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# Evidence for oxygen-limiting conditions during tertiary fixed-film nitrification

Robert W. Okey, Orris E. Albertson

**ABSTRACT:** A study of highly loaded (greater than  $1.2 \text{ g/m}^2 \cdot \text{d}$ ) tertiary nitrification systems was conducted to determine the reason for the substantial variations seen in the rate and extent of  $\text{NH}_4\text{-N}$  oxidation at the higher loading rates. It was determined that variation and scatter were not random, but seemed to be related to the level of dissolved oxygen in the tower. The "scattered data" evolved into a family of curves, each member representing a different effluent  $\text{NH}_4\text{-N}$  value in the load versus removal relationship. *J. Water Pollut. Control Fed.*, **61**, 510 (1989).

**KEYWORDS:** dissolved oxygen, fixed film processes, nitrification, temperature effects, tertiary treatment.

Since the increase in fuel costs in the 1970s, there has been a resurgence of interest in the use of fixed-film treatment systems, either alone or in combination with short detention activated sludge facilities. Substantial economy has been realized through the aerobic treatment of many strong wastewaters with fixed-film systems. Furthermore, sludge volume index (SVI) control has been facilitated in multi-stage biological systems treating wastes that are easy to assimilate.

Recently, there has been more interest in the use of fixed-film systems for nitrification, both in combination with biochemical oxygen demand (BOD) removal and in tertiary treatment systems. Despite this increased interest and use, there are still many uncertainties about correct design procedures. The impacts of temperature change on the rate of nitrogen oxidation and the effect of hydraulic loading are poorly understood. Also, there actually remains considerable question as to the kinetic order of the nitrogen removal step in the range between 1.0 and 10.0 mg/L  $\text{NH}_4\text{-N}$ . Finally, there is considerable uncertainty about oxygen supply availability and the impact of limited oxygen concentration on nitrification rate.

These fundamental questions have been dealt with in a series of studies. The present work deals with the problem of the oxygen supply, or lack thereof, in natural draft towers. Necessarily, this phase of the work includes a study of the relevant kinetic issues and an evaluation of temperature effects.

## Review of Relevant Literature

**Kinetics.** The contemporary design of fixed-film nitrification systems is based on the concept that the entire oxidation process is zero order for  $\text{NH}_4\text{-N}$  removal; that is, there is a specific nitrification rate, in  $\text{g/m}^2 \cdot \text{d}$ . Yet, an

analysis of the literature<sup>1-9</sup> indicates that these systems will have at least two kinetic regimes.

Several fundamental relationships describing nitrification in biological films have been developed.<sup>4-6</sup> Substantial proof for the correctness of the relationships has been provided through the execution of pilot studies, combined with the correlation of substantial quantities of data described elsewhere.<sup>10-13</sup> Observations indicate that the kinetic order can be zero, half order, and, at low concentrations, first order for  $\text{NH}_4\text{-N}$ .<sup>4-6</sup> The zero-order  $\text{NH}_4\text{-N}$  region is half order for oxygen.<sup>4-6</sup> Therefore, in the region that is zero order for  $\text{NH}_4\text{-N}$ , a different removal rate should exist for each oxygen concentration. That is, the film is not fully penetrated by oxygen. As an example, the nitrification rate was found to be as high as  $5 \text{ g/m}^2 \cdot \text{d}$  in rotating disc systems operated at high concentrations (about 29 mg/L) of dissolved oxygen.

The information obtained through a solution of a nomograph<sup>1</sup> and plate diffusion graphs yields a similar relationship. Also, the data provided in a model verification<sup>1</sup> show a relationship between oxygen and nitrite flux which is very close to half order (0.5) for oxygen.

A series of equations using mass balances to describe the rate of nitrogen oxidation has been developed.<sup>7,8</sup> At high concentrations of  $\text{NH}_4\text{-N}$ , the rate is zero order.<sup>7,8</sup> The oxidation rate changes to one of residual concentration dependence at low concentrations. The change in reaction order with changes in oxygen or  $\text{NH}_4\text{-N}$  concentration was not considered. The oxygen flux is reported to be a half-order function of the concentration of that species in the bulk phase. The design equation developed<sup>7</sup> contains a zero-order term and an "empirical" term to describe the removal in the lower reaches of the tower. The decrease in rate noted in the lower reaches of the tower is caused by incomplete film coverage of the media.<sup>7</sup>

The bulk of the fixed-film work<sup>1,3,4,8</sup> tends to indicate that resistance to diffusion outside of the biofilm does not have a significant impact on rate. However, others<sup>4</sup> found that at the low end of the concentration spectrum, that is, below 3.0 to 4.0 mg/L of  $\text{NH}_4\text{-N}$  in the bulk medium, the rate became first order and liquid film diffusion controlled the rate. This concept is supported in part by the work of another.<sup>14</sup> He suggests significant external resistance is likely in large-media low-flow systems, unlikely in small-media high-flow systems, and possible in intermediate systems. Fixed-film nitrification on plastic media

concentration of oxygen in the free flow than if only one regime existed. This is supported by a theoretical analysis of filter performance.<sup>18</sup>

**The impact of temperature change.** There are few data on the effects of temperature that can be used to quantify the impact of temperature on nitrification rate. The temperature corrections used are summarized here. Many workers have selected an Arrhenius-type correction for estimating the impact of temperature change on rate.<sup>7,19,20</sup> The Arrhenius equation predicts the change in rate with temperature for a biosystem operating at its maximum velocity. Also, the Arrhenius-type corrections predict changes in endogenous respiration. However, the use of such procedures to predict the rate change in biological films not fully penetrated by one substrate (oxygen) seems dubious at best.

