FACTORS AFFECTING

THE PERFORMANCE

OF ACTIVATED SLUDGE IN A

MODIFIED LUDZACK ETTINGER PROCESS

FED WITH HIGH PURITY OXYGEN

by

PETER HAGAR

A Thesis

Submitted to the Faculty of Graduate Studies

in Partial Fulfilment of the Requirements

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Department of Civil and Geological Engineering

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ABSTRACT

This research studied activated sludge systems in a Modified
Lutzack Ettinger configuration, with high purity oxygen fed to
sealed aerobic reactors under a gauge pressure of 7 cm water.
Primary effluent was fed to two systems' anoxic reactors,
which were intended to denitrify recycled nitrate, that was
formed in the subsequent aerobic reactors. One system with an
aerobic HRT of 2 h nitrified up to 40% of the influent NH_3,
and denitrified no more than 4 mg/l NO_3-N in the 2 h anoxic
reactor at 12^0C, with fluctuating solids retention times
(SRT's) of 3-15 days. The other system, with an aerobic HRT
of 4.5 h showed a trend towards complete nitrification at 12^0C
with a stable SRT of 15 days, nitrifying nearly 80% of the
ammonia before the research was terminated, but mass balances
showed less than 4 mg/L NO_3-N denitrification in the 1.5 h
anoxic reactor. System mass balances showed further
denitrification, which was correlated to the amount recycled.
Analysis showed that the 1.5 h HRT was too short for complete
denitrification and that denitrification potential was
restricted due to limited carbon. Both systems showed
denitrification was inhibited by dissolved oxygen from recycle
streams. SOC removal was due to adsorption and could not be
correlated to nitrate removal. This was confirmed by a batch
study. Complete nitrification was obtained at 24^0C in the
larger system, but denitrification was poor.

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ACKNOWLEDGEMENTS

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NOMENCLATURE

ALK	Alkalinity
ANOXIC	Condition promoting nitrate reduction
APHA	American Public Health Association
ASCE	American Society of Civil Engineers
BOD	Biochemical Oxygen Demand
BSOC	Biodegradable Soluble Organic Carbon
C	Carbon
C/N or C:N	Carbon to Nitrogen Ratio
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
HRT	Hydraulic Retention Time
MCRT	Mean Cell Residence Time
MLE	Modified Ludzack Ettinger (process)
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids
NEWPCC	North End Water Pollution Control Centre
N	Nitrogen
NH_3	Ammonia
NH_3-N	Ammonia nitrogen
NO_2^-	Nitrite
NO_2-N	Nitrite nitrogen
NO_3^-	Nitrate
NO_3-N	Nitrate nitrogen
ORP	Oxidation-Reduction Potential

ORP	Oxidation-Reduction Potential
P	Phosphorous
Q or Q_{RAW}	Flow of raw wastewater
R	Recycle flow
R1	Reactor 1, the anoxic reactor
R2	Reactor 2, the aerobic reactor
RAS	Recycle Activated Sludge
SOC	Soluble Organic Carbon
SRT	Solids Retention Time
SS	Suspended Solids
TKN	Total Kjeldhal Nitrigen
TN	Total Nitrogen
TRAIN A	System with 1.5 hour HRT in anoxic reactor and 4.5 hour HRT in the aerobic reactor
TRAIN B	System with 2 hour HRt in anoxic reactor and 2 hour Hrt in th eaerobic reactor
TSS	Total Suspended Solids
WAS	Waste Activated Sludge

1.0 INTRODUCTION AND PURPOSE

Three key pollutants discharged into waterways are carbon (C), nitrogen (N), and phosphorous (P). Carbon and nitrogen compounds that are biodegradable will be degraded by microorganisms, but in doing so consume oxygen, possibly to the point of depleting oxygen to levels that are too low for fish to survive. Nitrogen and phosphorous are key nutrients required by microorganisms, and their presence can stimulate microbial populations because they are the limiting factors restricting the population, rather than carbon.

Phosphorous is often considered the most critical nutrient, but the role of nitrogen must also be recognized, and its effect as a pollutant goes beyond being a nutrient that may stimulate carbon consuming microbial populations.

Nitrogen can exist in several forms which can cause different problems. As ammonia, particularly as un-ionized NH_3 rather than ionized NH_4^+, it is toxic to fish and other lifeforms. Both forms exert a chlorine demand during chlorination of potable water or wastewater, and residual chlorinated amines from wastewater chlorination are also toxic to fish. Ammonia is also corrosive to copper, which is important for industries using water for cooling purposes, where copper heat exchangers are common.

Nitrogen in the form of nitrate (NO_3^-) or nitrite (NO_2^-) has the potential to cause methaemoglobinaemia, particularly in infants 3-6 months of age (Hammer 1986). Nitrate levels are restricted in potable water supplies by many countries.

One common source of nitrogen and phosphorous in water supplies is the discharge from sewage treatment plants, many of which provide high levels of carbon removal.

The North End Water Pollution Control Centre (NEWPCC) is the largest of the City of Winnipeg's three wastewater treatment plants. It has been able to meet the carbon removal requirements (as carbonaceous biological oxygen demand) using a high purity oxygen activated sludge system within the design hydraulic retention time (HRT) of 2.16 hours. Sears (1995a) indicated that ammonia discharges from Winnipeg's wastewater control centres are the reason that concentrations of un-ionized ammonia (NH_3) sometimes exceed the Manitoba Surface Water Quality Guideline Objectives in certain areas of the Red and Assiniboine Rivers.

A study by Wardrop/TetrES (1991) reviewed measures to reduce ammonia loadings and concluded that nitrification of ammonia, which is the biological conversion of ammonia to nitrate, would require significant capital expenditures at the NEWPCC.

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The purpose of this research project conducted at the University of Manitoba was to study the Modified Ludzack Ettinger configuration, which consists of an anoxic reactor ahead of an aerobic reactor, with recycle from the aerobic reactor and the clarifier to the anoxic reactor. This system was to be constructed such that the aerobic reactor would have a sealed headspace and be fed high purity oxygen. The conditions the research system would have would thus reflect the conditions of a full scale high purity oxygen plant such as the NEWPCC. This document presents the findings of the research conducted on nitrification and denitrification, suggests that there are limits to performance and design, and recommends areas for additional research.

LITERATURE REVIEW

2.1   Biological Nitrogen Removal Principles

Some nitrogen cannot easily be broken down and will leave the
treatment process as a point source of nitrogen in the
receiving stream. Some nitrogen is incorporated into the
biomass that forms the activated sludge, and some nitrogen in
solids may be removed in primary clarification. The focus of
biological nitrogen removal is on the remainder of the
biodegradable nitrogen.

Figure 2-1 shows some of the transformations of nitrogen in a
biological treatment process. The first step is the bacterial
decomposition and hydrolysis of the organic nitrogen to
ammonia. The next step, called nitritification, converts the
ammonia to nitrite (NO_2^-). Nitritification is generally
considered to be a step carried out by a group of
microorganisms called *Nitrosomonas*.

Nitritification is almost immediately followed by conversion
of the nitrite to nitrate (NO_3), called nitratification.
Nitratification is generally considered to be carried out by
a group of microorganisms called *Nitrobacter*.   The two
microorganism groups, called nitrifiers, are autotrophs, which
Prescott et al. (1993) define as organisms that obtain their

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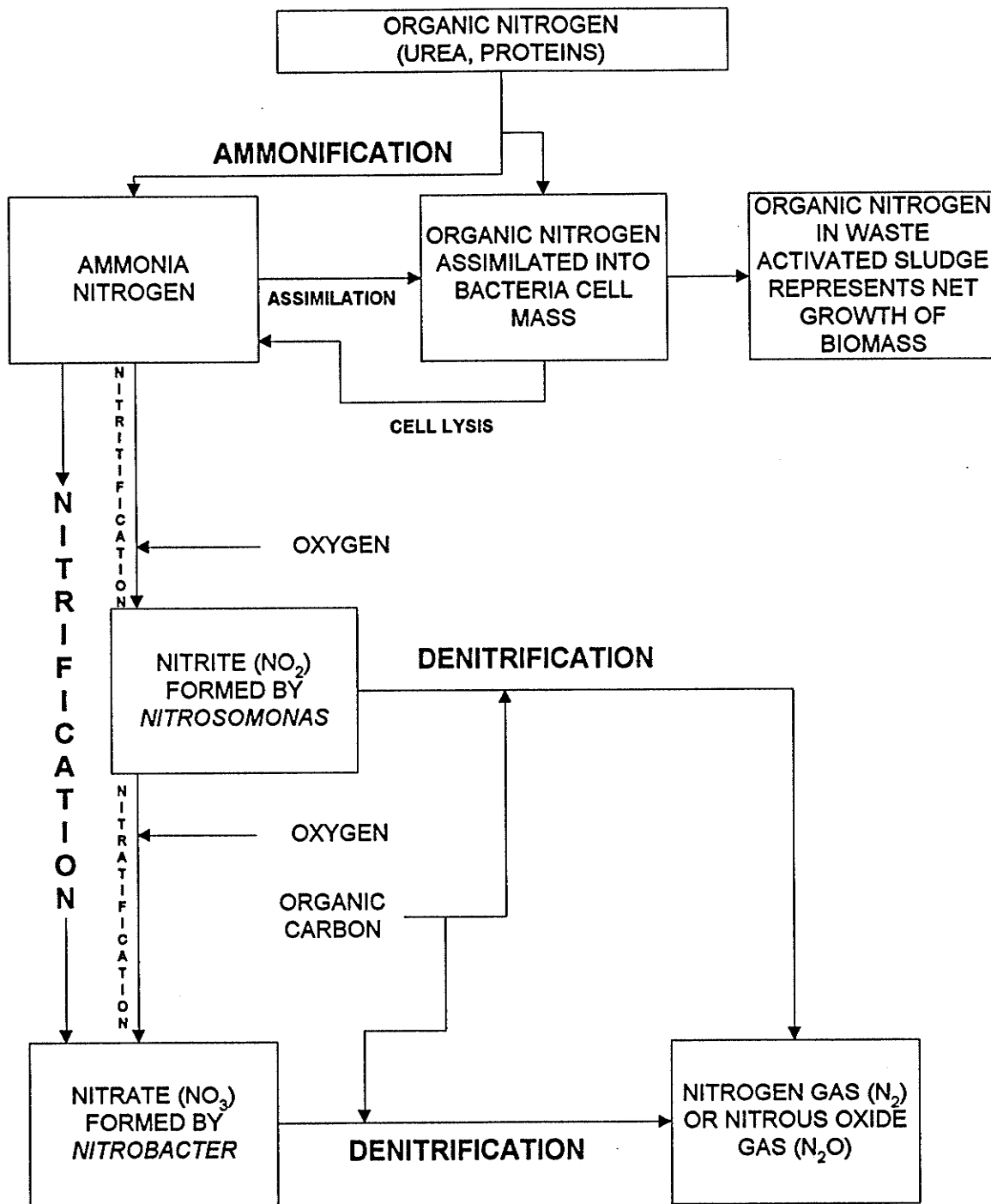
Figure 2-1: Transformations of Nitrogen in
Biological Treatment

carbon from CO_2.

The two step conversion of ammonia to nitrate is referred to as nitrification. Metcalf and Eddy (1991) indicate that the conversion of nitrite to nitrate is usually rapid and essentially complete, so little nitrite is noticed. Thus the overall nitrification process is typically limited by the performance of *Nitrosomonas.*

Randall et al. (1992) noted that other autotrophic genera such as *Nitrosococcus* and *Nitrospira* also nitrify, as do some heterotrophic bacteria, fungi and actinomycetes. He indicated that the heterotrophic rates are one tenth those of the autotrophs, and that in wastewater treatment, *Nitrosomonas* and *Nitrobacter* are the autotrophs that predominate.

The chemistry of the nitrification reactions, from McCarty et al. (1970), are:

$$NH_4^+ + 1.5\ O_2\ ---Nitrosomonas--> NO_2^- + 2H^+ + 2H_2O$$
$\Delta G^0 = -65.0$ kJ (from Prescott et al. 1993)

$$NO_2^- + 0.5\ O_2\ ---Nitrobacter--> NO_3^-$$
$\Delta G^0 = -17.4$ kJ (from Prescott et al. 1993).
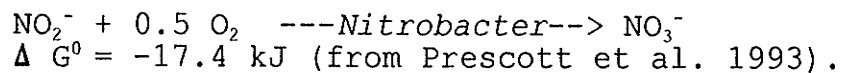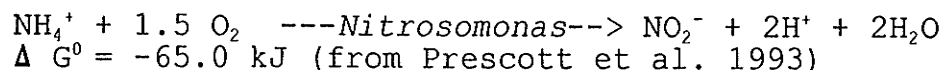
The nitritification step produces H^+, which consumes alkalinity in the system. The stoichiometric equation that accounts for cell synthesis, with a cell formula of $C_5H_7NO_3$, is

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given by EPA (1975) as:

$$NH_4^+ + 1.83O_2 + 198HCO_3 \text{ --nitrifiers--> } 0.021C_5H_7NO_3 + 1.041H_2O$$
$$+ 0.98NO_3 + 1.88H_2CO_3$$
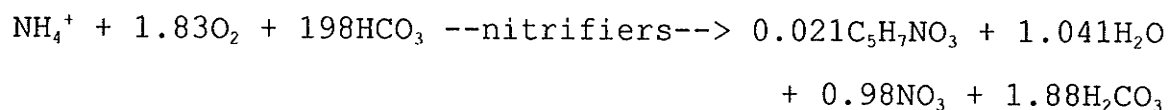
From the above equation, conversion of 1.00 gram of ammonia nitrogen consumes 7.14 grams of alkalinity. The equation also demonstrates that the nitrifiers require 4.18 grams of oxygen in order to make the conversion to NO_3. In activated sludge, nitrifiers must compete for oxygen with organic carbon using heterotrophs.

Conversion of ammonia to nitrate does not remove the nitrogen, but merely changes its form. This means that the nutrient loading to a receiving stream is changed very little by the nitrification process. In order to actually remove nitrogen, the final step of denitrification is required.

The stoichiometric equation describing the denitrification process that accounts for cell synthesis, with a cell formula of $C_5H_7NO_3$ and using methanol as an organic carbon source, is given by EPA (1975) as:

$$NO_3^- + 1.08CH_3OH + 0.24H_2CO_3 \text{ --denitrifiers--> } 0.06\ C_5H_7NO_3 + 0.47N_2$$
$$+ 1.68\ H_2O + HCO_3^-$$
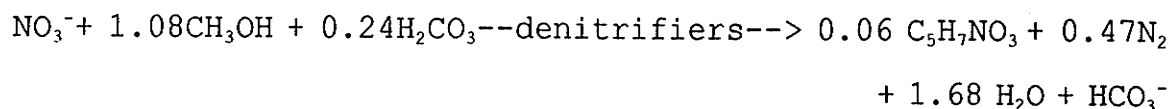
From this equation, the conversion of 1.00 grams of nitrate to nitrogen gas requires 0.93 grams of organic carbon and produces 3.47 grams of alkalinity. Thus the nitrification and denitrification process together consumes about 3.7 (7.14-3.47) grams of alkalinity per gram of ammonia nitrogen removed.

The "denitrifiers" are heterotrophic, and EPA (1975) indicated that they are ubiquitous in most natural environments, as well as in activated sludge. Monteith et al. (1979) listed *Pseudomonas, Micrococcus, Archromobacter,* and *Bacillus* as capable of denitrification. Metcalf and Eddy (1991) stated that denitrification takes place under anoxic conditions, where, due to the absence of oxygen, nitrate or nitrite serves as the electron acceptor.

Sawyer and McCarty (1978) reported that the aerobic degradation of acetate has a ΔG of -105.8 kJ. In anoxic denitrification the degradation ΔG is -99.4 kJ, whereas in anaerobic degradation of acetate with SO_4 or H_2O as the electron acceptor, the ΔGs are -6.4 and -3.6 kJ respectively. From this it can be seen that denitrification under anoxic conditions provides much more energy for microorganism growth than anaerobic reactions, and nearly as much as under aerobic conditions.

Sherrard and Silvasubramanian (1978) pointed out that nitrate reduction is actually classified as assimilatory or dissimilatory denitrification. Assimilatory denitrification converts the nitrate to ammonia, which is assimilated by the microorganism for use in synthesis reactions. Dissimilatory denitrification results in conversion to the gaseous end products NO, N_2 and N_2O, which dissimilate into the environment.

Sherrard and Silvasubramanian (1978) mentioned that the assimilatory process is both an anaerobic and aerobic process, whereas dissimilatory denitrification is an anaerobic one, although Metcalf and Eddy (1991) noted that the term anoxic is more appropriate. It is the latter process that is important in wastewater denitrification.

Grady and Lim (1980) indicated that the biochemistry of the dissimilatory denitrification pathway was not well understood, but the general model, given by Metcalf and Eddy (1991) as:

$$NO_3 \rightarrow NO_2 \rightarrow NO \rightarrow N_2O \rightarrow N_2$$
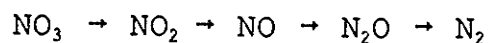
is essentially a simplified version of the pathway proposed by Fewson and Nicholas (1961):

Oxidation State of Nitrogen

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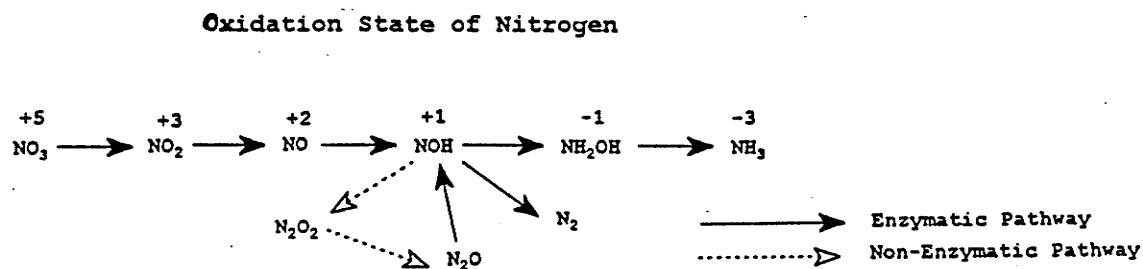
Payne (1981) reported that the pseudomonads are the predominant denitrifiers in wastewater systems, and are able to use substrates such as methanol, organic acids or carbohydrates with nitrate or nitrite.

Other microorganisms can denitrify. One group of microorganisms whose denitrifying capabilities are of significance is the phosphorous removing bacteria, *Acinetobacter*. Danesh (1995) demonstrated denitrification with simultaneous luxury uptake of phosphorous in SBR's, corroborating the findings of Barker and Dold (1995). Wentzel et al. (1989a,b) indicated that bench scale systems with phosphorous removing organisms had minimal denitrification rates, whereas Barker and Dold (1995) achieved rates comparable to other heterotrophs.

Zitomer and Speece (1993) noted the denitrifying capabilities of autotrophic bacteria *Paracoccus denitrificans*, and *Thiobacillus denitrificans*. The latter was used in bench scale in packed bed reactors containing elemental sulphur. Batchelor and Lawrence (1978) reported that applicability depended upon the price of methanol and sulphur.

2.2 FACTORS AFFECTING NITRIFICATION

2.2.1 CARBON

As noted previously, there is a competition between heterotrophs and autotrophs for oxygen. The higher the carbon-to-nitrogen (C/N) ratio, the greater the substrate for the heterotrophs, and the higher their demand for oxygen. It is due to the inequality of this competition for oxygen, where the heterotrophs utilize the majority of the oxygen, that the process of nitrification becomes difficult and, from the engineering standpoint, costly.

Hanaki (1990a, 1990b) demonstrated that the presence of biodegradable carbon inhibited ammonia oxidation, inhibition being exacerbated by low dissolved oxygen (DO) levels, apparently due to competition with heterotrophs. Hanaki (1990a) hypothesized that heterotrophs, which assimilate ammonia, hinder the transport of ammonia to the nitrifiers. If this were the case, then high doses of ammonia or lower C/N levels should increase the rate of nitrification at low DO levels; that is, if the autotrophs are competitive with the heterotrophs and get the oxygen, then nothing should stop their progress. However, Hanaki's own results showed that at DO levels below 0.5 mg ammonia oxidation was inhibited, indicating that heterotrophs are winning the competition for

oxygen, not ammonia.

Because of this competition for oxygen, sewage treatment is
sometimes considered a two step process: the first stage of
carbonaceous oxidation, the second of nitrification.
Treatments plants that have to nitrify are sometimes designed
in a two stage process, or as a single stage process where
both processes occur, although the size is dictated by
nitrification considerations.

2.2.2   SOLIDS RETENTION TIME (SRT)

McKinney (1962) is credited with describing the biological
basis in activated sludge for biochemical oxygen demand (BOD)
removal, but Marais (1973) described the process in terms of
solids retention time (SRT). Downing et al. (1964) originally
advanced the SRT concept, in particular regarding
nitrification. He indicated that below a certain SRT - later
defined as the minimum SRT for nitrification (SRT_{min}) - the
nitrifying population would be "washed out", losing
nitrification. Burchett and Tchobanoglous (1974) recommended
SRT or MCRT (mean cell residence time) as the means of control
of activated sludge process.

Jones and Sabra (1980) extended Marais' theory using SRT as
the key parameter to nitrification and denitrification

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processes, giving each an SRT based on the fraction of reactor space that was aerated (for nitrification) and anoxic (for denitrification). This has led to the terms: aerobic SRT, which is used to determine SRT_{min}, anoxic SRT, and System SRT (SSRT). Research into nitrification in a system having both aerobic and anoxic zones could then be done using the aerobic SRT as a key parameter, and compared to results in a conventional aerated system using its SSRT.

The SRT can be increased to build up solids levels and allow further conversion in the case of nitrification (Burchett and Tchobanoglous (1974)), or the degradation of resistant compounds, such as phenolics (Holladay et al. (1978)). However, the typical application of SRT was to keep the SRT low so as to avoid nitrification. Wild et al. (1971) reported that from 1940 until the late 1960's, the main objective in the United States was to minimize nitrification, because BOD removal could be removed at much lower cost without nitrification. The biological treatment plants of the 1930's were designed to produce a highly nitrified effluent that would not putrefy.

Another problem with nitrified sludge was that it could denitrify in the clarifier resulting in a loss ("bulking") of solids out of the system, which could lead to fines as a result of not meeting the environmental discharge criteria for

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suspended solids. Henze et al. (1993) indicated that at 20^0C, rising sludge from denitrification in the clarifier could be expected if the nitrate level were around 6-8 mg/l.

2.2.3   pH AND ALKALINITY

Downing and Knowles (1967) described nitrifier growth rate as a function of pH:

$$\frac{\mu}{\mu_{max}} = 0.833 * pH - 4.998 \qquad (5.9 \leq pH < 7.2)$$

where: μ =   specific growth rate of *Nitrosomonas*, 1/day

μ_{max} =   maximum specific growth rate of *Nitrosomonas*, 1/day

Hong and Anderson (1993) gave an unpublished correlation in the form of a polynomial equation found by researchers of the pure oxygen activated sludge system:

$$\frac{\mu}{\mu_{max}} = -0.7166 * pH^2 + 10.415 * pH - 34.8744 \qquad (5.9 \leq pH < 7.2)$$

Painter and Loveless (1983) studied nitrifying organisms with sewage as feed, at different pH values and three temperatures. The highest rate for nitrification was 0.61 /day at a pH of 7.0. However, no nitrification occurred at pH of 6.0 under temperatures as high as 25^0C, with HRT's of at least 8 hours

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and sludge growth rates of 2-5% per day, which translates to an SRT of >20 days, since the sludge wastage per day to maintain an SRT is the same as the growth rate per day. Thus 1/0.05 gives 20 days. The study did not give alkalinity, but BOD values in the influent were 150-200 mg/l with ammonia levels of 50-60 mg/l. The inability to nitrify at pH of 6.0 agreed with previous results indicating a pH threshold at 6.2.

Wild et al. (1971) found optimum pH for nitrification at 8.4 and a rate 15% of the optimum at pH of 6.0. Haug and McCarty (1972) could not nitrify at a pH of 5.5. Conversely, Stankewich (1972) achieved nitrification at pH's as low as 5.8 and temperatures of 20^0C using pure oxygen feed in pilot scale and Sears (1995a) was able to achieve nitrification at pH of 5.5, also using pure oxygen feed in lab scale reactors.

Anthonisen et al. (1976) explained the upper pH limit as being due to the presence of free ammonia, which is in equilibrium with NH_4^+ but in greater proportion at higher pH, and the lower limit as due to the accumulation of free nitrous acid (HNO_2^-) which exists in equilibrium with nitrite (NO_2^-), but in greater proportion at lower pH. Anthonisen et al. (1976) stated that although there appeared to be a pH threshold, the research did not allow for acclimation.

