Impact of Elevated Refinery Wastewater Temperature on Nitrification Rates in the Activated Sludge Process

William J. Cunningham, P.E.

KEYWORDS: High temperature nitrification, activated sludge, Monod kinetics, nitrification, ammonia removal, nitrate.

ABSTRACT

This paper summarizes prior research undertaken to assess the impact of elevated wastewater temperature on nitrification rates in the activated sludge process. Research work of others who have used Monod kinetics to model nitrification performance and describe the affect of temperature on nitrification rates is summarized. Observed data are presented; temperaturede-pendant nitrification rates calculated; and temperature correction coefficients using the Arrhenius equation are developed for the range of temperatures typically found in refinery wastewaters. Other environmental conditions, including pH, are known to affect nitrification rates, and this paper explores the role of pH in establishing a nitrification treatment strategy during periods of elevated wastewater temperature.

Some of the reported observations on nitrification rates are made in the 35°C to 45°C range, the temperature range where the performance of temperature-sensitive nitrifying organisms is reported to decline. This is also the temperature range that is common for refinery wastewaters and current global environmental policies now require near complete nitrification of elevated ammonia-containing refinery wastewater, and in some cases, total nitrogen removal to less than 10 mg/L.

This paper presents an empirical model for predicting the affect of wastewater temperature on nitrification in activated sludge systems and presents treatment strategies that can be used to optimize nitrification design and operation for refinery wastewaters, particularly for refineries located in warm-weather climates.

THE pH EFFECT

Wild et al. (1) (2) investigated the ability of nitrifying sludges to convert ammonia to nitrate under various temperature and pH conditions. Summarizing the work of earlier investigators, Wild presented the results of research conducted by J.A. Borchardt, University Michigan, Ann Arbor, in the mid 1960’s that reportedly showed that temperature had little effect on nitrification in the 15°C to 35°C temperature range. The widely referenced Borchardt data is presented graphically in Figure 1.

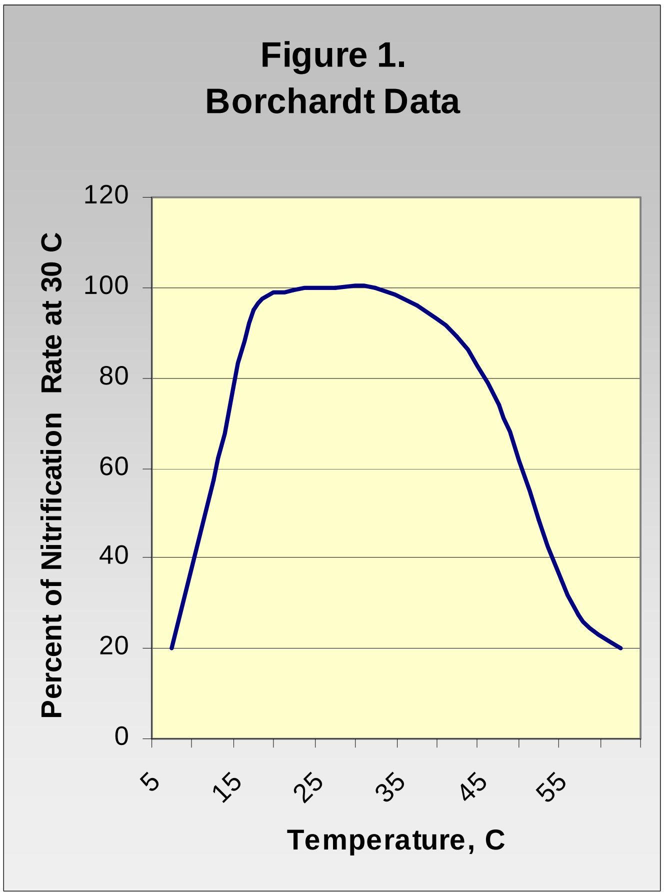

Figure 1. Borchardt Data

The effect of pH on the respiration rate of nitrosomonas as reported by Meyerhof (1917), and Engel and Alexander (1958) is shown in Figure 2; the effect on nitrobacter, as reported by Meyerhof (1916) is shown in Figure 3. The Engel and Alexander work indicates a wide pH range of 6.9 to 9.3 where 90 percent of the maximum rate of oxidation of ammonia is achieved, whereas the Meyerhof work indicates a tighter pH band width exists, 8.4 to 9.0 for ammonia oxidation by nitrosomonas, and pH 8.1 to 9.5 for oxidation of nitrite by nitrobacter. The Wild et al. work set out to clarify some of these apparent discrepancies.

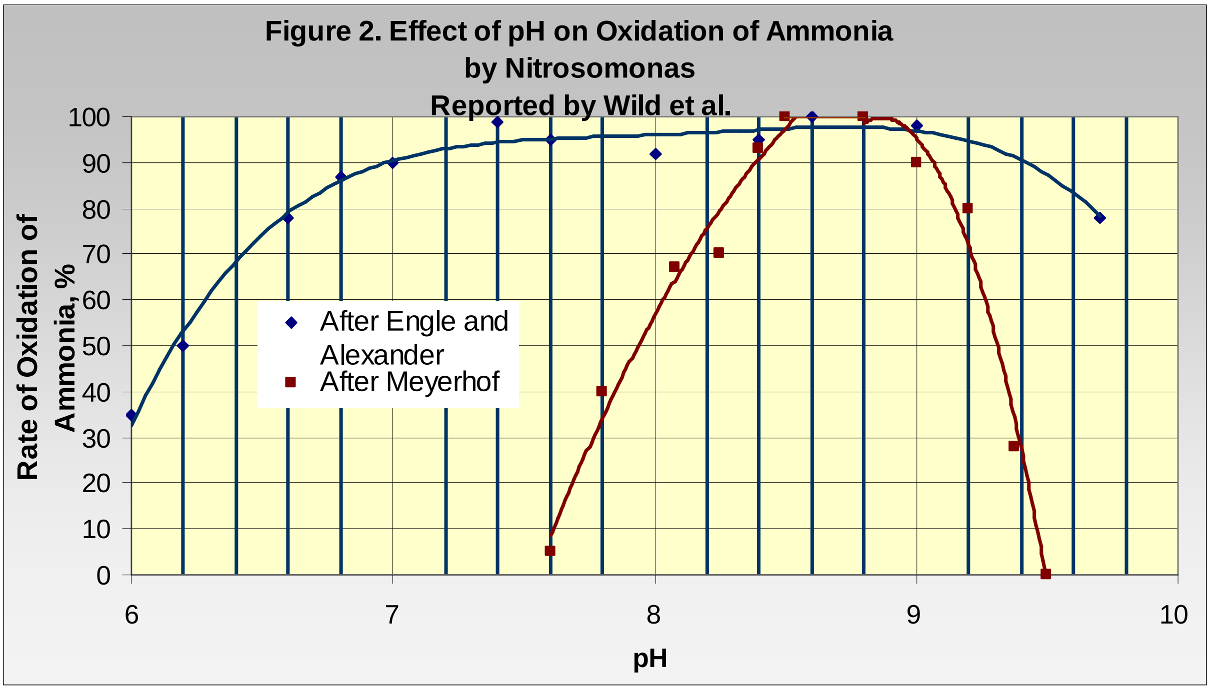

Figure 2. Effect of pH on Oxidation of Ammonia by Nitrosomonas Reported by Wild et al.

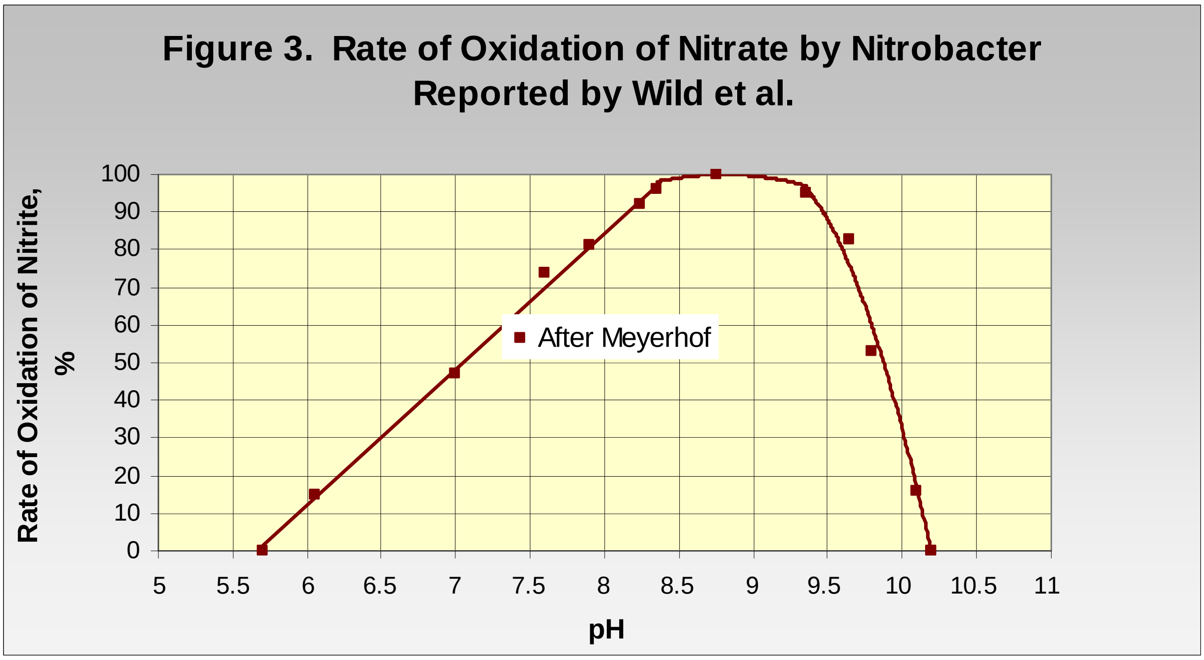

Figure 3. Rate of Oxidation of Nitrate by Nitrobacter Reported by Wild et al.

