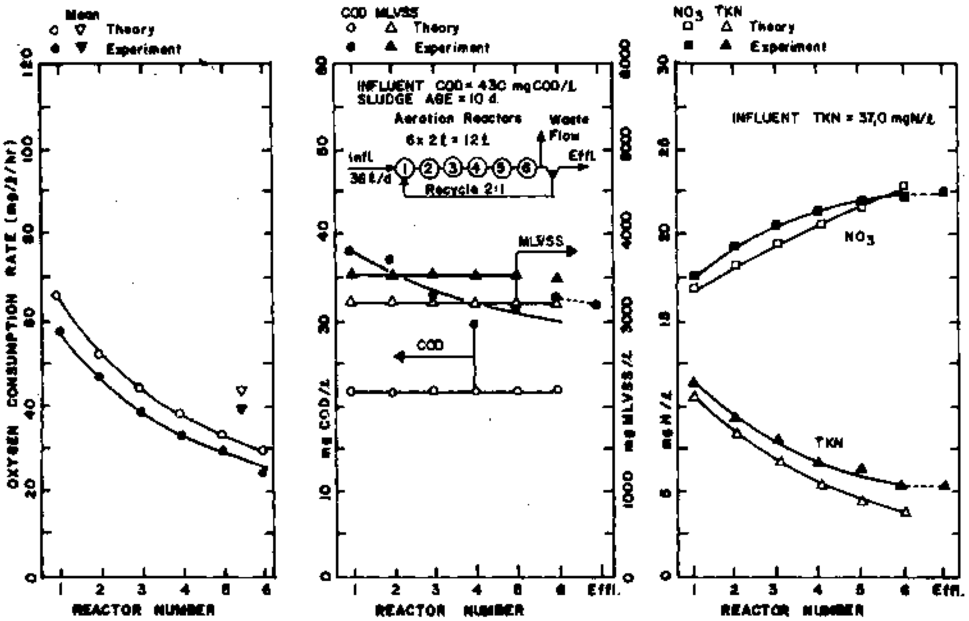

FIGURE 13. Comparison of process variable response profiles by the theoretical model with those observed experimentally in a series reactor process under constant loading conditions at 10 days sludge age, pH 6.05, and 20°C.

numerical values of the fractions for settled and raw wastewater are given in Table II. The soluble and particulate biodegradable fractions are considered as one for the purpose of modeling. The soluble unbiodegradable fraction passes unchanged through the plant, and the unbiodegradable solid fraction accumulates in the sludge and is discharged via the daily sludge wastewater.

The model of Marais and Ekama[19] was applied directly to predict the response behavior under dynamic conditions of loading. A comparison of the predicted and experimental responses under daily cyclic square wave loading conditions at 2.5, and 20 days sludge age are given in Figures 2 and 3. At a sludge age of 2.5 days, the predictions do not correlate with the experimental observations. The attenuation of the oxygen consumption rate over the feed and nonfeed periods can almost certainly be attributed to storage of substrate (COD) on the sludge mass. Furthermore, the theoretical filtered (that is, soluble) reactor COD concentration is far more sensitive to influent loading conditions than the experimentally observed values. Indeed, the experimental values seem to be completely insensitive to both square wave loading conditions and the sludge age. This insensitivity of the filtered reactor COD concentration can also be attributed to the storage of substrate capacity of the sludge. At a sludge age of 20 days, a reasonable correlation is obtained. Similar deficiencies were also observed with the McKinney[2] model.

