

# Effects of oxygen transport limitation on nitrification in the activated sludge process

Michael K. Stenstrom, Stephen S. Song

**ABSTRACT:** A pseudohomogeneous model of the nitrifying activated sludge process was developed to investigate the effects of mass-transport resistance and heterotrophic/nitrifier competition on the apparent relationship between dissolved oxygen (DO) concentration and nitrification. The kinetics of both heterotrophic carbon oxidation and autotrophic ammonia oxidation within activated sludge flocs were described by an interactive-type, multiple-substrate-limiting model. The values for the model's parameters were estimated from a series of experiments that were conducted in laboratory-scale nitrifying activated sludge reactors. Using the estimated parameter values, the model was used to simulate the effect of organic shock loads and steady-state nitrification efficiency over a typical range of mean cell retention times (MCRTs), DO concentrations, and levels of mass-transport resistance. Varying oxygen transport effects, MCRTs, and heterotrophic/autotrophic competition for DO can combine to give apparent nitrification-limiting DO concentrations that range from 0.5 mg/L to as high as 4.0 mg/L. *Res. J. Water Pollut. Control Fed.*, 63, 208 (1991).

**KEYWORDS:** activated sludge, dissolved oxygen, nitrification, *Nitrobacter*, *Nitrosomonas*.

The activated sludge process has been employed in many secondary treatment facilities constructed since 1973, in large part because of its ability to consistently meet secondary standards in a wide variety of situations. Although the process is highly efficient for the removal of dissolved and colloidal organic pollutants, it is sometimes unreliable in removing ammonia. Ammonia is often discharged in the effluent of activated sludge plants, not only as an unremoved constituent of wastewater but also as a byproduct of the treatment process itself. The typical activated sludge process treats domestic wastewater ammonia in concentrations ranging from 10 to 50 mg N/L.

Nitrification is the sequential two-step autotrophic oxidation of ammonia. This process is effected primarily by two genera of chemoautotrophic bacteria, *Nitrosomonas* and *Nitrobacter*. Oxidation of ammonia to nitrite is effected by *Nitrosomonas*. The second step, oxidation of nitrite to nitrate is effected by *Nitrobacter*. A particularly economical implementation of nitrification, especially for upgrading existing activated sludge plants, accomplishes these reactions within the same reactor as that used for the heterotrophic oxidation of carbonaceous matter. For simultaneous carbon and ammonia oxidation to occur, reactor conditions must be conducive to the growth and activity of both heterotrophic and nitrifying bacteria.

Factors considered relevant to the growth and activity of heterotrophs are also relevant to nitrifiers. Such factors include sludge age (MCRT), pH, temperature, dissolved oxygen (DO) concentration, electron donor substrate concentration, substrate composition, loading rate, and the presence of toxic substances. The impact of these factors on each of the two microbial populations is different. The nitrifying population, being less robust

than the heterotrophic population, requires more favorable environmental conditions. Painter (1977), Sharma and Ahlert (1977), and Focht and Chang (1975) review these conditions.

Of the many factors that are known to affect nitrifiers, DO concentration is one of the more important. Dissolved oxygen is required for nitrification, and many plant operators maintain high DO concentration to promote nitrification; however, maintaining excessively high DO concentration to ensure that the nitrifiers are not oxygen limited is uneconomical. An optimal DO concentration to achieve nitrification while reducing aeration costs has not been established.

Current models (Lawrence and McCarty, 1970, and Poduska and Andrews, 1975) of the nitrifying activated sludge process have used homogeneous approaches by assuming that the nitrifying bacteria are evenly dispersed with the heterotrophic bacteria in the mixed liquor. It is further assumed that the activity of nitrifiers is not affected by the presence of heterotrophic bacteria and vice versa, that is, there is no interaction between the two populations. The rate of nitrification is described by the Monod function with ammonium-nitrogen as the only limiting substrate. Therefore no interactions between the two populations can be simulated.

The suspended microbial cultures used in the nitrifying activated sludge process usually contain mixed liquor suspended solids (MLSS) ranging in concentration from 1000 to 4000 mg/L. At these concentrations, heterotrophic and nitrifying microorganisms do not exist in the suspension as dispersed individuals, but as flocs. Parker *et al.* (1970) reported that the size of activated sludge flocs range from 50 to 1000  $\mu\text{m}$ , with the average in the range of 200 to 500  $\mu\text{m}$ .

In their review of the literature, Stenstrom and Poduska (1980) found a wide variation in the reported effects of DO concentration on nitrification. They reported values of the limiting DO concentration ranged from 0.5 to 4 mg/L. Correspondingly, the reported values of the Monod half-saturation coefficient for DO ranged from 0.1 to 2 mg/L. Part of the large variability was attributed to differences in techniques used by the various researchers; determinations were made under pure culture conditions, activated sludge conditions, steady-state conditions, and non-steady-state conditions. They also suggest that the large range in reported DO concentrations could be the consequence of not recognizing the existence of synergistic factors such as mass-transport limitation and multiple-substrate-limiting kinetics.

To achieve efficient nitrification, a clearer quantification of the effects of DO concentration and the identification of other interdependent factors and their effects are needed. The objectives of this research are to resolve the incongruities in the literature and to develop a model of the nitrifying activated sludge process in terms of the relationships between DO concentration

and other synergistic factors. We investigated synergism among mass-transport limitation, multiple-substrate-limiting conditions, and heterotroph/nitrifier competition and present a mathematical model describing the effects of synergism on the relationship between DO concentration and nitrification.

### Model Development

The formulation of our model follows the pseudohomogeneous approach of Froment (1972). In adopting this approach, the activated sludge flocs are modeled as porous catalyst particles into which substrates diffuse and where autotrophic and heterotrophic competition for the substrates occurs. The effect of this diffusion and reaction process on intrinsic substrate uptake rates is summarized in terms of global reaction rates. By envisioning that these global rates occur homogeneously throughout the reactor volume, the entire reactor can be modeled.

**Kinetics.** A number of models (Poduska and Andrews, 1975, and Parker *et al.*, 1970) have been developed to describe the kinetics of microbial growth under single-substrate-limited conditions, and the Monod model is one of the most popular. The principal deficiency of Monod kinetics is its inability to saturate rapidly enough. Dabes *et al.* (1973) used a number of different sets of experimental data to show that in many instances the Blackman model and the exponential model provide a better data fit. The Blackman model makes a sharp transition from zero-order to first-order when the substrate concentration exceeds the half-saturation coefficient. It does not allow for a gradual transition from zero-order to first-order kinetics. The exponential model is somewhat of a compromise between the Monod model and the Blackman model and is given by

$$\mu = \mu_m \left[ 1 - \exp\left(-(\ln 2) \frac{S}{K_s}\right) \right] \quad (1)$$

This model allows a continuous transition from zero-order to first-order, but this transition is sharper than that allowed by the Monod model. Bader (1978) concluded that most of the published kinetic data fall somewhere between the curves for the Blackman model and the exponential model.

Models of multiple-substrate kinetics have been reviewed by Bader (1978 and 1984). Such models were categorized as either noninteractive or interactive. The noninteractive model can be represented as

$$\mu = \text{MIN} [\mu_1(S), \mu_2(S), \dots] \quad (2)$$

The function MIN [ ] takes the minimum of the arguments, and  $\mu_1, \mu_2, \dots$  are rate coefficients for single-substrate kinetic formulations. Equation 2 allows more than one limiting substrate, but only one substrate can be limiting at a time; no substrate interactions are allowed. Ryder and Sinclair (1972) proposed a model using this formulation.

The interactive model allows simultaneous substrate limitation and can be represented as

$$\mu = f[\mu_1(S), \mu_2(S), \dots] \quad (3)$$

The function  $f[ ]$  represents any arbitrary operator that is multiplication or arithmetic averaging. Stenstrom and Poduska (1980) performed an analysis for ammonium-nitrogen and oxygen uptake by nitrifying bacteria using this model with  $f[ ]$  being a multiplicative operator and  $\mu$  being the Monod function. They showed that nitrification can be alternately limited by either

ammonium-nitrogen or DO or be simultaneously limited by both, depending on nitrifier growth rate (MCRT of the system) and bulk substrate concentrations.

**Mass-transport limitation.** Though activated sludge flocs are relatively small, their size is insufficient to preclude mass-transport limitation. In the extensive literature on the modeling of heterogeneous chemical reactions, the extent of mass-transport limitation in a porous catalyst is often characterized by two dimensionless parameters, the Biot number and the Thiele modulus. The Biot number characterizes the influence of external resistance (the resistance of the bulk liquid) and is given by

$$\text{Bi} = \frac{kL}{D_e} \quad (4)$$

Where

Bi = Biot number, dimensionless;

$k$  = the liquid-phase, mass-transfer coefficient, L/T;

$L$  = a characteristic dimension, L;

$D_e$  = the effective diffusivity in the porous solid phase,  $L^2/T$ ;

$$= D_L \frac{\epsilon}{\tau};$$

$\epsilon$  = particle porosity; and

$\tau$  = particle tortuosity.