Wild et al. ran a pilot nitrification unit using settled trickling filter effluent supplemented with ammonium chloride to provide sufficient nitrogen substrate. Figure 4 presents experimental results of ammonia nitrification at two ammonia concentrations (26.4 mg/L and 46.5 mg/L) conducted at constant pH and temperature conditions. The observed rate of decline in ammonia concentration is constant, and the slopes of the decline rates are parallel, leading the investigators to conclude that nitrification is not inhibited by the concentration of ammonia tested, levels that are typically found in domestic wastewater. The ammonia levels tested are about half that found in refinery wastewater, and the potential impact of refinery ammonia levels are explored later in this paper.

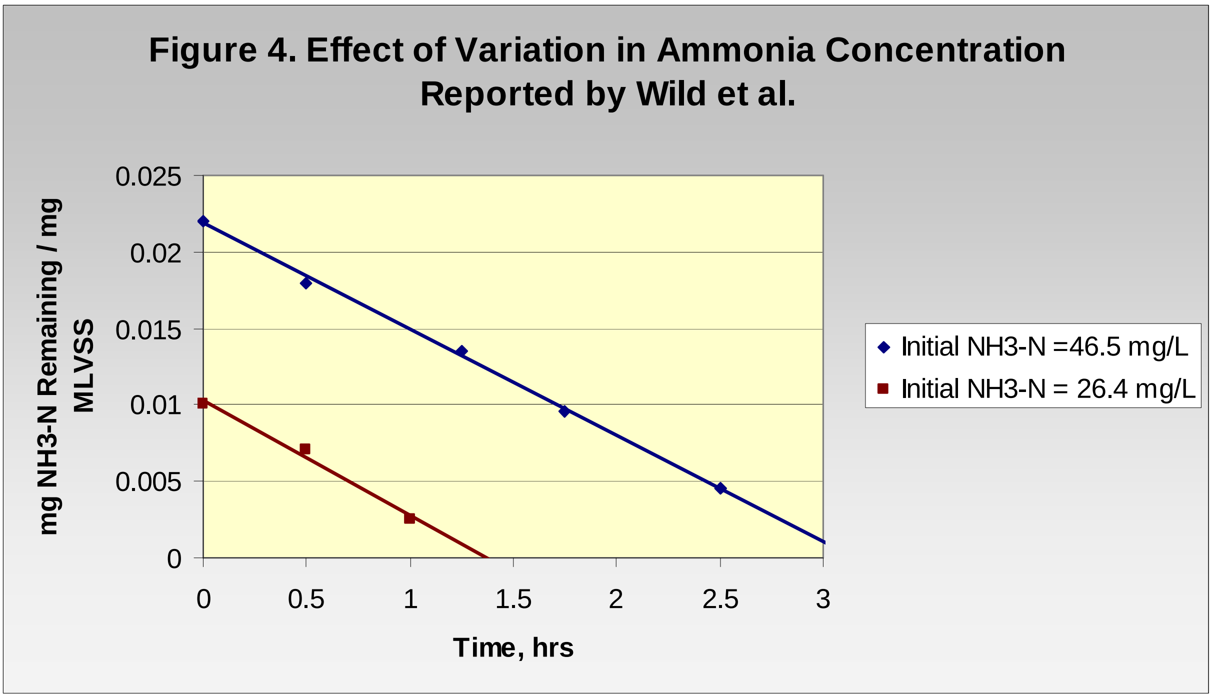

Figure 4. Effect of Variation in Ammonia Concentration Reported by Wild et al.

Wild at al. investigated the effect of pH on nitrification over a pH range of 6.0 to 10.5. Figure 5 presents time plot results for two experimental runs, each run at a constant temperature of 20°C. The investigators observed that there was no apparent initial ammonia nitrogen uptake by the nitrifiers; there was no lag time for nitrification to take place; and the nitrification rate was constant for the entire length of the experiment for each pH condition investigated.

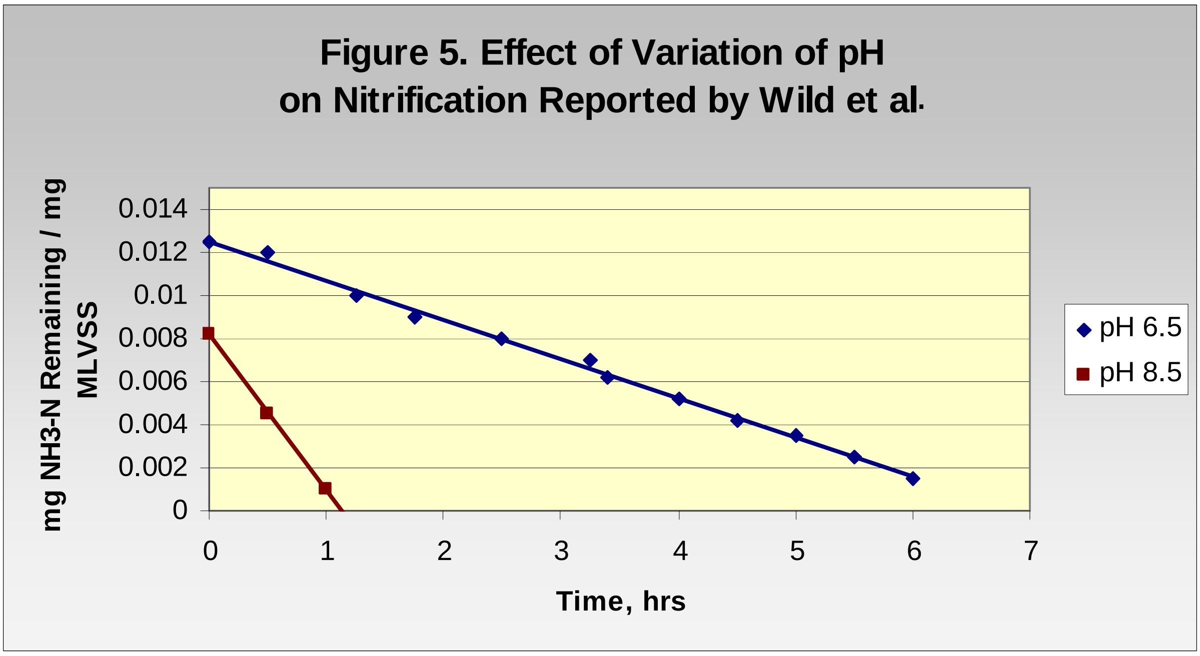

Figure 5. Effect of Variation of pH on Nitrification Reported by Wild et al.

Figure 6 presents the experimental results of observed ammonia nitrification at 20°C for the range of pH conditions investigated.

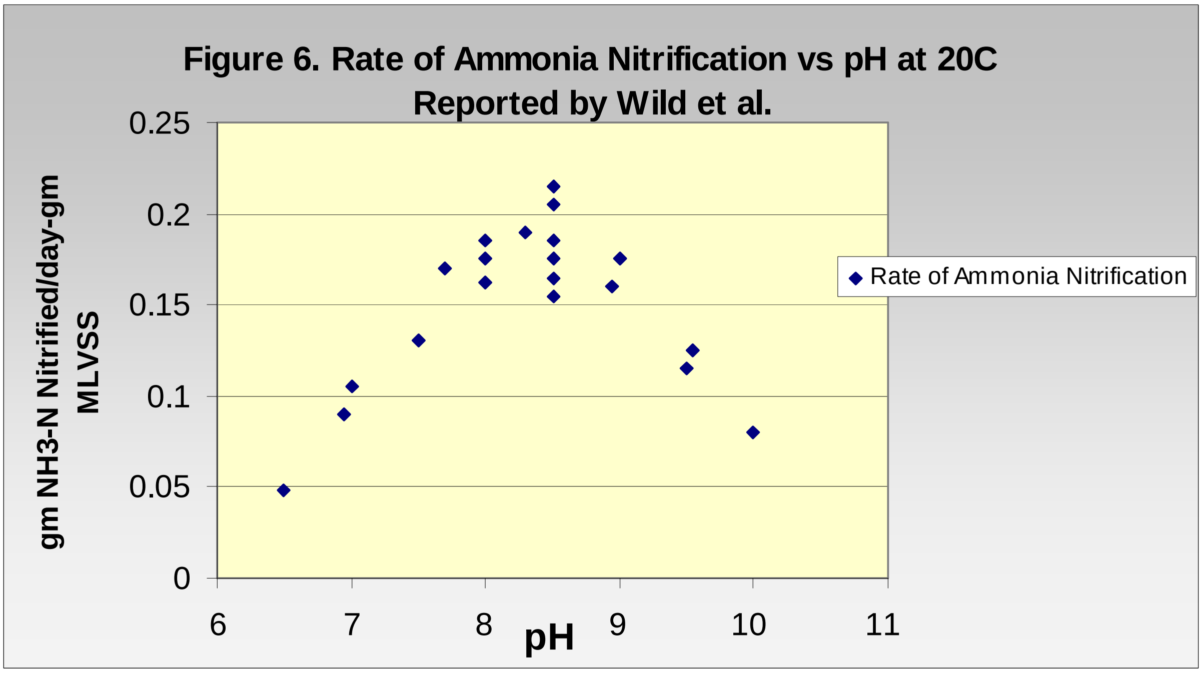

Figure 6. Rate of Ammonia Nitrification vs pH at 20C Reported by Wild et al.