One important difference between the studies of Stankewich

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(1972) and Sears (1995a) that nitrified, and those such as Wild et al. (1971), Haug and McCarty (1972) and Painter and Loveless (1983) that did not, is that the pH in the pure oxygen systems formed naturally as a result of containment of CO_2 in the sealed reactor headspace and alkalinity destruction due to nitrification. The other researchers, who did not have a sealed headspace, appear to have adjusted the pH of their systems with acid, which would have consumed the alkalinity.

Alkalinity is required by the nitrifiers, so it can be considered a substrate for the nitrifiers, and perhaps a diffusion limitation exists at low concentrations. Carbon dioxide may also be thought of as a substrate for the nitrifiers. Thus in the cases of Sears' (1995a) and Stankewich's (1972) research there may also have been an effect from increasing the carbon source for the nitrifiers, which is carbon dioxide.

2.2.4   TEMPERATURE

Temperature is a significant factor affecting nitrification, and one area of interest to researchers is nitrification at low temperatures. Adams and Eckenfelder (1974) cited a nitrification optimum of 28^0C-32^0C, with cessation below 5^0C; and recommended that serious consideration be given to the feasibility of nitrification at 12^0C.

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Sears' (1995a) results were achieved at 12⁰C and 22⁰C.
Oleszkiewicz and Berquist (1988) achieved nitrification at
temperatures as low as 2⁰C by increasing the SSRT. Sutton et
al. (1978) studied systems at various temperatures, nitrifying
at 7⁰C, but had to increase system HRT's and SRT's in order to
nitrify.

According to Levenspiel (1972), many chemical reaction rates
are functions of temperature, and follow Arrhenius' Law,
defined by:

$$K = Ae^{-E/RT}$$

where: A is a constant, moles/time

   E is the activation energy, joules/mole

   R is the gas constant, joules/mole∘K

   T is the absolute temperature, degrees Kelvin

   K is the rate of reaction, moles/time

This equation has been applied to chemical reactions and,
according to Johnson and Schroepner (1964), to some microbial
reactions.

Like other microbial processes, nitrification kinetics
exhibited Arrhenius behaviour in several studies but the
temperature range of study was important, as demonstrated by
Henry (1974). Henry noted that at lower temperatures,
Arrhenius plots of 30 pure cultures deviated from the straight

line of log K vs 1/T that indicates Arrhenius behaviour.

Oleszkiewicz and Berquist (1988) reported that the nitrification and denitrification kinetics in their SBR system exhibited discontinuous Arrhenius behaviour, with 7^0C being the critical point.

Painter and Loveless (1983) reported similar Arrhenius behaviour, and attributed the differences between the published results to undefined environmental factors. He warned that using the published results should not be used in the case of weak wastewaters. One reason for this is that weak wastewaters may have a different carbon to nitrogen ratio, which affects nitrification. In addition, Ulmgren (1974) reported that in northern Sweden, biological processes were incapable of removing BOD from dilute wastewater at cold temperatures and low biomass levels. Because of this, solids losses typical for a clarifier (20 mg/l) lowered the SRT's to below the SRT_{min} needed for nitrification. Knight (1980) noted a similar problem in the two-stage nitrification Egan Plant, where underloading resulted in the MLSS of the second aerobic reactor falling below 500 ppm, with a loss of nitrification efficiency.

2.2.5   OXYGEN

The recommended dissolved oxygen (DO) level for nitrification varies. At least 2 mg/l DO is recommended by Metcalf & Eddy (1991) and EPA (1993). Adams and Eckenfelder (1974) suggested that a nitrification system be design at 2.5-3 mg/l, but indicated that lab systems had achieved nitrification at levels below 1 mg/l. Nagel and Haworth (1969) found that nitrification rates doubled when the DO was increased from 1 mg/l to 3 mg/l.

Stentstrom and Song (1991) found that during organic shocks loads, the limiting DO was as high as 4 mg/l. Benefield and Randall (1980) reported on pilot studies with weak wastewaters and indicated maximum nitrification efficiency at DO's of 1 mg/l or higher, suggesting that there was less competition for the oxygen.

Knight (1980) observed that power failures lowered DO concentrations, leading to drops in nitrification efficiency.

2.2.6   TOXINS

In conducting a BOD test, it is important to inhibit the nitrifiers so that only the carbonaceous BOD is given. APHA's "Standard Methods of Water and Wastewater Analysis" (1989)

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recommends 2-chloro-6(trichloromethyl) pyridine to inhibit the nitrifiers. Other compounds are inhibitory to nitrifiers, amine compounds in particular receiving attention from Hockenbury and Grady (1977).

One concern in treatment plants is the polymers used to help dewater solids in centrifuges, which can return in the centrate to the activated sludge units. If the centrate is high in carbon compounds, then the impact of centrate may be the combination of the additional carbon load as well as the polymer, some of which Randall et al. (1992) noted are toxic to *Nitrosomonas*.

Barnes and Bliss (1983) reported that nitrification is inhibited by a wide variety of organic and inorganic inhibitors, heavy metals being the most significant inorganic inhibitors.

One of the problems with an upset to a nitrifying population is its restoration. Knight (1980) indicated that after a four hour power failure, the effect on nitrification efficiency lasted from the time of the power outage in early December until well into February. A previous repair work resulted in loss of nitrification efficiency that lasted several days.

2.3 FACTORS AFFECTING DENITRIFICATION

2.3.1 OXYGEN

Barnes and Bliss (1983) indicated that for most cases optimum
results would occur with zero dissolved oxygen concentration.
Barnes and Bliss (1983) indicated that under conditions where
the dissolved oxygen is low or zero an alternative electron
acceptor to oxygen is required, with nitrate being the
electron acceptor that is most favoured. They indicated that
since a nitrified wastewater would have a larger concentration
of nitrate than other competing ions such as sulphate,
biological denitrification could be expected to occur, and
defined such low or zero dissolved oxygen conditions as anoxic
in order to distinguish them from other anaerobic processes.

Grady and Lim (1980) reported that the effect of oxygen upon
nitrate reduction is upon the enzyme system. They stated that
one effect of oxygen is that it represses the synthesis of the
nitrate reducing enzyme, so that the enzyme is not synthesized
until there is an oxygen deficiency. Körner and Zumft (1989)
concurred, noting that enzyme synthesis was reduced to a low
level in the presence of oxygen. Von Schulthess et al. (1994)
added that enzyme activity was inhibited by oxygen.

Skerman and MacRae (1957), Terai and Mori (1975), and Dawson

and Murphy (1972a) reported inhibition of denitrification of a *Pseudomonas* culture treating domestic sewage at DO levels of 0.2 and above. Grady and Lim (1980) indicated that the floc structure complicates the determination of oxygen's effects upon denitrification, as large flocs may have an inner region with no oxygen, allowing denitrification in an aerobic medium.

Grady (1989) indicated that the IAWPRC model uses a Monod kinetic term in denitrification to account for DO inhibition, that switches denitrification on and off with varying O_2 concentration. It is coupled with a similar term for aerobic growth so that the model does not give an exact kinetic expression, but switches to start-and-stop aerobic and anoxic processes. Grady (1989) indicated that experimental evidence justified the use of these switching functions, but pointed out that the form of the kinetic term for denitrification deserved further study, in particular possibly separating reduction of NO_2 from NO_3.

Von Schulthess et al. (1994) obtained denitrification rates at DO levels of 0, 0.5, 1, 2 and 4 mg O_2/l, noting higher N_2O and minimal NO production at the higher oxygen levels, and maximum NO and N_2 production at 0 mg O_2/l. They indicated that oxygen inhibited the fast reduction rate of N_2O, more than it inhibited the reduction of either nitrate or nitrite.

2.3.2   pH

EPA (1975) and Moore and Schroeder (1971) reported an optimum denitrification rate between pH's of 6.5 and 7.5, with 70% of the optimum rate at pH's of 6 and 8. Dawson and Murphy (1972a) found an optimum denitrification rate at pH 7, with 50% of the optimum rate at 6 and 8. Randall et al. (1992) reported that other researchers have found a linear decrease in efficiency as pH declined from 7.0 to 4.0, or as pH rose from 8.0 to 9.5.

2.3.3   TEMPERATURE

Dawson (1971) reported Arrhenius type behaviour for denitrification between 3^0C and 27^0C. Stensel (1971), observed Arrhenius behaviour between 10^0C and 20^0C, but not between 20^0C and 30^0C for a continuous flow through system, and also observed Arrhenius behaviour in batch studies from 15^0C-25^0C. Sutton et al. (1974a) showed that Arrhenius type behaviour could predict denitrification kinetics in the 5^0C-25^0C range for both continuous stirred tank reactors and upflow packed column reactors, using a weighted least squares method to fit the data. Sutton et al. (1974b) indicated that a previous study by Dawson and Murphy (1973) resulted in denitrification effectively ceasing at 3^0C although the Arrhenius plot by Dawson and Murphy (1972b) included a point at 3^0C, which did

fit within the 95% confidence interval; this is the same point referred to by Sutton et al. (1974b).

Sutton et al.(1978) reported good agreement on an Arrhenius plot between data from researchers using methanol, and results using raw sewage as the carbon source for denitrification. They also demonstrated little temperature effect on denitrification relying on endogenous respiration, which Barnard (1974) stated was highly temperature sensitive.

2.3.4   SRT

Sutton et al. (1974a) reported different denitrification rates at different SRT's for different temperatures. The rate at a three day SRT was 1.5 times that of the six day SRT at 6°C.

Sutton et al. (1978) reported further experiments indicating the same trend during endogenous respiration, citing corroborating research by Stern and Marais (1974). Christensen and Harremoës' (1977) also found that the denitrification rate decreased as the aerobic SRT increased.

The HRT of the different reactors is a factor which determines the anoxic and aerobic SRT's. Therefore, the HRT must be considered as a parameter which can affect the aerobic and anoxic SRT's in nitrification/denitrification systems.

2.3.5   CARBON SOURCE

Organic carbon is critical, being a substrate in the heterotrophic denitrification reaction. There is degradable carbon in the wastewater in some but not all cases, particularly with industrial wastes, so alternate carbon sources have been sought for many years to carry out denitrification reactions.

The degradability or form of carbon is important, and methanol was considered the best source by McCarty et al. (1970) due to its economical cost and low sludge yield. Barnard (1975) showed that in raw wastewater there are three types of carbon sources that give different rates of denitrification: soluble easily degraded compounds such as acetic acid, slowly hydrolysed hydrocarbon compounds, and carbon from the microbial mass, or endogenous carbon.

Several authors have studied different compounds, with the consensus being that methanol was the most cost effective. However, Bell (1994) reported that the cost of methanol had risen from $0.40/USgal in 1993 to $1.55 by the end of 1994, fuelled by a surge in demand for cleaner burning fuels. While one broker suggested that the cost would drop to an equilibrium value of about $0.55/USgal by 1997, it seems that there is an economic incentive to find alternative carbon sources.

One area of research in waste treatment is fermentation of primary sludge, which utilizes the incoming carbon and converts it to a form more readily used by microorganisms removing phosphorous or nitrogen.

One problem with primary sludge fermentation is that methane production tends to occur. Danesh (1995) has successfully fermented raw wastewater in a controlled sequencing batch reactor (SBR), rather than using primary sludge in a subsequent SBR system for nutrient removal. This approach has avoided methanogenesis and produced more than 90% acetic acid, whereas primary sludge fermentation yields no more than 60% acetic acid. Acetic acid is regarded as the most usable volatile fatty acid for phosphorous or nitrogen removal.

One goal of engineering design is to maximize the use of highly degradable carbon for nutrient removal. Before nitrate can be denitrified ammonia has to be converted to nitrate which, as noted above, requires the absence of organic carbon, because the nitrifiers have to compete for oxygen. The result of research into nitrification and denitrification has been the development of different processes that have the same objective. The Modified Ludzack Ettinger process is one and is discussed in the next Section.

2.4 The Modified Ludzack Ettinger Process

Several nitrogen and phosphorous removal processes have been developed, with differences occurring in some of the recycle points, or number of stages. Examples of some are Bardenpho (with three, four and five stage processes), University of Capetown (UCT) and University of Virginia (VIP) (Metcalf and Eddy 1991).

For nitrogen removal only, a simple process which uses an anoxic reactor followed by an aerobic reactor with recycle was investigated by Ludzak and Ettinger (1962). It is called the Modified Ludzak Ettinger process (MLE), and is shown in Figure 2-2.

Kunihiro et al.'s (1993) review of the 24 suggested plant retrofits at Chesapeake Bay indicated that 9 were recommended to adopt the MLE system. This indicates that the MLE system can be practically applied and warrants further research.

Each process requires a certain amount of carbon. The carbon-to-phosphorous or carbon-to-nitrogen ratios are used for process design. Carley (1988) indicated that a COD:TKN ratio of 6.2:1 was considered sufficient for denitrification, with methanol as a carbon source. Elefsiniotis et al. (1989) found that recycle ratios above 6Q:1Q were unstable, using Carley's

INFLUENT

PREDENITRIFICATION
REACTOR

AEROBIC
REACTOR

CLARIFIER

EFFLUENT

RECYCLE
FROM
AEROBIC
REACTOR

RECYCLE ACTIVATED SLUDGE (RAS)
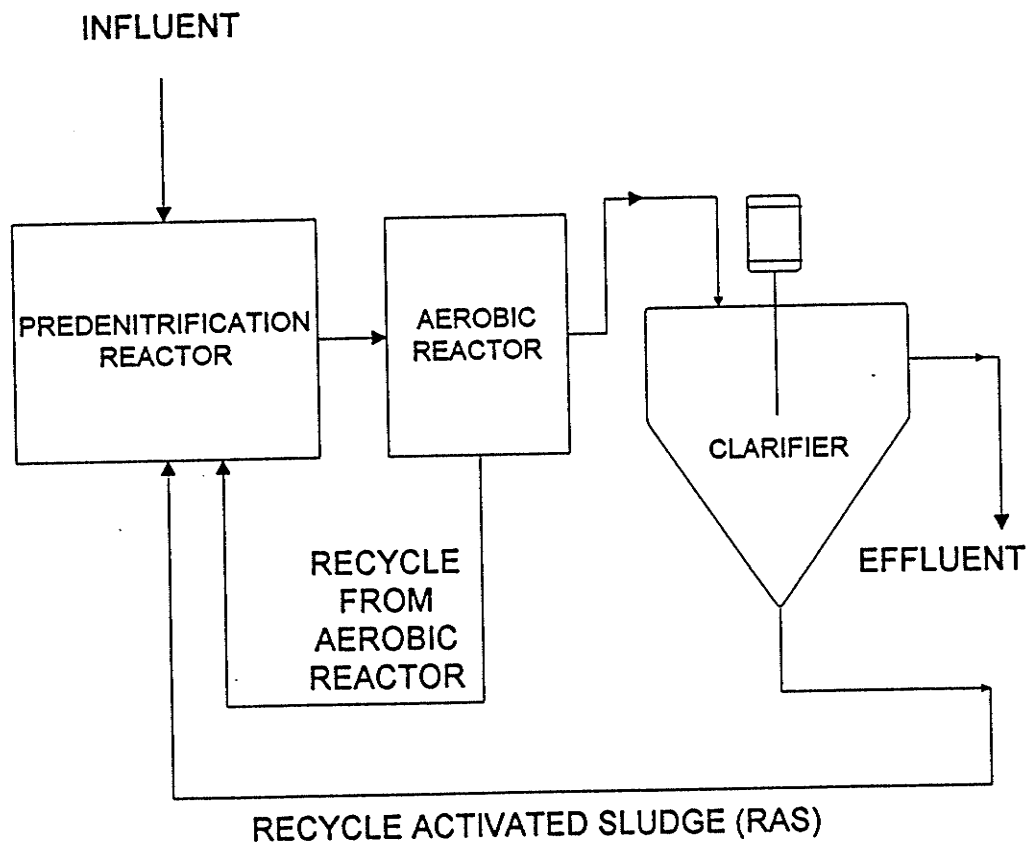
Figure 2-2:   Schematic of MLE System

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COD:TKN ratio. The ultimate nitrogen removal depends upon the amount of recycled nitrate, which Brannan and Randall (1987) have indicated has an economic limit at a recycle ratio of 4:1, which is less than the unstable performance level found by Elefsiniotis et al. (1989).

In the processes removing phosphorous and nitrogen, the carbon requirement is higher, in order to remove the phosphorous. Ekama and Marais (1984) recommended that when the COD/TKN ratio is less than 9.5, the MLE system should be selected instead of the Bardenpho system, which removes nitrogen and phosphorous. This implies that another means of phosphorous removal is required because the MLE system does not remove phosphorous.

2.4 PURE OXYGEN SYSTEMS

Caponetto (1994) studied the MLE process using pure oxygen rather than air, and indicated that such a study was the first she could find to do so.

One problem encountered in her pilot scale research was that the aerobic reactor which was fed pure oxygen was not sealed, thus allowing considerable amounts of CO_2 to escape. This prevented a large drop in pH which may have allowed nitrification to proceed in the pilot scale, whereas Zaleski

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(1993) indicated that the simultaneous full-scale trial experienced pH fluctuations and loss of nitrification more than once during the trial.

Speece and Humenick (1973) pointed out that one way to allow nitrification to proceed was to open one of the sealed reactors to vent CO_2, to avoid the pH drop, thereby allowing nitrification. This comes at the expense of wasted oxygen, but the authors claim the loss is small.

Hong and Andersen (1993) compared the pH drop with the fraction of nitrifiers and concluded that without CO_2 stripping, the HRT of a pure oxygen system would have to be double that of an air fed system. They also indicated that biological nutrient removal in a pure oxygen system required stripping of CO_2 from the second stage of a four stage reactor system for practical reasons, although the ideal point of CO_2 removal is the first stage.

Therefore pure oxygen plants that must meet today's more stringent ammonia discharge limits face a difficult and potentially costly challenge. Furthermore, with the trend towards nutrient removal, the pure oxygen system process must prove itself capable of meeting such targets economically, if new pure oxygen plants are to be built.

The advantages the ASCE (1983) gave for pure oxygen over conventional air feed are that high oxygen transfer rates can be met with low power inputs while maintaining a high DO residual, can operate at higher substrate loading rates, and can also operate at high MLSS levels, while exhibiting good sludge settling characteristics.

In a system that is to nitrify and denitrify, or remove phosphorous, some of these benefits may not apply. For instance, the MLE and phosphorous removal processes begin with an anoxic or anaerobic reactor, which is the high substrate loading rate point, so this advantage is to some extent negated.

Likewise, the effect of these units on settling characteristics may take away some of the advantages pure oxygen plants had over air activated sludge. The ability to aerate at high MLSS is an advantage for nitrification, if one considers that competition for oxygen is one of the problems with nitrifiers. However, the consequence of carrying a high MLSS is that there is a high carbon dioxide production rate, which can lead to the depressed pH condition, and possible nitrification difficulties noted above.

The consensus seems to be that these difficulties are not an obstacle. For example the Deer Island Plant, which will

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nitrify, is being outfitted with a Pure-Ox feed. An attractive feature of FMC's system trade-named "MAROX" is that it uses a very fine diffuser with such high oxygen transfer efficiency that sealing of the headspace is not required. This would avoid the nitrification difficulties at low pH, assuming that these nitrification difficulties are real. Cohen (1972) described the open tank process and reported that the oxygen transfer rate was approximately six times more efficient than any other oxygenation method.

The performance of nitrification and denitrification in an MLE system with pure oxygen feed under sealed conditions largely remains unknown, and became an objective of this thesis research.

3.0 OBJECTIVES

The objectives of this thesis research were to:

1)   Demonstrate the feasibility of an experimental MLE system
     in which the aerobic reactor is fed pure oxygen to
     nitrify primary effluent containing ammonia levels of 25-
     35 mg/l.

2)   Demonstrate the feasibility of denitrifying the nitrate
     formed.

3)   Examine relationships between SOC and NO_3.

4)   Explain the performance results of the experimental MLE
     systems.

5)   Provide some direction for further research into nitrogen
     removal in a pure oxygen plant.

4.0   MATERIALS AND METHODS

4.1   The Collection of Primary Effluent

Primary effluent was collected at the NEWPCC and delivered by courier on Monday, Wednesday and Friday. Collection from the NEWPCC was to done at 1:00 P.M. to coincide with the 7:00 A.M. surge of sewage. This resulted in wastewater which would be among the most difficult to treat.

The effluent was then transferred into 20 L storage buckets that were stacked in a cool chamber kept at 4^0C. A 100 L plastic lined chemical drum was used to store the feed for these and two other reactors run by Sears (1995a). The storage buckets were emptied into the drum as needed.

4.2   Reactor Setup and Equipment

Two predenitrification reactor trains were assembled in the Department of Geological and Civil Engineering, University of Manitoba (Figure 4-1). The train data are shown in Table 4-1.
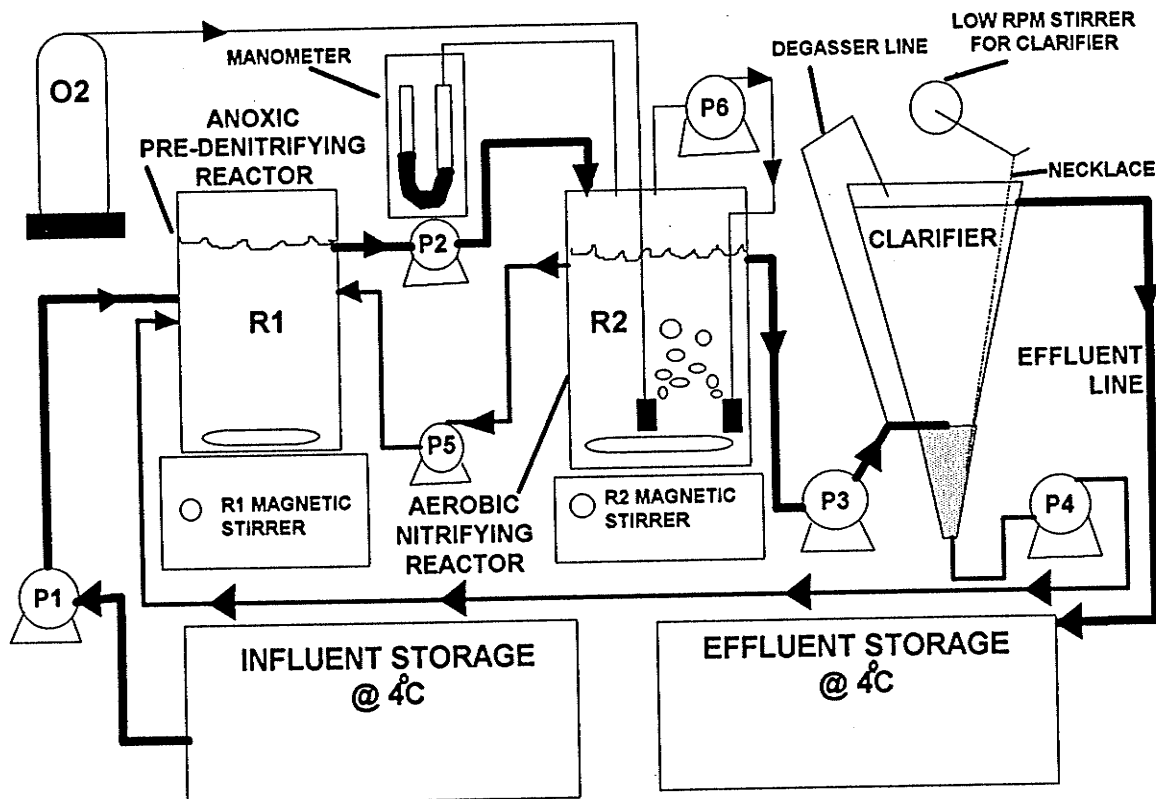
REACTOR #
R1   Anoxic Pre-Denitrifying Reactor
R2   Aerobic Nitrifying Reactor

PUMP #
P1   Influent Feed Pump
P2   Pump from R1 to R2
P3   Pump from R2 to Clarifier
P4   Recycle Activated Sludge Pump
P5   Recycle Pump from R2 to R1
P6   Gas Recirculating Pump

Figure 4-1: Reactor Setup and Equipment

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Table 4-1: Operational Parameters

Parameter	Train A	Train B
System SRT (days)	15	15
Anoxic Reactor HRT_{RAW} (h)	1.5	2
Aerobic Reactor HRT_{RAW} (h)	4.5	2
Temperature before Nov. 5	22^0C	22^0C
Temperature after Nov. 5	12^0C	12^0C
Recycle Ratio	$1.5-3.1xQ_{RAW}$	$1.8-2.8xQ_{RAW}$
Clarifier HRT (h)	3.5	3.5

Pure oxygen was supplied by pure oxygen tanks, flowing through Grade VI 1/4" Nalgene tubing to an air regulator normally used for household aquariums. The air flow was measured by Gilmont G-4340 flowmeters. The pressure of the reactor was controlled at approximately 7 cm of water by maintaining that height of water above the air discharge line in an Erlenmeyer flask.