In an attempt to improve the correlation between theoretical and experimental responses, the Marais and Ekama[19] model was modified to incorporate substrate storage and synthesis of cell mass, using the stored substrate mechanism as proposed by Blackwell[33] (Equations 8 and 10). Because Blackwell's model implies that the rate of substrate disappearance is independent of the substrate concentration in the liquid phase, S_b, (that is, zero order), at certain stages in the cycle this resulted in negative S_b values. Blackwell's equation consequently was modified to a first-order rate with respect to substrate concentration in the liquid phase, S_b. Furthermore, after noting the large fraction of inert material generated at long sludge ages and that there is no reason to believe that such material can store energy, the total volatile solids concentration, X_v, of Equation 8 was changed to the active volatile solids concentration, X_a.

$$dS_b/dt = -K_a S_b X_a (f_{ma} - X_s/X_a) \quad (11)$$

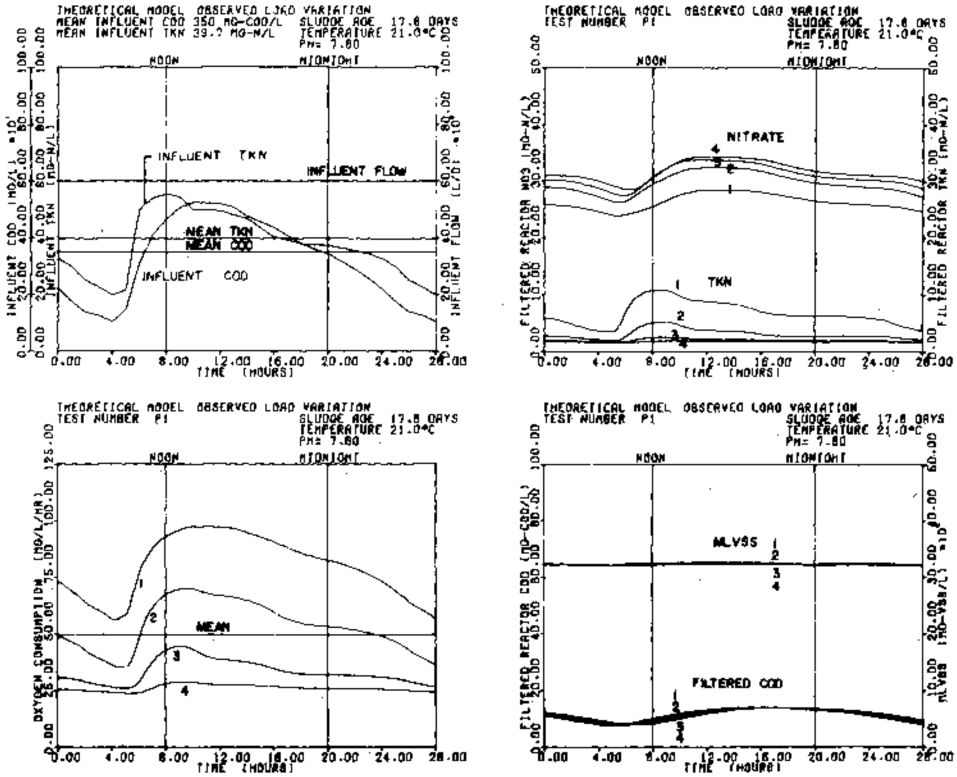

FIGURE 14. Theoretical process variable response waves predicted for the series reactor pilot plant under cyclic loading conditions at 18 days sludge age, pH 7.8, and 21°C.

where

K_a = substrate adsorption rate constant, and

f_{ma} = maximum fraction of substrate that can be incorporated on the *active* sludge mass, mg vss/mg vss.

Andrews and Busby's modification (Equation 9) of Blackwell's equation (Equation 8), which introduces a variable storage potential, was found to lead to inconsequential differences, probably because the storage potential is large compared with the actual storage that takes place. Also, when the biodegradable substrate in the liquid S_b attained values near zero, the storage potential becomes virtually zero and the equation then showed desorption tendencies.