The investigators observed an optimum pH for nitrification of pH 8.4, consistent with the results reported in the earlier investigations of Meyerhof and Engel et al. Figure 7 presents the nitrification data as a percent of the maximum observed rate; Wild et al. observed that 90 percent of the maximum nitrification rate occurred in the 7.8 to 8.9 pH range.

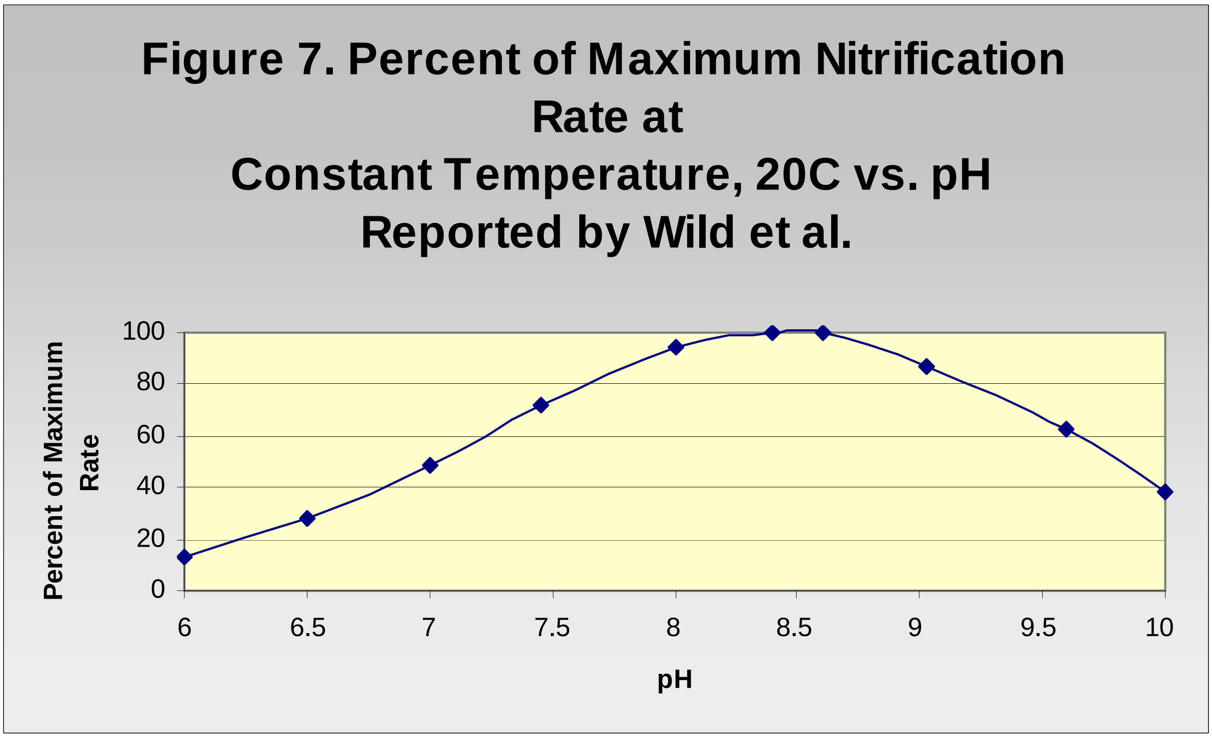

Figure 7. Percent of Maximum Nitrification Rate at Constant Temperature, 20°C vs. pH Reported by Wild et al.

IMPACT OF TEMPERATURE TYPICALLY FOUND IN WASTEWATERS

Wild et al. conducted temperature studies over a range of 5°C to 31.5°C. Figure 8 presents the results of two experiments run at 8°C and 31.5°C. Both experiments were run at pH 8.5. There was no lag observed in nitrification nor was any decrease in the nitrification rate as ammonia concentration declined.

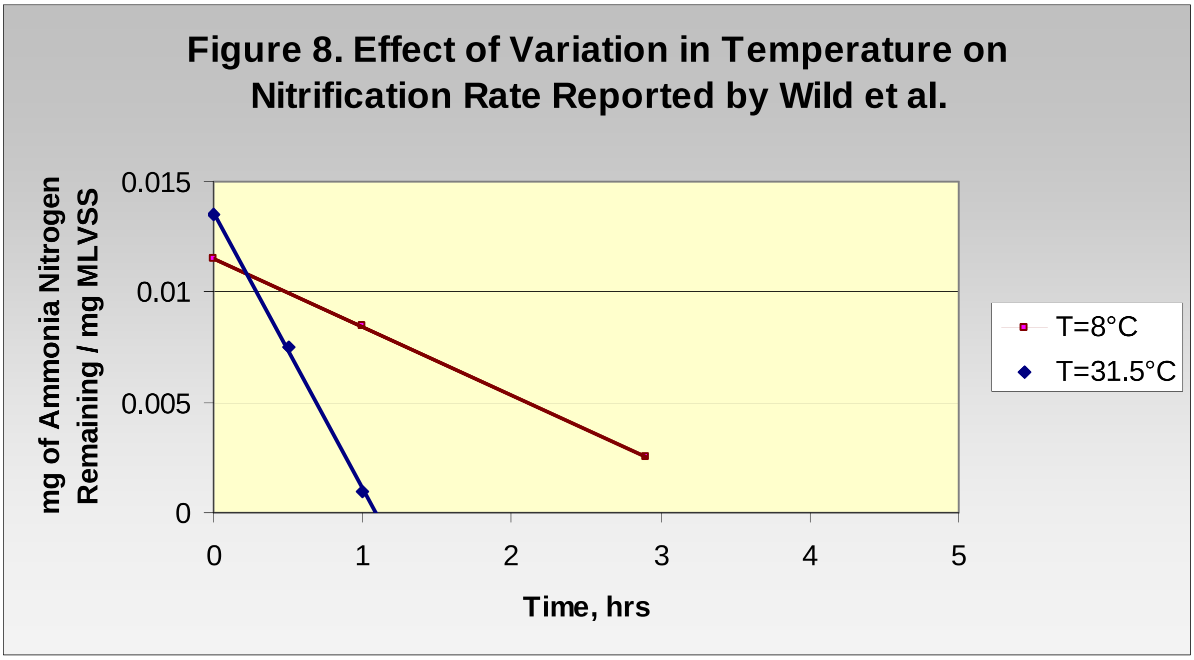

Figure 8. Effect of Variation in Temperature on Nitrification Rate Reported by Wild et al.

The rate of nitrification at all temperatures investigated is summarized as a percent of the nitrification rate observed at 30°C in Figure 9.