The anoxic reactor was not perfectly sealed, since air entered through the hole for the ORP probe, but it still ran at a slight vacuum. Neither reactor would discharge a sample without removal of a rubber stopper to open the reactor to atmospheric pressure.

The 10 cm inner diameter reactors (R1 and R2) were made of plexiglass. The clarifier was a hybrid of a 10 cm plexiglass cylinder and a 1 L plastic Imhoff cone, glued together, and sealed for leaks with silicon caulking.

In order to prevent biomass accumulation on the inner surface, a Cole Parmer #7553-80 peristaltic pump motor was suspended above the clarifier on a retort stand. A small piece of flexible wire shaped like a hockey stick was attached to the pump shaft. As the shaft rotated, the unattached edge of the wire (the "blade") would travel a circular path that was approximately the same as the clarifier circumference. A 75 cm silverplated necklace from K-mart was suspended from the blade, and contacted most of the internal surface, providing the required cleaning action at about 6 rpm.

Cole Parmer 23 cm X 23 cm magnetic stirrers provided mixing. The aerobic reactors also received mixing action from the aeration stones (and later nozzles) that diffused the pure oxygen and the recirculated headspace gases.

Cole Parmer #7553-80 peristaltic pumps with Masterflex 7014 pump heads and #14 sized Masterflex tubing were used to pump most liquids. For recirculating the headspace gases, 7020 heads and #20 tubing were used, and 7015 heads and #15 tubing were used for pumping recycle in Train A. Tygon tubing

conveyed liquids from the pump to the reactor, with PVC plastic connectors joining the Tygon tubing to the pump tubing or reactor.

Dissolved oxygen was monitored in Train A with a Fisher YSI model #54A DO meter, and in Train B with a Fisher YSI model #51B DO meter. Both trains' anoxic reactor ORP's were measured by a Chemcadet pH meter/controller, set to read millivolt potential, using a Fisher 13-620-82 ORP probe.

4.3 Measurements and Sampling Schedule

The daily (Monday-Friday) measurements were air flow, pump RPM, reactor temperature, pH, DO, ORP, clarifier sludge volumes and total effluent volume collected. Saturday, Sunday and holiday measurements were restricted to total effluent volume, and ensuring that the DO was at least 2 mg/L. Monday, Wednesday and Friday were sampling days for TKN, NH_3, SOC, NO_3, MLSS and alkalinity analyses, which were conducted according to APHA et al.'s (1989) "Standard Methods" procedures. CO_2 levels in the headspaces were also routinely conducted in a GOW MAC 550 gas chromatograph.

The samples were vacuum filtered through 0.45 µ Whatman 934-AH microfibre filters. About 2 mL of 1N sulphuric acid were added and the samples were stored at 4^0C while awaiting testing.

Pump rpm was measured with a Shimpo DT-105 tachometer. Temperature was measured with a mercury thermometer, and pH measurements were taken using a Fisher #230 pH meter.

4.4 Calculations

The solids retention time (SRT) was calculated by:

$$SRT = \frac{M_S}{M_{LS} + WAS} \qquad (1)$$

$$M_S = M_{R1} + M_{R2} + M_C \qquad (2)$$

$$M_{R1} = MLSS_{R1} \times V_{R1} \qquad (3)$$

$$M_{R2} = MLSS_{R2} \times V_{R2} \qquad (4)$$

$$M_C = RAS \times V_C \qquad (5)$$

$$WAS = (\frac{M_S}{SRT_T} - M_{LE}) + MLSS_{R2} \qquad (6)$$

$$M_{LE} = MLSS_E \times F \qquad (7)$$

with:
SRT =	Solids retention time (d)	
M_S =	Mass in the system (g)	
M_{LS} =	Mass lost in the system (g/d)	
WAS =	Waste activated sludge (g/d)	
M_{R1} =	Mass in reactor R1 (g)	
M_{R2} =	Mass in reactor R2 (g)	
M_C =	Mass in clarifier (g)	
$MLSS_{R1}$ =	Mixed liquor suspended solids in reactor R1 (g/L)	
V_{R1} =	Volume of liquid in reactor R1 (L)	
$MLSS_{R2}$ =	Mixed liquor suspended solids in reactor R2 (g/L)	
V_{R2} =	Volume of liquid in reactor R2 (L)	
RAS =	Recycled activated sludge (g/L)	
V_C =	Volume of sludge in clarifier (L)	
M_{LE} =	Mass lost in effluent (g/d)	
$MLSS_E$ =	Mixed liquor suspended solids in effluent (g/L)	
F =	Flow (L/d)	
SRT_T =	Target sludge retention time (d)	

For WAS<0, the SRT is calculated using WAS=0.

The hydraulic retention time (HRT) was calculated by:

$$HRT = \frac{V_R \times T}{V_E} \qquad\qquad (8)$$

$$R_\% = \frac{I - O}{I} \times 100\% \qquad\qquad (9)$$

with:
V_R =		Volume of the reactor (L)
T =		Time from last measurement (h)
V_E =		Volume of the effluent (L)
$R_\%$ =		Percent removals from a unit or system
I =		Incoming substance (SOC, TKN, etc.)
O =		Outgoing substance (SOC, TKN, etc.)

It was recognized that in the case of NH_3, TKN could possibly form more NH_3 and another calculation would be needed. For the sake of simplicity the above calculations were used, because the graphical interpretation from either calculation would yield the same conclusions.

4.5 Process Control

Although there was a desire to keep SRT, DO and HRT fairly consistent, these parameters varied daily. Temperature control was very stable in both the 22^0C condition, which was simply the laboratory ambient temperature, and in the 12^0C cool chamber. The cool chamber did break down, and temperature control was lost from March 11 to March 15. The temperature during this time could be considered as 22^0C.

The HRT_{RAW} was fairly consistent, changing slightly due to

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variation in influent flow, which was affected by plugging and unplugging of the influent line. The HRT of the reactor based on total flow was not only subject to variations in influent flow, but also variations in RAS and recycle.

There were inaccuracies in the measurements used to determine the effluent daily flow. The volume was calculated based on the height of the effluent collected, which was measured with a ruler, and could be taken as accurate to ± 0.32 cm. Also, the time of the measurement could be taken as ± 15 min.

SRT control was often dictated by solids losses in the effluent, and by spills that rendered SRT calculation impossible. These events reduced the SRT to below the target values. In addition, a certain amount of biomass buildup was desired at times, notably at low carbon loadings, in which case no sludge was wasted and the SRT exceeded the target value.

DO control was based on Metcalf and Eddy's (1991) recommendation that the DO level for nitrification be at a minimum of 2 mg/L. The DO reached a maximum level of 16 mg/L, which can happen in a pure oxygen fed environment, as control of DO was limited by the equipment. The oxygen flows were at 5 mL/min. Attempting to go below 5mL/min caused the ball in the flowmeter to stick, plugging oxygen feed totally.

Controlling the rpm of the gas recirculating pump enabled control in the 2-8 mg/L range with higher levels occurring periodically.

A larger system with higher feed rates would circumvent the problem by allowing more biomass which can consume more than this minimal 5 mL/min oxygen flow, thus allowing better control of DO levels.

5.0 RESULTS

5.1 Characterization of Influent Data

The feed to the reactors from May-September 1993 was very dilute due to record rainfalls in Winnipeg. Because of these record rainfalls, one cannot say without further data what are the "normal" summer conditions.

The histograph in Figure 5-1 of the SOC levels shows that the August levels were much lower than the levels after mid-September. Also shown in Figure 5-1 are data of the NEWPCC centrate TSS. The centrate data appear to have behaviour similar to the average SOC data.

Figures 5-2 indicates that the TKN levels were also lowest during August, 1993, as does Figure 5-3 for ammonia.

Figure 5-4 shows the relationship between the influent SOC and the influent TKN from July 19, 1993 to March 20, 1994. The data shows that the soluble TKN is about half the value of the SOC. Figure 5-5 shows the relationship between the influent TKN and influent NH_3. The influent ammonia is about 80% of the influent TKN. These relationships may be useful for design calculations.
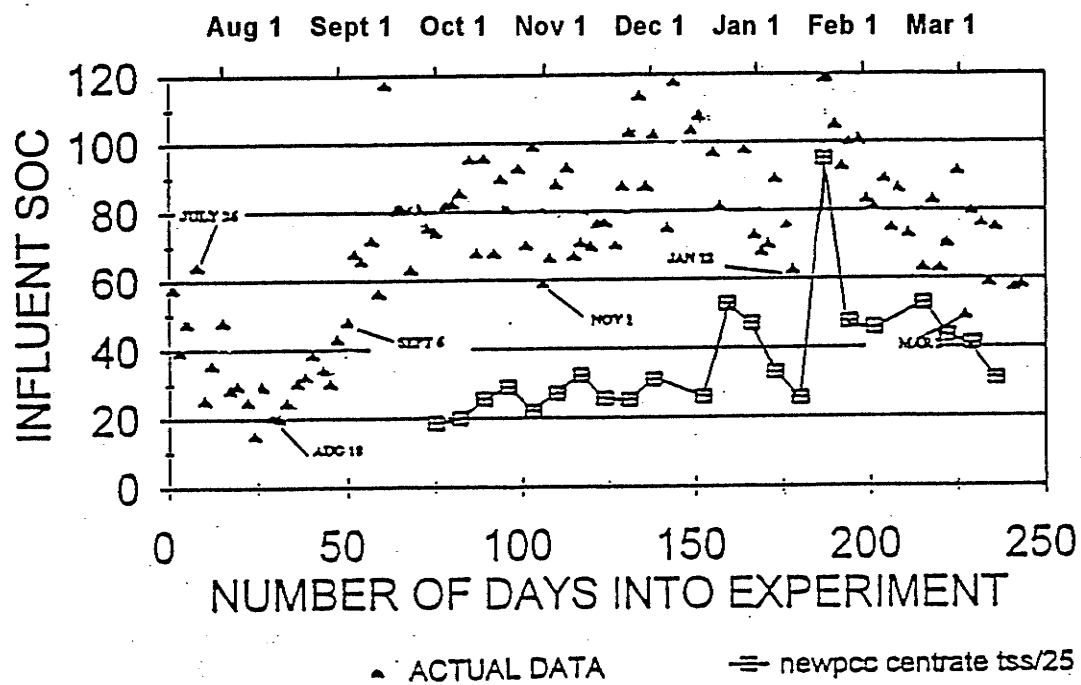
Figure 5-1: Histograph of Influent SOC
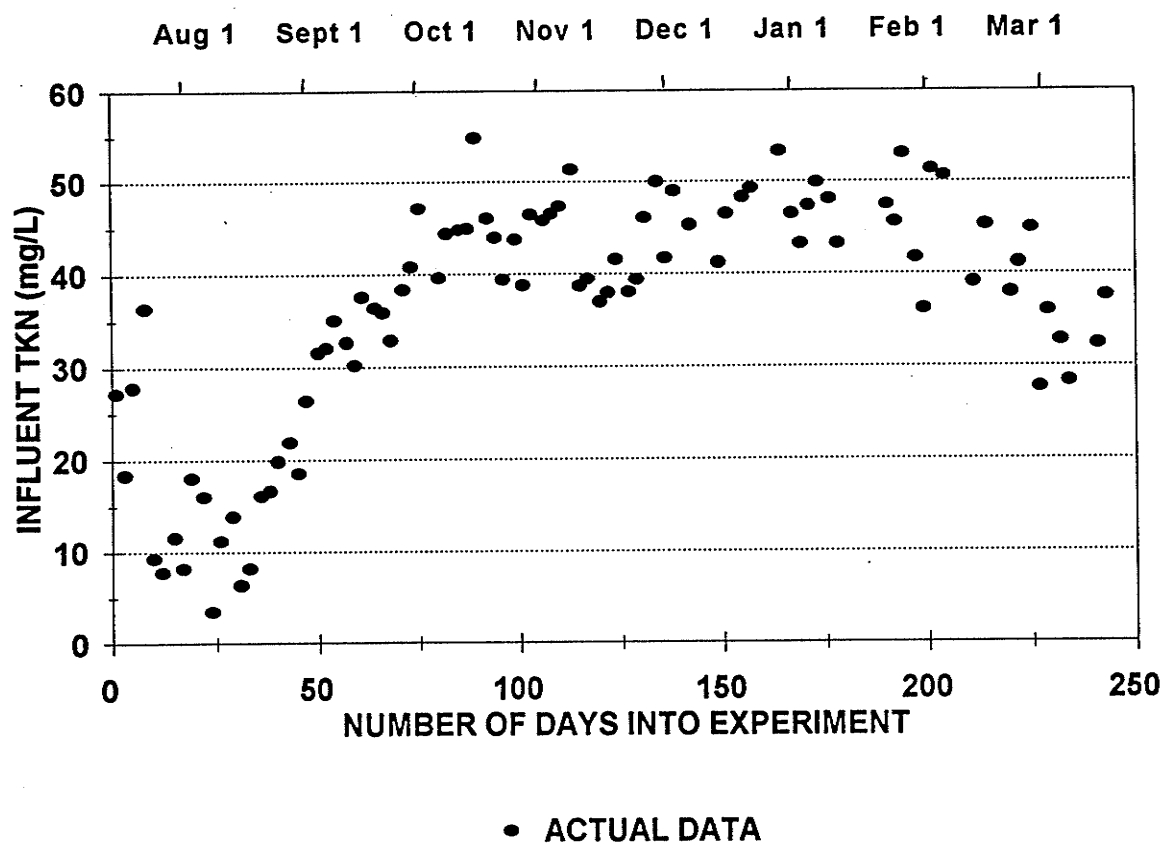
Figure 5-2:   Influent TKN Histograph:
July 19, 1993 - March 20, 1994
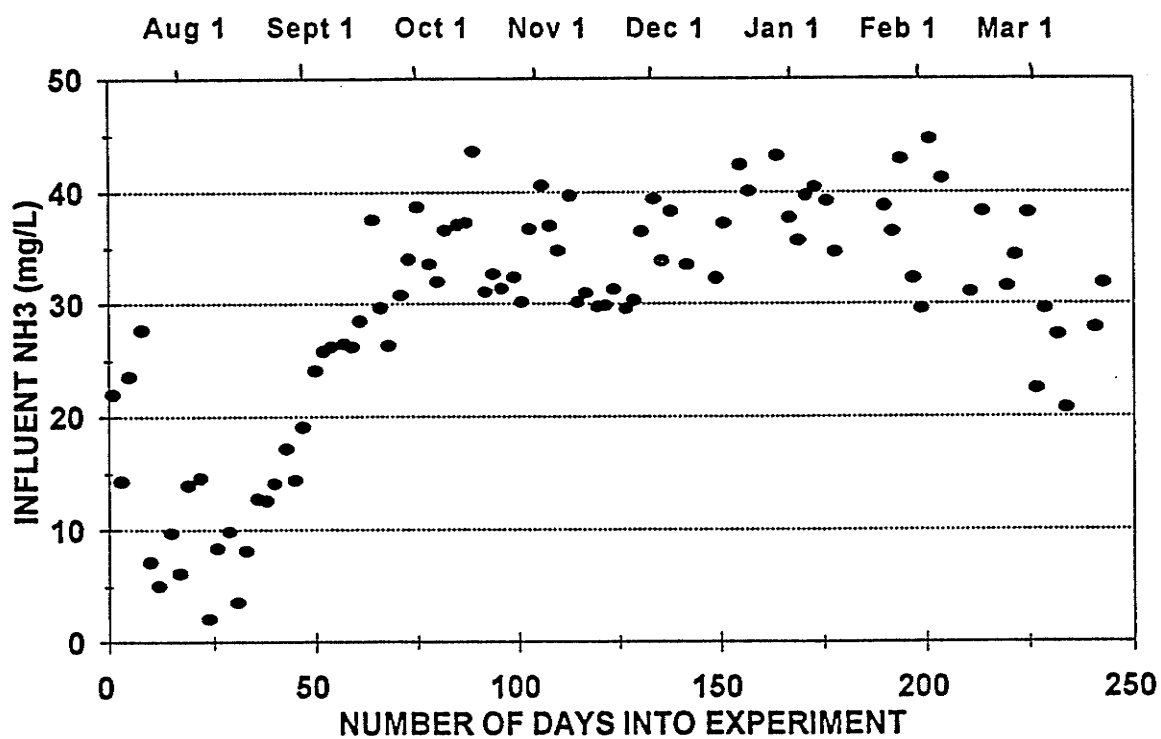
Figure 5-3:   Influent NH₃ Histograph:
              July 19, 1993 - March 20, 1994
              NH3 is reported as NH3-N

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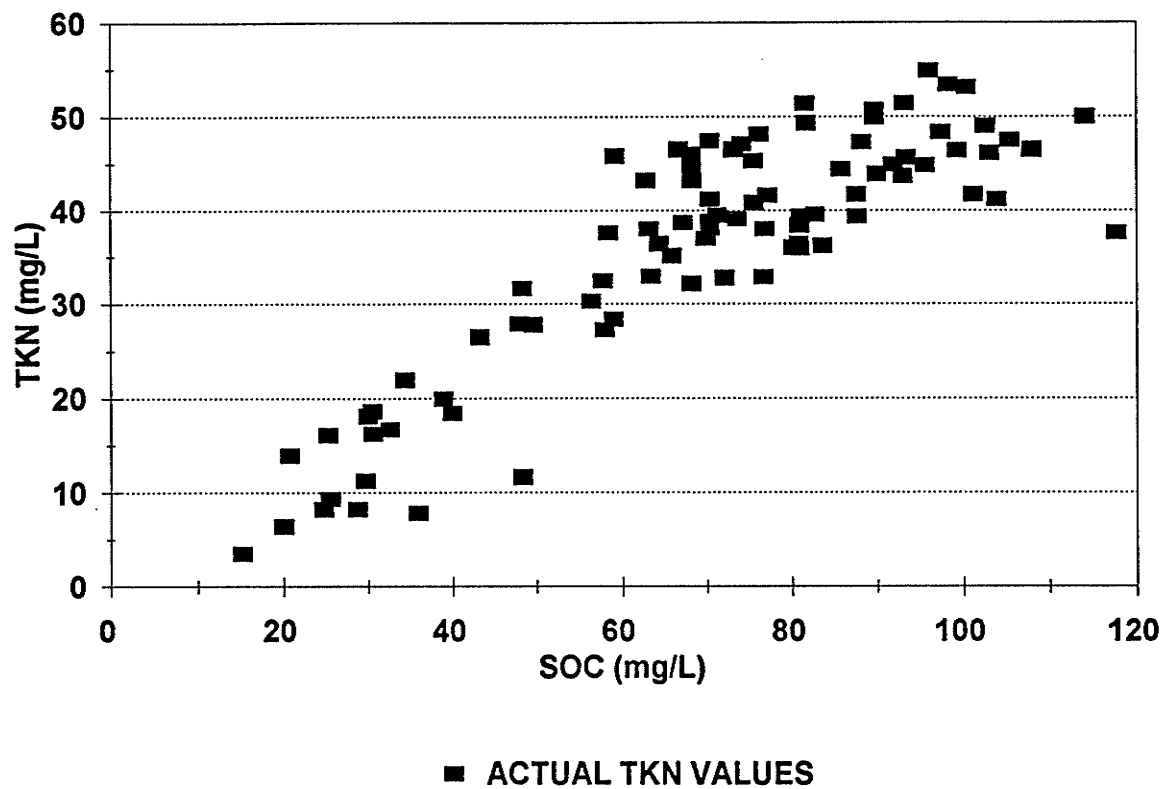
Figure 5-4: Influent Characteristics - Influent
TKN vs. Influent SOC
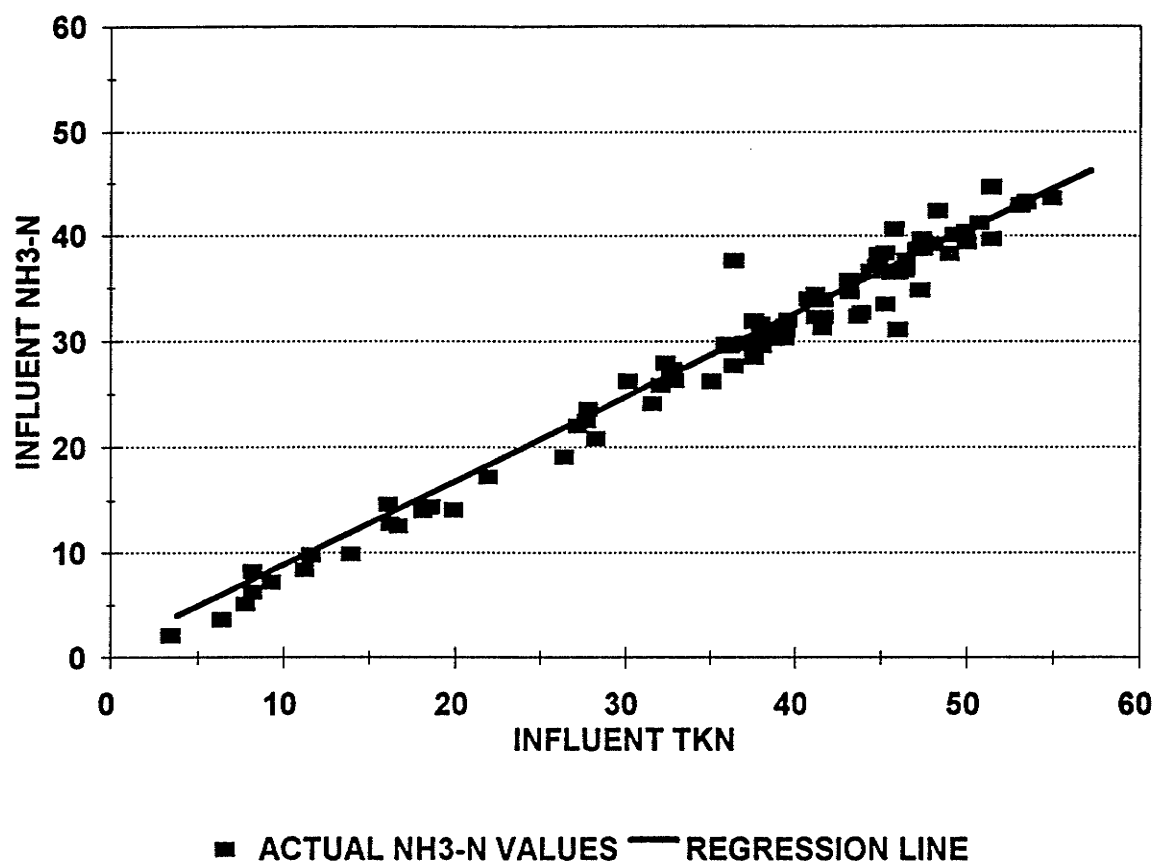
Figure 5-5:   Influent Characteristics - Influent
             NH₃ vs. Influent TKN

The raw SOC:TKN ratio histograph is shown in Figure 5-6. The SOC:TKN ratio varied more in the first 60 days than it did over the next 180 days, as seen from Figure 5-6. Part of this may be attributed to the rain during that period, and also to the fact that some of the influent was mixed with effluent from the previous day. It was necessary to add the effluent because of shortages of influent.

5.2   Operating Results @ 22°C

Between July 19 and November 5, the systems ran at 22°C. System B, with the 2 h aerobic HRT, experienced high solids losses which resulted in no control over the SRT. Instead, the SRT was dictated by the solids losses, and nitrification could not be sustained due to insufficient aerobic SRT.

System A, with a 4.5 h HRT, did not experience solids loss to the same extent and was able to nitrify more than 90% of the influent ammonia. However, system mass balances showed that the system usually did not denitrify at 100% efficiency in the anoxic reactor.