The Biot number is the ratio of the characteristic time for diffusion across the porous particle to the characteristic time for diffusion across the boundary between the fluid phase and the particle surface. Hence, transport limitation is dominated by external resistance when this ratio is small.

Petersen (1965) demonstrated, by using realistic values of mass-transport parameters, that external mass-transport limitation cannot exist without the presence of internal mass-transport limitation. The influence of internal resistance (the resistance of the particle matrix) is characterized by the Thiele modulus. The square of the Thiele modulus is given by

$$\phi^2 = \frac{L^2 \bar{R}(C_B)}{D_e c_B} \quad (5)$$

Where

$\phi$  = Thiele modulus, dimensionless;

$\bar{R}(C_B)$  = the intrinsic rate of reaction,  $M/L^3 - T$ ; and

$c_B$  = the concentration of the reactant in the bulk fluid,  $M/L^3$ .

This modulus can be interpreted as being the ratio of the characteristic time for diffusion to the characteristic time for reaction. Alternately, it can be interpreted as the ratio of the intrinsic rate of reaction to the maximum rate of diffusion. Hence, the extent to which internal mass-transport limitation is significant is dependent on the relative rates of reaction and diffusion.

Kossen (1979) used the Thiele modulus to show that oxygen depletion can occur within flocs that are larger than about 500  $\mu\text{m}$ . His results suggest that oxygen depletion can occur in smaller flocs if the oxygen uptake rate is higher; therefore, one might expect oxygen transport to be limited by diffusional resistance for floc sizes commonly encountered in the activated sludge process (Parker *et al.*, 1970). Atkinson and Rahman (1979) attempted to predict the rate of carbonaceous uptake as a function of a Thiele-type modulus. They concluded that there will be no internal limitation when the value of the modulus is less

than 0.5. Mueller *et al.* (1968) and Bailod and Boyle (1970) experimentally demonstrated that mass-transport resistance can significantly affect the rate of carbonaceous substrate uptake in the activated sludge process. In each study, the influence of substrate transport limitation was assessed by measuring the rate of substrate uptake for a pure culture of floc-forming bacteria in both flocculated and dispersed states. Mueller *et al.* (1968) measured oxygen uptake rates and Bailod and Boyle (1970) measured both glucose and oxygen uptake rates. Glucose was the only limiting substrate in these experiments. Both studies reported that the uptake rates of the dispersed cultures were significantly higher than those of the flocculated cultures at low bulk glucose concentrations, while no differences in uptake rates were observed at high bulk glucose concentrations.

LaMotta and Shieh (1979) performed similar experiments using an enriched culture of nitrifying bacteria. In batch experiments, the initial rate of ammonia uptake was measured as a function of floc size. The initial concentration of ammonium-nitrogen was 1 mg N/L and ammonium-nitrogen was selected as the only limiting substrate by maintaining a DO concentration of 15 mg/L. Because maximum initial uptake rates were obtained only for small flocs, they concluded that floc size can significantly affect the nitrification rate.

Similar approaches to modeling transport resistance have been made by Jenkins and co-workers (Lau *et al.*, 1984, and Hao *et al.*, 1983). They have implicated intrafloc DO concentration and reaction rates to preferential growth rates of bulking and nonbulking microorganisms.

**Floc model.** The model was developed to use the Thiele modulus and the Biot number to characterize diffusional resistance (Song, 1986, and Stenstrom and Song, 1987). Both parameters account for particle geometry through the characteristic length parameter,  $L$ . Characteristic length is sometimes defined as the ratio of the gross volume of the particle (solid plus void volume) to the external surface area of the particle. This definition has the advantage of avoiding the difficulty of defining the shape of the highly irregular activated sludge flocs and minimizing the effect of floc shape on the Thiele modulus.

The following dimensionless equation was derived to describe mass transport:

$$\frac{d^2 c_i}{dx^2} + \frac{a-1}{x} \frac{dc_i}{dx} + \frac{a^2 L^2}{D_{e,i} S_{B,i}} \dot{R}_i = 0 \quad (6)$$

The dimensionless forms of the center and surface boundary conditions are

$$\frac{dc_i}{dx} \Big|_{x=0} = 0 \quad (7)$$

$$\frac{dc_i}{dx} \Big|_{x=1} = a \text{Bi}_i (1 - c_{i,s}) \quad (8)$$

Where

- $D_{e,i}$  = effective diffusivity of species  $i$ ,  $L^2/T$ ;
- $\dot{R}_i$  = rate of reaction for species  $i$ ,  $M/L^3T$ ;
- $x$  = dimensionless radius,  $r/r_f$ ;
- $c_i$  = dimensionless concentration,  $s_i/S_{B,i}$ ;
- $c_{i,s}$  = dimensionless concentration at the floc surface;
- $a$  = geometry factor: 1 for slab, 2 for cylindrical, and 3 for spherical;
- $L$  = ratio of floc volume to floc surface area,  $L$ ;
- $S_{B,i}$  = concentration of species  $i$  in bulk liquid,  $M/L^3$ ;

- $S_i$  = concentration of species  $i$  in the floc,  $M/L^3$ ;
- $s_{i,s}$  = concentration of species  $i$  at floc surface,  $M/L^3$ ;
- $r_f$  = radius of floc,  $L$ ; and
- $\text{Bi}_i$  = Biot number for species  $i$ .

**Reaction rates.** The physical and biochemical reactions that occur in the nitrifying activated sludge process are numerous and complex. To produce a manageable model, it is assumed that only soluble substrates are involved and that the only major reactions are (1) the oxidation of carbonaceous substrate (glucose) by heterotrophic bacteria, (2) the oxidation of ammonium-nitrogen to nitrate by nitrifying bacteria, and (3) the endogenous decay of both heterotrophic and nitrifying bacteria. The subscripts on concentration, half-saturation coefficients, and rates are denoted as follows: 1 = oxygen; 2 = ammonia nitrogen; 3 = glucose; 4 = nitrate nitrogen; H = heterotrophic; and N = nitrigenous.

Under these conditions the rate of glucose uptake can be described as

$$\dot{R}_3 = -q_{H3}\rho U\left(\frac{c_1}{K_{1H}}\right) \cdot U\left(\frac{c_3}{K_{3H}}\right) \quad (9)$$

Where

- $q_{H3}$  = maximum specific glucose uptake rate for heterotrophs ( $1/T$ ), (mass glucose/total sludge mass -  $T$ );
- $\rho$  = density of total sludge mass within floc,  $M/L^3$ ;
- $U[x]$  = exponential rate function given by  $1 - \exp[-(\ln 2)x]$ ;
- $c_i$  = concentrations of species  $i$  inside floc,  $M/L^3$ ; and
- $K_{iH}$  = half-saturation coefficient of species  $i$  for heterotrophs,  $M/L^3$ .

The rate of ammonia oxidation is described as

$$\begin{aligned} \dot{R}_2 = & -q_{H2}\rho U\left(\frac{c_1}{K_{1H}}\right) \cdot U\left(\frac{c_2}{K_{2H}}\right) \cdot U\left(\frac{c_3}{K_{3N}}\right) \\ & - q_{N2}\rho U\left(\frac{c_1}{K_{1N}}\right) \cdot U\left(\frac{c_2}{K_{2N}}\right) + q_{D2}\rho U\left(\frac{c_1}{K_{1H}}\right) \end{aligned} \quad (10)$$

Where

- $q_{H2}$  = maximum specific ammonium-nitrogen uptake rate for heterotrophs ( $1/T$ ) (mass  $\text{NH}_4^+ - \text{N}$ /total sludge mass -  $T$ );
- $q_{N2}$  = maximum specific ammonium-nitrogen uptake rate for nitrifiers ( $1/T$ ) (mass  $\text{NH}_4^+ - \text{N}$ /total sludge mass -  $T$ );
- $q_{D2}$  = maximum specific ammonium-nitrogen production rate from endogenous decay ( $1/T$ ) (mass  $\text{NH}_4^+ - \text{N}$ /total sludge mass -  $T$ ); and
- $K_{iN}$  = half-saturation coefficient of species  $i$  for nitrifiers,  $M/L^3$ .