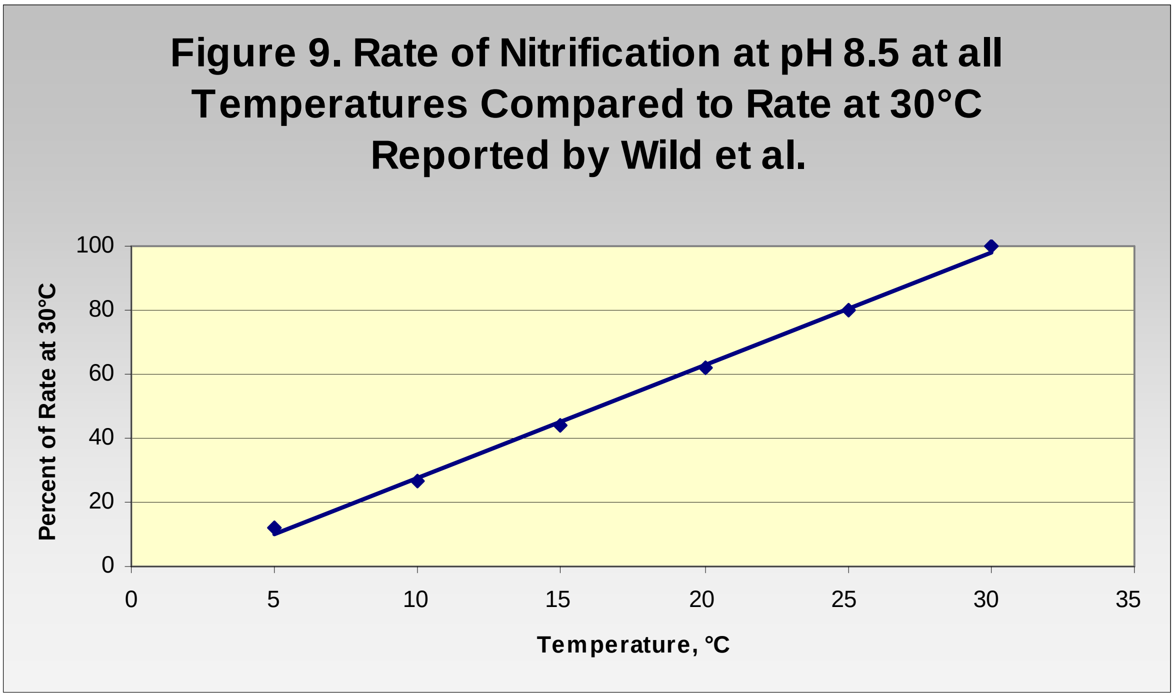

Figure 9. Rate of Nitrification at pH 8.5 at all Temperature Compared to Rate at 30°C Reported by Wild et al.

The results of the Wild et al. work show significant temperature impact on nitrification, in contrast to the earlier referenced Borchardt work. Wild et al. concluded that the Borchardt data showed less temperature influence in the 15°C to 35°C temperature range because the Borchardt experimental units were not being stressed with elevated levels of ammonia and the rate of nitrification occurring at given temperatures was sufficient to achieve complete nitrification.

The Wild et al. work concluded at a maximum temperature of 31.5°C, so no observations were made at higher temperatures to help define when elevated temperatures begin to have an adverse impact on nitrification rates.

IMPACT OF ELEVATED TEMPERATURE

Willers et.al. (3) investigated nitrification rates in two types of animal slurry, pig and veal-calf, over a temperature range of 20 °C to 60 °C. Short-term rapid nitrification assays were performed on veal-calf slurry and digested pig slurry and nitrification rates calculated for each temperature run. The results are presented in Figures 10 and 11.

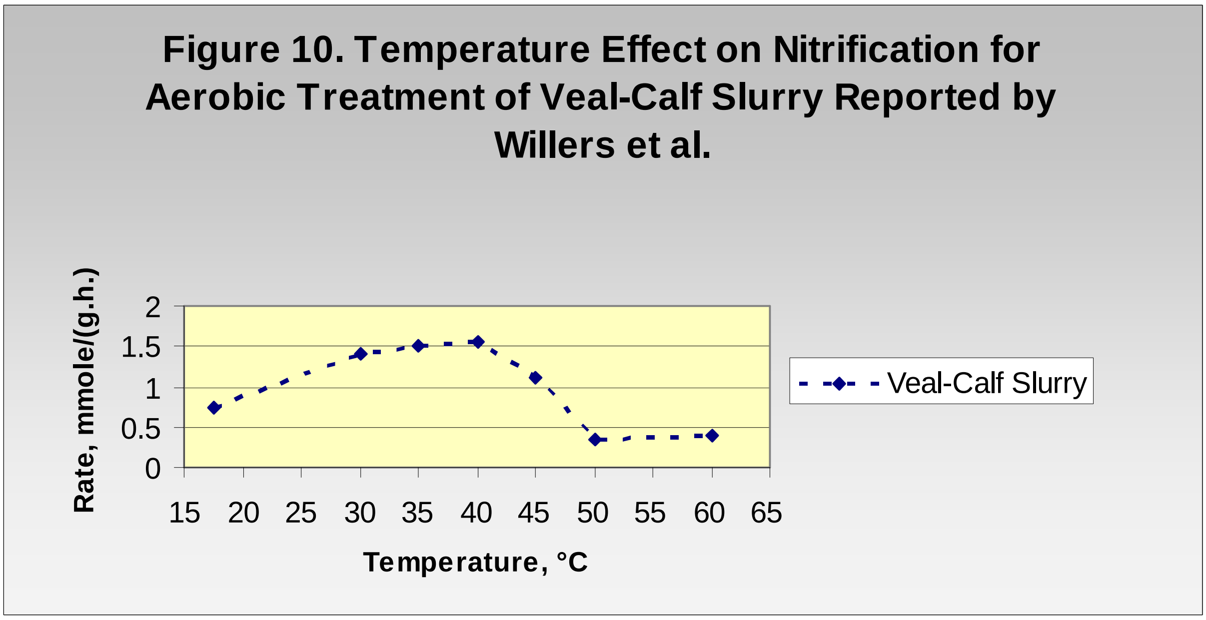

Figure 10. Temperature Effect on Nitrification for Aerobic Treatment of Veal-Calf Slurry Reported by Willers et al.

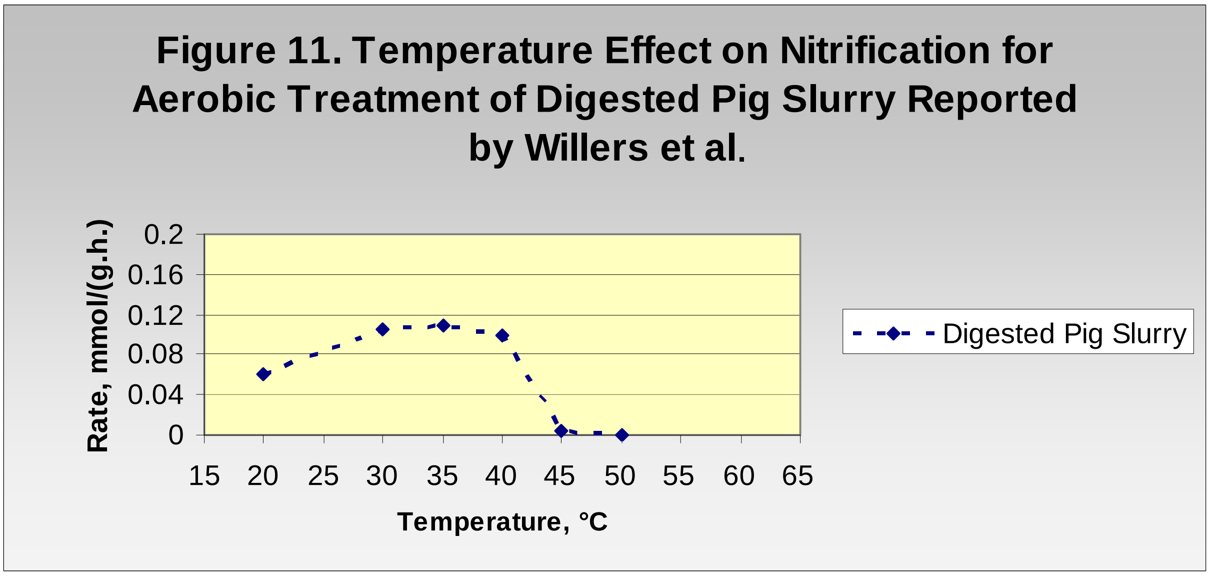

Figure 11. Temperature Effect on Nitrification for Aerobic Treatment of Digested Pig Slurry Reported by Willers et al.

The highest nitrification rates occurred at 40°C for the veal-calf slurry. Apparent significant nitrification occurred at 50°C and 60°C but this loss of ammonia was later attributed to ammonia volatilization from the liquid phase, not nitrification, as the assay MLSS pH exceeded 9.0 at the end of the assay work.

The highest nitrification rates occurred at 35 °C for the pig slurry and complete absence of nitrification was observed above 45 °C. Willers et al. reported that the rapid assay tests conducted during this investigation are only valid for the prediction of short-term temperature effects, and that operation at elevated temperatures could have a long-term negative effect on the growth rate of nitrifiers, and loss of nitrification capacity.

When testing was repeated at longer incubation times, the maximum nitrification rates were depressed below that observed during the short-term assays. Willers et al. reported that other factors, including the observed elevated pH (>9.0) may have contributed to greater free ammonia concentration and inhibition of nitrifying bacteria, contributing to the observed depressed nitrification rate. Willers et al. reported that the nitrifying bacteria population could adapt to high temperature environments after long-term exposure to elevated temperature. However, elevated wastewater temperature environments in refineries are transient, and predominately occur in refinery wastewaters during the warmest summer period when heat extraction within the refinery is already at its maximum. Thus, it is unlikely that a long enough period of time at elevated temperature operation would exist to acclimate the nitrifiers and restore good nitrification performance.

Neufeld et al. (4) investigated the potential causes of biological nitrification instability including interaction of organics, free ammonia, elevated temperature, cyanide, and phenolics using coke plant wastewater. The impacts of elevated temperature and free ammonia are summarized here.