The operating control of dissolved oxygen was not well established during this time and excessive feeds of pure oxygen were needed to maintain the headspace pressure. Better control of oxygen was achieved by adding pumps to recirculate
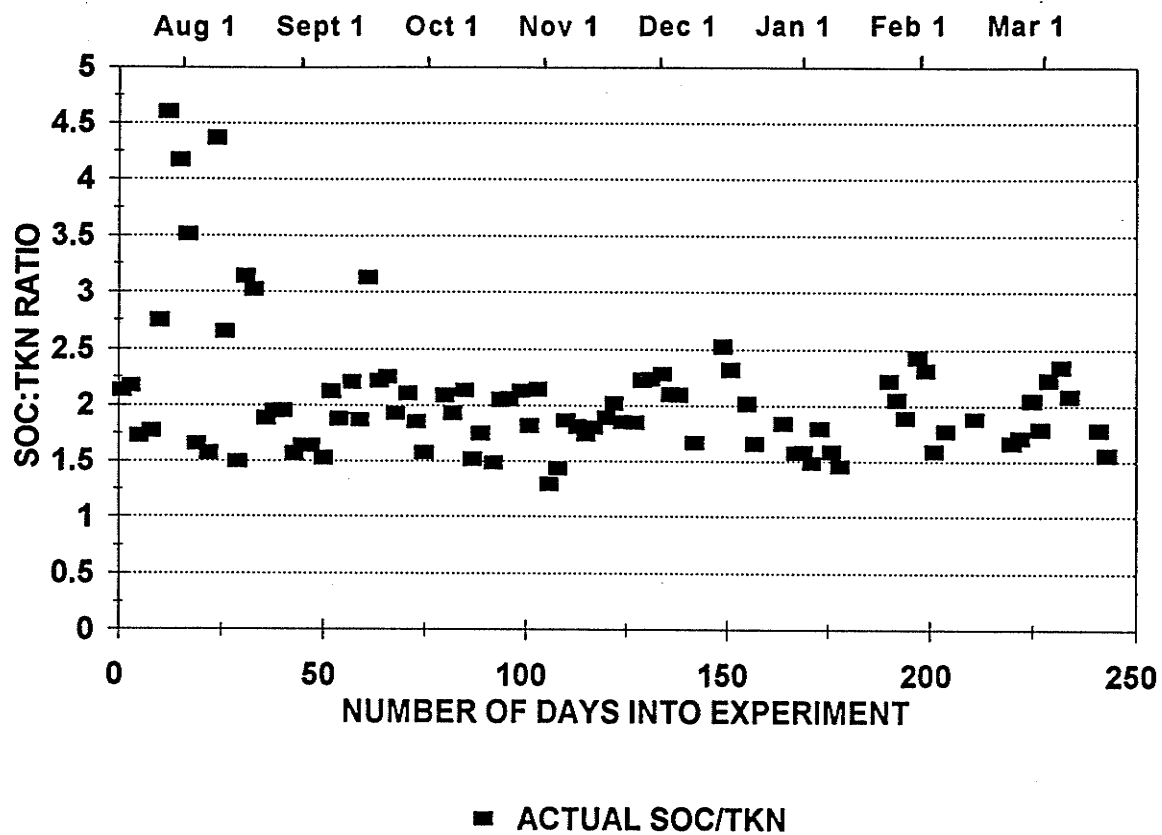
Figure 5-6:   Raw SOC:TKN Ratio

the headspace gases, resulting in a drop of pure oxygen feed from 50 mL/min into the 5-10 mL/min range. This was the lowest feed that could be controlled, as lower levels would result in the ball in the flow meter plugging the flow of oxygen completely.

5.2.1   Data from Train A @ 22^{0}C

Figure 5-7 shows the SOC in the anoxic reactor R1 plotted against the influent SOC. The best exponential fit of the data was a straight line. Figure 5-8 shows the SOC in the aerobic reactor R2 plotted against the influent SOC and Figure 5-9 shows the Effluent SOC plotted against the Influent SOC. As with Figure 5-7, the best exponential fit was a straight line. This linearity is explored further in Section 6. The linear regression data are given in Appendix 1.

Despite variable influent SOC, the carbon removal process can be considered steady state, as seen in the histograph of the effluent SOC in Figure 5-10.

Figure 5-11, 5-12 and 5-13 show the linear fit between TKN and NH$_3$ for each part of the process, with the best fits occurring in the two reactors.

The histograph in Figure 5-14 shows the percentage of TKN that
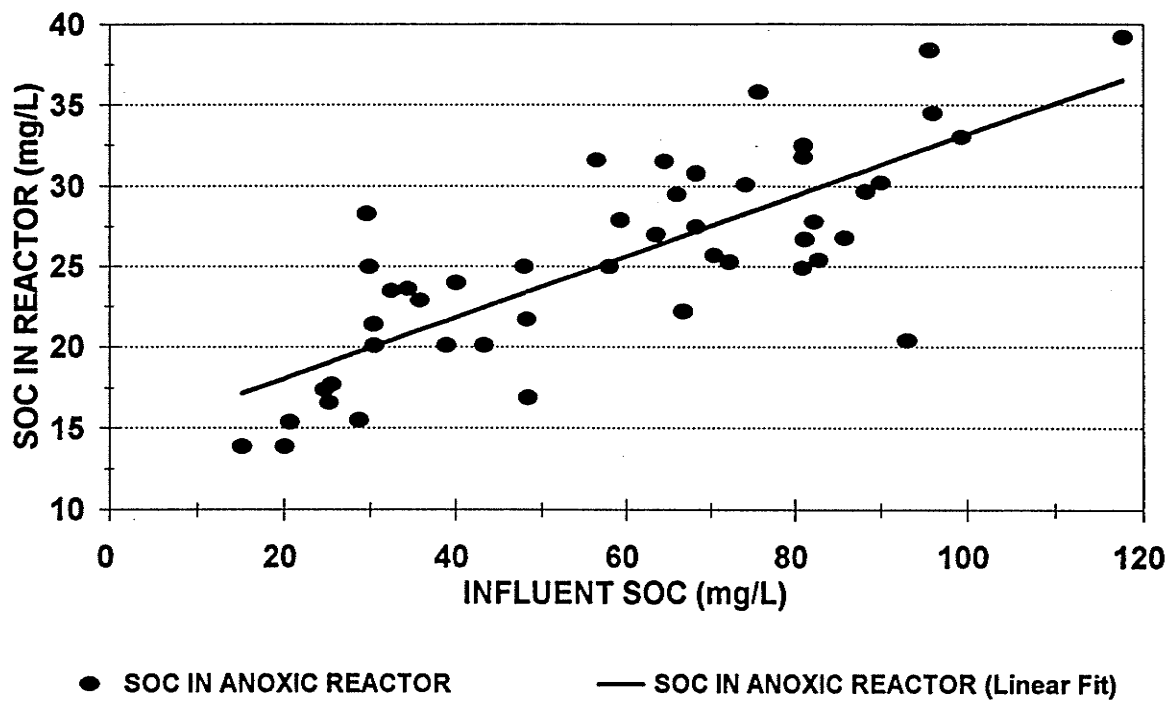
Figure 5-7:   SOC in Anoxic Unit vs SOC of Influent
             Train A @ 22°C
             1.5 h anoxic; 4.5 h aerobic
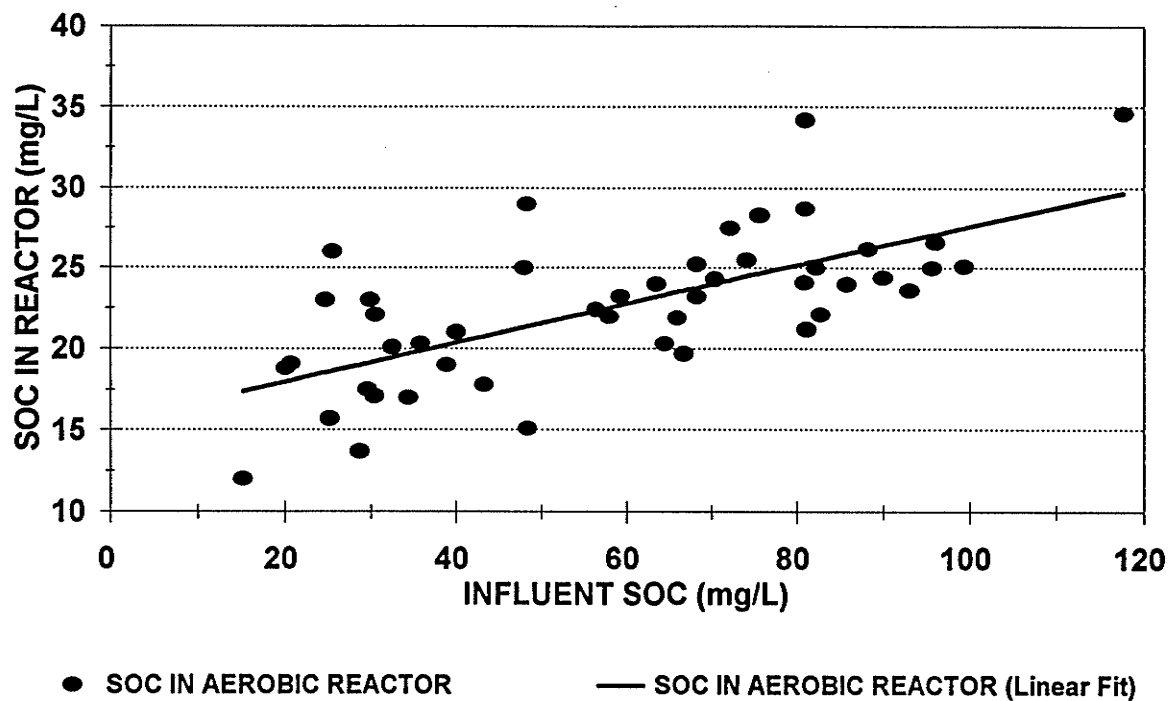
Figure 5-8:   SOC of Aerobic Reactor vs SOC of
              Influent Train A @ 22^{0}C
              1.5 h anoxic; 4.5 h aerobic
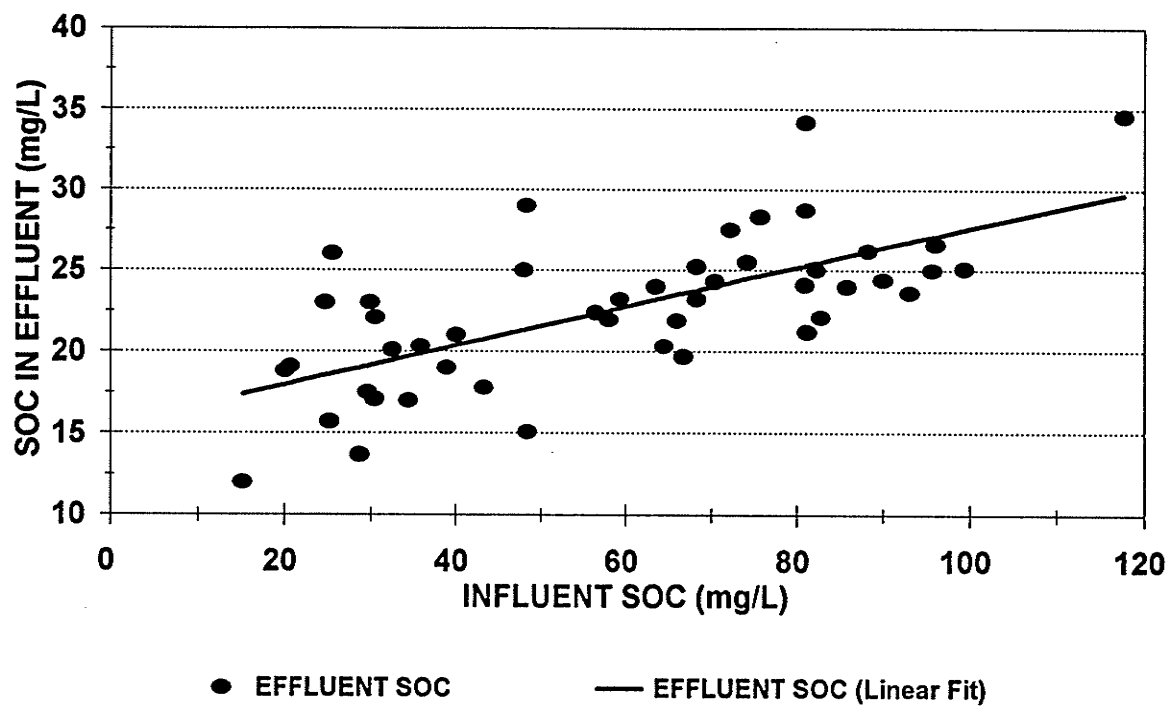
Figure 5-9:   SOC of Effluent vs SOC of Influent
             Train A @ 22°C
             1.5 h anoxic; 4.5 h aerobic
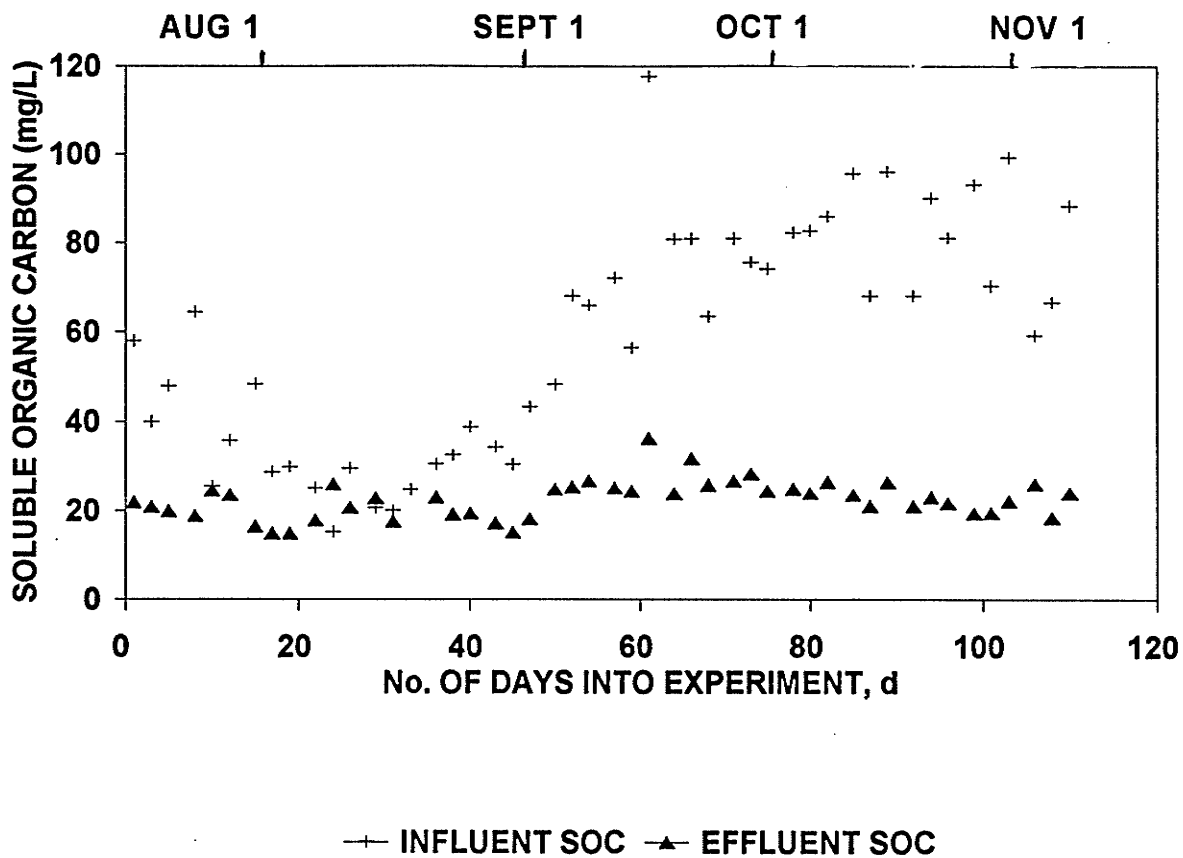
Figure 5-10:   Influent and Effluent SOC,
              July 19, 1993 - November 5, 1993
              Train A @ 22⁰C
              1.5 h anoxic; 4.5 h aerobic
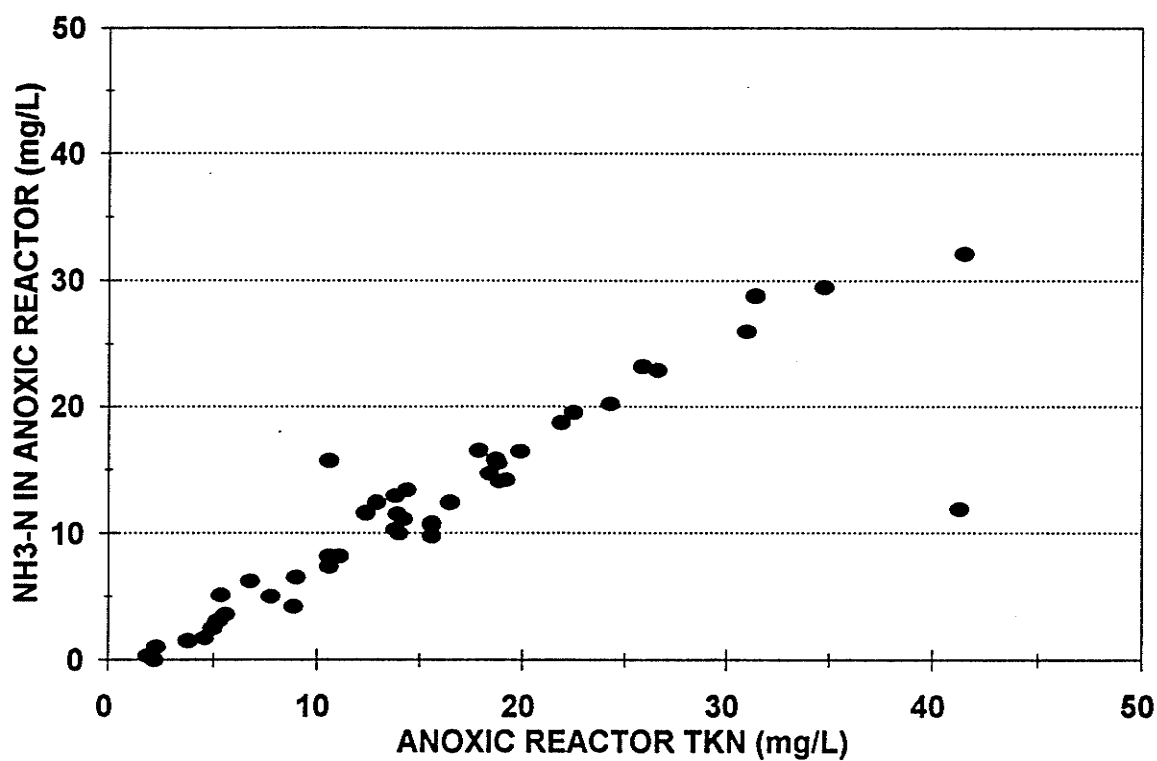
• NH3-N IN R1

Figure 5-11:   Characterizing NH_3 and TKN
Relationship in the Anoxic Reactor
(R1), Train A @ 22^0C
1.5 h anoxic; 4.5 h aerobic
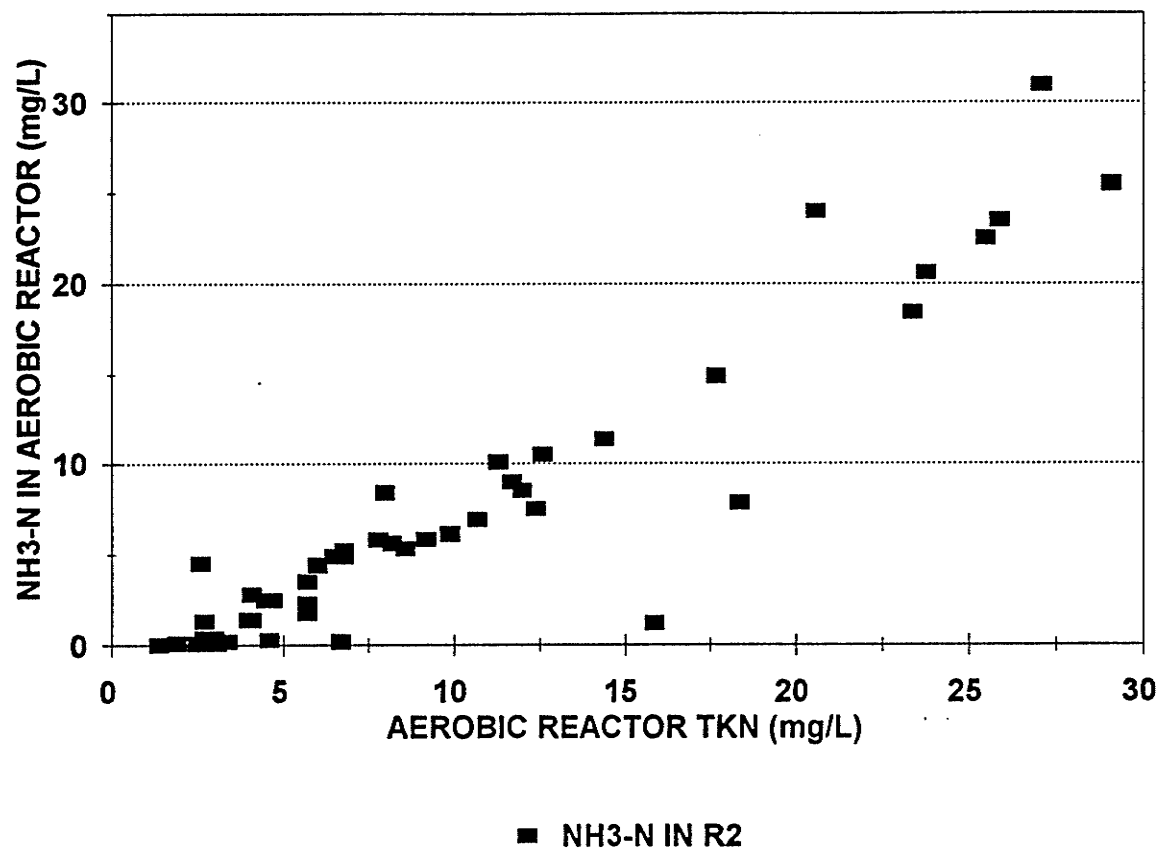
Figure 5-12: Characterizing NH₃ and TKN
Relationship in the Aerobic Reactor
(R1), Train A @ 22⁰C
1.5 h anoxic; 4.5 h aerobic
NH3 is reported as NH3-N
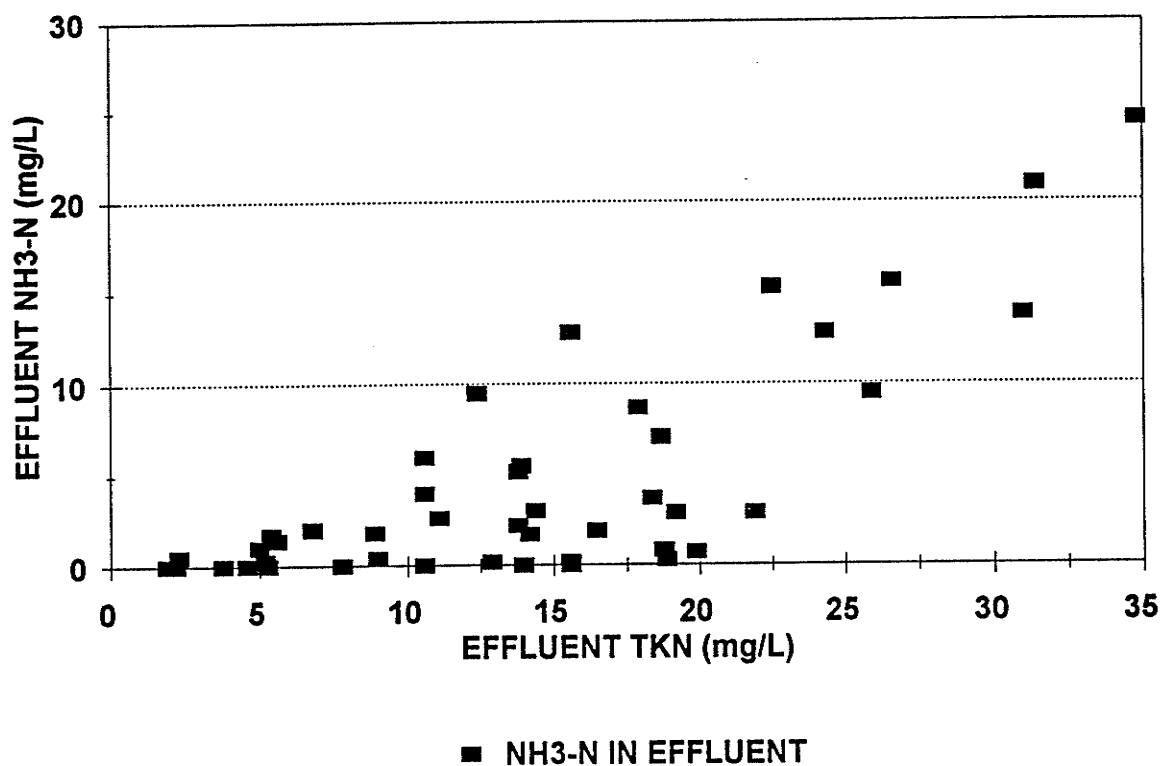
Figure 5-13:   Characterizing NH_3 and TKN
Relationship in the Effluent,
Train A @ 22°C
1.5 h anoxic; 4.5 h aerobic
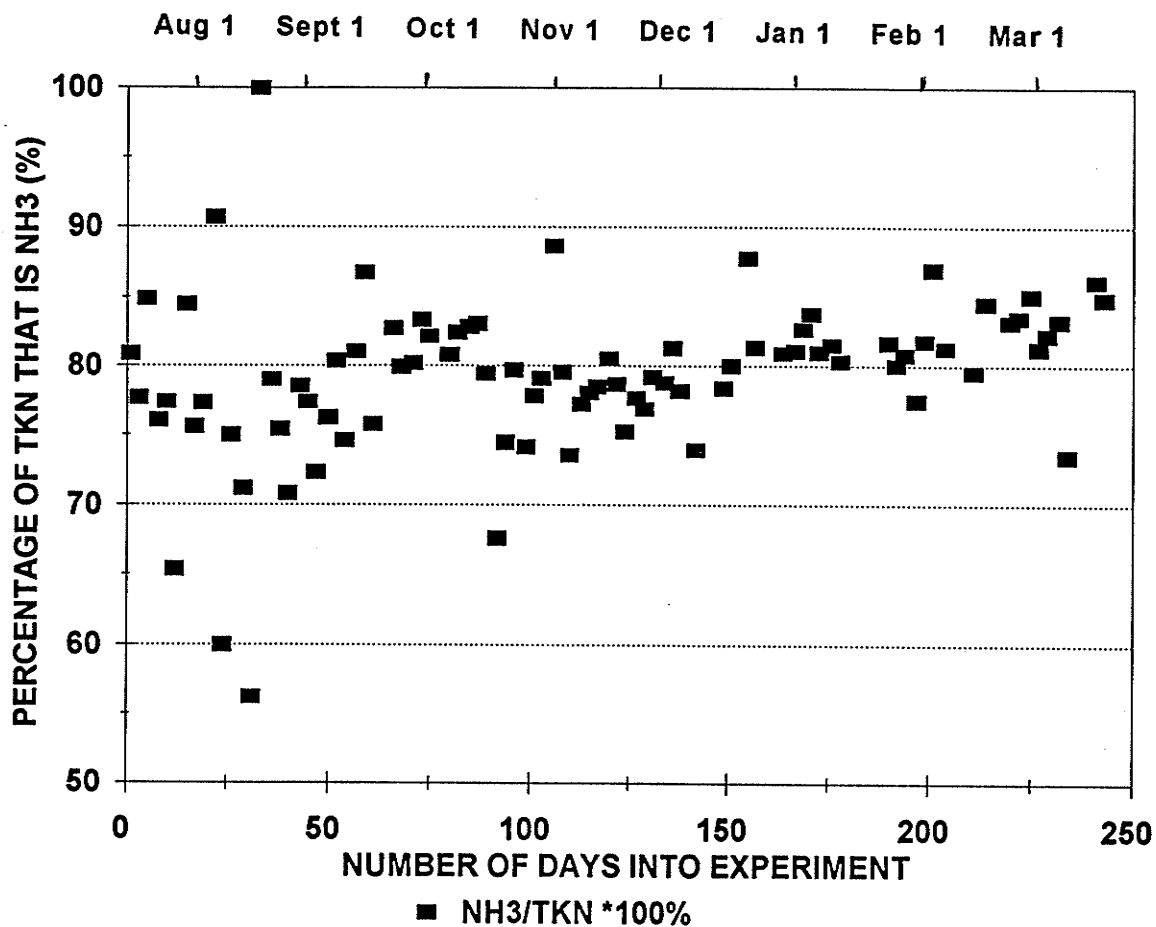
Figure 5-14: Percentage NH$_3$ in the Influent TKN
July 19, 1993 - March 20, 1994