The responses predicted by the modified model are shown in Figures 4 and 5. In these figures an additional variable—the mass concentration of COD stored on the organisms—is shown. At a sludge age of 2.5 days, the prediction of the total oxygen consumption rate is greatly improved with respect to the experimental data, while at 20-days sludge age the fit remains satisfactory. At 2.5 days sludge age, however, the observed oxygen consumption rate shows a precipitous decrease at feed termination, whereas the predicted response does not show such a decrease. Furthermore, the theoretical filtered reactor COD concentrations still did not show similar insensitivity to cyclic square wave loading conditions. It was eventually concluded that the insensitivity of the filtered reactor COD concentration to cyclic square wave loading conditions results from the nature of the influent wastewater. In the model of Andrews and Busby,[38] no distinction is made between soluble and particulate substrate, and all the substrate is assumed to be of a particulate nature. This assumption is reasonable when one notes that all the substrate in municipal wastewater is essentially of a particulate nature.

There is also no distinction made between soluble and particulate influent substrate in

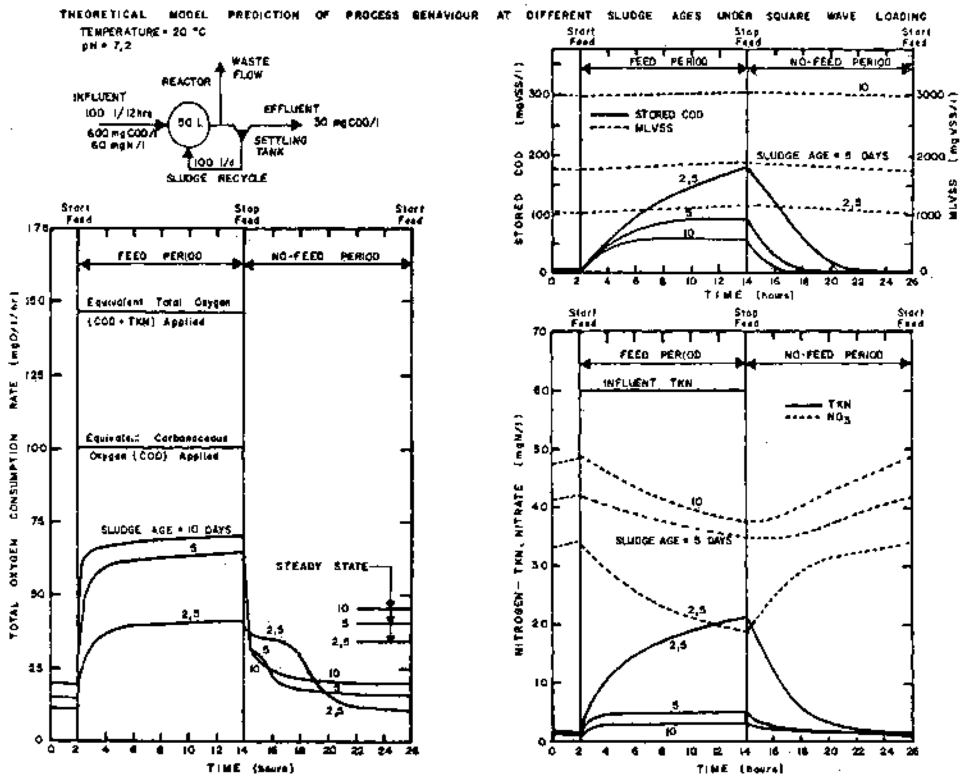

FIGURE 15. Behavior of the CMAS process under daily cyclic square wave loading conditions at 20°C and pH 7.20.

the modified theoretical model. Nevertheless, it is implicitly assumed to be all soluble. The theoretical model was modified so that all the substrate is assumed to be particulate. This was done by allowing the unadsorbed substrate to remain enmeshed in the sludge flocs, to be densified in the settling tank, and to be recycled back to the reactor. Note that the substrate enmeshed in the sludge flocs is *not* stored substrate. The effluent and filtered reactor COD concentrations are therefore principally the soluble unbiodegradable fraction of the influent COD. The responses predicted by the theoretical model incorporating these modifications are given in Figures 6 and 7. The insensitivity of the filtered reactor COD is now well reproduced by the theoretical model. This approach finds support from the experimental observation that there is no significant difference between the soluble effluent COD concentration at a sludge age of 2.5 or 20 days, at 20° and 12°C. However, the modifications have made no improvement to the prediction of the precipitous decrease in the oxygen consumption rate at feed termination at a sludge age of 2.5 days.