In evaluating the effect of temperature on enzyme reactions, it has been argued that Arrhenius is applicable only at high substrate concentrations,<sup>21,22</sup> that is, when the intrinsic zero-order rate is extant. If additional sites exist for substrate (first-order range), the system will, with a decreasing temperature, come to a new steady state with the substrate occupying the vacant sites. In the present case, this implies deeper film penetration by the limiting substrate. It is possible to conclude from this analogy that, where the systems are not truly zero order with respect to all substrates, changes in rate will not occur to the extent anticipated by Arrhenius and seen in many high substrate concentration systems. The significant point here is that even in the zero-order portion of the nitrification system the film is not fully penetrated by DO. In fact, penetration by oxygen into the film seems very limited.

Others<sup>1,3,4</sup> did not deal specifically with temperature effects. In fact, in one experiment,<sup>4</sup> a data correlation plot was compiled using data for all experimental temperatures. The suggestion is that bulk-phase concentration, the rate of diffusion, and the resulting impact on concentration in the film have a far more significant impact on rate than significant changes (5° to 10°C) in temperature.

**Summary of relevant issues.** In general, there is agreement among the many workers who have contributed to the study of fixed-film metabolism that more than one kinetic order exists in a nitrifying tower. There is, at the same time, the almost unspoken suggestion that the only significant kinetic regime is zero order.

While it is probably true that, in most cases, the bulk of the tower is zero order for NH<sub>4</sub>-N, the precise zero-order rate cannot be determined with confidence without specific knowledge about the DO concentration. This point is probably more significant than the fact that more than one kinetic regime exists in all towers that produce 0 to 3.0 mg/L of NH<sub>4</sub>-N in their effluent.

Temperature effects are not well defined by the available literature. No workers have attempted to interrelate diffusivity and saturation concentration (oxygen) along with the anticipated increase or decrease in the endogenous metabolism. No one has studied the incidence of only modest film penetration and what this means with respect to the application of an Arrhenius-type correction. Some have ignored temperature-related metabolic effects altogether, implying that they are of secondary concern. This

at 90 to 150-m<sup>2</sup>/m<sup>3</sup> surface area would be classed in the latter category.

Fixed-film models generally use Fickian diffusion concepts to describe movement through the liquid film, into, and where applicable, through the biological film. The diffusivity in the film is usually assumed to be identical or similar to that through water. Also, most workers<sup>1,3,8</sup> use Monod kinetics to describe the metabolic conversions. The use of Monod kinetics has been questioned by other researchers,<sup>15,16</sup> who indicate that the kinetic relationships of enzymes in structured media often cannot be described by the Monod or Michaelis-Menten relationship.

The oxidation rate in the zero-order portion of the tower will be controlled by the bulk flow oxygen concentration<sup>6</sup> according to the following equation:

$$r_{an} = \frac{1}{K_{ao}} \left( S_o \right)^{0.5} \quad (1)$$

Where

- $r_{an}$  = NH<sub>4</sub>-N oxidation rate, g/m<sup>2</sup> · d;
- $K_{ao}$  = half-order rate constant, g<sup>0.5</sup>/m<sup>0.5</sup> · d;
- $S_o$  = oxygen concentration in the bulk phase, g/m<sup>3</sup>;
- $n$  = stoichiometric relationship between NH<sub>4</sub>-N and oxygen, 3.94 mg O<sub>2</sub>/mg NH<sub>4</sub>-N.

The tower will remain zero order until the concentration ratios are as described in the following inequality:<sup>1,2,4</sup>

$$\frac{S_o}{D_o} > \frac{S_n}{D_n} \quad (2)$$

Where

- $S_n$  = bulk concentrations of NH<sub>4</sub>-N, g/m<sup>3</sup>;
- $D_o$  = diffusivity of O<sub>2</sub>, m<sup>2</sup>/s · 10<sup>-10</sup>; and
- $D_n$  = diffusivity of NH<sub>4</sub>-N, m<sup>2</sup>/s · 10<sup>-10</sup>.

The literature indicates that oxygen is limiting in most cases. In fact, it has been fully stated that oxygen will always be rate limiting.<sup>6</sup> These workers examined the impact of oxygen with NH<sub>4</sub>-N in excess and found that nitrification up to an oxygen concentration of 2.0 to 4.0 mg/L is first order for oxygen because of control at the liquid film, and then half order for oxygen at higher concentrations.

Saturation values of dissolved oxygen (DO) in the tower can be expected at no or low load; lesser values occur at higher loading. A recent study<sup>17</sup> indicated that there is a marked difference between the actual and calculated residence time in percolating biological filters. This work has suggested the presence of two distinctly different films: a free flowing superficial film outside the margin of the biological surface, and a captured film moving much more slowly through the channels in the rough surface of the biofilm.

The implications of these conclusions<sup>7</sup> are substantial, although there are some similarities to previous assumptions. The significant point is that it seems likely that there are two diffusion regimes, not one, leading to lower-than-expected concentrations of oxygen next to the biofilm. This configuration would require a much higher

seems reasonable where strong substrate concentration dependence has been demonstrated.

While the literature does not deal with temperature effects in a meaningful fashion, or the impact of varying hydraulic loads, the issue of oxygen concentration is often mentioned. The literature indicates that it is mandatory to consider the interrelationship between the diffusivity of the two principal substrate species ( $\text{NH}_4\text{-N}$  and  $\text{O}_2$ ) and the saturation concentration of oxygen as a function of temperature as having a significant and perhaps a dominant role in regulating the rate of  $\text{NH}_4\text{-N}$  oxidation in fixed-film systems.

#### Presentation of Data

The data used in this study were derived from the installations and under the conditions described in Table 1. The data were reduced as follows:

- All total Kjeldahl nitrogen (TKN) or  $\text{NH}_4\text{-N}$  sent to the tower with the exception of the effluent organic nitrogen was considered part of the load, including recycled  $\text{NH}_4\text{-N}$ . The effluent organic nitrogen was deducted because it is not a part of the potential oxidative load.
- Several strength or load parameters were investigated, including the total areal load and several different concentrations. However, to provide a basis for analyzing all data together, the areal load ( $\text{g}/\text{m}^2 \cdot \text{d}$ ) was found to be the most appropriate parameter and is used for most of the correlations here.