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is NH_3 during the period July 19-Nov 5. Figure 5-5 gave the relationship between the influent TKN and NH_3 data for the entire experiment.

5.2.2   Data from Train B @ 22^{0}C

Figure 5-15 shows the histograph of the percent TKN and NH_3 removals for Train B @ 22^{0}C. There is little indication that the system ever sustained steady-state nitrification, which limits the use of the data for this system. However, Figure 5-16 shows that carbon removal was steady-state, with effluent SOC being stable as compared to the influent SOC.

5.3 Operating Results at 12^{0}C

After November 5 (the 117th day), the systems were run at 12^{0}C, a temperature at the time considered to be more important to study. Once again System B suffered from solids losses, although spill containment allowed for some solids recovery, and decanting of effluent buckets to recover effluent solids was instituted. Also, an adjustment to the clarifier was made to prevent the discharge flow from lifting the settling sludge. Despite these adjustments, the control of SRT in System B at 12^{0}C was not stable enough to approach steady state nitrification.

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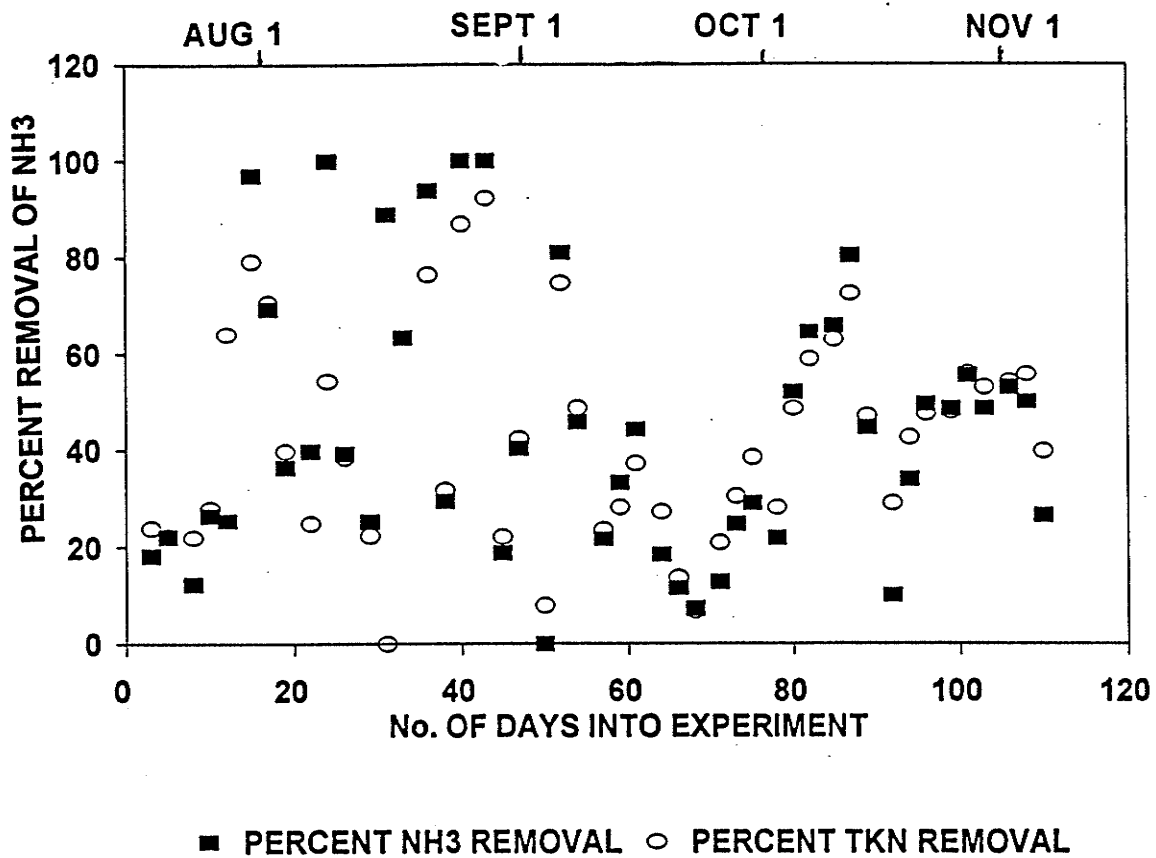
Figure 5-15:   Histograph of %TKN and NH_3 Removals from Train B @ 22°C

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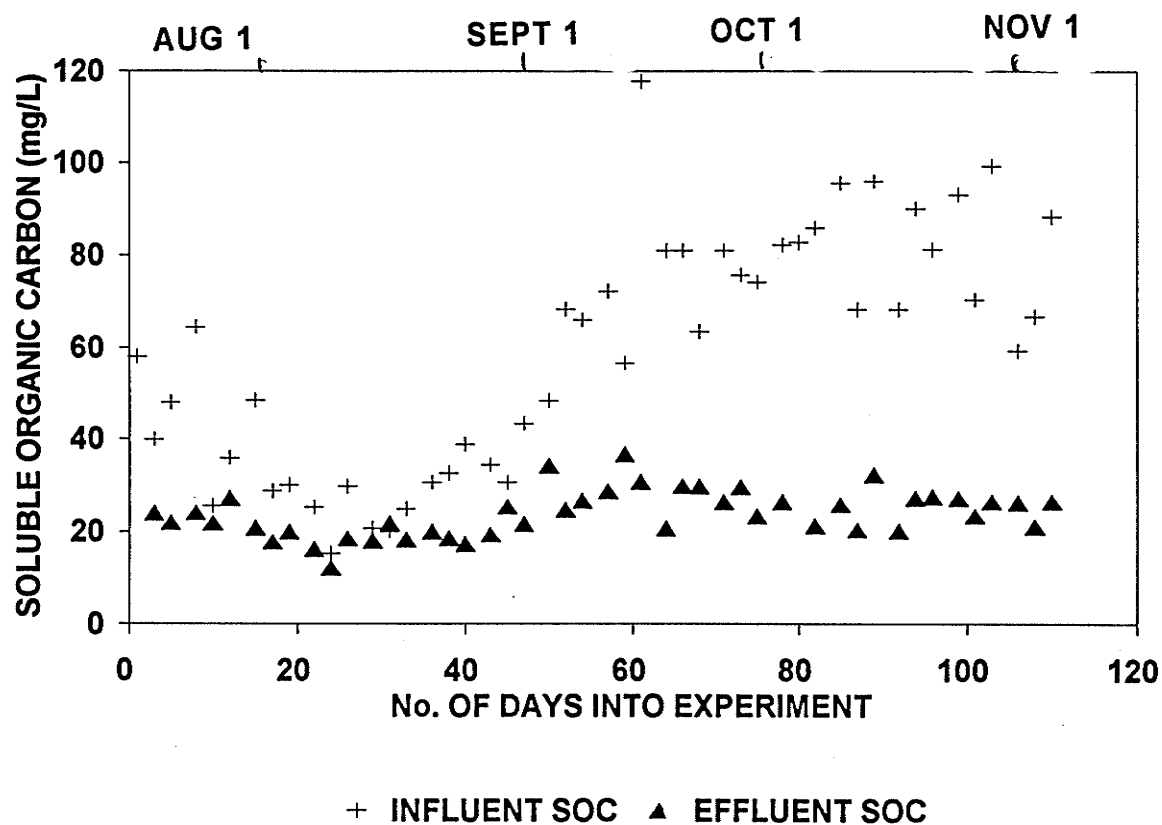
Figure 5-16:   Histograph of Influent and Effluent
                SOC from Train B @ 22°C

System A also suffered from the same problem, although it had much better SRT control. The period from January 1 to February 18 was one where the SRT was consistently above 15 days. After a major spill on February 18, the SRT was again controlled above 15 days, except for a spill on April 5, where biomass was recovered and waste activated sludge from Sears(1995a) was also added to replenish the lost mass. About three days after the spill, the SRT remained above 15 days until the end of the experiment.

5.3.1   Data from Train A @ 12°C

Figure 5-17 shows a histograph of the percentage TKN and NH_3 conversion for System A after February 18 until April 25. The spill of April 5 is indicated, since over 95% of the system mass was lost. A new start is considered from February 19 as waste biomass from other reactors was added.

A trend is apparent in Figure 5-17 that shows that percent nitrification increased over time. This represents the acclimation of the nitrifiers. By extrapolation, an acclimation period of about 75 days should result in >90% nitrification at 12°C. It is valid to make the extrapolation as Sears (1995a), running units in parallel, did achieve >90% nitrification after sustaining a 15 day SRT for 70 days.

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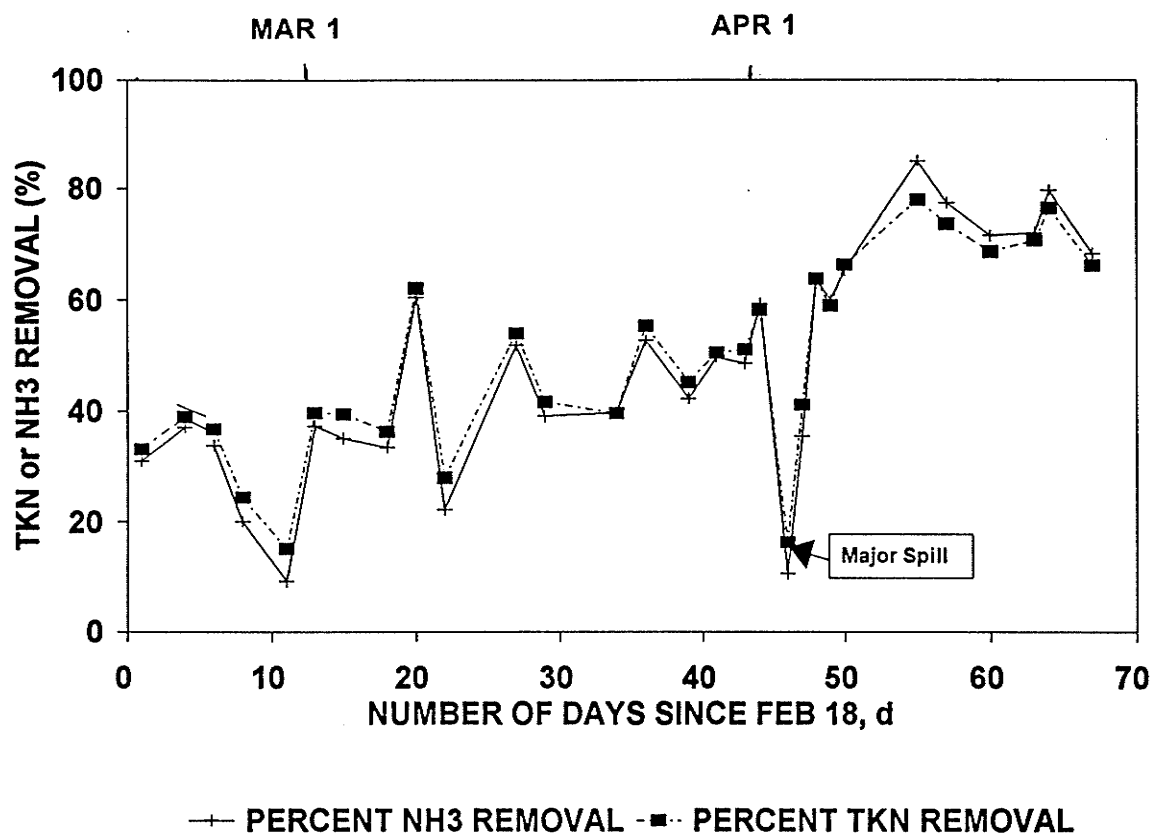
Figure 5-17:   Percentage TKN and NH₃ Removals
                February 18 - April 25 , 1994
                Train A @ 12⁰C
                1.5 h anoxic; 4.5 h aerobic

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Figure 5-17 also shows that TKN removal and NH_3 removal behave very similarly. Since NH_3 is the major component of TKN, this is logical.

The ORP was recorded, and a plot of the ORP and the percent nitrification histographs are shown in Figure 5-18. This graph shows an apparent relationship such that as the ORP increases, the percent nitrification increases. However this is not the entire story. The % Nitrogen Removal and ORP histographs are plotted in Figure 5-19. Figure 5-19 shows that the ORP is like a mirror image of the total nitrogen removal. Both nitrogen removal and % nitrification increase with time. Therefore, correlations between ORP and these two parameters is confounded by time. However, a relationship is indicated by virtue of the data in Tables 5-1 and Table 5-2, which indicates the changes of direction of ORP and percent nitrification or percent nitrogen removal.

5.3.2   Data from Train B @ 12^0C

As noted, Train B suffered from operating problems that resulted in SRT's being lower than the target 15 days. Consequently, the aerobic SRT of Train B was frequently low enough to wash out the nitrifiers in the system, as indicated by the SRT data in Appendix 3. The aerobic SRT at the target SRT may also have been too low to support a fully nitrifying

65
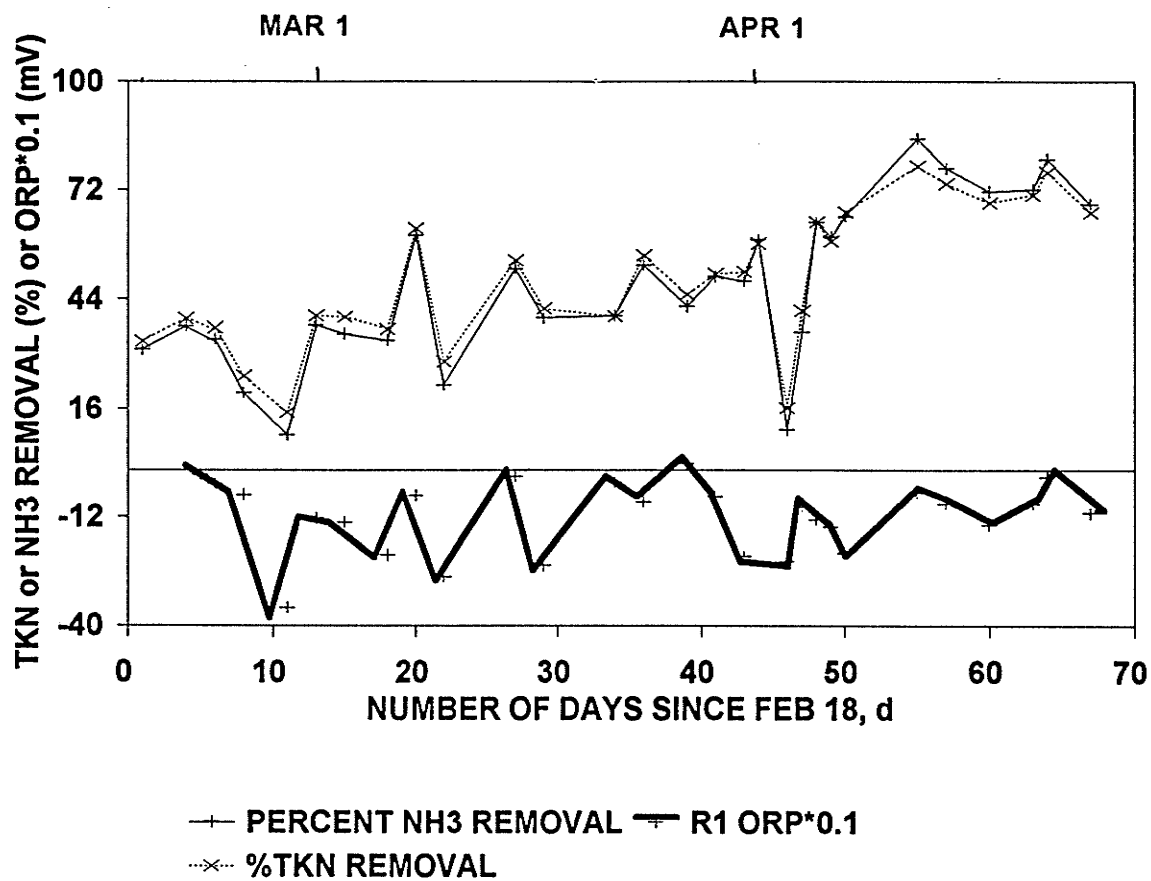
Figure 5-18:   Percentage TKN and NH_3 Removals and
                Anoxic Reactor Oxidation Reduction
                Potential (ORP) Train A
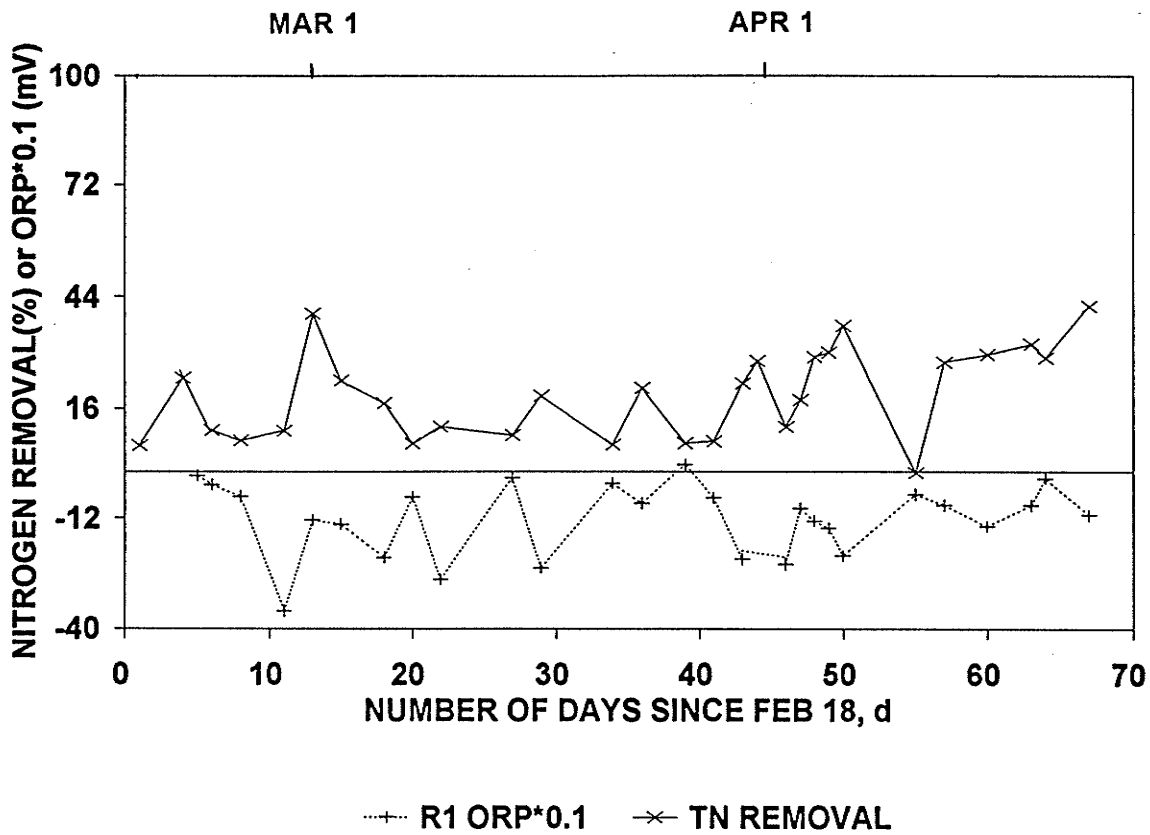
Figure 5-19:   Percentage Total Nitrogen Removal and
Anoxic Reactor Oxidation Reduction
Potential (ORP) Train A
February 18 - April 25, 1994

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Table 5-1: Number of Points Corresponding to Increases or
Decreases of ORP and Ammonia Removal

	Increase in NH_3 Removal	Decrease in NH_3 Removal
Increase in ORP	12	3
Decrease in ORP	1	7

Table 5-2: Number of Points Corresponding to Increases or
Decreases of ORP and Nitrogen Removal

	Increase in N Removal	Decrease in N Removal
Increase in ORP	2	6
Decrease in ORP	12	1

but the system was never stable enough to prove or disprove this. Examples of two washouts are evident in Figure 5-20 between days 35-58 and days 68-85, where the percent nitrification falls after reaching a maximum.

Due to the low amount of nitrate produced by nitrification, the anoxic reactor was essentially 100% efficient. From the standpoint of defining a rate though, the data are not useful because the indications are that the reactor could denitrify more, if more nitrate were put into it.