The rate of oxygen uptake is the sum of the rate due to heterotrophic activity, the rate due to nitrifier activity, and the rate due to endogenous respiration. The net rate is given by

$$\begin{aligned} \dot{R}_1 = & -q_{H1}\rho U\left(\frac{c_1}{K_{1H}}\right) \cdot U\left(\frac{c_3}{K_{3H}}\right) \cdot U\left(\frac{c_2}{K_{2N}}\right) \\ & - q_{N1}\rho U\left(\frac{c_1}{K_{1N}}\right) \cdot U\left(\frac{c_2}{K_{2N}}\right) - q_{D1}\rho U\left(\frac{c_1}{K_{1H}}\right) \end{aligned} \quad (11)$$

Where

- $q_{H1}$  = maximum specific oxygen uptake rate for heterotrophs (1/T) (mass  $\text{NH}_4^+ - \text{N}$ /total sludge mass - T);  
 $q_{N1}$  = maximum specific oxygen uptake rate for nitrifiers (1/T) (mass  $\text{NH}_4^+ - \text{N}$ /total sludge mass - T); and  
 $q_{D1}$  = maximum specific oxygen uptake rate for endogenous respiration (1/T) (mass  $\text{NH}_4^+ - \text{N}$ /total sludge mass - T).

The rate of nitrate production is given by

$$\dot{R}_A = q_{NA}\rho U\left(\frac{c_1}{K_{1N}}\right) \cdot U\left(\frac{c_2}{K_{2N}}\right) \quad (12)$$

Where

- $q_{NA}$  = maximum specific nitrate production rate (1/T) (mass  $\text{NO}_3^- - \text{N}$ /total sludge mass - T).

All maximum specific rates in equations 9 through 12 are based on total cell mass and the floc density is the total cell mass of a floc divided by the gross volume of the floc. Global rates are obtained by averaging these distributions over the volume of the floc.

**Reactor model.** The floc model and associated reactions must be used with a reactor model in order to calculate bulk concentration. The liquid and gaseous substrate mass balances for one to four CSTRs in series are shown in equations 13 and 14, respectively.

$$V \frac{dS_i}{dt} = (S_{IN,i} - S_i)Q + X_T \bar{R}_i V \quad \text{for } i = 2, 3, \text{ and } 4 \quad (13)$$

$$V \frac{dS_1}{dt} = K_L a (S_1^* - S_1) + X_T \bar{R}_1 V \quad (14)$$

Where

- $Q$  = influent flow rate,  $\text{L}^3/\text{T}$ ;  
 $S_{IN,i}$  = influent concentration of substrate  $i$ ,  $\text{M}/\text{L}^3$ ;  
 $S_i$  = effluent concentration of substrate  $i$ ,  $\text{M}/\text{L}^3$ ;  
 $\bar{R}_i$  = global specific reaction rate of substrate  $i$ , (mass of substrate/mass of total sludge - T);  
 $X_T$  = mixed liquor solids concentration,  $\text{M}/\text{L}^3 - \text{T}$ ;  
 $V$  = volume of aeration basin,  $\text{L}^3$ ;  
 $K_L a$  = volumetric oxygen-transfer coefficient, 1/T; and  
 $S_1^*$  = saturation DO concentration,  $\text{M}/\text{L}^3$ .

Assuming that the microorganism concentration in the influent and effluent are negligible, the mass balance for the nitrifiers and the heterotrophs, respectively, are

$$\frac{dX_N}{dt} = \frac{-1}{\theta_c} X_N + X_T (\bar{R}_N + f_N \bar{R}_D) \quad (15)$$

$$\frac{dX_H}{dt} = \frac{-1}{\theta_c} X_H + X_T (\bar{R}_H + f_H \bar{R}_D) \quad (16)$$

Where

- $\theta_c$  = MCRT [T] or  $Q_w/V$  where  $Q_w$  is waste flow rate from the aeration basin;  
 $X_N$  = concentration of nitrifiers,  $\text{M}/\text{L}^3 - \text{T}$ ;  
 $X_H$  = concentration of heterotrophs,  $\text{M}/\text{L}^3 - \text{T}$  (note that  $X_N + X_H = X_T$ );

- $\bar{R}_N$  = global specific growth rate for nitrifiers, mass of nitrifiers/mass of total sludge - T;  
 $\bar{R}_H$  = global specific growth rate for heterotrophs, mass of heterotrophs/mass of total sludge - T;  
 $f_H$  = heterotroph fraction,  $X_H/X_T$ ;  
 $f_N$  = nitrifier fraction,  $X_N/X_T$ ; and  
 $\bar{R}_D$  = global specific decay rate, 1/T.

The reactor model consists of equations 13 through 16. If the DO concentration in the reactor is controlled, the DO is known and equation 14 is unnecessary.

The global specific rates in the reactor model are obtained from the simultaneous solution of the floc model (equation 9 for  $i = 1, 2$ , and 3). The two models are linked by the boundary conditions given by equations 9 and 10 and equations 15 and 16 as follows:

$$q_{N2} = q'_{N2} \cdot f_N \quad (17)$$

$$q_{H3} = q'_{H3} \cdot f_H \quad (18)$$

Where

- $q'_{N2}$  = maximum specific ammonium-nitrogen uptake rate for nitrifiers, mass  $\text{NH}_4^+ - \text{N}$ /mass of nitrifiers - T; and  
 $q'_{H3}$  = maximum specific glucose uptake rate for heterotrophs, mass glucose/mass of heterotrophs - T.

These equations state that the maximum specific rates that are based on total sludge mass,  $q_{N2}$  and  $q_{H3}$ , can vary as the relative sizes of the nitrifying and heterotrophic populations shift. It is assumed that the maximum specific rates based on specific populations,  $q'_{N2}$  and  $q'_{H3}$ , are intrinsic properties of those populations and are therefore constant.

### Experimental Procedures

An experimental investigation was designed to demonstrate the effects of mass-transport limitation and to verify the proposed mathematical model. Three laboratory-scale activated sludge reactors were constructed as shown in Figure 1. The reactors were designed to vary mixing and aeration rates independently. This was accomplished by varying the mixer rpm while controlling the DO by adjusting gas-flow rate and oxygen content in the gas. Each cylindrical reactor had a maximum volume of 18 L, with a working liquid volume of 14.5 L. The jacketed reactors were constructed from 38 cm long sections of concentric 25 and 30 cm diameter plexiglass pipe. Water from a temperature-controlled bath was circulated through each jacket at rates up to 75 L/hr to maintain the MLSS temperature to within  $\pm 0.1^\circ\text{C}$  of the set point. Because the large wall surface area to volume ratio of the experimental reactors was not typical of full-scale activated sludge systems, a motorized scrapper/baffle assembly was constructed from 316 SS and inserted into the reactor. The baffles were 2.2 cm wide and were equipped with polytetrafluoroethylene squeegees on the sides and bottom. The baffle assembly was turned for several rotations several times per day by a timer-activated 0.5-rpm motor. Mixing was provided by two 13 cm diameter impellers (marine-type, axial flow) mounted 7.6 and 28 cm above the bottom of the reactor. Liquid depth was normally 34.3 cm. Aeration was provided by a 2.5 cm diameter, spherical fine pore ceramic diffuser, located directly below the lower impeller. Air flow rates of up to 2.3 L/min were possible, but generally air flow was kept to less than 1 L/min.

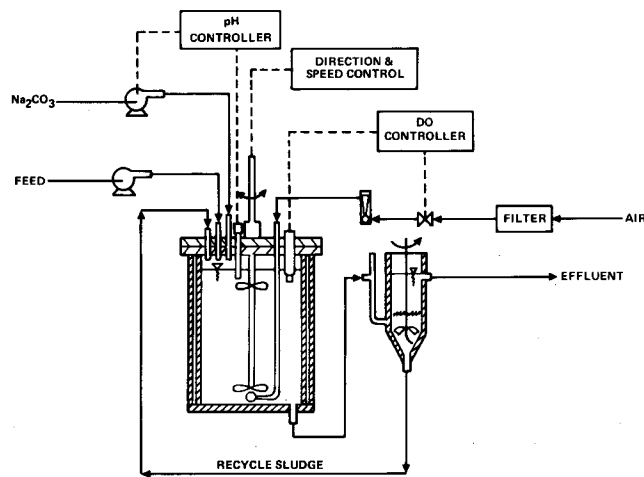


Figure 1—Laboratory reactor.

Dissolved oxygen concentration was monitored with YSI model 57 meters. To precisely control DO concentration, a differential gap controller was constructed using two comparators that were interfaced to the DO meter's recorder output. The output of the comparators were used to turn off and on a solenoid valve, which slightly increased air flow to the diffuser. To assure that the same mixing conditions were present over the wide range of biological oxygen uptake rates, the air feed was blended with high purity oxygen. This allowed the same gas-flow rate to be used at differing biological conditions and mixer rpm to obtain the desired set-point DO. Therefore gas-flow rate had no effect on mixing. The DO was successfully maintained to within  $\pm 0.1$  mg/L of the set point. The reactor pH was maintained to  $7.5 \pm 0.1$  by adding 2N  $\text{Na}_2\text{CO}_3$  using a Horizon model 599-20 pH meter/controller.