The data from all facilities investigated were reduced and the oxidizable  $\text{NH}_4\text{-N}$  areal load on the tower was plotted against the observed rate of  $\text{NH}_4\text{-N}$  removal. These data are contained in Figure 1. The graph contains in excess of 250 data sets.

Two facts concerning the data are immediately apparent. First, below a loading rate of  $1.2 \text{ g}/\text{m}^2 \cdot \text{d}$ , the correlation is of a high order. Second, above  $1.2 \text{ g}/\text{m}^2 \cdot \text{d}$ , the scatter seems to indicate no correlation. The key point of interest in this plot is that there can be excellent removals occurring above  $1.2 \text{ g}/\text{m}^2 \cdot \text{d}$ , up to  $2.5 \text{ g}/\text{m}^2 \cdot \text{d}$ . The key

is to identify the conditions which provide excellent performance.

If oxygen is limiting the rate of oxidation above  $1.2 \text{ g}/\text{m}^2 \cdot \text{d}$  and the data are not merely randomly scattered, there should be an orderly array of the "scattered" data based on either loading rate, removal rate, effluent  $\text{NH}_4\text{-N}$ , or a combination of the three. Furthermore, the ratio of the removal rate and estimated DO should be a constant for a given effluent value. This ratio should be related to the stoichiometric relationship between oxygen and  $\text{NH}_4\text{-N}$ . With these points in mind, the data have been analyzed and reorganized.

The DO lines plotted on Figures 2, 3, 4, and 5 are based on the method of others.<sup>4</sup> The half-order constant of  $4.30 \text{ g O}_2^{0.5}/\text{m}^{0.5} \cdot \text{d}$  was developed using Figures 4 and 5 to first establish the position of the saturation level of oxygen, presumably at the maximum rates of oxidation. Next, back calculating was done to obtain the appropriate constant. An oxygen diffusivity of  $22 \times 10^{-10} \text{ m}^2/\text{s}$  was used in the calculation.<sup>25</sup>

The Arizona Nuclear Pilot Plant (ANPP) (corrugated vertical media) and Garland (crossflow) data have been analyzed and segregated as described. These data are presented in Figures 2, 3, 4, and 5. The data represent an orderly array based on effluent  $\text{NH}_4\text{-N}$  loading and removal, as would be expected if oxygen limitations controlled performance.

There are a number of differences between the data developed at low hydraulic load as compared to the high and data developed on the cross- and vertical-flow plastic media. To see these differences more clearly, the mean rates have been obtained by regression and are shown in Figure 6. The low hydraulic load ANPP data clearly produces a poorer quality effluent than the higher loadings. Furthermore, the crossflow media appears to operate at lower oxygen levels than the vertical flow media, but the reasons are unknown.

The relationship between the estimated DO levels and the removal of  $\text{NH}_4\text{-N}$  is seen best in Figure 4. This is consistently found to be about 1:4. That is, the change in

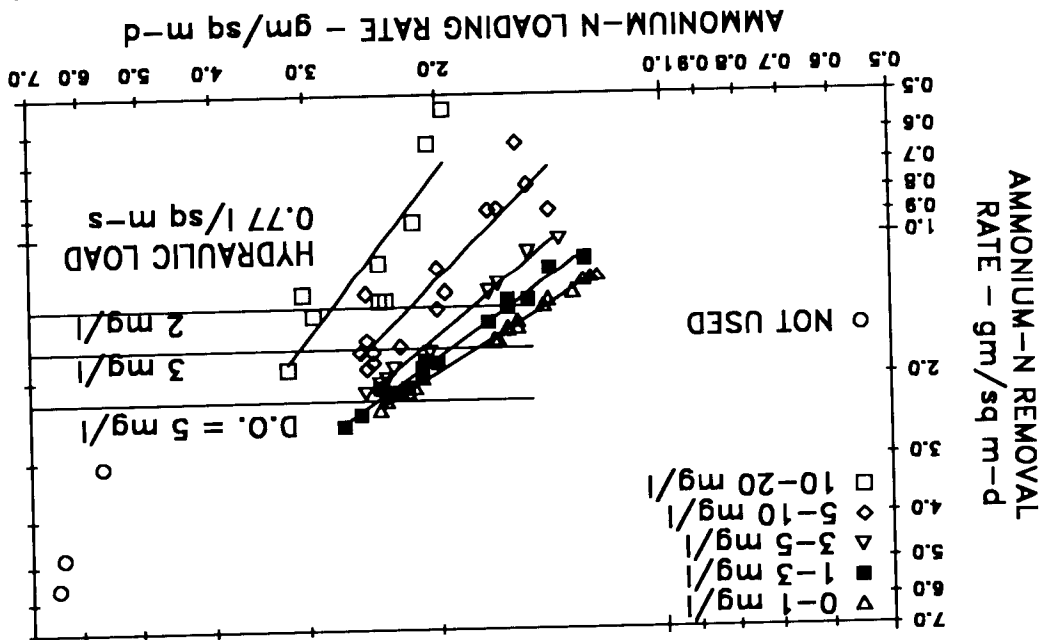
Table 1—Description of pilot plant data used in this study.

Location	Hydraulic load		Temperature, °C	Reference
	$Q_{inf}^a$ , $\text{L}/\text{m}^2 \cdot \text{s}$	$Q_R^b$ , $\text{L}/\text{m}^2 \cdot \text{s}$		
Arizona Nuclear Pilot Plant (ANPP)	0.54	0	28-32	23
ANPP	0.54	0.34	28-32	
ANPP	0.68	0.34	28-32	
Midland, Mich.	1.02	0.39	16-18	24
	0.68	0.46	17-19	
Sunnyvale, Calif.	0.82	1.09	13-20	25
Bloom Township, Ill.	0.82	1.09	7-23	26
Garland (Duck Creek), Tex.	Total hydraulic load = 0.77		16-29	27

<sup>a</sup>  $Q_{inf}$  = influent flow.

<sup>b</sup>  $Q_r$  = recycle flow.