Figure 5-21 for Train B at 12^0C shows a similar symmetry between nitrogen removal and ORP. This is significant because the relationship has been replicated in an independent system.

How can ORP appear to correlate to both nitrogen removal and % nitrification? This is discussed in Section 6.
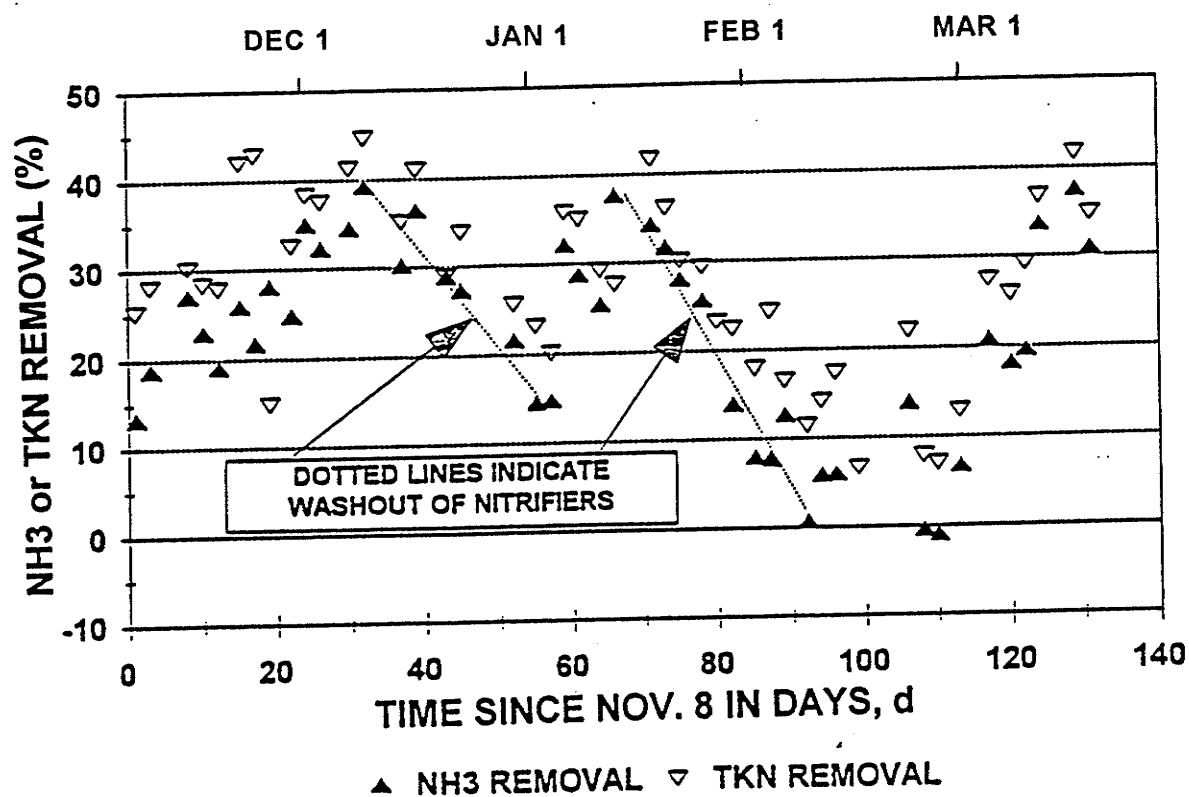
Figure 5-20: Percentage TKN and NH₃ Removals
November 8, 1993 - March 20, 1994
Train B @ 12°C
2 h anoxic; 2 h aerobic
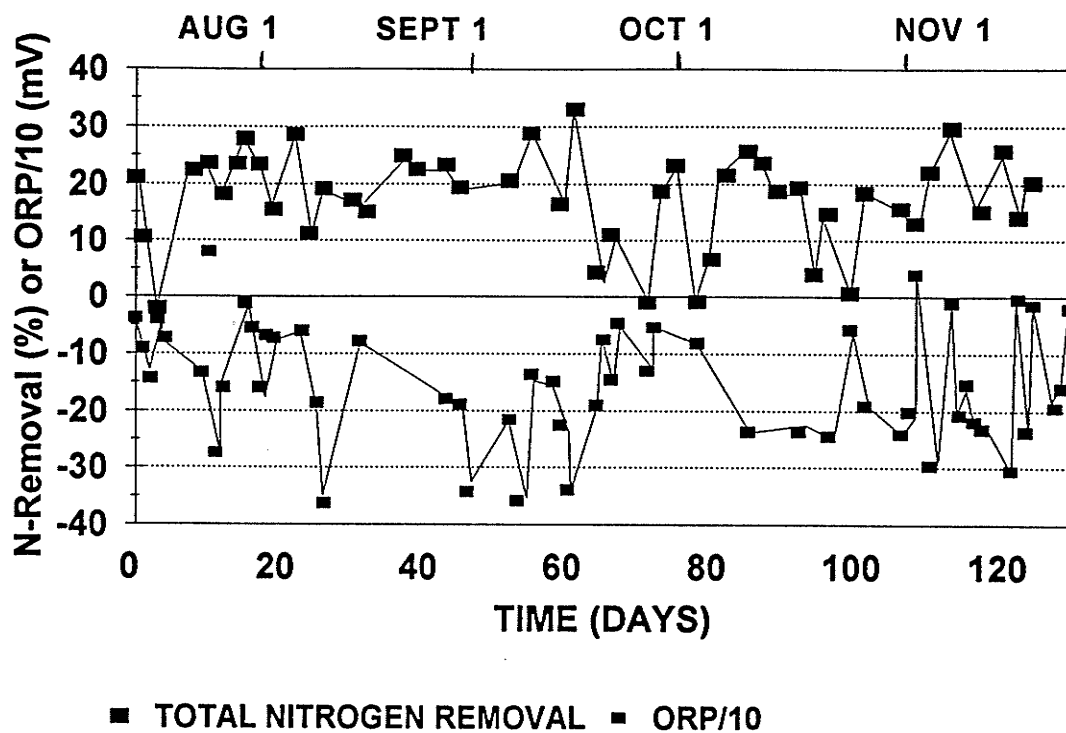
Figure 5-21:   Percentage Total Nitrogen Removal and Anoxic Reactor Oxidation Reduction Potential (ORP) Train B @ 12^{0}C

2 h anoxic, 2 h aerobic

6.0 DISCUSSION

6.1 Characterization of Influent

The concern over ammonia is greatest in the summer months, which, due to the warmer temperatures increases the toxic effect of ammonia and eutrophication process. It was observed (see Figure 5-1) that the wastewater was more dilute from August to mid-September. Characterizing the summer wastewater data has potential uses: for missing data, an estimate can be made; the value of a data point can be questioned; and by observing how the relationships change through the process units, process behaviour might be understood.

The histographs of SOC (Figure 5-1), and TKN and NH_3 (Figure 5-2) indicated that the concentrations changed over time. The design for a nitrification treatment train for 20^0C should be based on the characteristics of the wastewater for that temperature regime. Analysis of relationships for each individual period could improve the characterization process.

Figure 6-1 shows the influent SOC and TKN characteristics are related for the period from July 19 to November 8. In Figure 6-2, the data from November 8 to March 20 are plotted. A comparison of the linear fits shows that there was not a great change in the influent SOC and TKN relationship, therefore the

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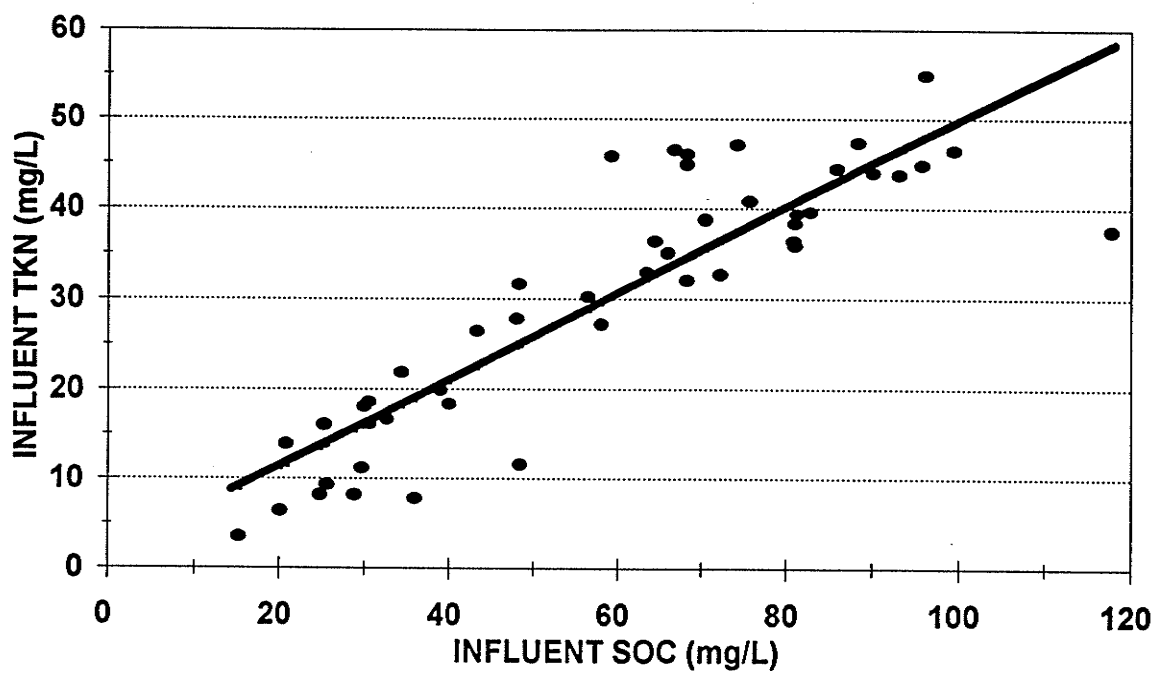
Figure 6-1:   Influent TKN and SOC Relation
             from July 19 - November 8, 1993
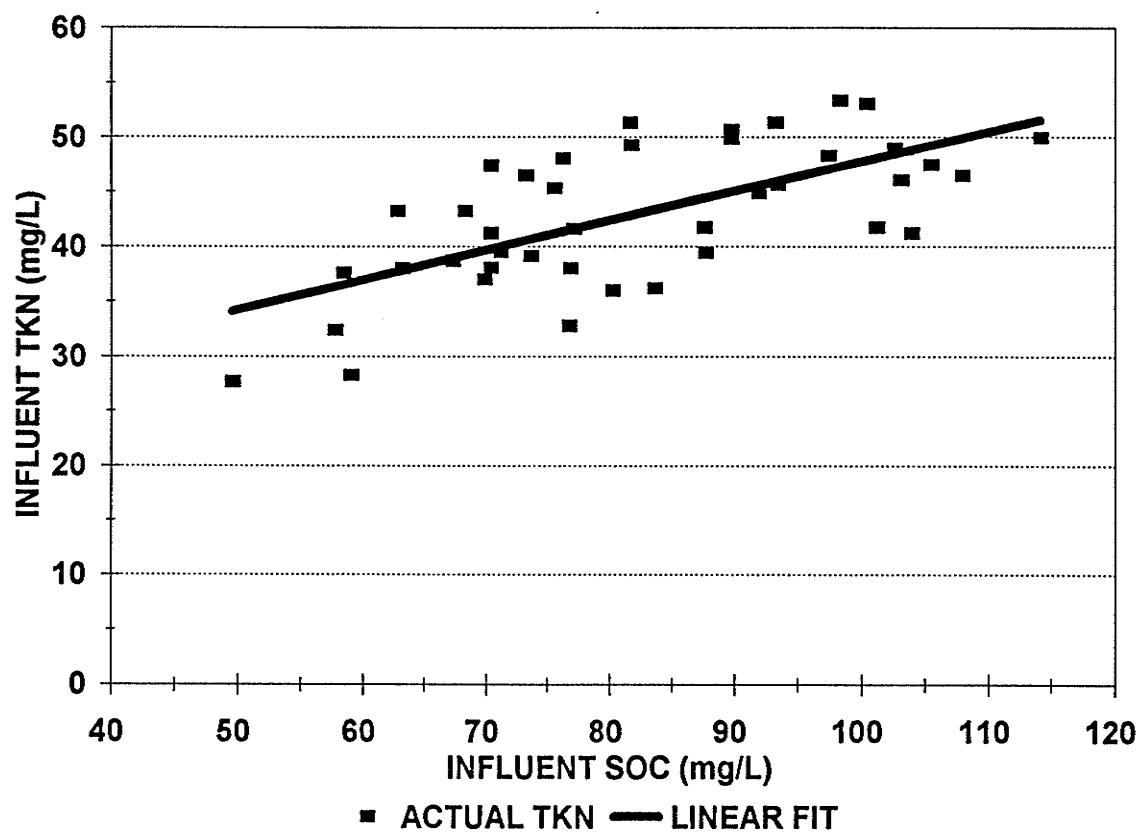
Figure 6-2:   Influent TKN and SOC Relation
              from November 8, 1993 - March 20, 1994

characterization that included all the data in Figure 5-4 seems reasonable for design purposes. That is, the influent SOC:TKN ratio is about 2:1. A similar analysis for the NH_3:TKN ratio, by comparing Figures 6-3 and 6-4, indicate that the ratio of 0.8:1, obtained using all the data in Figure 5-5, is also valid.

There may be other time-dependent relationships that could be studied, such as during melt, or drought, or rainfalls, to help the characterization process. A design for summer performance could be inaccurate if a key design parameter such as BOD or NH_3 were highly influenced by winter data. An important and relevant example is the carbon availability for denitrification. The higher SOC values that occur in winter inflate the mean of the available SOC.

6.2 Similarities in Reactor Values Due to Recycle

Figures 5-7, 5-8 and 5-9 from the three reactors in Train A exhibited the same SOC removal behaviour. Because effluent was recycled to R1 and there was recycle from R2 to R1, this should be expected. Any phenomena occurring downstream of R1 should appear in R1, since behaviour in one unit is "exported" to another due to the effect of recycle.
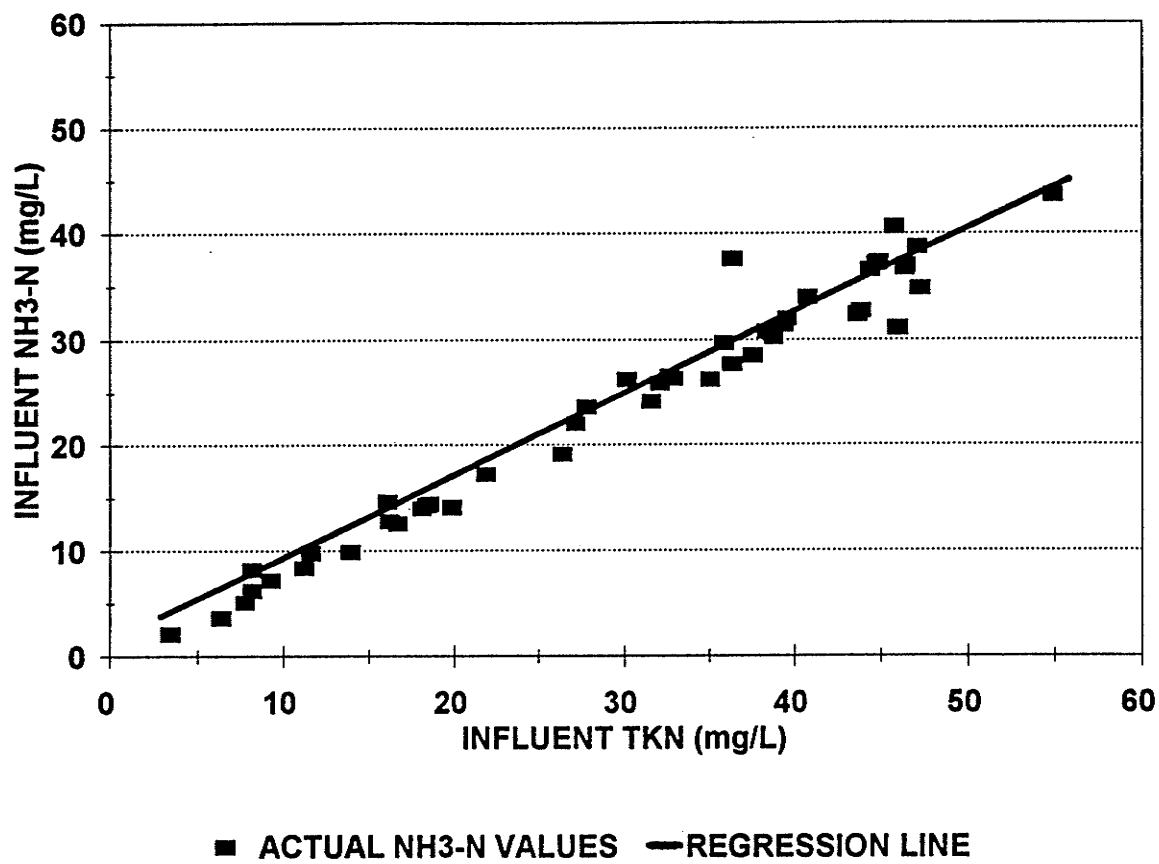
Figure 6-3:   Influent NH_3 and TKN Relation
from July 19 - November 8, 1993
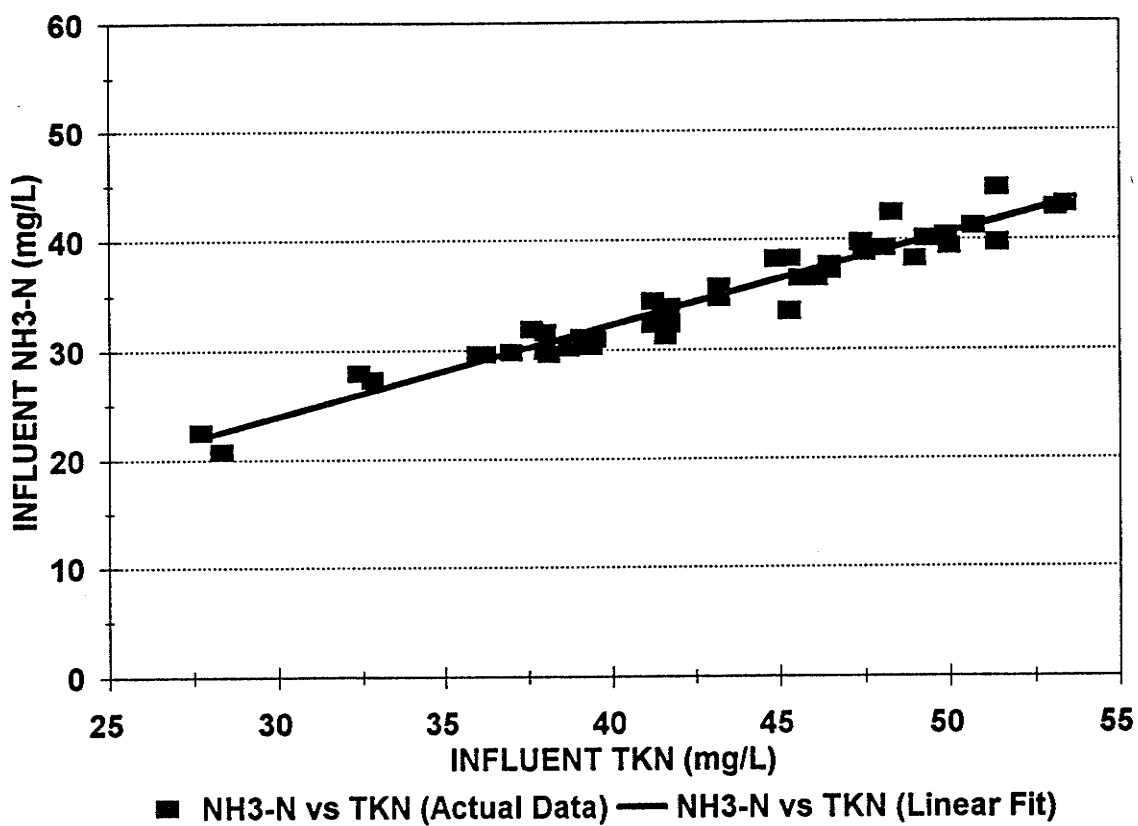
Figure 6-4: Influent NH$_3$ and TKN Relation
           from November 8,   - March 20,

6.3 Reactions Occurring in Clarifier

If the clarifier were a unit in which nothing happens then the effluent results should equal the results for the aerobic reactor (R2). A comparison of R2 and effluent values for Train A at $22^\circ C$ are shown in Figure 6-5. While it appears that there are more points where the effluent SOC is lower than the R2 SOC, one cannot conclude this based on the statistical t-test, which was done for Figures 6-5 through 6-12 in Appendix 1. The t-test indicates if one can conclude whether the data follow the identity: R2 result = Effluent result, which has a slope of 1.0 and intercept at the origin.

Figure 6-6 compares the R2 NH_3 with the effluent NH_3 for the same system. It shows, as confirmed by the t-test in Appendix 1, that the effluent NH_3 was lower than R2, raising the possibility that the clarifier acted as a reactor.

The effluent samples were taken as a 24 hour cumulative sample, whereas the R1 and R2 samples were taken from the reactor on a grab basis. If an upset such as a spill occurred in the morning, the system units would reflect reduced performance due to a loss of biomass. The effluent sample, however, would not be significantly impacted by the spill and might explain why more points seem below the 45^0 line, which is the line passing through the origin with a slope of 1.0.

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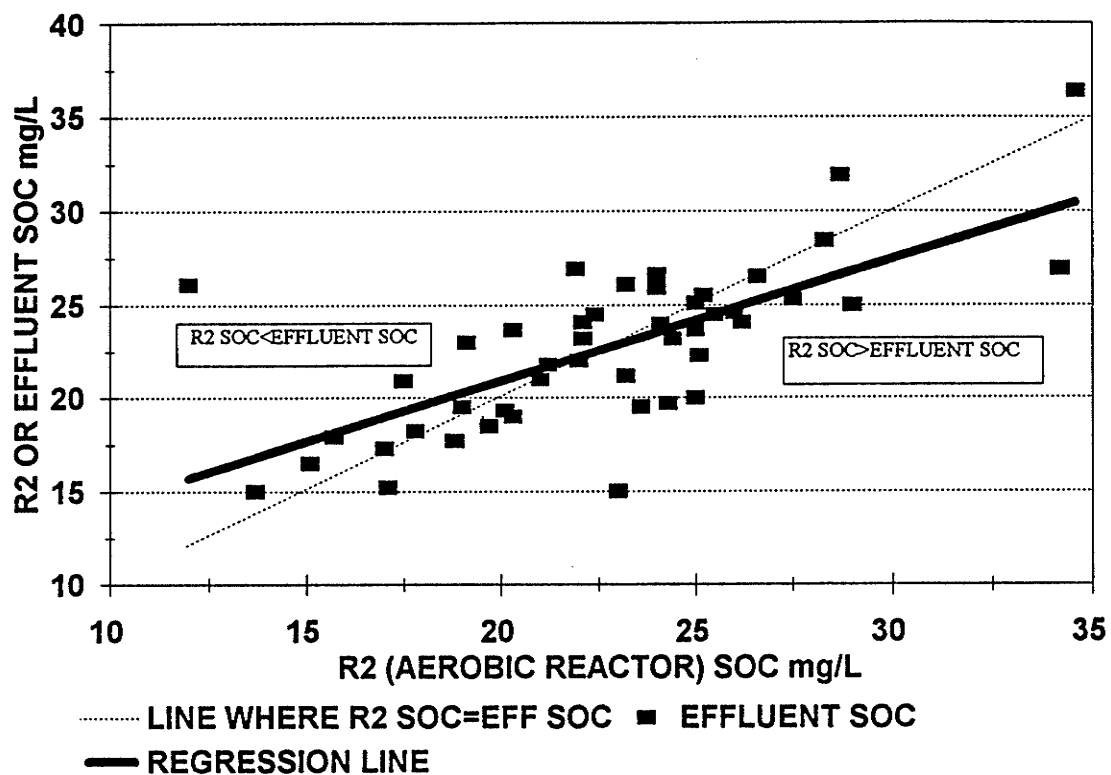
Figure 6-5:   Comparison of Effluent and Aerobic Unit
              (R2) SOC Values in Train A @ 22°C
              1.5 h anoxic; 4.5 h aerobic
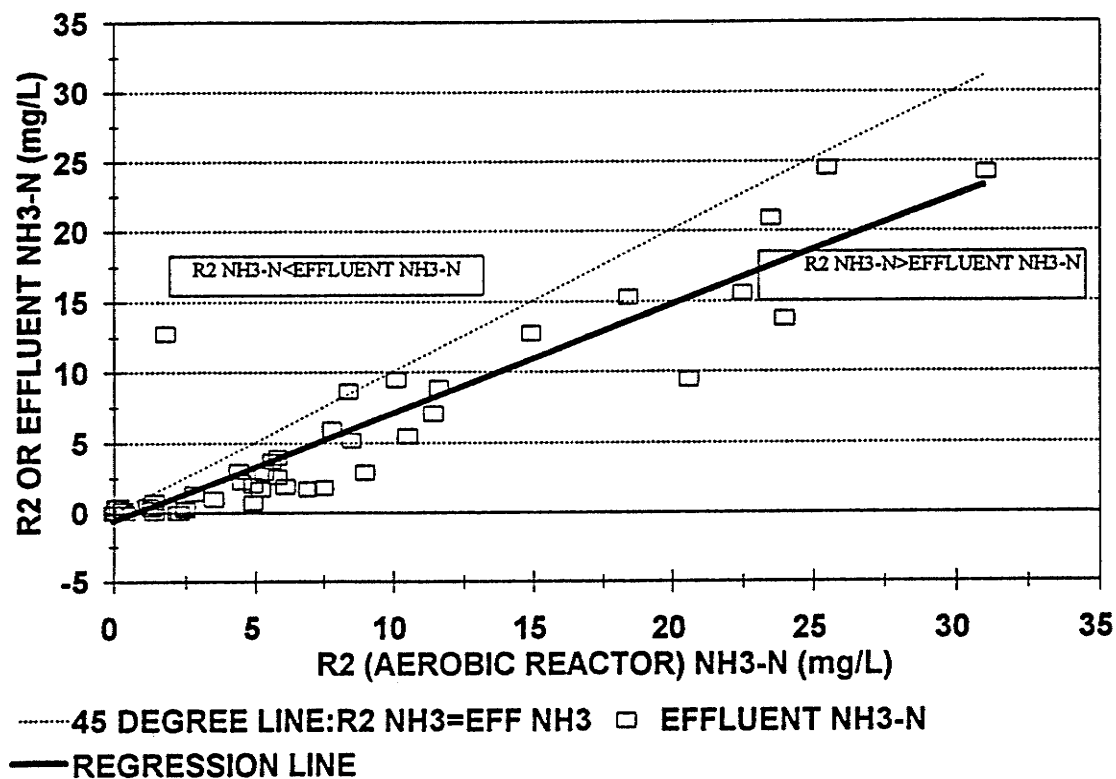
Figure 6-6:   Comparison of Effluent and Aerobic Unit
(R2) NH₃ Values in Train A @ 22°C
1.5 h anoxic; 4.5 h aerobic

Another possible explanation is that reactions occurred in the effluent buckets at 4^0C. If the reactions occurred in the bucket, the data at high NH_3 values would be the same, because these are points of poor system nitrification. If larger differences between R2 and effluent NH_3 values occurred at higher NH_3 values, that would mean that the reactions in the bucket at 4^0C would have to be more extensive than at 12^0C. That is impossible, because even though the HRT was 5-10 times higher, the MLSS was about 1/50 that of the system, and the temperature was 8^0C lower. Therefore this explanation cannot be correct.