The clarifiers were constructed of 30.5-cm sections of 10 cm diameter PVC pipe. The bottom of the clarifiers were formed by a 60-deg polypropylene funnel cone. The mixed liquor flowed from the reactor to the clarifier by gravity, which allowed the reactor's liquid level to be controlled by the clarifier elevation. A rake was used to prevent bridging in the clarifier and was operated intermittently by a clock motor connected to a timer. With the exception of the rake, the clarifier was operated continuously.

In general, standard analytical techniques ("Standard Methods," 1985) were used. Ammonium and nitrate were measured using specific ion electrodes. Nitrite was determined using Method 419 ("Standard Methods," 1985). Table 1 shows the normal range of reactor operation. Additional details of the experimental program are presented elsewhere (Song, 1986, and Stenstrom and Song, 1987).

To verify the model, it was necessary to estimate the various parameters or combinations of parameters. Four subproblems were created in such a way to isolate groups of model parameters for experimental measurement. Because this investigation emphasizes certain features of the model, the grouping of parameters into subproblems and the subproblem solution method reflect the relative importance of each subset of parameters. Table 2 shows the four subproblems and their objectives. Subproblems 1, 3, and 4 were performed in reactors shown in Figure 1; subproblem 2 was performed in 1-L beakers containing aliquots of mixed liquor taken from the reactors. Each subproblem was

Table 1—Range of normal experimental conditions.

Range of normal steady-state operation conditions	
pH	7.5–7.6
Temperature	22–25°C
Impeller speed	170–200 rpm
DO concentration	5–6 mg/L
Sludge age	4–8 days
Hydraulic retention time	7 hours
MLSS	1500–2500 mg/L
MLVSS	89–97%
Sludge volume index (SVI)	70–150
Specific oxygen uptake rate (SOUR)	18–25 mg/g · hr
Effluent	
SS	5–40 mg/L
TOC	4–10 mg/L
$\text{NH}_4^+\text{-N}$	0.1–0.5 mg/L
$\text{NO}_2^-\text{-N}$	0.05–0.2 mg/L
$\text{NO}_3^-\text{-N}$	45–60 mg/L

composed of two or more sets of experiments with two or more runs (replications). Reactors were operated at steady-state conditions for at least three MCRTs before initiation of experiments. Generally, the MCRT ranged between 4 and 5 days but in some cases was as high as 8 days. Hydraulic retention time was generally 7 hours. Precise conditions are noted later.

The model was solved using a FORTRAN program. The flocc model is a split boundary problem, and was solved using second-order correct analogs. The nonlinear terms were linearized using a direct iteration procedure. After making an initial guess, the problem was solved and the results were compared to the initial guess. If the guess and result did not agree (e.g. <1% difference) a new guess was made and the problem resolved. Convergence was easily reached after a few iterations. The ordinary differential equations comprising the reactor model were integrated using Gear's method. All three procedures are described by Ferziger (1981).

In several cases, we used a nonlinear program to estimate model parameters. This was accomplished by changing the parameter values and observing the sum of squares error between the observations and the calculations. The objective function for each subproblem was different. A steepest decent gradient technique was used (Kuester and Mize, 1973).

Table 2—Subproblems and their experimental objectives.

Subproblem no.	Experimental conditions	Parameters to be estimated
1	Four sets of short-term experiments at various DOs with minimum mass-transport resistance and heterotrophic oxygen uptake	$K_{1N}$ , verify the exponential growth rate function
2	Two sets of batch experiments with minimum mass-transport resistance	$q_{N2}$ , $Y_{N2}$ , $q_{D1}$ , $q_{D2}$ , $q_{H3}$ , and $Y_{H3}$
3	Long-term, steady-state experiments with minimum mass-transport resistance	$K_{1H}$ , $K_{2N}$ , and $K_{3H}$
4	Three simultaneous runs, different DOs, and different mass-transport resistances	$L^2\rho$ , $\epsilon$ , and $\tau$ ; demonstration of mass-transport resistances

## Experimental Results

**Subproblem 1—determination of nitrifier growth rates with minimum transport resistance.** The objective of this series of experiments was to determine the oxidation rate of ammonia as a function of DO concentration without competition from heterotrophs for DO. Before beginning each experiment, the feed to each reactor was shut off and the mixed liquor was allowed to aerate for 30 minutes at DO = 4 mg/L. After 30 minutes, the oxygen uptake rate decreased to a relatively constant 5–8 mg O<sub>2</sub>/L·hr, which is the endogenous uptake rate. At the beginning of each experiment the NH<sub>4</sub><sup>+</sup> concentration was increased to 80 mg/L using NH<sub>4</sub>Cl. The DO was next adjusted to the desired set point and controlled within ±0.1 mg/L. The pH was controlled at 7.5 ± 0.1 by adding Na<sub>2</sub>CO<sub>3</sub>. Ammonia and nitrate were measured at hourly intervals.

Three initial experiments, set I, were performed to determine the minimum impeller rpm at which no mass-transport limitation occurred. Figure 2 shows the specific ammonia nitrogen oxidation rate at DO = 0.7 mg/L for the mixer rpms. Error bars represent the analytical precision of the measuring technique for ammonia, nitrate, and suspended solids. Reaction rate was not affected above 170 rpm, suggesting that mass transfer was no longer rate limiting; therefore, 170 rpm was selected for subsequent experiments in this series. Figure 2 also shows the shear rate, as indicated by the *G* factor associated with each rpm. Power input was measured directly by a torque meter. The no-load torque, corresponding to bearing resistance, was subtracted from the total torque. The *G* factor versus rpm relationship is the same for subproblems 3 and 4.

Three more sets of experiments were performed to estimate  $K_{1N}$  and  $q_{N2}$ . Parameters were estimated using both the exponential and Monod models. A two parameter, nonlinear least squares was performed to simultaneously estimate both parameters. A single parameter procedure was also used to estimate  $K_{1N}$  by using the normalized form of the growth rate equations (by dividing equation 1 by  $\mu_m$ ).

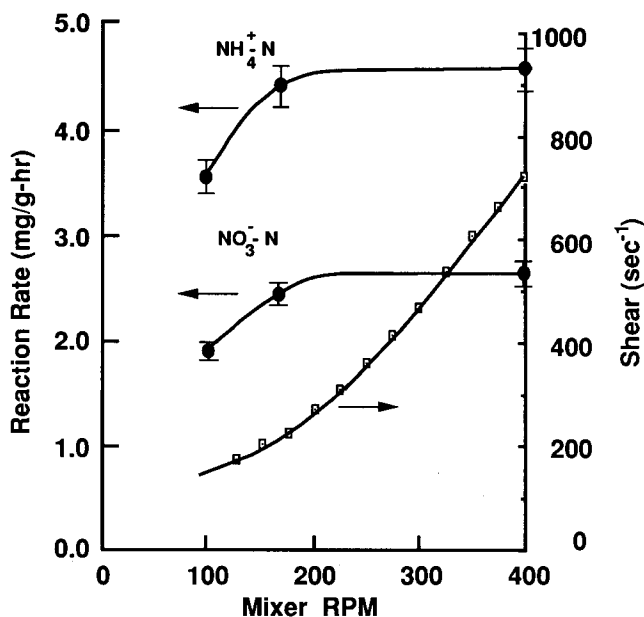


Figure 2—Specific ammonia oxidation and nitrate production rate as a function of mixing intensity.

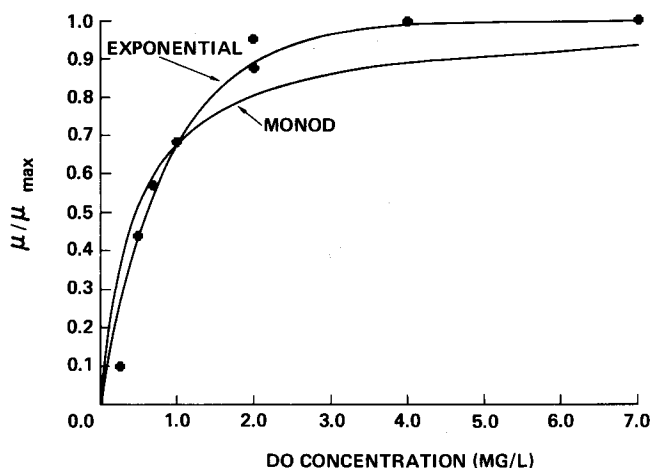


Figure 3—Normalized ammonia oxidation rates and theoretical rates for the Monod and exponential models.

The exponential model ( $R^2 = 0.98$ ) fits the data shown in Figure 3 better than the Monod model ( $R^2 = 0.91$ ) and was adopted for this reason. The values of  $K_{1N}$ , estimated from the two-parameter procedure, ranged from 0.727 to 0.560 mg DO/L. The single parameter procedure estimate was 0.62 mg/L. The range of estimates for  $q_{N2}$  was 7.10 to 5.38 mg NH<sub>4</sub><sup>+</sup>-N/g·hr.