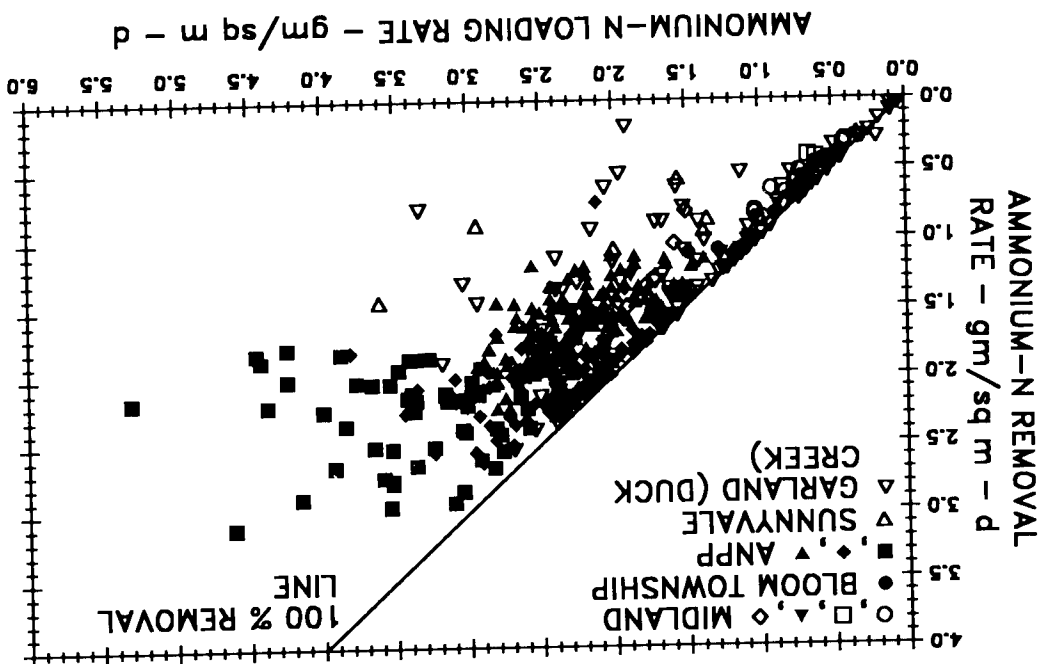
Figure 2—Effluent  $NH_4-N$  for a loading rate of  $0.77 L/m^2 \cdot s$  and temperatures between  $16^\circ$  and  $29^\circ C$ . Data are from the Duck Creek Pilot Plant, Garland, Tex.



**Discussion**  
 Kinetic regimes. During the tertiary trickling filter oxidation of  $NH_4-N$ , at least two kinetic regimes exist. These easily definable reaches are zero and first order, both for  $NH_4-N$ . At a high concentration, the system is zero order for  $NH_4-N$  and limited by the DO concentration. The zero-order reach is apparent in those instances where the effluent  $NH_4-N$  is greater than  $3.0$  to  $4.0$  mg/L. At low concentrations, the oxidation seems to be first order for

the removal rate is about  $0.25 g NH_4-N/m^2 \cdot d$  for each 1 mg/L DO increase in the estimated bulk liquid. In the present analysis, no temperature effects were observed. The impact of a limited oxygen supply overwhelms any and all temperature effects, if any truly exist. In the same fashion, limited sampling provides only a narrow view of the effect of altering the hydraulic load, although the effect of increases in the hydraulic load is probably related to increases in  $NH_4-N$  loading.

Figure 1—Oxidizable  $NH_4-N$  areal load versus the observed rate of  $NH_4-N$  removal.



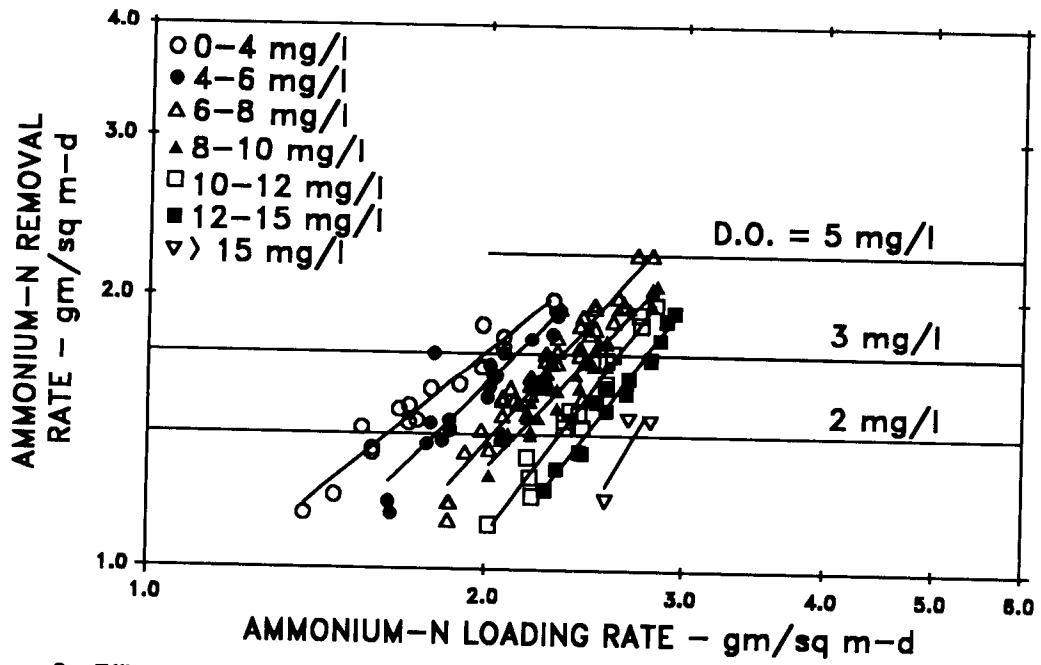


Figure 3—Effluent  $\text{NH}_4\text{-N}$  for a loading rate of  $0.54 \text{ L/m}^2 \cdot \text{s}$  and a temperature of  $30^\circ\text{C}$ . Data are from the Arizona Nuclear Pilot Plant.