If the influent line started to plug overnight, the reactors would have a higher HRT, allowing for better removal in the system than would be reflected in the effluent buckets. This could account for points well above the 45° line in any of the plots involving R2 and effluent value comparisons.

The plugging of a recycle line or RAS line would reduce the dilution of the influent by highly oxidized (and high ORP) wastewater. Because of this the ORP of the anoxic reactor would drop. Plugged recycle lines would also reduce the amount of nitrate returned to the anoxic reactor, limiting the amount of potential denitrification. However, during such a blockage, biomass would start to build up in the clarifier, where it could have a continuous source of oxygen to carry out

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nitrification or carbon oxidation. These reactions would increase the difference between the effluent and R2 values.

The SOC and NH_3 values are lower in the effluent than in R2 for Train A at 12^0C as seen from the NH_3 comparison in Figure 6-7 and the SOC comparison in Figure 6-8, and verified by the t-tests in Appendix 12. The tendency for effluent values to be lower than the aerobic reactor values was observed at both 12^0C and 22^0C for Train A. It should be noted from Figure 6-6 that for many of the points where the R2 NH_3 was below 5, the effluent NH_3 was lower. Such conditions have to be considered free of operating problems.

The plot in Figure 6-9 comparing the R2 SOC with the effluent SOC for Train B at 12^0C shows that for the majority of points, the effluent SOC was lower than the SOC in the aerobic reactor, and was also verified by the t-test in Appendix 12. The plot in Figure 6-10 comparing the R2 NH_3 with the effluent NH_3 for Train B at 12^0C also gives lower effluent values than R2 values, and was also confirmed by the t-test in Appendix 1. This Train B data proves that the cause for the difference between the reactor and effluent results applies to both systems.
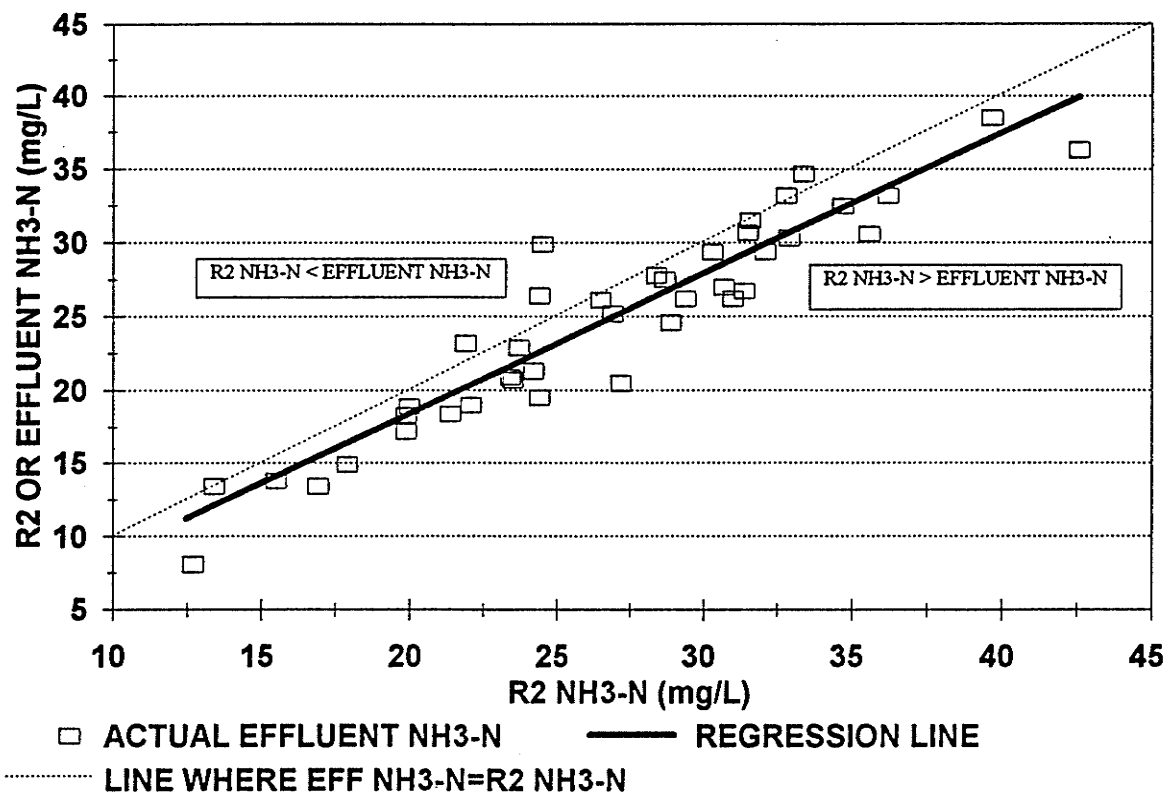
Figure 6-7: Comparison of Effluent and Aerobic Unit
(R2) NH$_3$ Levels in Train A @ 12^{0}C
1.5 h anoxic; 4.5 h aerobic
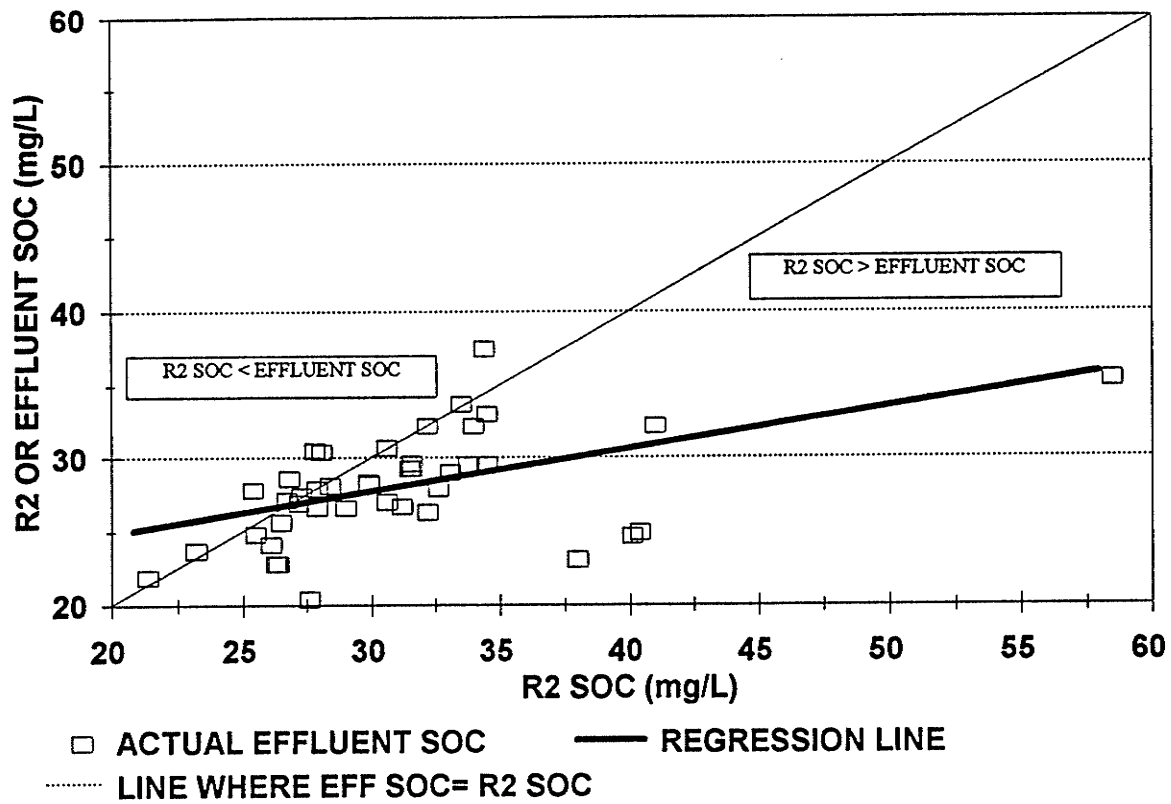
Figure 6-8:   Comparison of Effluent and Aerobic Unit
              (R2) SOC Levels in Train A @ 12°C
              1.5 h anoxic; 4.5 h aerobic
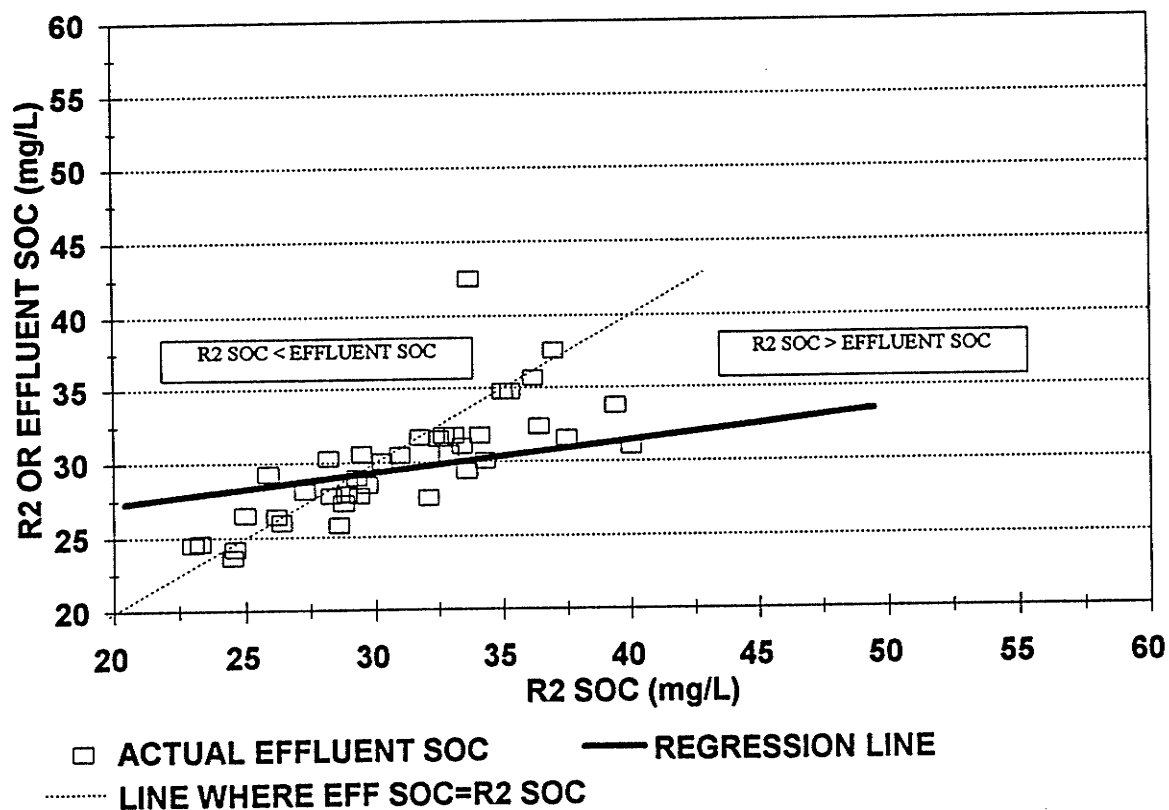
Figure 6-9:   Comparison of Effluent and Aerobic Unit
              (R2) SOC Levels in Train B @ 12°C
              2.0 h anoxic; 2.0 h aerobic
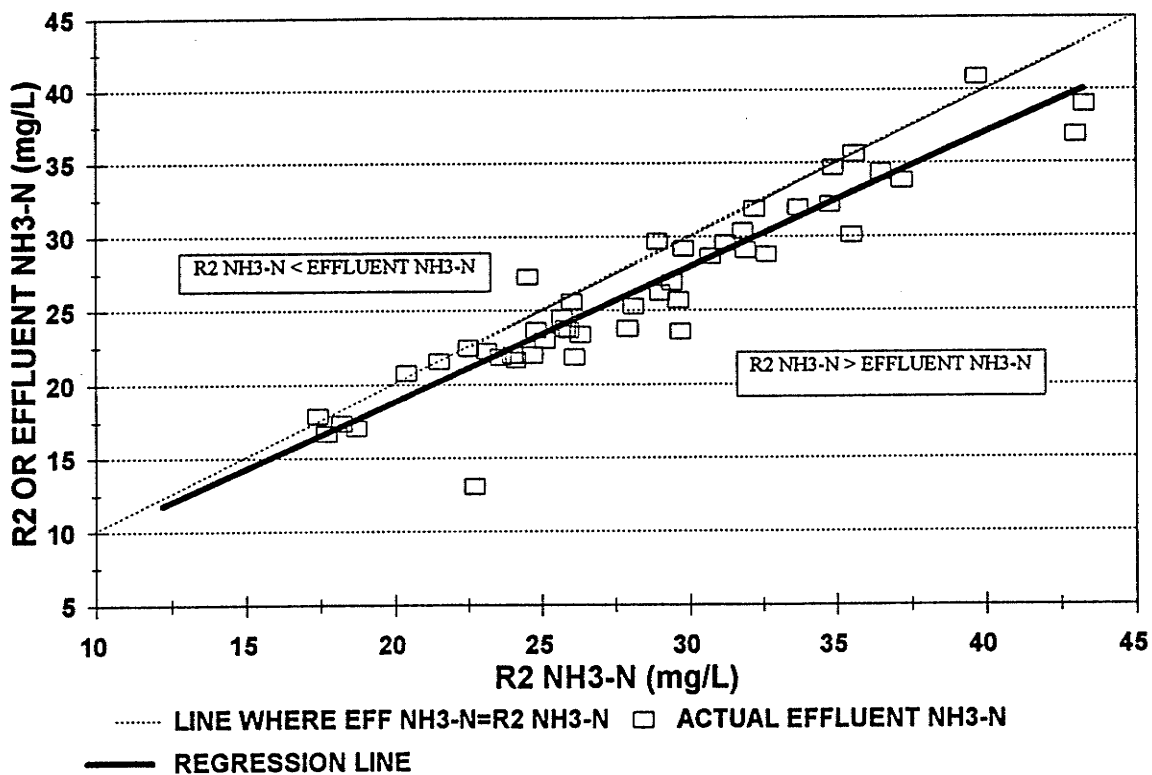
Figure 6-10:   Comparison of Effluent and Aerobic
                Unit (R2) NH₃ Levels
                in Train B @ 12°C
                2.0 h anoxic; 2.0 h aerobic

In Figure 6-8 it should be noted that below R2 SOC values of 30, about half the effluent data points are above the line and half below, whereas above R2 SOC values of 30, all but one is below the line. Similar behaviour exists for Train B in Figure 6-9. This suggests that the system SOC removal is near its limit, and both systems, one with a 50% larger HRT, have essentially the same limit. It also suggests that some SOC is released at low SOC values in the clarifier. This is reasonable since non-degradable SOC would be desorbed by the biomass, and only when the degradable SOC is removed, could such a phenomenon be detected. This might account for the lack of statistical evidence in Figure 6-5 to conclude that the effluent values were lower than the R2 values because those data include the period of August to mid-September which had low influent SOC values. From this evidence from two systems at two temperatures, it follows that while there is degradable carbon in the clarifier, it is being removed, and is being removed to very low levels. Furthermore, ammonia was also removed, which would mean that the clarifiers in each of the cases were aerobic. A method of verifying this is to check the R2 and effluent nitrates since the effluent nitrates should be higher than the R2 nitrates.

Figures 6-11 and 6-12 show that the effluent nitrates were higher than the R2 values, and the t-tests in Appendix 1 confirm it for Trains A and B at 12^0 C respectively. This
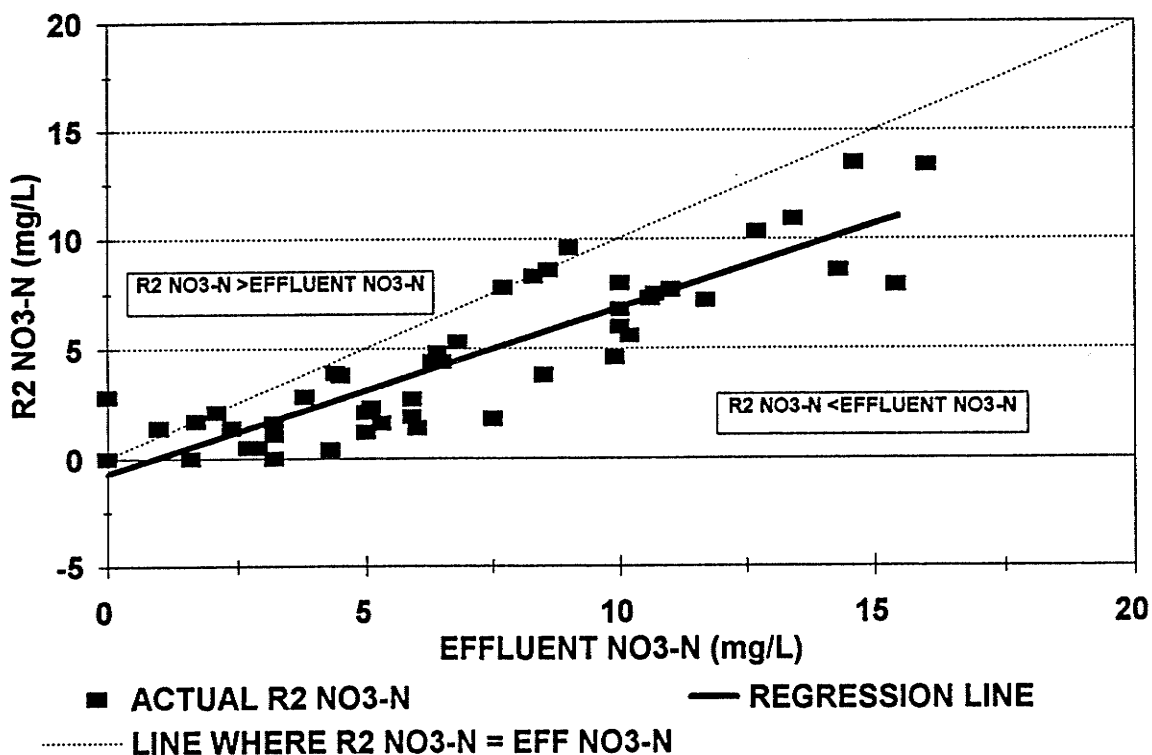
Figure 6-11:   Comparison of Effluent and Aerobic
                Unit (R2) NO$_3$ Levels
                in Train A @ 12^{0}C
                1.5 h anoxic; 4.5 h aerobic
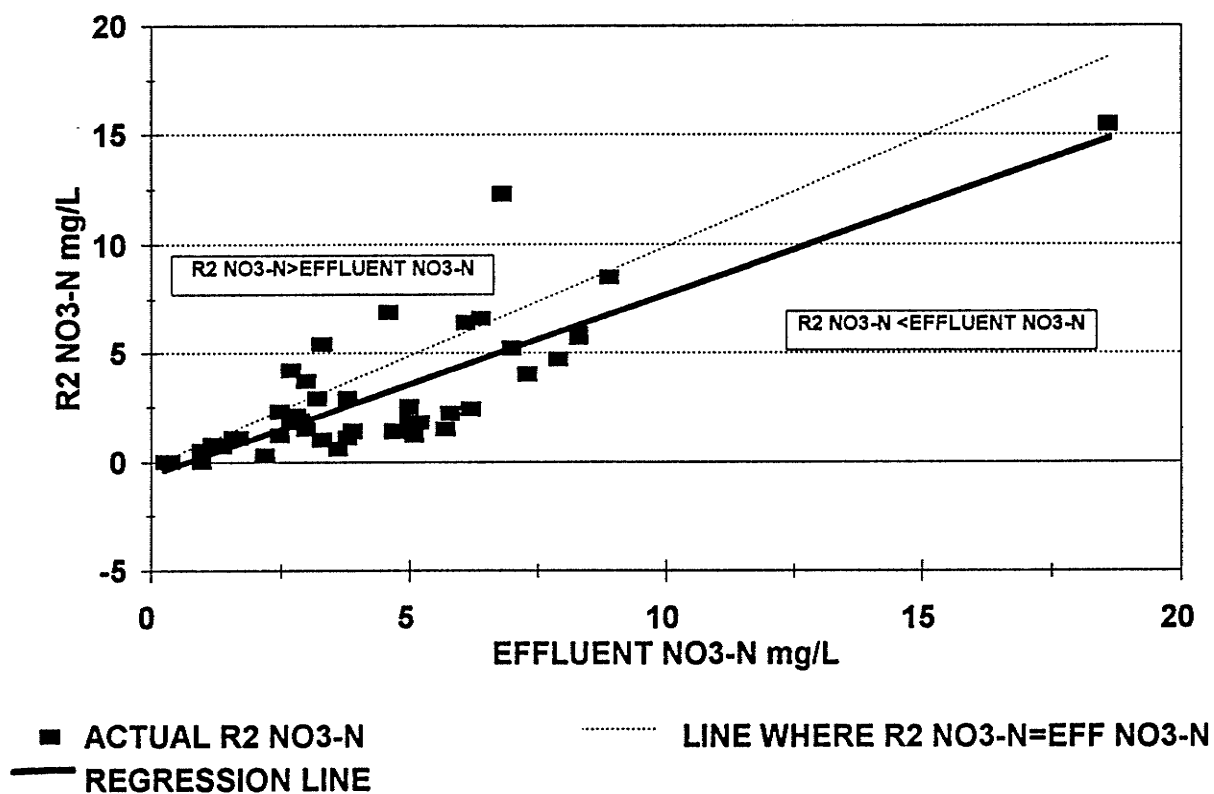
Figure 6-12:   Comparison of R2 and Effluent NO_3
Values for Train B @ 12^0C

supports the hypothesis that the clarifier was behaving as a reactor. However, it does not help differentiate between this explanation and the one that suggests operating problems led to poorer performance in the reactors.