**Subproblem 2—stoichiometry.** The objective of this subproblem was to determine and verify the stoichiometric parameters presented in the modeling sections. All of the experiments for this subproblem were conducted in a miniature analogue of laboratory-scale reactors, a specially equipped 1-L pyrex beaker with provisions for pH, DO, and temperature control. The mixed liquor used in these experiments was taken from the sludge that was wasted from laboratory-scale reactors. During these experiments the reactors were operated at a sludge age of 8 days. All other operating conditions were the same as those described previously. Waste sludge from all three reactors was combined, mixed, and allowed to settle for 30 minutes to concentrate at a factor of two (to obtain MLSS concentrations of 4000 mg/L). This concentrated mixed liquor was then transferred to the 1-L beaker reactor and aerated for 30 minutes before starting an experiment. The DO concentration throughout all experiments was maintained between 6 mg/L and 8 mg/L. The mixing rate was large enough to ensure that mass-transfer resistance did not affect results.

The procedure for both sets of experiments and replicates was similar, except that glucose was added in set II. A concentrated solution of NH<sub>4</sub>Cl was added to the beaker and NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>-N, and NO<sub>2</sub><sup>-</sup> were monitored over the following 3 to 6 hours.

Figure 4 shows the results for run 2 of set I. Nitrite accumulation was observed in all cases. It appears that when nitrite production in the beaker exceeded the acclimatized, steady-state production rate in the reactor, nitrite accumulation occurred. Since the model does not account for nitrite accumulation, it was necessary to assume that ammonia oxidation rate is unaffected by nitrite concentration. This assumption appears justified for the concentrations encountered in this study.

The parameters  $q_{N2}$ ,  $Y_{N2}$ , and  $q_{D2}$  were estimated from set I. To obtain accurate estimates, it was necessary for the total inorganic nitrogen species to balance. For the first hours of the

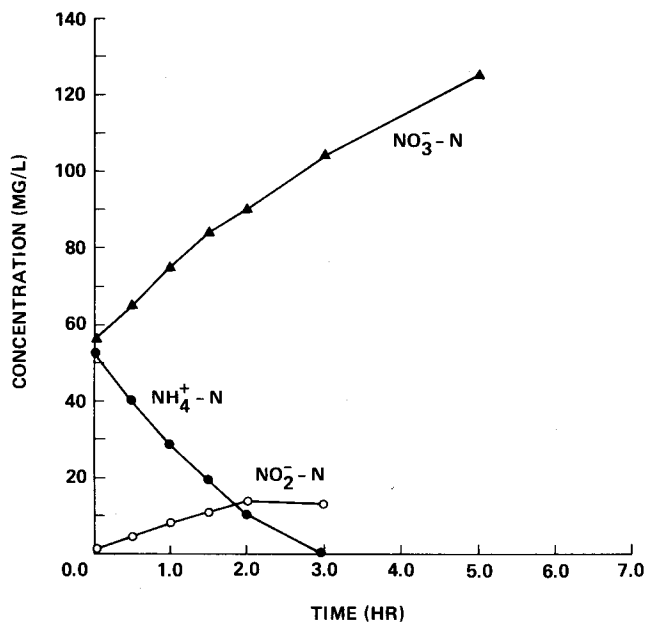


Figure 4—Ammonia, nitrite, and nitrate versus time for subproblem 2 (run 2, set I).

results, which comprise the linear portion of the data, the balance was  $\pm 2\%$  and  $\pm 8\%$  for runs 1 and 2, respectively. Estimates of  $q_{N2}$  and  $Y_{N2}$  were made from the rate of ammonia disappearance and oxidized nitrogen production and were 4.92 and 4.76 mg/g · hr and 0.11 and 0.07 g/g for runs I and II, respectively.

Set II was performed 1 day after set I and the procedure was identical except for glucose addition. TOC was measured during this run and served as an indirect indicator of glucose concentration (1 mg/L glucose  $\sim$  2.5 mg TOC/L). The TOC analysis also measures other carbonaceous compounds, but this error is small within the region of the data where the glucose concentration is high ( $\sim 450$  mg/L). Figure 5 shows the results of the first run.

It is known that during conditions such as those that existed in this set of experiments, storage products may be formed; however, it was not necessary to modify the model shown earlier to account for storage product formation. For the purposes of this investigation, it is only necessary to model the impact of this phenomenon on nitrification. This impact is manifest only through the potential competition for oxygen and nitrogen.

Estimates for  $q_{H3}$  and  $Y_{H3}$  were made using oxygen and nitrogen uptake data only. Using average values of  $Y_{N2}$  and  $q_{D2}$  estimated from set I, estimates for  $q_{H3}$  and  $Y_{H3}$  were 53 mg/g · hr and 0.37 g/g, respectively. The oxygen uptake rate accounted for only 58 and 53% of the TOC ( $\sim$  glucose/2.5) disappearance, suggesting that storage product formation is an important phenomenon. The rate of oxygen uptake due to ammonia oxidation was approximately 4.5 times the rate of ammonia uptake; therefore,  $q_{N1} = 4.5q_{N2}$ .

**Subproblem 3—kinetic parameter determination.** Results from set I experiments in subproblem 1 (ammonia oxidation rate as a function of impeller speed) provided partial evidence for the existence of mass-transport-limiting effects. Though differences in the maximum specific  $\text{NH}_4^+ - \text{N}$  uptake rates at different mixing speeds appear to be significant, better assessment of the effects

of mass-transport limitation on nitrification can be achieved in longer term experiments; any differences in rates can be magnified in terms of effluent concentrations over a longer period of time.

Four sets of experimental runs consisting of three runs per set (one run per reactor) were conducted to investigate the effects of different impeller speeds at different DO concentrations. For all four sets, the impeller speeds for reactors 1 and 2 were adjusted to approximately 60 and 200 rpm, respectively. Impeller speeds were chosen to represent reasonable extremes of mixing intensities that may be encountered in full-scale activated sludge plants. It is reasonable to expect that even at the lowest mixing intensities, the mixed liquor should still be completely suspended, and that at the highest mixing, the turbidity in the effluent should not be excessive. The low impeller speed (60 rpm) was the lowest speed that could be used and still maintain the mixed liquor in complete suspension. The high impeller speed was not high enough to significantly affect the turbidity of the effluent. Reactor 3 served as a control. Reactor 1 used air enriched with oxygen to obtain the proper DO concentrations at the same mixer rpm.

At the start of each experiment, the DO concentrations for reactors 1 and 2 were set to 4.0, 1.5, 1.0, and 0.75 for sets 1 through 4, respectively. After 20 hours (about three hydraulic retention times) after the start of an experiment, the effluent from each reactor was analyzed for TOC,  $\text{NH}_4^+ - \text{N}$ , and  $\text{NO}_3^- - \text{N}$ . The MLSS concentration at the beginning and end of the 20-hour period for each reactor was also measured. No mixed liquor was wasted during an experiment. At the conclusion of each set, the DO concentration for reactors 1 and 2 were turned to the normal operating conditions; the impeller speeds remained

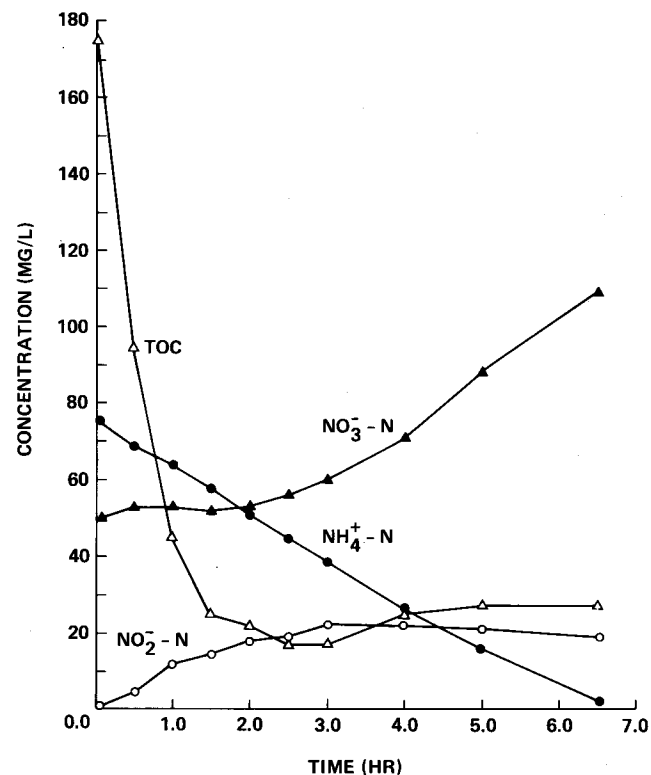


Figure 5—Ammonia, nitrite, nitrate, and TOC concentrations versus time for subproblem 2 (run 1, set II).