Experimental results showed that unionized ammonia acts as a toxic inhibitor beginning at 10 mg/L, and Neufeld et al. suggested operating the MLSS pH in activated sludge system at a pH of 7 for treating ammonia concentrations up to 250 mg/L, a level typical in steel industry wastewaters. Even though biokinetics for ammonia removal are slower at pH 7 contrasted with higher operating pH (see references 1 and 2 above), the authors concluded that enhanced stability due to ammonia/ammonium ion equilibrium favor this operating point for wastewaters with elevated ammonia concentration typical for the steel coke industry.

For refinery wastewaters, where maximum ammonia concentrations are typically less than 100 mg/L, higher operating MLSS pH can be implemented to take advantage of the increase in biokinetic activity without the consequential toxic effect of free ammonia concentration. For instance, at pH 8, where the nitrification rate can be more than 50% greater than the nitrification rate at pH 7, only 10% of the ammonia in solution exists as free ammonia. Thus, a refinery wastewater with 60 mg/L ammonia concentration, would have less than 6 mg/L free ammonia, well below the reported toxic threshold, and have enhanced nitrification kinetics to achieve the desired effluent nitrogen quality.

The investigators reported their results using classic Monod kinetics:

$v = V_{max}S/ (K_m + S)$

Where, v = nitrification rate, $gNH_3/gVSS$-day

S = ammonia level in solution, mg/L

V_{max} = maximum nitrification rate, $gNH_3/gVSS$-day

K_m = half velocity constant, mg/L

Experiments were conducted at pH 8 with nitrifiers acclimated to the elevated temperatures tested. Figure 12 is a summary of the maximum nitrification rate, V_{max} as a function of temperature.

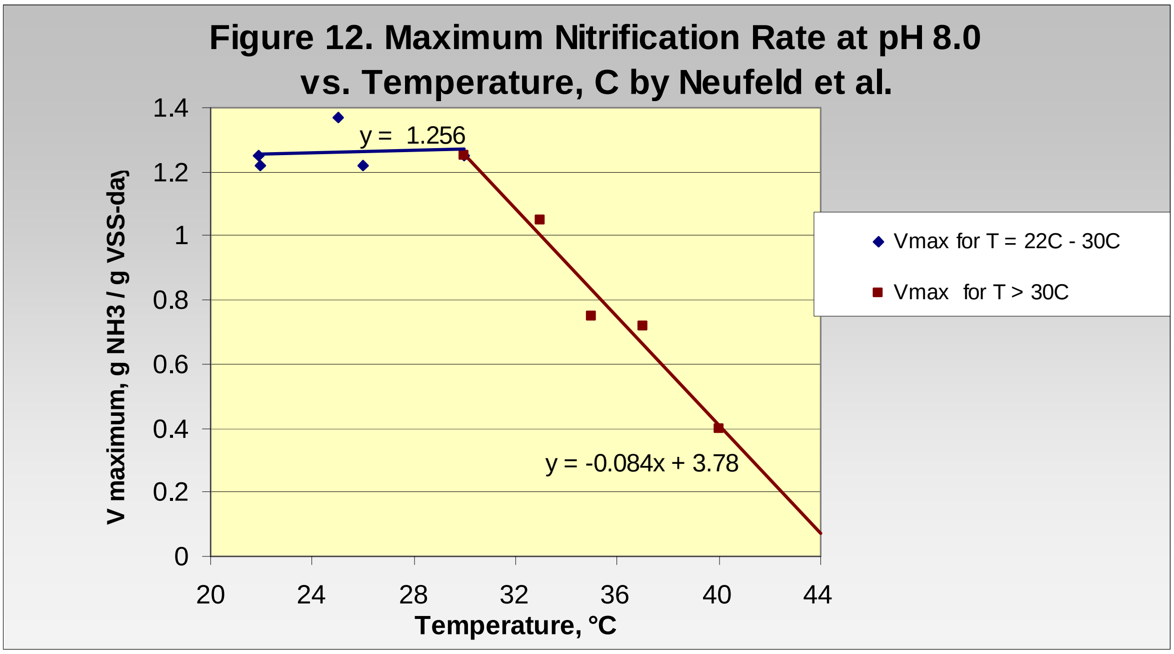

Figure 12. Maximum Nitrification Rate at pH 8.0 vs. Temperature, C by Neufeld et al.

At pH 8, V_{max} was observed to be constant over a temperature range of 22 to 30°C. Above 30°C, V_{max} dropped quickly, approaching zero at a temperature of about 45°C.

The investigators also evaluated K_m the Michaelis-Menten half velocity constant. Their results are presented in Figure 13.

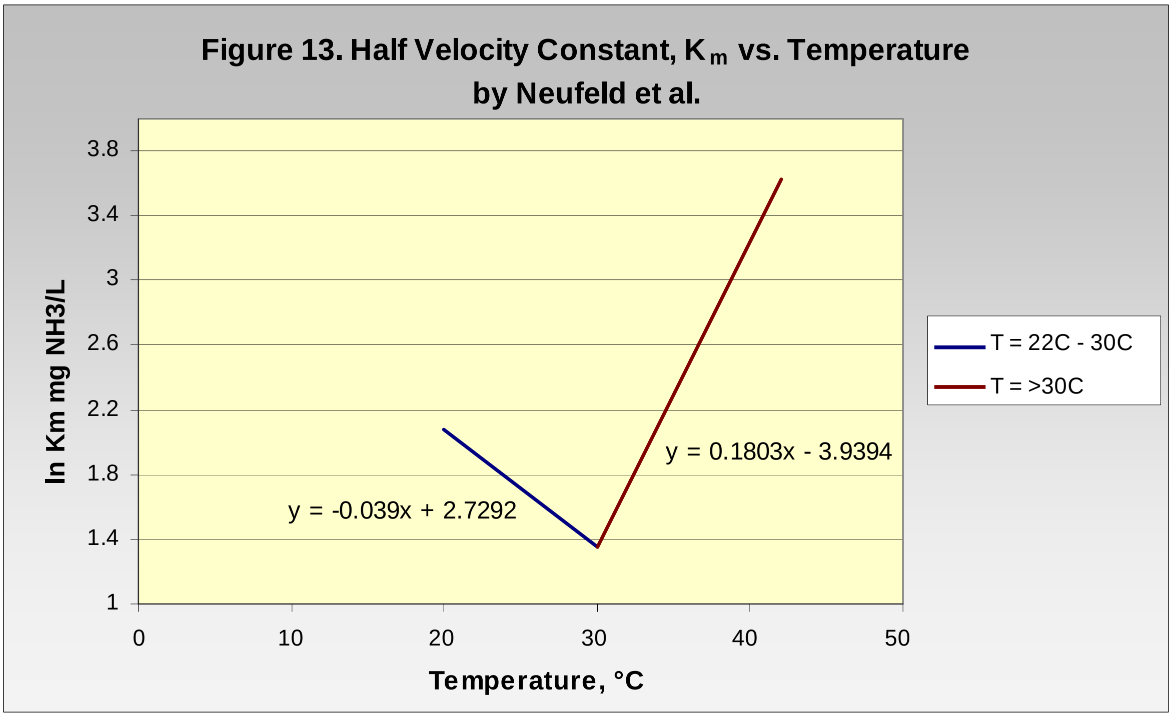

Figure 13. Half Velocity Constant K_m vs. Temperature by Neufeld et al.

As temperature increases to 30°C, K_m decreases, resulting in an increased nitrification rate for a fixed level of ammonia concentration. As temperature rises above 30°C, K_m rises significantly, resulting in significantly decreased nitrification rates.

Neufeld et al. (5) reported that this observed optimum temperature for biological nitrification occurs because bacteria, being made of proteins, are denatured by heat and become inactive as the temperature rises well above the optimum temperature.

Referencing the work of Wong-Chong and Hall (6), Neufeld et al. concluded that as temperature rises, "two simultaneous reactions are occurring with respect to nitrification: an increase in the rate of biological nitrification, coupled with an increase rate of chemical protein denaturation." This results in an apparent optimum temperature of approximately 30°C, where maximum nitrification kinetics occur. Above 30°C, nitrification kinetics rapidly decline below that observed at 30°C. The Neufeld et al. work showed that the decrease in nitrification kinetics continues to approximately 45°C, below which no measurable nitrification takes place.

By applying the Neufeld et al. data to a modified Arrhenius equation, an empirical model can be developed to derive the temperature correction coefficient, θ_n, for nitrification rates up to 30°C:

$$v_T = v_{20} \cdot \theta^{T-20}$$

and for nitrification rates greater than 30°C, but less than or equal to 45°C:

$$v_T = v_{30} \cdot \theta^{30-T}$$

Using the above empirical model, the following solutions can be derived for the temperature correction coefficient of each temperature band:

$\ln v_T = \ln v_{20} + (T\text{-}20) \ln \theta_{n,\leq 30}$ for temperatures ≤30°C; and
$\ln v_T = \ln v_{30} + (30\text{-}T) \ln \theta_{n,>30}$ for temperatures >30°C ≤ 45°C

Figure 14 presents the temperature correction coefficient solution for two conditions, 5 mg/L ammonia nitrogen, and 15 mg/L ammonia nitrogen for temperatures less than 30°C.