As nitrification occurred at both sludge ages, the experimental oxygen consumption rate responses consisted of both heterotrophic and autotrophic organism metabolic oxygen requirements. Ekama and Marais [46] hypothesized that the precipitous decrease in the experimental oxygen consumption rate at feed termination is a behavioral characteristic of autotrophic nitrification. The acceptance of this hypothesis led to the development of a modified model for nitrification that incorporated the following concepts:

- A fraction of the TKN concentration (probably proteinaceous nitrogen) is not directly available for nitrification, but must first be converted to free and saline ammonia before it can be nitrified. This conversion to ammonia seemed to be a relatively slow process.
- The conversion of ammonia to nitrate is instantaneous.
- With the storage of COD, a certain mass of nitrogen is also stored.

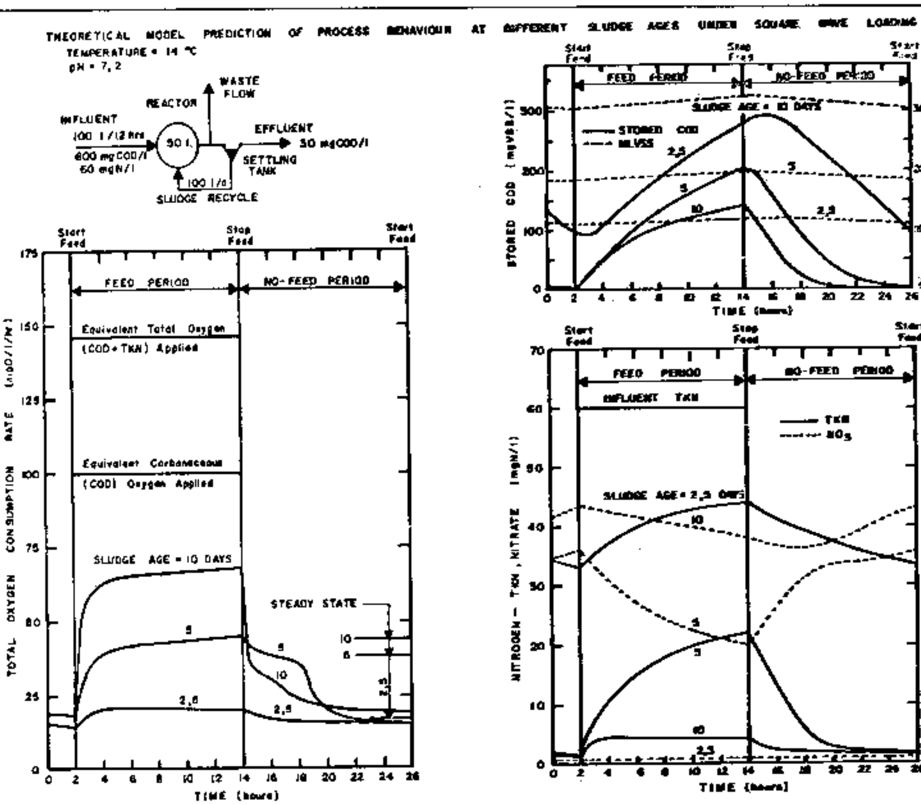

FIGURE 16. Behavior of the CMAS process under daily cyclic square wave loading conditions at 14°C and pH 7.20.

In terms of the modified nitrification model, the precipitous decrease in the total oxygen consumption rate at feed termination is caused by the sudden termination of influent ammonia addition. The acceptance of the modified nitrification model implies that the application of the Monod relationship to modeling nitrification under daily cycle square wave loading conditions is inappropriate.