$\text{NH}_4\text{-N}$ . The general agreement with previous findings<sup>4</sup> serves to support the correctness of this conclusion.

Therefore, the tower contains at least two kinetic regimes under most operating conditions if the effluent  $\text{NH}_4\text{-N}$  is less than 3.0 to 4.0 mg/L. The upper portion of the tower is zero order. The point of transition probably is as

described<sup>1</sup> and used elsewhere.<sup>28</sup> This transition occurs at a bulk  $\text{NH}_4\text{-N}$  concentration of 2.0 to 4.0 mg/L. Because the DO concentration in trickling filters seems to be so low (less than 4 to 5 mg/L), the half-order reach noted by others<sup>4</sup> in RBCs probably is not seen. A consequence of this finding is that all load versus removal data plot as if

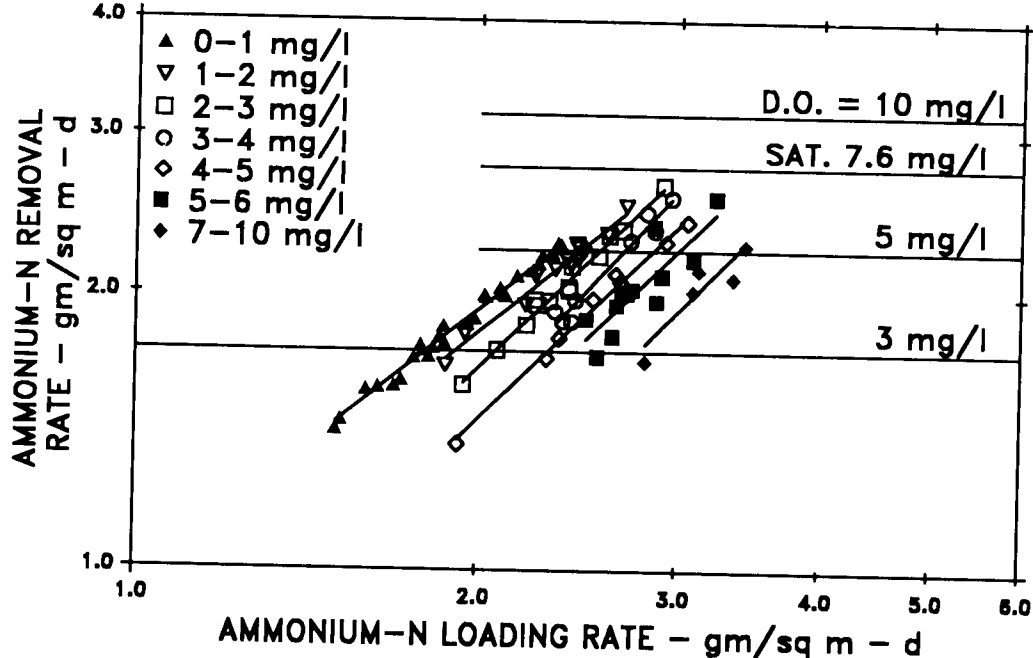


Figure 4—Effluent  $\text{NH}_4\text{-N}$  for a loading rate of  $0.87 \text{ L/m}^2 \cdot \text{s}$  and a temperature of  $30^\circ\text{C}$ . Data are from the Arizona Nuclear Pilot Plant.

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Figure 6—Regression analyses of effluent  $NH_4-N$  for the Arizona Nuclear Pilot Plant (30°C) and the Duck Creek Pilot Plant, Garland, Tex. (16° to 29°C).

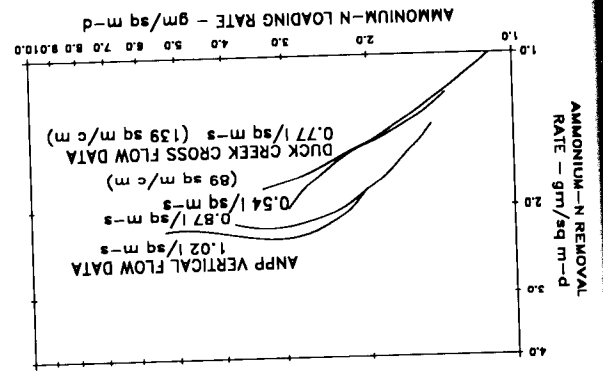
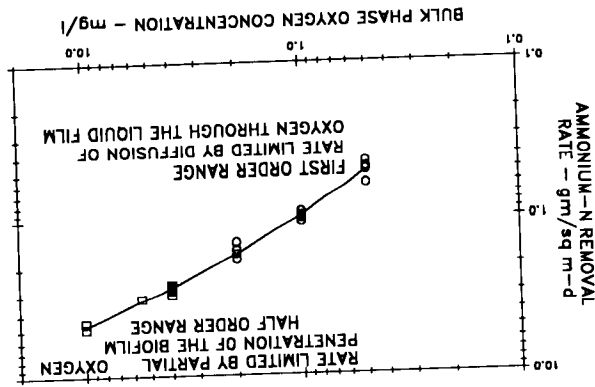


Figure 7—Nitrification rate as a function of bulk phase oxygen concentration.