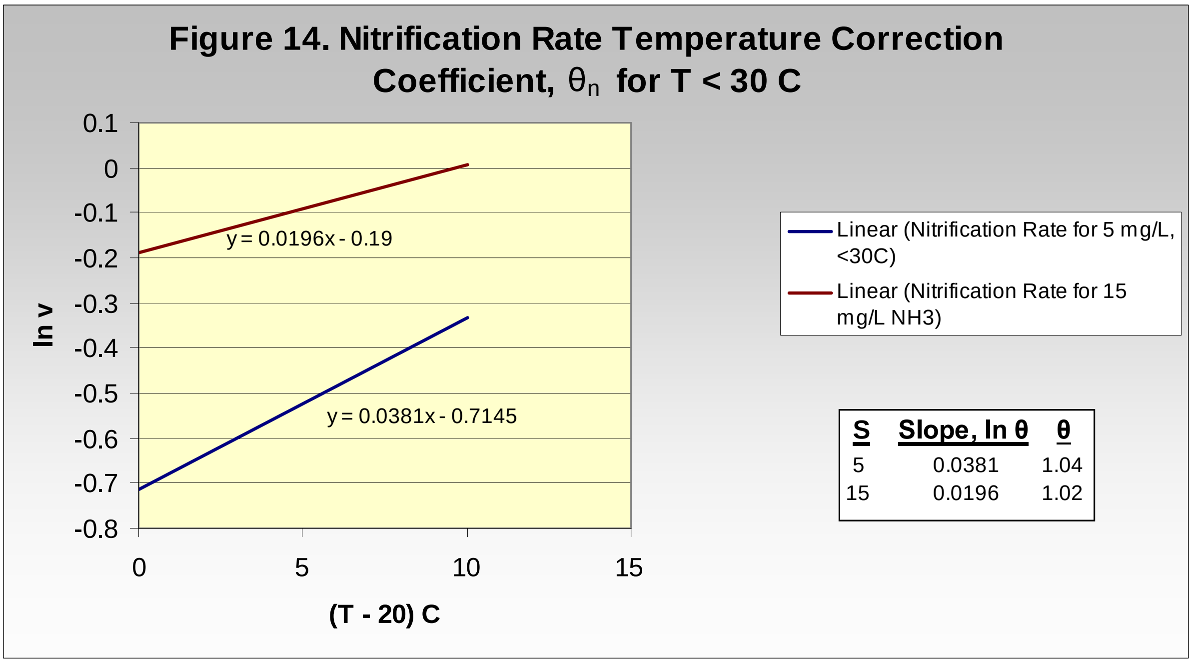

Figure 14. Nitrification Rate Temperature Correction Coefficient θ_n for T <30 C

The empirically derived temperature correction coefficient, $\theta_{n,<30}$, ranged from 1.02 to 1.04 for temperature less than 30°C.

Figure 15 presents the temperature correction coefficient solution for two conditions, 5 mg/L ammonia nitrogen, and 15 mg/L ammonia nitrogen for temperatures exceeding 30°C.

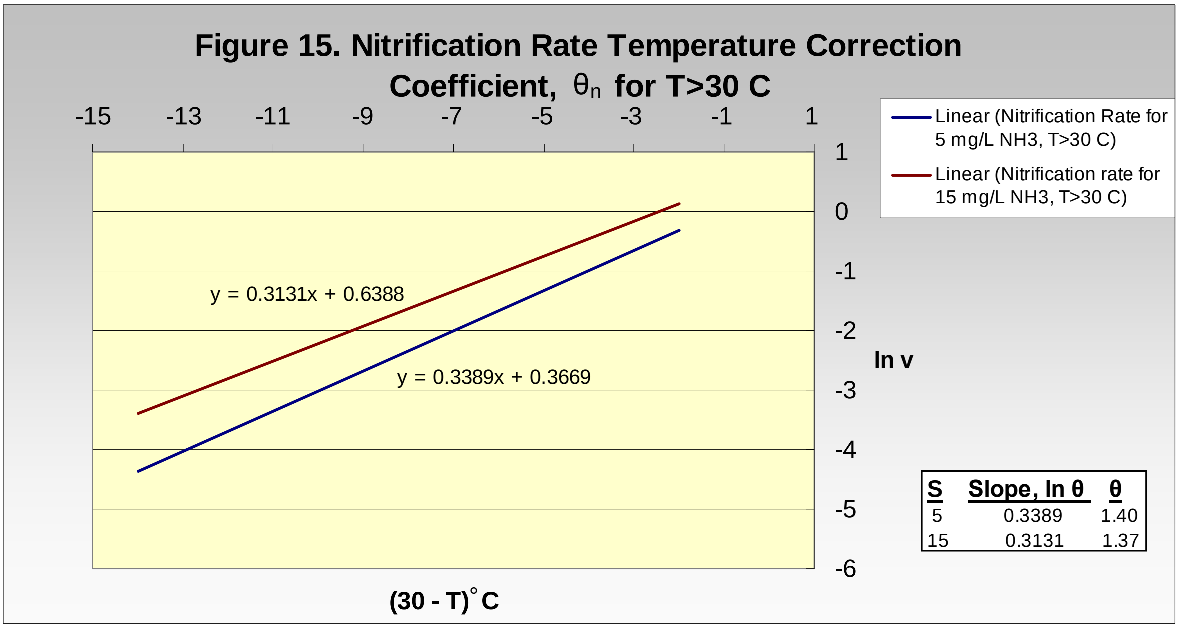

Figure 15. Nitrification Rate Temperature Correction Coefficient θ_n for T >30 C

The slope of the lines increase nearly ten-fold, compared to the less than 30°C data, indicating much greater temperature sensitivity when temperature exceeds 30°C. The empirically derived temperature correction coefficient, $\theta_{n,>30}$, ranged from 1.37 to 1.40 for temperature greater than 30°C, but less than or equal to 45°C.

The percent of the maximum nitrification rate, v, calculated using the modified Arrhenius equation over a temperature range of 20 to 45°C for 5 mg/l and 15 mg/l ammonia nitrogen concentration is presented in Figure 16. When compared to the maximum nitrification rate at 30°C as supported by the Neufeld et al. data, nitrification rates quickly drop off with temperatures greater than 30°C, such that at the 35°C to 38°C temperature range, a temperature range common in warm weather refinery effluents, the prevailing nitrification rate may be as low as 20 to 40% of the achievable nitrification rate at 30°C.

Keeping in mind that the maximum nitrification rates developed by Neufeld et al. were developed at a pH of 8.0 (where nitrification rates are near maximum) and that the pH of activated sludge MLSS typically occurs in the 7.2 to 7.5 range, the projected nitrification rates due to operating at an elevated temperature range of 35°C to 38°C at a pH of 8.0 would represent a nitrification rate approximately 40 to 75% of the projected maximum nitrification rate occurring in the 7.0 to 7.5 pH range at 30°C. The system design solids retention time (SRT) would have to be adjusted to accommodate this reduced nitrification rate and produce the desired effluent nitrogen quality.

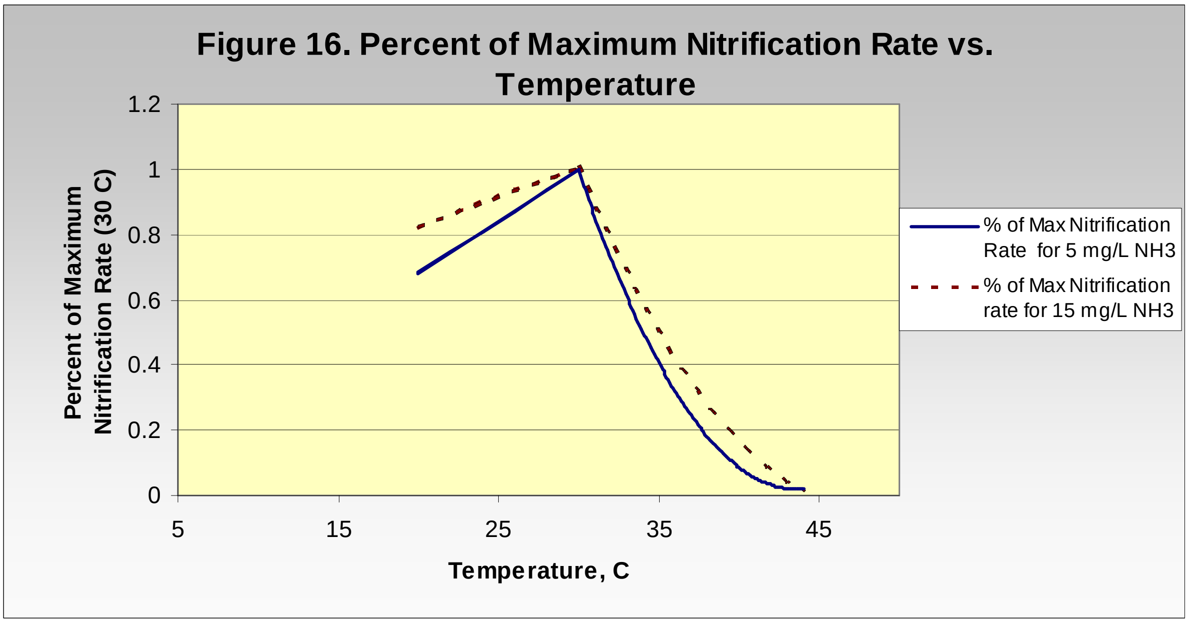

Figure 16. Percent Maximum Nitrification Rate vs. Temperature

Shammas (7), citing fragmented and sometimes contradicting data and information available to describe the effect of temperature and pH on nitrification rates undertook research to study the interaction of biomass concentration, temperature, and pH on ammonia oxidation rates in nitrifying activated sludge.