Incorporation of the modified nitrification model into the general model gave the response shown in Figure 8 for 2.5-days sludge age. The precipitous decrease in the total oxygen consumption rate was now adequately predicted, but the correlation could be obtained only after it was accepted that the free and saline ammonia fraction of the influent TKN is only 20% and the organic bound fraction 80%. This conflicts with experimental measurements for municipal wastewater that give approximately 80% of the TKN as free and saline ammonia and 20% as organic bound nitrogen. The exclusion of the tested Monod relationship for nitrification in favor of a different nitrification theory could not be accepted unless very powerful supporting evidence can be presented.

Work by Wilson and Marais [25] on biological denitrification in the activated sludge process led to a reassessment of the model. From their work it is apparent that the rapid removal of substrate from the liquid phase is an energy-requiring adsorption mechanism. This observation suggested an alternative explanation for the precipitous decrease in the total oxygen consumption—that the precipitous drop is a behavioral characteristic of heterotrophic organisms caused by the cessation of an energy requirement for the adsorption of the substrate, resulting from the termination of substrate addition. This hypothesis has been verified by Ekama and Marais.[27]

The mathematical model was modified to incorporate the energy requirements for adsorption and the nitrification theory, based on the Monod function relating the ammonia concentration to the rate of growth of *nitrosomonas*, was reinstated in the model. Adsorption energy requirements were incorporated on the basis of 8% of the substrate

(COD) transferred from the liquid phase to the stored phase is required to provide energy for storage; an identical mass of oxygen is used for this purpose. The influent TKN fractions of ammonia and organic bound nitrogen were taken as those measured experimentally—that is, approximately 80% free and saline ammonia and 20% organic nitrogen. Nevertheless, the concepts of organic nitrogen storage and slow conversion to free and saline ammonia as set out in the previous model were retained. The comparison of the theoretical and experimental responses are shown in Figures 9 and 10. There is a significant improvement in the predictive capabilities of the modified mathematical model for the oxygen consumption rate, TKN, and nitrate concentration responses at both 2.5- and 20-days sludge age. The values of the kinetic constants are given in Table II.

The temperature effects of the process were evaluated by repeating the experimental test runs at 12°C at both 3.3- and 30-days sludge age. The results of two such tests are shown in Figures 11 and 12. The temperature dependency of the kinetic constants is given in Table II. These constants show that the rate of adsorption is very temperature dependent, the synthesis rate less so, and the endogenous respiration rate relatively insensitive. The first two temperature dependency constants were determined by repeated simulation studies until the best fit at 12°C was obtained; that for endogenous respiration was determined by measuring oxygen utilization rates with time in batch studies of aerobic mixed liquor suspended solids (MLSS) digestion at different temperatures.[19]

At 3.3-days sludge age (Figure 11), the oxygen consumption rate is attenuated to a virtually constant value between the feed and no-feed periods. From the theoretical model a concentration of biodegradable COD (±50 mg COD/l) is enmeshed in the sludge and is not adsorbed. Similarly, a large concentration of *stored* solids remains unmetabolized. Both these concentrations are removed from the process during daily sludge wasting. The continued high storage level is the principal reason why the oxygen consumption rate remains virtually constant over the 24-hour cycle. No nitrification was observed—a fact successfully predicted by the model. At 30-days sludge are (Figure 12), the predicted oxygen consumption rate behavior is somewhat different from the observed behavior. At the termination of the feed period the experimental oxygen consumption rate rapidly decrease, whereas, theoretically, the decrease is more gradual. These differences in behavior have not been explained. Nevertheless, the oxygen consumption rate is reasonably well predicted during the feed period. Concentrations of MLVSS and filtered COD are also satisfactorily simulated. The stored solids concentration (mg VSS/l) varies considerably between the feed and non-feed periods, resulting in the variation in oxygen consumption rate of the 24-hour cycle.