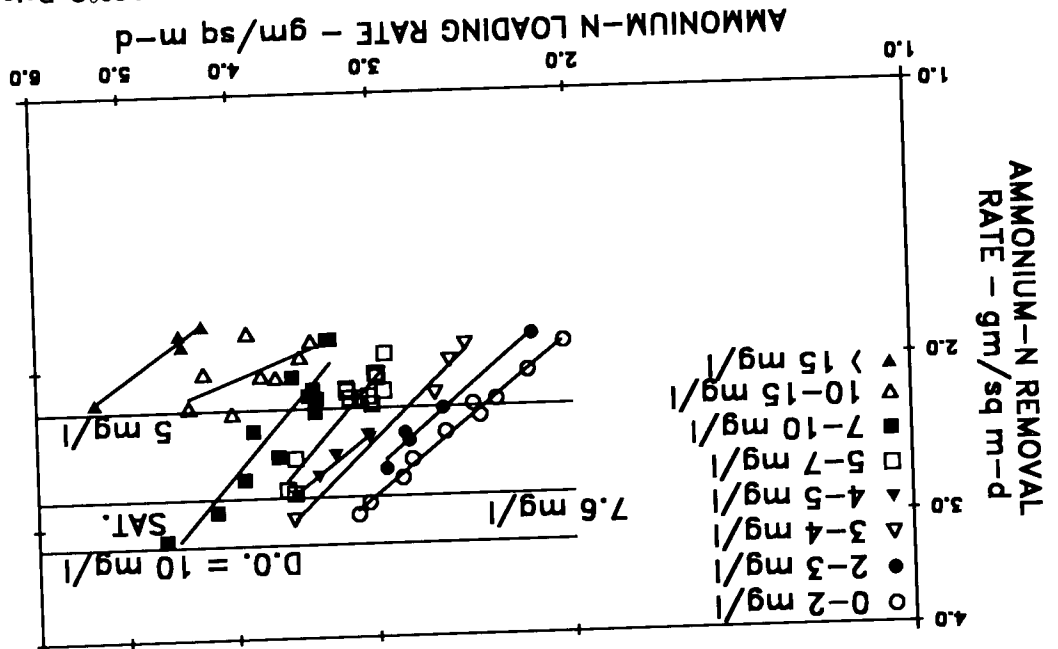


The entire tower was concentration dependent; that is, first order, even if only the bottom 100 cm is actually first order in  $NH_4-N$  under conditions of low load and adequate oxygen supply. Oxidation rates in the two regimes seem to be limited by diffusion. The controlling resistance is in the biological film in the zero-order range and in the liquid film in the first-order range.<sup>4,6,14,17</sup> In addition, this resistance is supported by the apparent reaction order. The most significant finding derived from the present analysis confirms the existence of a region in which the nitrification rate seems to be regulated by the oxygen concentration. The presence of this region has been confirmed through pilot work,<sup>4</sup> and others have served to quantify it further.<sup>5,6,17,18</sup> The relationship shown in Figure 7 was developed from pilot plant data.<sup>6</sup> In this case, an excess of  $NH_4-N$  was supplied and

the oxygen concentration varied. The liquid film seemed to control rate until the bulk oxygen concentration was 2.0 to 4.0 mg/L, after which the kinetic order changed to one-half. It is presumed that the tower bulk concentration of oxygen is usually great enough to assure half-order kinetics (with respect to oxygen), although the oxidation rate of 3.0 gm/m<sup>2</sup>·d, which was seen here at 30°C, indicates a concentration of only 4.0 to 5.0 mg/L in the bulk phase. The family of curves explains the apparent scatter of the data obtained at the higher loadings in Figure 1; that is, greater than 1.2 gm/m<sup>2</sup>·d. What appears to be scatter in reality a reflection of the range of DO available in the tower and the resulting oxidation rates and effluent values for a range of applied loads. The system breaks sharply at 1.2 gm/m<sup>2</sup>·d. The data indicate a rough equivalence of 0.25 gm/m<sup>2</sup>·d per 1 mg/L oxygen (a 1:4 ratio). The implication is that oxygen de-

pendent; that is, first order, even if only the bottom 100 cm is actually first order in  $NH_4-N$  under conditions of low load and adequate oxygen supply. Oxidation rates in the two regimes seem to be limited by diffusion. The controlling resistance is in the biological film in the zero-order range and in the liquid film in the first-order range.<sup>4,6,14,17</sup> In addition, this resistance is supported by the apparent reaction order. The most significant finding derived from the present analysis confirms the existence of a region in which the nitrification rate seems to be regulated by the oxygen concentration. The presence of this region has been confirmed through pilot work,<sup>4</sup> and others have served to quantify it further.<sup>5,6,17,18</sup> The relationship shown in Figure 7 was developed from pilot plant data.<sup>6</sup> In this case, an excess of  $NH_4-N$  was supplied and

Figure 5—Effluent  $NH_4-N$  for a loading rate of 1.02 L/m<sup>2</sup>·s and a temperature of 30°C. Data are from the Arizona Nuclear Pilot Plant.





mands of over 4.8 mg/L (four times 1.2) often create an oxygen deficiency in the tower. The resolution of this question must await further work.

The implication is that heavily loaded systems probably operate at somewhere between 20 and 40% of oxygen saturation, or perhaps at an even lower level. There is great uncertainty as to what the DO level really is. Measured effluent DO values are not a valid measure of what is actually happening in the tower. Designing a tower with confidence requires some knowledge of the oxygen level in the tower. That knowledge cannot be obtained with complete assurance for natural draft towers.

In another work,<sup>29</sup> the forces contributing to natural draft in tertiary towers were investigated. Three important facts resulted from the analysis:

- The maximum driving force (difference in air density) across a 6.7-m (22-ft) tower is often approximately 0.25 mm H<sub>2</sub>O under normal temperature and humidity conditions.
- There are normally two reversals in air flow each day, meaning that there are two periods during which the driving force is zero.
- It is possible to devise a scenario under normal weather conditions in which the driving force is less than 0.25 mm of H<sub>2</sub>O for most of the day in a 6.1-m (20-ft) deep tower and less than 0.13 mm of H<sub>2</sub>O in a 1.2-m (4-ft) deep filter.

One other significant point made in the work is that the normal air and liquid flow generated in trickling filters is orders of magnitude below that required for meaningful gas transfer by turbulent surface removal.

It is likely that most towers that do fail to meet the effluent goals do so because the towers are usually oxygen limited. This conclusion has been reached by others.<sup>5,6</sup>

It would appear, therefore, that there is strong reason to investigate the feasibility and cost effectiveness of forced ventilation. These findings point also to the absolute necessity of knowing the minimum DO concentration in the system to accurately and confidently estimate the rate of nitrogen oxidation. There are no known data available to estimate the DO saturation as a function of the volume of air/volume of wastewater in trickling filters.