Shammas' work was presented using classic Monod kinetics:

$v = Vm \cdot S/ (K_s + S)$
$\quad = kX \cdot S/ (K_s + S)$
Where:
v = nitrification velocity, mg/L-day
S = ammonia level in solution, mg/L
V_m = maximum nitrification velocity, mg/L-day
K_s = half velocity constant, mg/L
k = maximum rate constant, 1/day
X = MLVSS concentration, mg/L

The maximum rate constant, k, and maximum nitrification velocity, V_m results are presented in Figures 17 and 18 respectively.

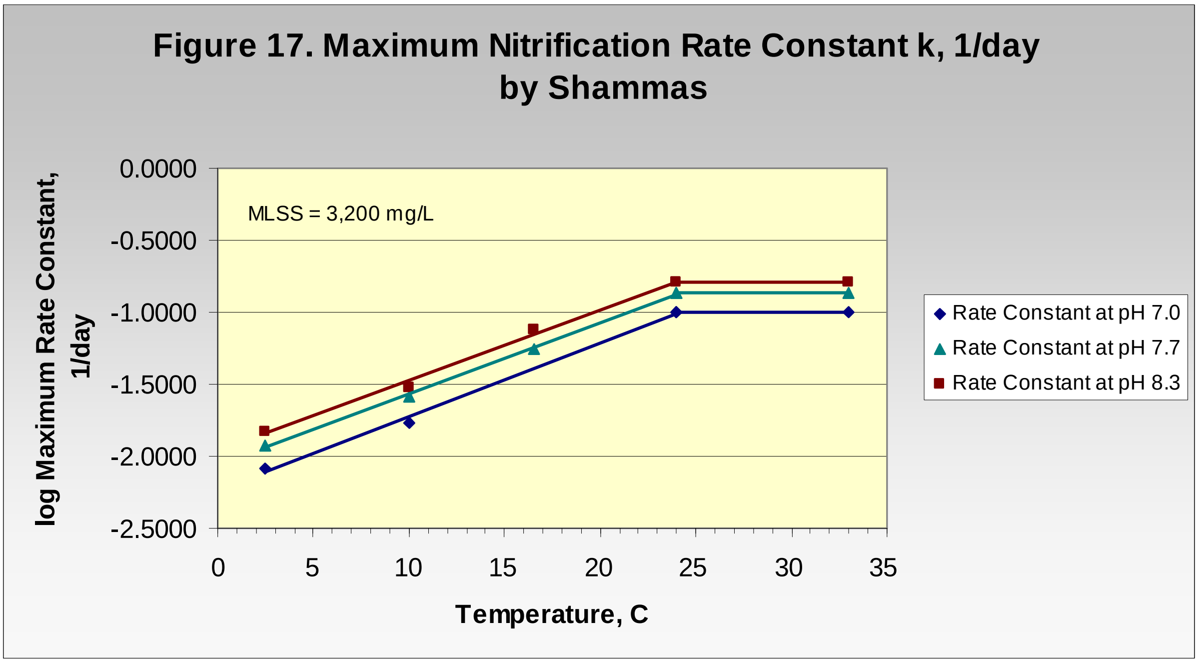

Figure 17. Maximum Nitrification Rate Constant k, 1/day by Shammas

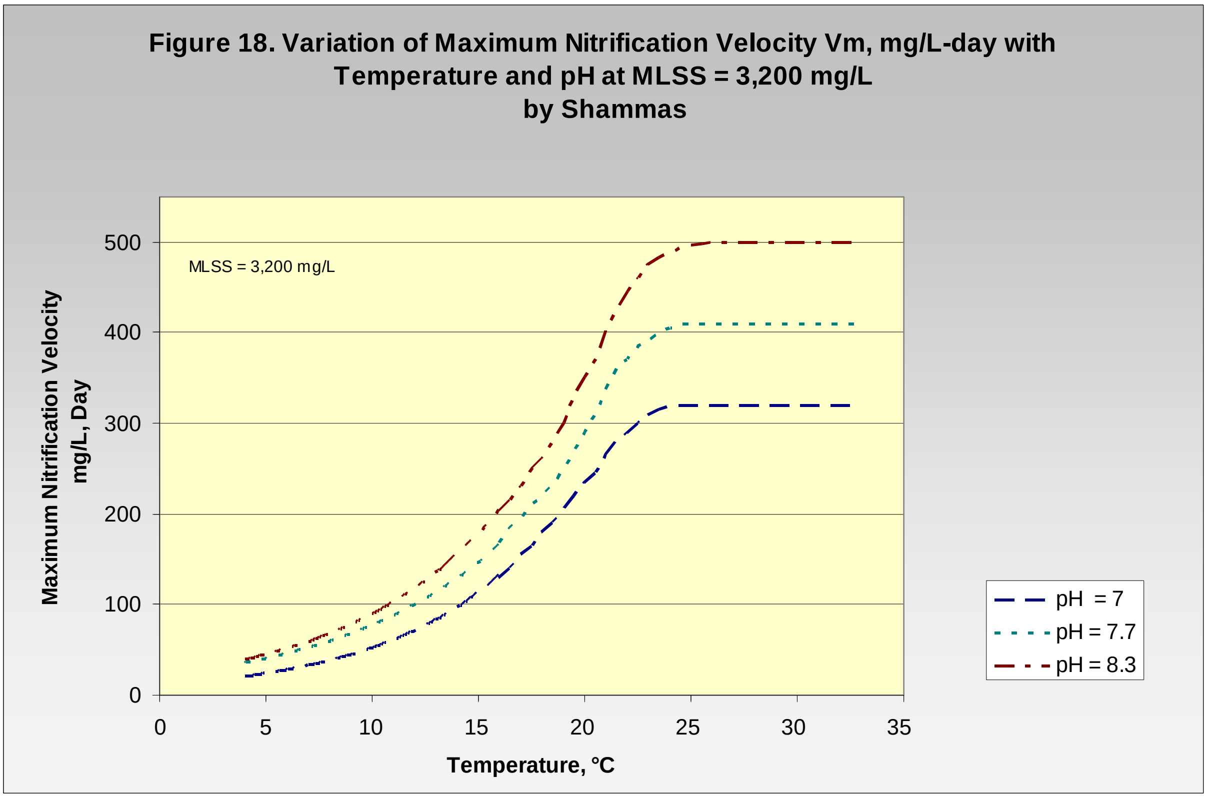

Figure 18. Variation of Maximum Nitrification Velocity Vm, mg/L-day with Temperature and pH at MLSS = 3,200 mg/L by Shammas

Shammas concludes that there was no interaction between pH and temperature in their effect on the nitrification rate; each affected the maximum nitrification rate independently. However, MLVSS concentration had an influence on the extent of temperature and pH effects. This work also showed that at the maximum MLVSS concentration run (3,200 mg/L), the maximum nitrification velocity was obtained at 33°C, the maximum temperature run during this work. This increases the temperature by 3° above that observed by Neufeld et al. for the maximum nitrification velocity.

Using the Monod constants determined by Shammas for several experimental temperature runs, an estimate of the nitrification temperature correction coefficient can be obtained. Figure 19 presents the solution for θ_n, the nitrification temperature correction coefficient using the modified Arrhenius equation described previously.