To determine the effect of spatial variations, a set of experiments was run on a series process configuration consisting of six completely mixed reactors in series under constant loading conditions at 10-days sludge age and 20°C. The theoretical model was used to predict the behavior of this process configuration (Figure 13). The kinetic constants used in the simulation study are those values given in Table II. The experimental data are averages of the daily measurements of the process variables over one sludge age. With the variability to be expected in biological systems, the experimental and theoretical data are in excellent agreement.

Following the success of the theoretical model in predicting time- and space-vary behavior, it was felt the biological kinetic mechanisms were adequately delineated to undertake pilot-scale studies involving space- and time-varying conditions (Category 4), which impose the most severe test on the validity of the model.

The pilot plant, situated at Pretoria, consisted of four 5-m^3 aeration reactors in series. A constant flow of 60 m^3/d settled wastewater was imposed on the pilot plant. The cyclic load resulted from the diurnal variation in influent COD and TKN concentrations. The pilot plant was operated at 18-days sludge age and a sludge recycle ratio of 2:1 at approximately 21°C. The experimental data, including the influent COD and TKN concentrations, observed over a 24-hour cycle are given in Figure 1. The input data were used in a simulation study with the kinetic and other constants for settled wastewater listed in Table II. The theoretical predictions are shown in Figure 14. However, to obtain the good correlation, a value of the maximum specific growth of the *nitrosomonas* μ_{nm} of 0.21 had to be accepted, a value three times lower than that for the unsettled wastewater (Table II). Such a decrease is not unjustified because Pretoria wastewater contains an appreciable industrial fraction, whereas the wastewater of Cape Town, used as influent in the laboratory studies, was principally from domestic sources. From an inspection of the experimental data and the theoretical data in Figures 1 and 14 which are plotted to identical scales to facilitate a direct comparison, it can be seen that an excellent correlation is obtained even under the severe dynamic conditions.

GENERAL BEHAVIOR OF THE MODEL

To provide an overall impression of the response of the activated sludge process at different sludge ages and temperatures, the theoretical behavior of a plant operated under square wave loading conditions at 20° and 14°C was studied at sludge ages of 2.5, 5, and 10 days. The volumes of the plants were maintained at a constant value so that the concentrations and rates are proportional to masses and mass rates of the different parameters per mass input. The simulations are shown in Figures 15 and 16.

An important result is that to ensure reasonably complete nitrification during winter (14°C), the minimal sludge age should be 10 days. Another interesting point is that at short sludge ages and low temperatures, the stored COD becomes an appreciable fraction of the MLVSS that is discharged with the daily sludge wastage. Furthermore, because of the continuous high level of stored COD, the fluctuation of the oxygen consumption rate tends to be highly attenuated and the rate remains at a low level. In effect, at low sludge ages and temperatures, the plant operates principally as a bioflocculation process. At sludge ages of 10 days and longer, temperature has very little effect on the behavior of the plant. Not shown on the diagrams is the effluent COD, which in all cases was 30 mg COD/l. This insensitivity of the effluent COD to changes in temperature and sludge age is attributable to the particulate nature of the influent COD and storage of substrate on the sludge mass.

This paper dealt only with the basic biological mechanisms and their kinetics as hypothesized by the authors. The process equations were not discussed as these can be readily developed once the biological mechanisms are known. The biological mechanisms proposed by the authors are unlikely to be final and must be looked on only as a further advance in understanding biological behavior. The explanation of adsorption and its oxygen demand in particular needs greater scrunity and cannot be said to be positively proved. A major conclusion from this work is that the oxygen utilization rate is a most important parameter in any attempt to unravel the mechanisms and kinetics of the activated sludge process.