**Hydraulic effects.** Perhaps the most significant point noted concerning hydraulic loadings is the marked suppression of oxidation rates in the lowest of the three hydraulic loadings from the ANPP facility. The two upper loading rates produced almost identical rates of oxidation. However, the lowest of the three, the 0.54 L/m<sup>2</sup> · s loading, was markedly suppressed. Because the temperatures and all other features were identical, it must be concluded that the lower hydraulic loading was responsible for the depressed oxidation rates. Also, in the same fashion, the data from Duck Creek seemed to show some suppression of nitrification at 0.77 L/m<sup>2</sup> · s. These data were obtained on crossflow media, which may require a somewhat higher driving force for good oxygenation.

While high effluent NH<sub>4</sub>-N values were coincident with high application rates for Sunnyvale, Bloom Township, and Midland, this is attributable to high areal loading and possibly concurrent oxygen limitations. It may be this

phenomenon that others<sup>28,30,31</sup> referred to by indicating that increased hydraulic load while increasing the removal percentage also appeared to increase the effluent NH<sub>4</sub>-N levels. The National Research Council formula for rock filters projects significant improvement in performance with a recycle ratio of 2:1 to 3:1. Increased oxygenation resulting from the recirculation is an obvious conjecture.

**Evaluation of temperature impacts.** As the limiting feature in both the zero-order and first-order reach seems to be diffusion, Arrhenius-type corrections are insufficient to explain any temperature effect. The rather astonishing lack of sensitivity to temperature confirms that factors other than metabolic phenomena are controlling the rate at which NH<sub>4</sub>-N is oxidized.

The important aspects that enter into the analysis of temperature effects include the following:

- Diffusivity is related to temperature and viscosity as follows:

$$D_o = \left( \frac{T_{ABS}}{\mu_{ABS}} \right) \quad (3)$$

Where

$T_{ABS}$  = absolute temperature, and

$\mu_{ABS}$  = absolute viscosity in compatible units.

- The change in the oxygen mass transfer driving force with temperature, (saturation concentration ( $C_s$ ) minus the actual operating concentration ( $C_o$ )).
- The incomplete film penetration; that is, the depth of inner water layer and aerobic film.
- The nature of the relationship between diffusivity, oxygen concentration, and rate.

The change in diffusivity may be estimated by a number of methods; the procedure used here is described elsewhere.<sup>23</sup> The oxygen saturation data are handbook values.

Because of the incomplete film penetration, estimates using the Arrhenius equation with a "μ" (activation energy) value of 10 000 to 15 000 cal are invalid. The intrinsic rate and endogenous respiration will increase or decrease with temperature, but the film will become more fully penetrated as the temperature increases or less as the temperature decreases and the external concentrations respond to that change. Therefore, the actual zero-order rate of nitrogen conversion will be controlled by the rate at which the substrate (oxygen) reaches active sites in the biofilm, which is controlled by the concentration and the diffusivity.

As shown earlier in Equation 1, the rate of oxidation was defined<sup>4</sup> to be a function of the half-order constant and the DO concentration. Further, the constant is

$$K_{ao} = (2D_o)(K_o)^{0.5} \quad (4)$$

Where

$D_o$  = diffusivity of oxygen, m/s × 10<sup>-10</sup>, and

$K_o$  = specific oxygen utilization rate, g/m<sup>3</sup> · s.

Noting the form of these equations, the key temperature relationship is as follows:

$$\frac{r_{anT_1}}{r_{anT_2}} = \left( \frac{D_{oT_1}}{D_{oT_2}} \right)^{0.5} \left( \frac{C_{sT_1}}{C_{sT_2}} \right)^{0.5} \quad (5)$$

When and 5° values

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• All tertiary towers studied in the present work, when loaded at rates greater than 1.2 g/m<sup>2</sup> · d of NH<sub>4</sub>-N, periodically demonstrated an oxygen deficient condition, as evidenced by a reduced rate and extent of oxidation. Rates

ing:  
From the analysis, it is possible to conclude the following:

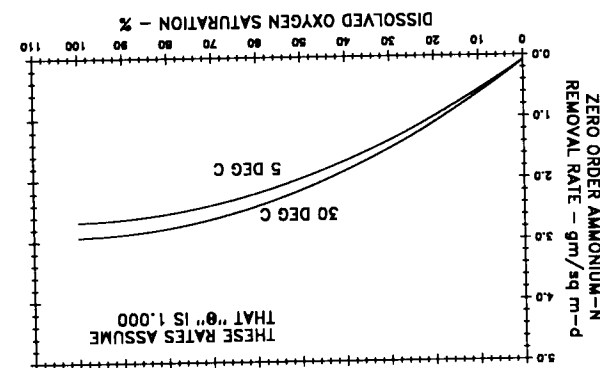
An analysis of data from five pilot tertiary treatment plant facilities has been carried out. The purpose of this analysis was to evolve design procedures which could be supported by the theory of oxidation in fixed biological films. The study was particularly directed toward the resolution of questions about the actual kinetics of NH<sub>4</sub>-N oxidation under varying operating conditions, the impact of DO levels on NH<sub>4</sub>-N removal rate, the origin and magnitude of temperature effects (if any), and finally, the impact of varying the hydraulic load. In carrying out this work, basic fixed-film theory was used as a base for formulating procedures for data reduction and analysis.

**Summary and Conclusions**

With adequate ventilation, a design can be based on a loading rate 1.2 g/m<sup>2</sup> · d or less to 3.0 to 4.0 mg/L NH<sub>4</sub>-N with reasonable assurance of good performance on either vertical or crossflow media, although good estimates of performance in the first-order range have not yet been published. This method, however, does not constitute an economic design procedure.