**Table 3—Effluent concentrations measured in subproblem 3.<sup>a</sup>**

Series no.	Reactor 1, 60 rpm			Reactor 2, 200 rpm			Reactor 3, DO = 4.0 mg/L			
	DO	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	TOC	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	TOC	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	TOC
I	4.0	0.22	45	7	0.28	42	7	0.15	47	7
II	1.5	0.16	47	7	0.14	46	7	0.12	48	7
III	1.0	0.20	45	7	0.18	47	7	0.10	48	7
IV	0.75	10	20	7	0.32	42	6	0.13	48	6

<sup>a</sup> All concentrations in mg/L.

at 60 and 200 rpm, respectively. Each set of experiments was conducted 2 days apart.

The results are shown in Table 3. Nitrification rate was significantly affected in only the experiment in which the impeller speed was 60 rpm and the DO concentration was 0.75 mg/L. The effluent concentrations of NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N in the other experiments fell within the typical range of concentrations measured under normal operating conditions. The activity of the heterotrophic population was not significantly affected in any of the experiments.

The results from set IV clearly demonstrate that nitrification can be affected by the reactor mixing intensity. For the same concentration of DO (0.75 mg/L), a difference in the mixing intensity resulted in a vast difference in the rates of nitrification. The results also demonstrate that the heterotrophic population is more competitive than the nitrifying population under oxygen-limiting and/or mass-transport-limiting conditions. In reactor 1 of series IV, where nitrification was already significantly limited, the heterotrophic uptake of glucose was not at all affected. It should be noted that within 1 day (and probably much earlier) after being returned to a DO concentration of at least 4 mg/L, the concentrations of NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N in the effluent from this reactor were again within the range of normal effluent concentrations. It can be reasoned that the observed effect was not the result of any significant shifts in the composition of the microbial population and that the effect did not cause any such shifts over a 20-hour period.

The steady-state data obtained in this subproblem were used to estimate  $K_{2N}$ ,  $K_{3H}$ , and  $K_{1H}$ . Parameter values were selected to produce model estimates matching steady-state observations. The value of  $K_{2N}$  was selected by requiring the model's prediction to match the observed effluent NH<sub>4</sub><sup>+</sup>-N concentration under high DO concentration. A value of 0.13 mg/L was selected for  $K_{2N}$ . A similar process could be used to select  $K_{3H}$ , except that steady-state effluent glucose concentrations were never measured.

**Table 4—Subproblem 4 reactor conditions.**

Reactor no.	Impeller speed, rpm	DO concentration (mg/L) at time (h)			
		-48-0	0-9	9-24.5	24.5-27
1	60	4.0	0.20	0.75	4.0
2	200	4.0	0.20	0.75	4.0
3	150	4.0	4.0	4.0	4.0

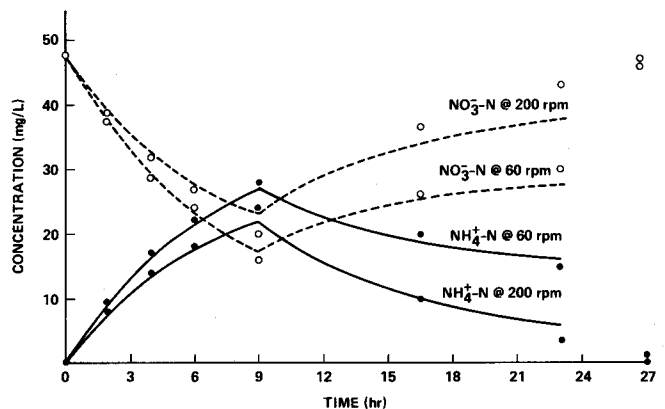
However, it is known that effluent glucose concentration would be low, perhaps just a few mg/L. It was decided to select a value of  $K_{3H}$  of about the same magnitude as the expected effluent concentration. A value of 3.0 mg/L was selected.

The value of  $K_{1H}$  was selected so that the effluent TOC concentration would be independent of DO concentration over the range of measured DOs, or 0.2 to 4.0 mg/L. Also,  $K_{1H}$  should be consistent with values reported previously in the literature. A value of 0.01 mg/L satisfied both constraints.

**Subproblem 4—demonstration of oxygen-transport resistance.** In preparation for the experiments, the mixed liquors from all three reactors were collected, mixed together, and operated at the impeller speeds and DO concentrations shown in Table 4. Runs were performed at 60 and 200 rpm.

Figure 6 shows the results of subproblem 4. The decrease in nitrification efficiency at time zero, evidenced by increasing NH<sub>4</sub><sup>+</sup>-N concentration and decreasing NO<sub>3</sub><sup>-</sup>-N concentration, indicates mass-transfer resistance. Resistance decreased markedly when DO was increased at 9 hours. These results were used to estimate parameters shown later and are significant evidence of mass-transport-limiting conditions. The smooth and broken lines shown in Figure 6 are the model simulation results for these conditions.

To estimate the values of  $L^2\rho$ ,  $\frac{\epsilon}{\tau}$ , and  $R_e$ , the model results were fitted to the observations using a nonlinear optimization technique. Estimates of  $D_{e,i}$  were obtained from "Perry's Chem-



**Figure 6—Ammonia and nitrate concentrations with model predictions versus time for subproblem 4.**



Table 5—Model parameters.

Half-saturation coefficients	Specific rates	Yields	Mass-transport parameters	Reactor parameters
$K_{1N} = 0.56 \text{ mg O}_2/\text{L}$	$q_{H3} = 70 \text{ mg glucose/gMLVSS-L}$	$Y_{H3} = 0.44 \text{ g/g}$	$\frac{\epsilon}{\tau} = 0.5$	$\theta_H = 7h$
$K_{1H} = 0.01 \text{ mg O}_2/\text{L}$	$q_{N2} = 6.8 \text{ mg NH}_4^+/\text{gMLVSS-L}$	$Y_{N2} = 0.09 \text{ g/g}$	$K_r A = 15.3 \text{ hr}^{-1}$	
$K_{2N} = 0.13 \text{ mg NH}_4^+/\text{L}$	$q_{D1} = 3.2 \text{ mg O}_2/\text{gMLVSS-L}$		$Re = 100$	
$K_{3H} = 3 \text{ mg glucose/L}$	$q_{D2} = 0.7 \text{ mg O}_2/\text{gMLVSS-L}$		$L^2\rho = 0.75 \times 10^{-5} \text{ cm}^2\text{-g/L}$	
			$D_{O,02} = 7.9 \times 10^{-2} \text{ cm}^2/\text{hr}$	
			$D_{NH3} = 7.2 \times 10^{-2} \text{ cm}^2/\text{hr}$	
			$D_{GLUCOSE} = 2.5 \times 10^{-2} \text{ cm}^2/\text{hr}$	

ical Engineering Handbook" (Perry *et al.*, 1969). The values of other parameters, estimated previously in subproblems 1, 2, and 3 were used. Next, plausible values of  $\frac{\epsilon}{\tau}$  (0.5) and  $R_e$  (100) were selected. The value of  $L^2\rho$  was estimated using a least-squares criterion with the ammonia observations. A second estimate was performed using the maximum likelihood criteria with both the ammonia and nitrate data. Next, the estimate of  $K_{1N}$  was refined using the nonlinear technique and the ammonia data. The best-fit value of  $K_{1N}$  was reduced to 0.46 mg/L. The parameter group  $L^2\rho \left/ \frac{\epsilon}{\tau} \right.$  remained constant at  $2 \times 10^{-3}$ . This

result was not unexpected because it is the "unknown" portion of the Thiele modulus. For the second run at different mixing conditions, the parameter group was estimated as  $1.5 \times 10^{-4}$ . The data and model results shown in Figure 6 show the validity of the model.

### Simulation

Previous experiments have shown that mass transport can limit the rate of nitrification in the 5- to 8-day MCRT range. This finding explains differences in previous observations of a limiting DO concentration to achieve nitrification. There is no single, limiting DO concentration to achieve nitrification. The DO concentration required to achieve nitrification is strongly influenced by reactor conditions such as temperature, MCRT, inhibitors, shear rate, and shock organic loads.

Parameters estimated for the model are shown in Table 5. These parameters, in conjunction with two sets of floc parameters ( $L^2\rho$ ), are used to demonstrate how mass-transport limitations may affect nitrification efficiency. These simulations use the integrated floc and reactor models.

Mean cell retention time strongly affects process performance. Three days MCRT is the least MCRT at which nitrification normally occurs. It has been shown that the rate of nitrification can be limited by mixing and DO concentration. It is therefore plausible to expect that the limiting MCRT for nitrification is also a function of DO and mixing rates (for example, floc size).