APPENDIX—List of symbols

b^* = General parameter for endogenous respiration, d^{-1}. Subscripts h or n refer to heterotrophic or nitrifying organisms, respectively.

f = Unbiodegradable fraction of the active sludge mass, mg VSS/mg VSS.

f_{ca} = Fraction of substrate (COD) required for adsorption, mg COD/mg COD.

f_{ma} = Maximum fraction of substrate (as VSS) that can be incorporated in the active volatile sludge mass, mg VSS/mg VSS.

f_{mv} = Maximum fraction of substrate (as VSS) that can be incorporated in the total volatile sludge mass, mg VSS/mg VSS.

f_n = Nitrogen fraction of the sludge, mg N/mg VSS.

f_{oe} = Organic nitrogen fraction of the nitrogen released by heterotrophic endogenous respiration, mg N/mg N.

f_{os} = Organic nitrogen fraction of the nitrogen required for heterotrophic cell synthesis, mg N/mg N.

f_{sn} = Free and saline ammonia fraction of the influent TKN, mg N/mg N.

f_{un} = Soluble unbiodegradable fraction of the influent TKN, mg N/mg N.

f_{up} = Particulate unbiodegradable fraction of the influent COD, mg VSS/mg COD.

f_{us} = Soluble unbiodegradable fraction of the influent COD, mg COD/mg COD.

K_a^* = Substrate adsorption rate constant, l/mg VSS·d.

K_m^* = Maximum heterotrophic specific growth rate constant, mg COD/mg VSS·d.

K_n^*† = Saturation coefficient for nitrification, mg N/l.

K_r^* = Conversion rate of organic nitrogen to free and saline ammonia, l/mg VSS·d.

K_s^* = Saturation coefficient for heterotrophic cell synthesis, mg COD/l.

K_{ss} = Saturation coefficient for storage of substrate, mg COD/l.

N = General parameter for nitrogen concentration, mg N/l. Subscripts a, n, o, t, and u refer to ammonia, nitrate, organic nitrogen, TKN, and unbiodegradable concentrations, respectively.

O = General parameter for oxygen consumption rate, mg O/l·d. Subscripts a, c, e, n, s, and t refer to adsorption, carbonaceous, endogenous respiration, nitrification, synthesis, and total fractions, respectively.

P = COD:VSS ratio, mg COD/mg VSS.

R_k = Substrate transfer rate constant, mg COD/mg VSS·d.

S = General parameter for substrate (COD) concentration, mg COD/l. Subscripts b, u, and t refer to biodegradable, unbiodegradable soluble, and total fractions, respectively.

t = Time (d).

X = General parameter for sludge concentration (mg VSS/l). Subscripts a, e, n, s, and v refer to active, endogenous, nitrifier, stored, and total volatile concentrations, respectively. Additional subscripts g or l refer to concentrations gained or lost as a result of process reaction.

Y_h = Heterotrophic organism yield coefficient using stored substrate, mg VSS/mg COD corrected for adsorption energy requirements.

Y'_h = Heterotrophic organism yield coefficient using substrate from the liquid phase (ignoring adsorption energy requirements, mg VSS/mg N.

Y_n = Nitrifying organism yield coefficient, mg VSS/mg N.

μ*† = General parameter for *specific* growth rate, d^{-1}. Subscripts h or n refer to heterotrophic or nitrifying organisms, respectively. Additional subscript m refers to maximum value.

μ'_h = Heterotrophic organism growth rate, d^{-1}.

θ = General parameter for the temperature dependency coefficient. Subscripts h and n refer to heterotrophic and nitrifying organisms, respectively. Additional subscripts a, e, and s refer to adsorption and endogenous respiration and synthesis values, respectively.

ϕ = General parameter for the pH dependency coefficient. Subscripts h and n refer to heterotrophic and nitrifying organisms, respectively. Additional subscripts a, e, and s refer to adsorption, endogenous respiration, and synthesis values, respectively.

* Additional subscripts T or 20 refer to the value at T or 20°C, respectively.

† Additional subscripts p or 7.2 refer to the value at pH equal to p or 7.2, respectively.

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