**Design considerations.** No heavily loaded natural draft tower design can be undertaken at present with complete confidence until more is known about the oxygen levels in the tower. Forced ventilation at a level designed to maintain a specific oxygen level under the warmest tower conditions and the heaviest load will permit the selection of a zero-order rate with more, if not complete, confidence. It is obvious that forced draft towers will perform consistently better than natural draft towers. Hence, the best natural draft rate oxygen data may be the place to begin to obtain good design information for forced draft towers. Certainly, the presently available design curves that are derived from philosophies that do not include a realistic view of these factors controlling oxidation are of little real design help. More specific data interrelating oxygen concentrations in or next to the biofilm are absolutely necessary.

**Figure 8—Effect of DO concentration on NH<sub>4</sub>-N oxidation.**



The essential aspects of the first-order portion of the lower have been studied and are the subject of another paper.

$\bar{Q}$  = flow rate, m<sup>3</sup>/d  
depth, g/m<sup>3</sup>; and  
(NH<sub>4</sub>-N)<sup>trans</sup> = NH<sub>4</sub>-N concentration at transition transition, D<sup>trans</sup>, m;  
L = tower depth, D<sup>lower</sup>, minus depth at  
K<sub>N</sub> = first-order constant, m<sup>-1</sup> · depth, m<sup>2</sup>;  
A<sup>trans</sup> = media surface area to the transition  
(NH<sub>4</sub>-N)<sub>R</sub> = NH<sub>4</sub>-N concentration removed, g/m<sup>3</sup>;

Where

$$\frac{\bar{Q}}{(NH_4-N)_R} = \frac{(K_{ao})^{0.5}(S_o^{0.5}A^{trans})}{(NH_4-N)^{trans}}(1 - e^{-K_N L}) \quad (8)$$

removal equation is of the form:  
The actual oxidation rate is a combination of two terms, one that describes the removal in the zero-order region and the second which is first order for NH<sub>4</sub>-N. Therefore, the first term in the removal equation applies down to the point of transition. Based on the findings of this study, the zero-order rate will vary between 1.0 and 3.0 g/m<sup>2</sup> · d depending on oxygen availability. The second term is first order for NH<sub>4</sub>-N and describes the removal below the point of transition in the tower. The removal equation is of the form:

It is recognized that  $\theta$  may be less or more; that is, 1.01 is only an estimate. The age of the cells in a tertiary nitrification tower will normally be substantial (greater than 10 to 15 days). Hence, the endogenous rate will be low and temperature effects will probably be negligible. The difference in rate brought about by temperature seems to be estimated most appropriately by the changes in oxygen concentration and diffusivity. The impacts of temperature and oxygen concentration on the zero-order rate based on diffusivity changes at 30°C and 5°C are shown in Figure 8.

$$\frac{r_{ant2}}{r_{ant1}} = \left(\frac{D_{OT2}}{D_{OT1}}\right)^{0.5} \left(\frac{C_{ST2}}{C_{ST1}}\right)^{0.5} 1.01^{(T2-T1)} \quad (7)$$

$$= (1.09)(1.28) = 1.40$$

The overall correction could include a modest correction for changes in endogenous respiration ( $\theta$ ); a  $\theta$  of 1.01 is included here. Therefore, the total correction might be

$$\frac{r_{ant2}}{r_{ant1}} = \left(28 \times 10^{-10}\right)^{0.5} \left(7.6\right)^{0.5} \left(12.8\right) = 1.09$$

When this relationship is applied, for example, for 30°C and 5°C, the following result is obtained using handbook values of diffusivity<sup>33</sup> and saturation concentration.

were consistent with low oxygen values as determined by a method described elsewhere.<sup>4</sup>

- There seems to be two kinetic regions operating in most fixed-film towers designed for the tertiary treatment of wastewater. The first is seen at high  $\text{NH}_4\text{-N}$  concentrations, a region which is zero order for  $\text{NH}_4\text{-N}$  and half order for oxygen. The second is a concentration-dependent reach which seems to be first order for  $\text{NH}_4\text{-N}$ .

- The temperature effects seem to be comparatively minor in the zero-order region because of the offsetting effects of temperature on diffusivity of oxygen and on the concentration of oxygen possible in the bulk-liquid flow.

- The effect of hydraulic loading seems to be complex and the data available do not serve to completely resolve the question of the impact of hydraulics on the system. However, there seems to be a point in the oxygen-limited zone where low hydraulic rates (in this case,  $0.54 \text{ L/m}^2 \cdot \text{s}$ ) result in suppressed oxidation rates. At the same facility (ANPP), rates of 0.88 and  $1.02 \text{ L/m}^2 \cdot \text{s}$  produced markedly higher rates of  $\text{NH}_4\text{-N}$  conversion. In addition, in the case of data from three different facilities (Garland, ANPP, Bloom Township) where scatter appeared at high  $\text{NH}_4\text{-N}$  loads and little or no scatter existed at low loadings (less than  $1.2 \text{ g/m}^2 \cdot \text{d}$ ), the increased effluent values seem to be caused by oxygen limitation rather than the increased hydraulic load.

- A single oxidation rate ( $\text{g/m}^2 \cdot \text{d}$ ) or inverse areal loading rate ( $\text{m}^2/\text{g} \cdot \text{d}$ ) does not constitute a rational basis for design. The design must consider such features as the DO concentration in the tower, the point of transition from oxygen to  $\text{NH}_4\text{-N}$  dependence, and the impact of temperature changes on these factors. Certainly, empirical procedures must still be used, at least in part. Completely rational design procedures must await the development of more DO and rate information.

- Although the evidence is indirect, it is clear that  $\text{NH}_4\text{-N}$  and oxygen diffusion control or limit nitrification rate and that temperature effects are minimal across the entire range of normal loadings. This seems to occur because the system operates at a fraction of the maximum oxidation rate.

- Caution should be used when applying the conclusions of this experiment because they were based on data that came from pilot plants. Full-scale units, even with the same depth, may have different hydraulic conditions and often, less effective natural draft ventilation.

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