Figure 7 shows this relation for three MCRTs of 12, 6, and 3 days as a function of bulk DO concentration for two mixing regimes. The two values of the parameter  $L^2\rho$ ,  $0.75 \times 10^{-5}$  and  $1 \times 10^{-3} \text{ cm}^2 \cdot \text{g/L}$ , are representative of the conditions investigated in subproblem 3 and correspond to floc diameters of 60 to 100  $\mu\text{m}$  and 200 to 400  $\mu\text{m}$ , respectively. The increased MCRT

provides greater nitrification efficiency at lower DO concentrations or greater floc sizes. Simulations predict that the nitrification-limiting DO concentration for a low MCRT (3 days), high mass-transfer activated sludge process to be approximately 1.5 mg/L. The limiting DO decreases to 0.5 mg/L if the MCRT is increased to 12 days. For low mass-transfer rates (for example, large floc diameters), the limiting DO is to 2.5 and 0.7 mg/L for 3 and 12 day MCRTs, respectively.

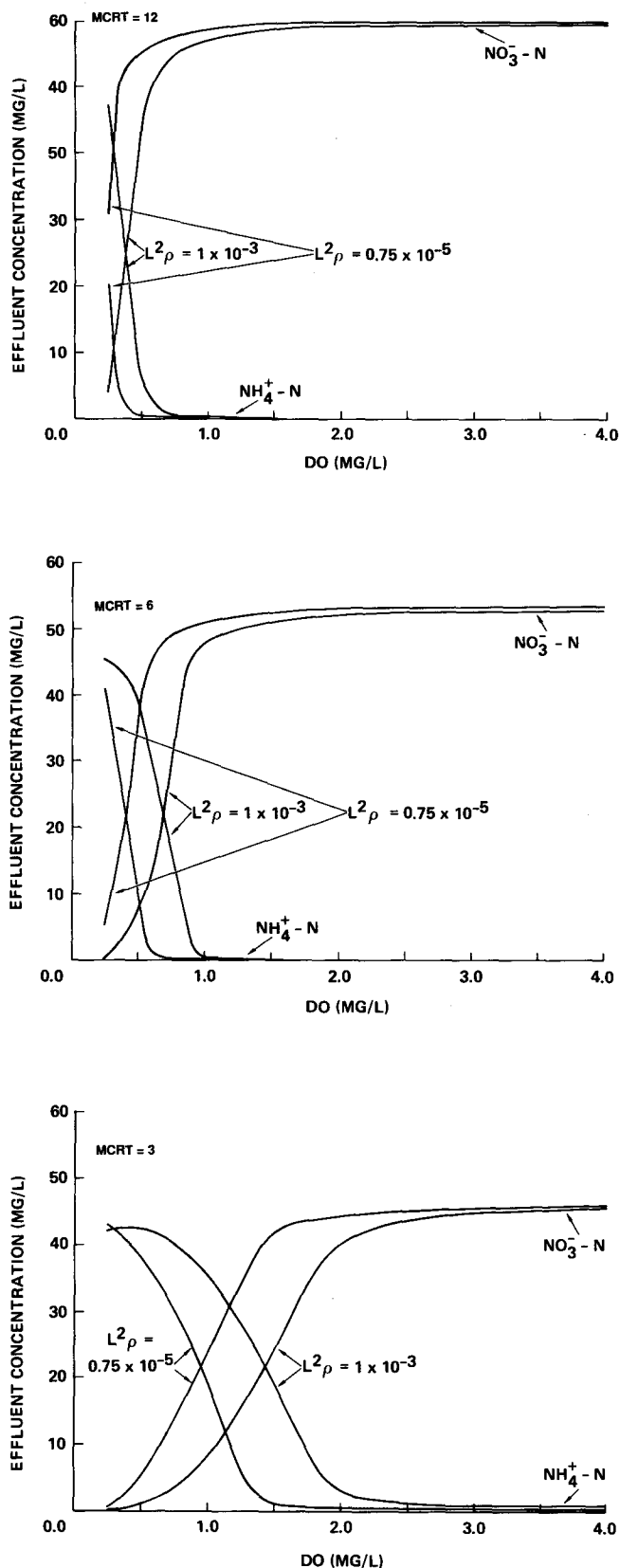
Nitrification can be temporarily inhibited, or impacted, by organic shock loads. The model can be used to simulate this condition. The increased organic load increases the heterotrophic DO uptake rate, competing with nitrogenous DO uptake.

Figure 8 shows the results of this simulation for two mass-transfer rates, with an instantaneous increase in carbonaceous substrate (glucose) applied at time zero. The points show where both the floc and reactor model solutions were obtained and are not data points. The simulation shown in the upper part of Figure 8, with high mass-transfer rates (small floc diameter), suggests that the process will tolerate the organic shock with an insignificantly small increase in effluent ammonia concentration. The simulation shown in the lower half of Figure 8, with lesser mass-transfer rates (greater floc diameter), suggests more impact of the organic shock. The effluent ammonia concentration increases to 3 mg/L and would have increased more had the bulk DO decreased below 1.0 mg/L.

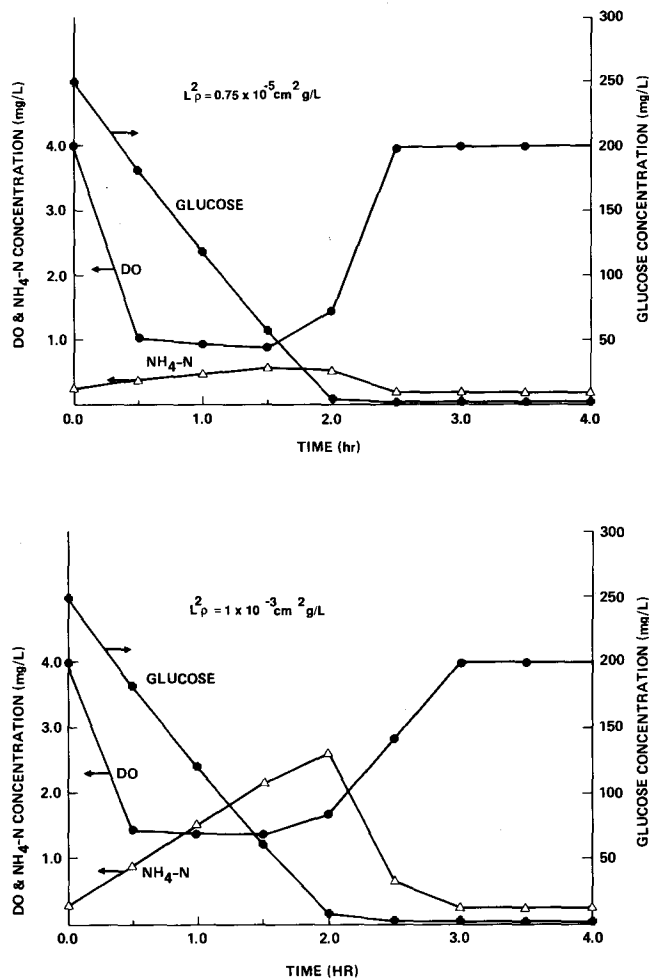
The difference in nitrification efficiency can be explained by the internal floc DO concentration. Figure 9 shows the internal concentration as a function of the floc radius for steady-state and shock-loading conditions (1 hour into the shock). The steady-state condition is in the upper part of Figure 9, and the shock load condition is shown in the lower part. The steady-state DO is high even in the center of the floc and is roughly 75% of the bulk fluid DO. For the organic shock condition, the DO is virtually 0 at the floc center. This decrease results because of reduced bulk DO concentration, mass-transport limitation, and heterotrophic competition.

### Conclusions

From previously described investigations and computer simulations, the following conclusions are presented. They are based on the assumption that experiments conducted herein using 100% soluble substrates are representative of actual treatment plants. Further experiments may be required to show that the results are valid for situations with a high percentage of particulate substrates.



**Figure 7—Steady-state effluent ammonia and nitrate concentrations versus bulk DO concentration for MCRTs of 12, 6, and 3 days (top to bottom).**



**Figure 8—Glucose, DO, and ammonia concentrations for low (top) and high (bottom) mass-transfer rates versus time during an organic shock load (points show where reactor and floc models were solved and are not data points).**

Mass-transport limitation can significantly affect the apparent relationship between DO concentration and nitrification under both steady-state and transient conditions.

Under the steady-state conditions investigated here, the apparent limiting DO concentration for nitrification in the activated sludge process ranges from 0.5 mg/L to 2.5 mg/L, depending on the MCRT and the degree of mass-transport resistance. This compares to less than 0.1 mg/L for pure cultures.

The wash-out MCRT can be expected to be dependent on both DO concentration and the degree of mass-transport resistance; a high MCRT may be required to ensure nitrification at lower DO concentrations and for higher mass-transport resistance.

The apparent relationship between DO concentration and nitrification under transient conditions may differ drastically from that under steady-state conditions. Because of mass-transport resistance and heterotrophic/nitrifier competition for DO, the apparent limiting DO concentration for nitrification can be as high as 4.0 mg/L during an organic shock load.