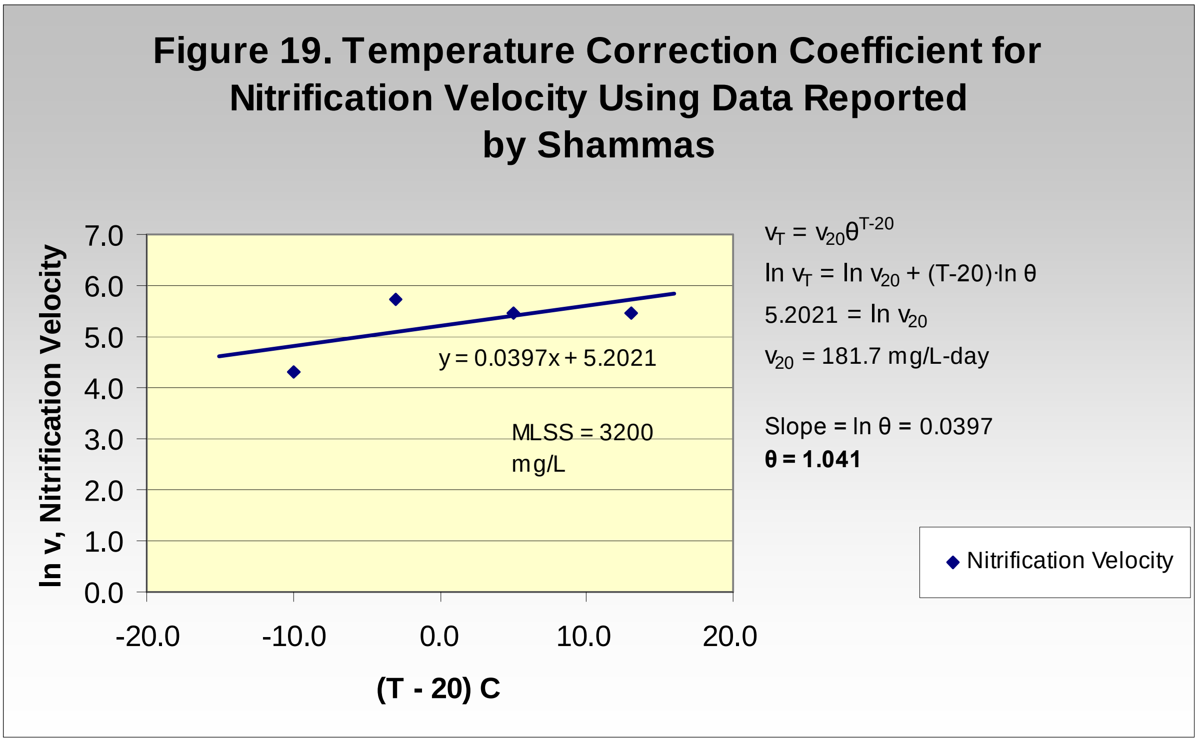

Figure 19. Temperature Correction Coefficient for Nitrification Velocity Using Data Reported by Shammas

The nitrification temperature correction coefficient calculates to 1.04, within the same range as that calculated using the data from Neufeld et al. (1.02 – 1.04) for temperature ≤ 30°C.

Sabalowsky (8) ran several high temperature bench-scale reactors to determine if consistent nitrification could be achieved at a local municipal wastewater treatment plant where 85% of the loading was contributed by industry, and summer wastewater temperature often exceeded 40°C. Sabalowsky evaluated several process configurations at a bench-scale level, including a separate nitrification step for the treated secondary effluent (post nitrification/denitrification), and a Modified Lutzack-Ettinger (MLE) process for the primary effluent.

Sabalowsky demonstrated that at “moderate” temperatures, 28 - 30°C, consistent nitrification and denitrification could be achieved with both secondary effluent and primary effluent (MLE) reactors. This baseline performance also demonstrated a lack of nitrification inhibitory compounds present in the wastewater, allowing the evaluation of nitrification at higher temperatures to take place.

In an attempt to simulate the sudden rise in wastewater temperature that occurred each spring, the operating temperature of the post nitrification/denitrification aerobic reactor (treatment of secondary effluent) was raised from 28°C to 39°C over a four-day period and then gradually increased to 47°C over the next 17-day period. Within seven days of the initial temperature increase, increases in effluent soluble Kjeldahl nitrogen (SKN) and ammonia nitrogen were observed. Nitrification, as measured by the increases in effluent ammonia and SKN concentrations, was severely inhibited within two weeks of the initial temperature increase and operating the aerobic reactor at a temperature ranging from 45°C to 47°C. This is the same maximum temperature range observed by Neufeld et al. where nitrification rates approached zero.

Sabalowsky also attempted to acclimate the nitrifying organisms to the high temperature operating condition of the wastewater treatment plant by gradually increasing the operating temperature of the bench-scale MLE process applied to the primary effluent from 30°C to 45°C, over a two month period. While effluent suspended solids were initially difficult to control at the elevated temperatures, some nitrification was observed as measured by the presence of nitrate in the effluent prior to bringing the anoxic reactor (to assess denitrification at the elevated temperature) on-line. Sabalowsky’s work demonstrated that some acclimation of nitrifying organisms is possible at elevated temperatures, however, long term acclimation may be required, and the system would likely be prone to upsets due to loss of solids in the effluent and poor mixed liquor suspended solids control.

CONCLUSIONS

The research work reviewed clearly demonstrated that elevated temperatures, such as those typically encountered in refinery wastewaters, can inhibit nitrification kinetics. Maximum nitrification kinetics are observed in the 30°C to 33°C temperature range. Nitrification rates decline with temperatures below and above 33°C and can be very well predicted using a modified Arrhenius equation. Over the temperature range of 5°C to 33°C, the following empirical relationship can be used:

$$v_{T\leq 33} = v_{20}\, \theta_{T\leq 33}^{(T-20)}$$

Where:
$v_{T\leq 33}$ = nitrification rate at temperature, T°C for temperature ≤ 33°C
v_{20} = nitrification rate at 20°C
$\theta_{T\leq 33}$ = computed nitrification temperature correction coefficient for T≤ 33°C; $\theta_{T\leq 33}$ = 1.04

When wastewater temperatures exceed 33°C, nitrification rates decline rapidly, and this rate of decline is much greater than that which occurs when temperature fall below 33°C . This, as described by Neufeld et al. may be due to chemical protein denaturing of the nitrifying bacteria.

When the observed nitrification rates for temperatures greater than 33°C are correlated using a modified Arrhenius equation, the following empirical relationship is derived:

$v_{T>33} = v_{33}\, \theta_{T>33}^{(33-T)}$
Where:
$v_{T>33}$ = nitrification rate at temperature, T°C for temperature >33°C
v_{33} = nitrification rate at 33°C
$\theta_{T>33}$ = computed nitrification temperature correction coefficient for T> 33°C; $\theta_{T>33}$ = 1.4

Thus, the nitrification rates for refinery activated sludge systems operating in the 35°C to 38°C temperature range, are estimated to be 50% to 18% respectively, of the maximum nitrification rate occurring at 33°C.

Shammas demonstrated that temperature and pH affect the nitrification rate independently. Three pH values were used in Shammas's ammonia oxidation experiments: pH 7.0, 7.7, and 8.3. Maximum nitrification rates occurred at pH 8.3, consistent with the earlier work of Wild et al.

A clear strategy for achieving maximum nitrification in high temperature wastewater environments would be to take advantage of the increased nitrification efficiency provided by operating at increased pH during high-temperature operating periods.

For instance, it is common for activated sludge systems to operate at a pH in the range of 7.2 to 7.4. Wild estimated that the optimum pH for nitrification occurs at pH 8.4. By increasing the operating pH of the aeration basin MLSS to pH 8.0 - 8.4 during elevated temperature periods, an estimated 50% increase in nitrification rate above that which would occur at pH 7.2 to 7.4 is possible. The higher operating pH also results in an equilibrium shift that favors the occurrence of free ammonia in solution. At pH 8.0 and a wastewater temperature of 35°C, approximately 10% of the ammonia in solution is as free ammonia. Free ammonia concentration must be limited to less than 10 mg/L to prevent ammonia toxicity. As long as influent ammonia concentration is less than 100 mg/l, pH adjustment to a pH of 8.0 can be implemented to maximize nitrification rates and overall nitrification performance. Influent ammonia concentrations less than 100 mg/L allow pH adjustment up to 8.4 to increase overall nitrification performance.

REFERENCES:

Wild, H.E., Sawyer, C.E., and McMahan, T.C., “Factors Affecting Nitrification Kinetics.” *Journal Water Pollution Control Federation*, 43(9): 1845 -1854

USEPA Technology Transfer Seminar Publication, “Nitrification and Denitrification Facilities.” EPA-625/4-73-004a Revised, (Revised February 1974)

Willers, H.C., Derikx, P.J.L., ten Have, P.J.W., and Vijin, T.K., “Nitrification Limitation in Animal Slurries at High Temperatures.” *Bioscience Technology*, 64: 47- 54

Neufeld, R.D., Greenfield, J.H., Hill, A. J., and Adekoya, D.O., “Nitrification Inhibition Biokinetics.” Project Summary, USEPA, Research and Development EPA-600/S2-83-111 (January 1984)

Neufeld, R.D., Greenfield, J.H., and Rieder, B., “Temperature, Cyanide and Phenolic Nitrification Inhibition.” *Water Resources*, 20(5): 633 - 642

Wong-Chong, G. and Hall, J.D. “Single Stage Nitrification of Coke Plant Wastewater.” *Symposium on Iron and Steel Pollution Abatement Technology*, Philadelphia, PA, pgs 395 – 456, EPA-600/9-81-017

Shammas, Nazih Kh. “Interactions of Temperature, pH, and Biomass on the Nitrification Process.” *Journal Water Pollution Control Federation*, 58(1):52 – 59

Sabalowsky, Andrew R. “An Investigation of the Feasibility of Nitrification and Denitrification of a Complex Industrial Wastewater with High Seasonal Temperatures.” Masters Thesis, Virginia Polytechnic Institute and State University, April 1999