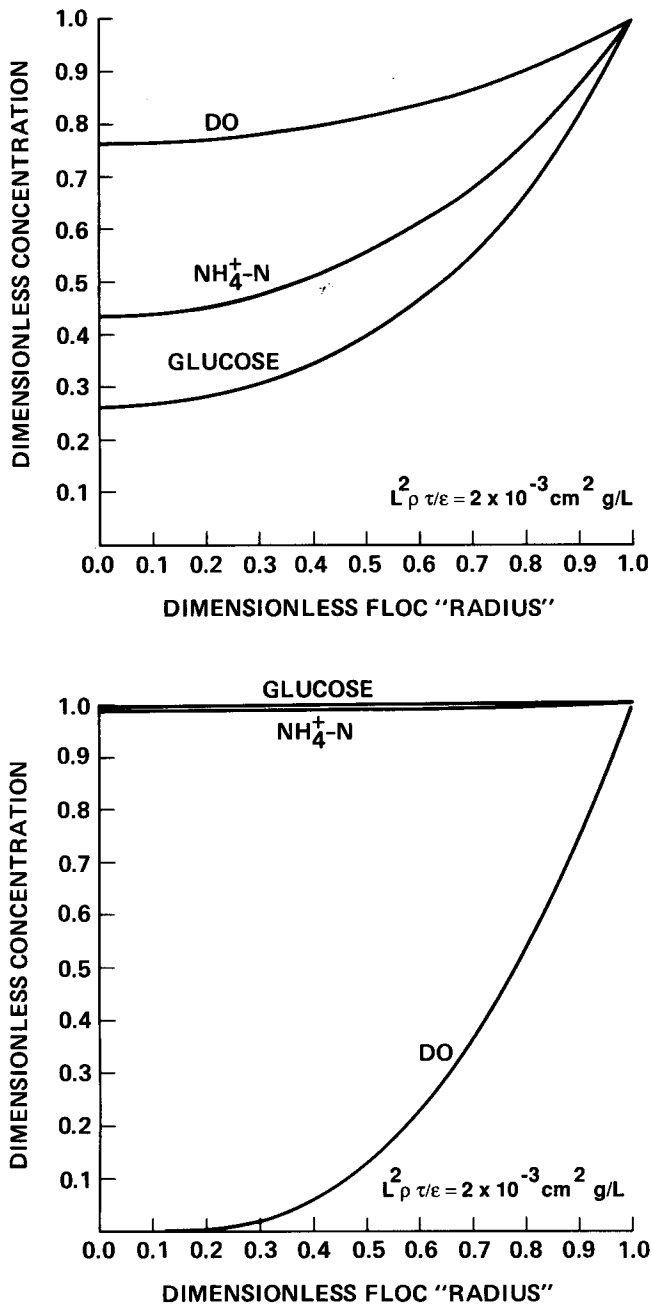


Figure 9—Intrafloc DO, ammonia, and glucose concentrations for steady-state (top) and organic shock (bottom) conditions.

Nitrification can occur under multiple-substrate-limiting conditions within activated flocs while single-substrate-limiting conditions prevail in the bulk liquid.

The exponential kinetic formulation more accurately describes the intrinsic relationship between DO concentration and the rate of oxidation of  $\text{NH}_4^+\text{-N}$  by *Nitrosomonas* than does the Monod model. The value of the half-saturation coefficient for the exponential model is between 0.45 mg/L and 0.56 mg/L.

The rate of  $\text{NH}_4^+\text{-N}$  oxidation by *Nitrosomonas* is typically the rate-limiting step under steady-state conditions, but the rate

of  $\text{NO}_2^-\text{-N}$  oxidation can become limiting under transient conditions. The accumulation of  $\text{NO}_2^-\text{-N}$  under transient conditions appears to be correlated with transient increases in the rate of  $\text{NO}_2^-\text{-N}$  production rather than with low DO concentrations.

#### Acknowledgments

**Credits.** This project was supported in part by the National Science Foundation Grant No. CME-7911792.

**Authors.** Michael K. Stenstrom is a professor of civil engineering at the University of California, Los Angeles. At the time this work was done, Stephen Song was a postgraduate research engineer at UCLA; he is now an environmental engineer at the General Motors Technical Center in Warren, Michigan. Correspondence should be addressed to Michael K. Stenstrom, Civil Engineering Department I, University of California, Los Angeles, CA 90024-1600.

Submitted for publication November 11, 1989; revised manuscript submitted September 25, 1990; accepted for publication December 14, 1990. The deadline for discussions of this paper is September 15, 1991. Discussions should be submitted to the Executive Editor. The authors will be invited to prepare a single Closure for all discussions received before that date.

#### References

- Atkinson, B., and Rahman, F.-UR (1979) Effect of Diffusion Limitation and Floc Size Distribution on Fermenter Performance and the Interpretation of Experimental Data. *Biotechnol. Bioeng.*, **21**, 221.
- Bader, F. G. (1978) Analysis of Double-substrate Limited Growth. *Biotechnol. Bioeng.*, **20**, 183.
- Bader, F. G. (1984) *Microbial Population Dynamics*. M. J. Bazin (Ed.), CRC Press, Boca Raton, Fla., 1.
- Baillo, C. R., and Boyle, W. C. (1970) Mass Transfer Limitations in Substrate Removal. *J. Sanit. Eng.*, **96**, 525.
- Dabes, J. N., et al. (1973) Equations of Substrate-limited Growth: The Case for Blackman Kinetics. *Biotechnol. Bioeng.*, **XV**, 1159.
- Ferziger, J. H. (1981) *Numerical Methods for Engineering Application*. Wiley-Interscience, New York, N.Y.
- Focht, D. D., and Chang, A. C. (1975) Nitrification and Denitrification Processes Related to Wastewater Treatment. *Adv. Appl. Microbiol.*, **19**, 153.
- Froment, G. F. (1972) Analysis and Design of Fixed Bed Catalytic Fixed Bed Reactors. In *Chemical Reaction Engineering*. Adv. Chem Series 109, Am. Chem. Soc., Washington, D.C.
- Hao, O. J., et al. (1983) The Half-saturation Coefficient for Dissolved Oxygen: a Dynamic Method for its Determination and Its Effect on Dual Species Competition. *Biotechnol. Bioeng.*, **25**, 403.
- Kossen, N. W. F. (1979) Oxygen Transport into Bacterial Flocs and Biochemical Oxygen Consumption. *Prog. Water Tech.*, **11**, 9.
- Kuester, J. L., and Mize, J. H. (1973) *Optimization Techniques with FORTRAN*. McGraw-Hill, New York, N.Y.
- LaMotta, E. J., and Shieh, W. K. (1979) Diffusion and Reaction in Biological Nitrification. *J. Environ. Eng.*, **105**, 655.
- Lau, A. O., et al. (1984) The competitive growth of floc-forming and filamentous bacteria: a model for activated sludge bulking. *J. Water Pollut. Control Fed.*, **56**, 52.
- Lawrence, A. W., and McCarty, P. L. (1970) Unified Basis for Biological Treatment Design and Operation. *J. San. Eng.*, **96**, 757.
- Mueller, J. A., et al. (1968) Oxygen Diffusion Through Zoogeal Flocs. *Biotechnol. Bioeng.*, **10**, 331.
- Painter, H. A. (1977) Microbial Transformations of Inorganic Nitrogen. *Prog. Water. Tech.*, **8**, 3.

- Parker, D. S., *et al.* (1970) Characteristics of Biological Flocs in Turbulent Regimes. SERL Rep. No. 70-5.
- Perry, R. H., *et al.* (1969) Perry's Chemical Engineering Handbook. 4th Ed., McGraw-Hill, New York, N.Y.
- Petersen, E. E. (1965) Chemical Reaction Analysis. Prentice-Hall, Englewood Cliffs, N. J.
- Poduska, R. A., and Andrews, J. F. (1975) Dynamics of nitrification in the activated sludge process. *J. Water Pollut. Control Fed.*, **47**, 2599.
- Ryder, D. N., and Sinclair, C. G. (1972) Model for the Growth of Aerobic Microorganisms Under Oxygen Limiting Conditions. *Biotechnol. Bioeng.*, **14**, 787.
- Sharma, B., and Alhert, R. C. (1977) Nitrification and Nitrogen Removal. *Water Res.*, **11**, 897.
- Song, S. (1986) The Effect of Mass Transport Limitation on Nitrification in the Activated Sludge Process. Ph.D. thesis, Civil Eng. Dept., Univ. Calif., Los Angeles.
- Standard Methods for the Examination of Water and Wastewater. (1985) 16th Ed., Am. Public Health Assoc., Washington, D.C.
- Stenstrom, M. K., and Poduska, R. A. (1980) The Effect of Dissolved Oxygen Concentration on Nitrification. *Water Res.*, **14**, 643.
- Stenstrom, M. K., and Song, S. (1987) The Effect of Mass Transport Limitation on Nitrification in the Activated Sludge Process. UCLA-Engr. Rep. No. 87-28, Univ. Calif., Los Angeles.