There is one possible operating problem that might have led to a discrepancy between the effluent and aerobic reactor values is that the chamber temperatures may have been different between the evening and the day. Since most samples were taken in the morning, the system could have been at its lowest efficiency during sampling. However, if this were true, the mass balances would not have worked. Furthermore, sampling at 12^0C was frequently taken later in the day, when the R2 results would be from a higher temperature. No change in the behaviour is noted between temperatures. Thus it must be concluded that neither sampling time nor chamber temperature caused the observed behaviour.

In order to prove that a difference could exist between the aerobic reactor and clarifier results, it should be possible to show that such difference could occur during periods in which there were no operating problems. In Figure 6-13, the comparison of the % Nitrification from both the aerobic reactor and the effluent buckets is shown along with the anoxic reactor ORP. The areas circled in the figure indicate
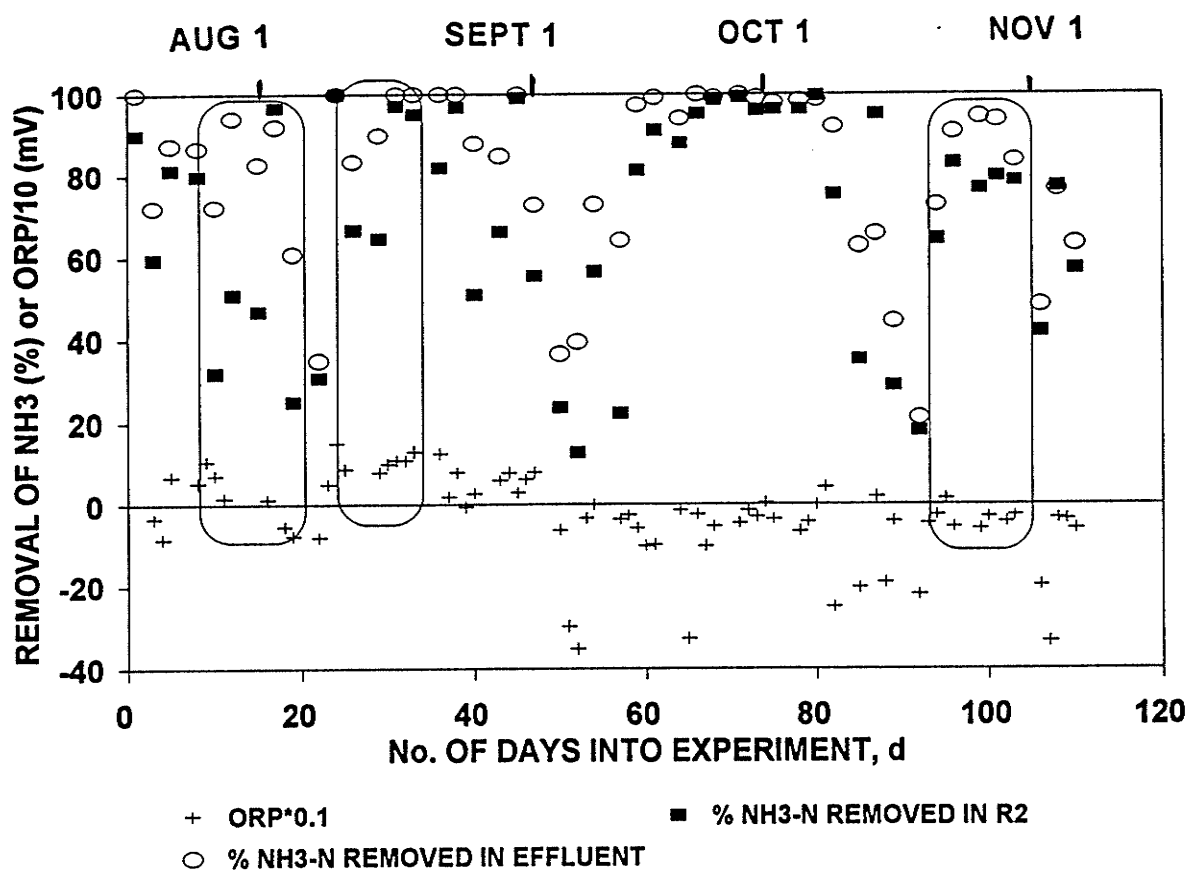
Figure 6-13:   Aerobic Unit (R2) and Effluent
                Percent NH$_3$ Removals and Anoxic Unit
                (R1) Oxidation Reduction Potential
                (ORP) in Train A @ 22°C
                1.5 h anoxic; 4.5 h aerobic

differences between the R2 and effluent results during periods of stable ORP of Train A at 22°C. The differences cannot be attributed to operating problems. If temperature changes were a factor, the difference would be more consistent. Therefore it must be concluded that the clarifiers exhibited reactor behaviour.

6.4   SOC Relationship to NO_3 Removal

Mass balances from the SOC data showed that SOC was removed in the anoxic reactor. Figure 6-14 shows the SOC removal at 12°C in Train A compared to the SOC that would be theoretically removed if there were 20 mg/L of denitrification (the equivalent of 10 mg/L of denitrification and 15 mg/L of dissolved oxygen in the recycle). Removal of 10 mg/L NO_3 never occurred, as is apparent from the removal of NO_3 shown in Figure 6-15, nor did the dissolved oxygen attain 15 mg/L. The SOC removal that did occur indicates that there was more than enough carbon removed to react with these amounts. Therefore, the SOC was either reacting with something besides the known reactants O_2 and NO_3, or SOC was removed by another mechanism. There is no reaction to explain the SOC removal because the anoxic reactor ORP tended to be too high for sulphate reduction (which occurs below -250 to -300 mV) and would not have occurred without first completing nitrate

92
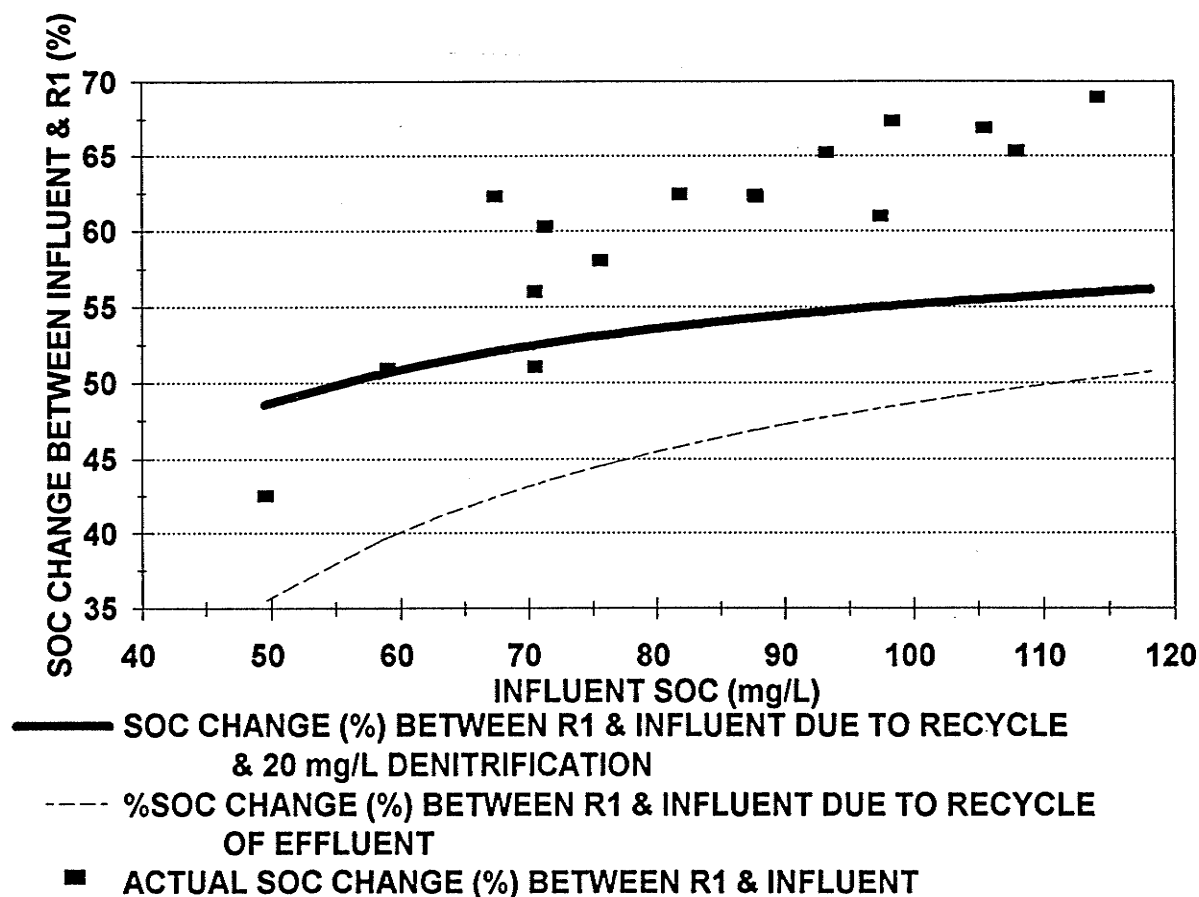
Figure 6-14:   Percentage Change between Influent
                and Anoxic Unit (R1) SOC based
                Actual Data, and also on Theoretical
                Calculations, One Assuming Only
                Dilution From the Recycle, the other
                Assuming Dilution from Recycle and
                also 20 mg/L of NO_3-N of
                Denitrification
                Anoxic Unit Train A @ 12^0C
                1.5 h anoxic; 4.5 h aerobic
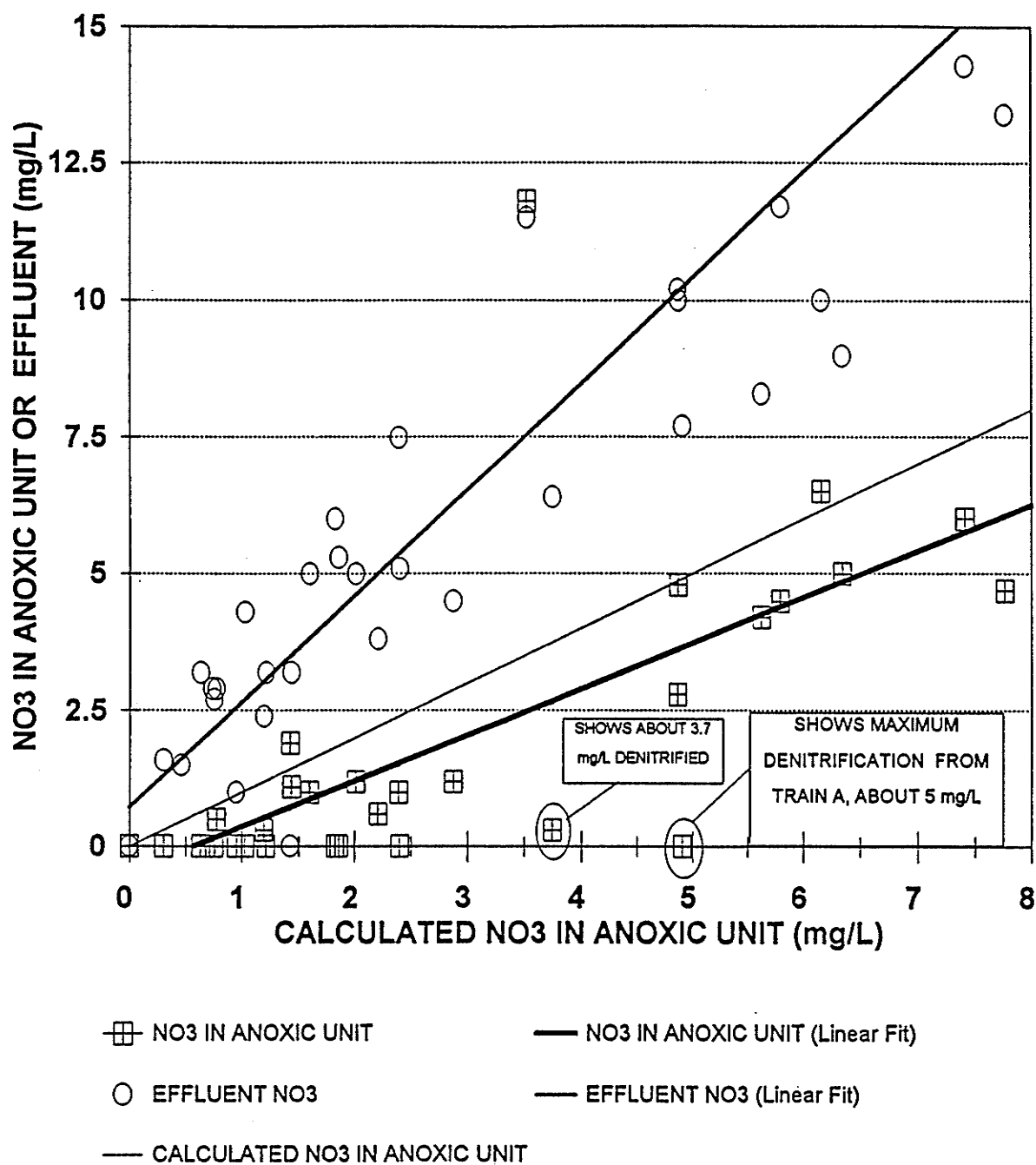
Figure 6-15:   Nitrate Balance for Anoxic Reactor
                using Aerobic Reactor, Effluent and
                Recycle Data for Train A @ 12°C
                1.5 h anoxic; 4.5 h aerobic
                NO3 is reported as NO3-N

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reduction. Any precipitation reactions would have occurred when the primary effluent was received. At times, some containers had to be stored at the operating temperature of 12^0C for over 24 hours, and no precipitation reactions were observed. Because of this, another SOC removal mechanism must be postulated.

Figures 5-7, 5-8 and 5-9 showed a plot of the SOC removed in the 1.5 h anoxic reactor versus the influent SOC at 22^0C. The best fit of the data was a straight line, which suggests that SOC removal is a first order reaction. Figures 6-16, 6-17 and 6-18 also show that SOC removal at each reaction stage at 12^0C was largely a linear function of the influent SOC. The data are scattered but the linear trends are apparent, corroborating the first order SOC removal findings at 22^0C. This also indicates that SOC removal in the anoxic reactor essentially depended upon the influent concentration, rather than denitrification or other parameters. Given that SOC measurements were taken in order to examine the relationship between SOC removal and NO_3 removal, it is important to explain the SOC removal behaviour.

SOC can be removed by adsorption, which is the basis for a selector reactor. Typical adsorption removal curves are the Langmuir and Freundlich isotherms (Montgomery Consulting Engineers 1982). Montgomery Consulting Engineers noted that
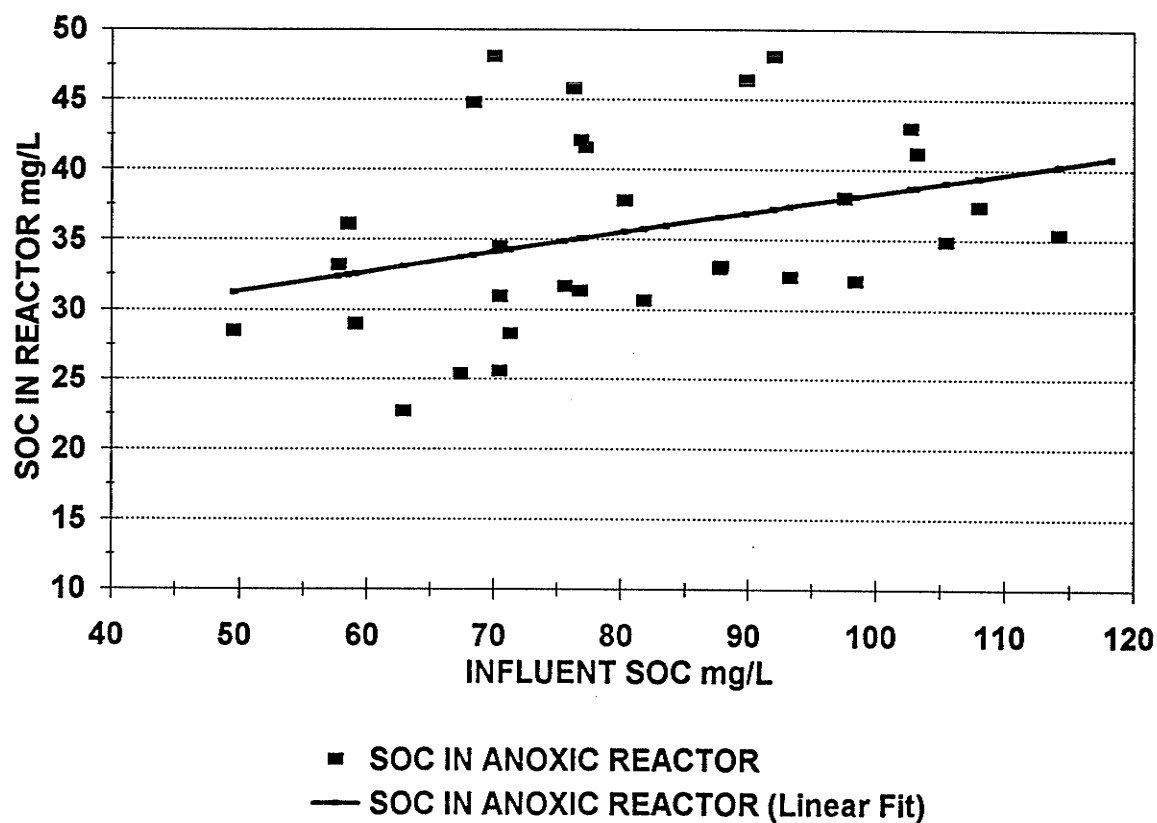
Figure 6-16: SOC in Anoxic Reactor (R1) vs
Influent SOC for Train A @ 12^{0}C
1.5 h anoxic; 4.5 h aerobic
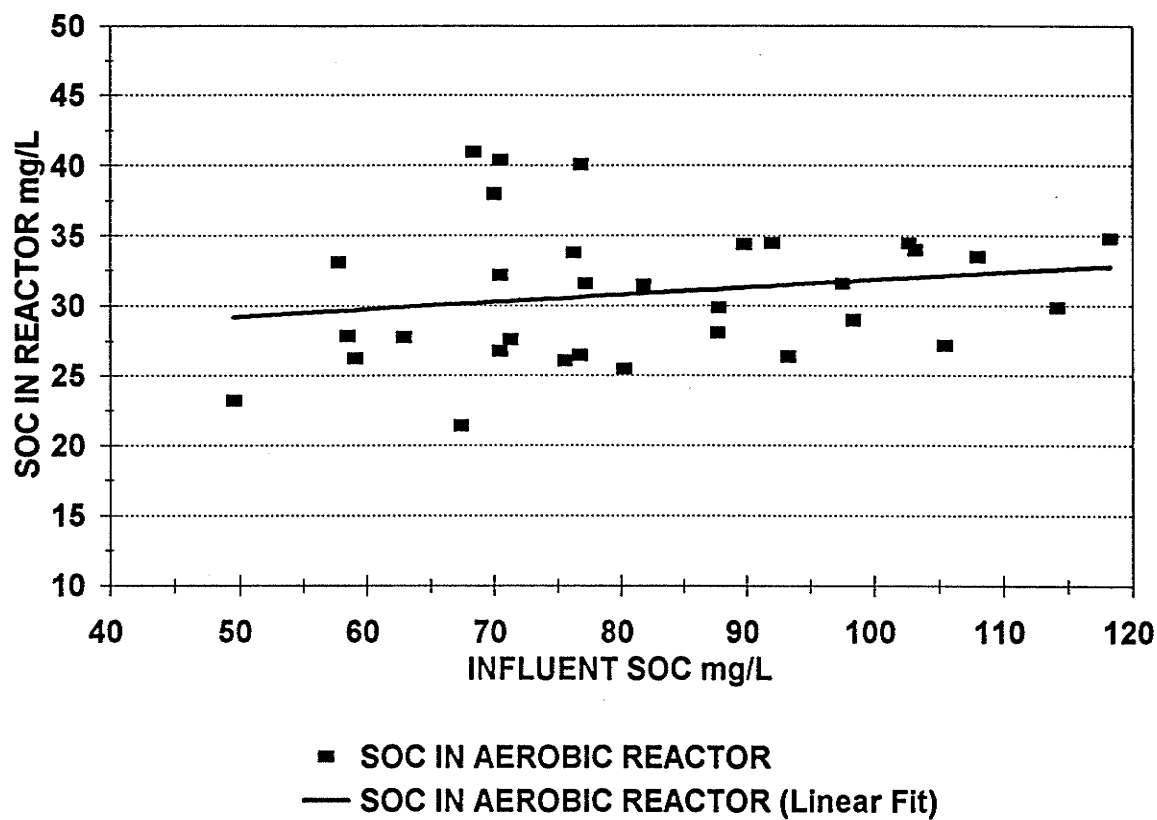
Figure 6-17: SOC in Aerobic Reactor (R2) vs
Influent SOC for Train A @ 12^{0}C
1.5 h anoxic; 4.5 h aerobic
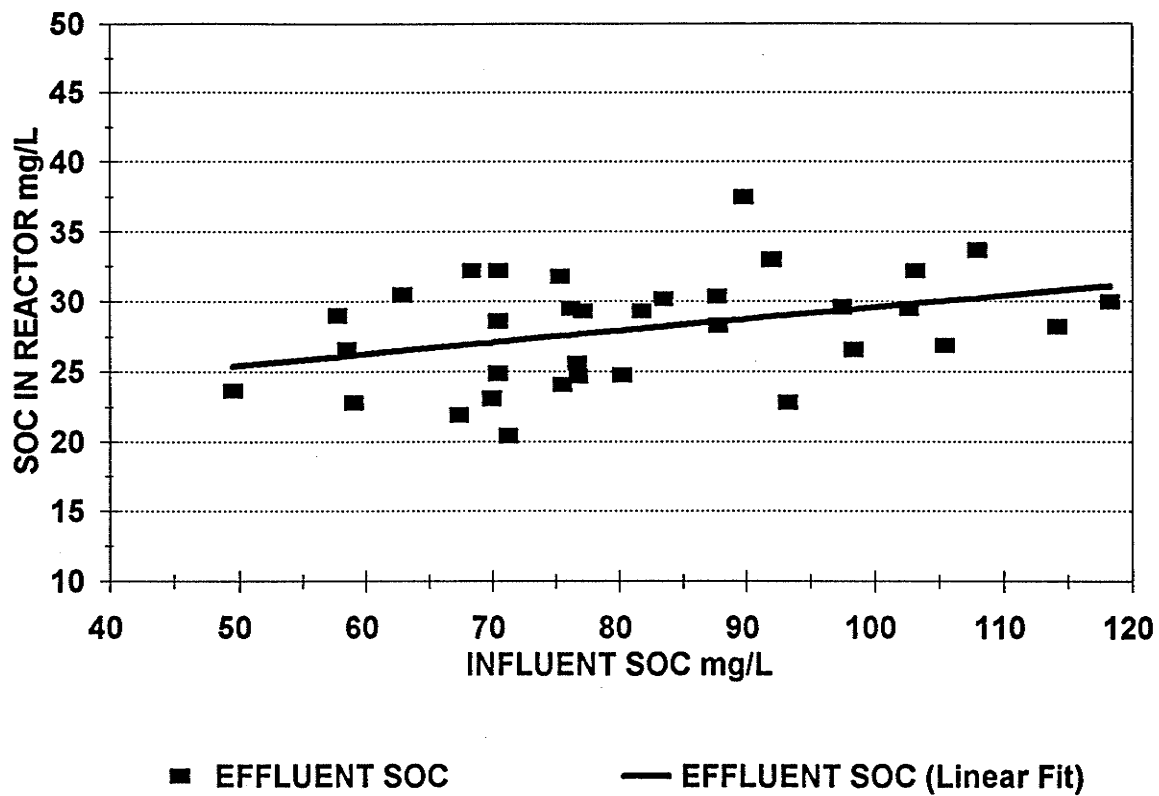
Figure 6-18: SOC Removal in Effluent vs Influent SOC for Train A @ 12^{0}C 1.5 h anoxic; 4.5 h aerobic

the Freundlich isotherm tries to account for heterogeneity of the adsorbent surfaces, which could describe activated sludge surfaces. The expression of the Freundlich isotherm given by Montgomery Consulting Engineers (1982) is: $q = aC^{1/n}$, where a and n are constants, C is the equilibrium concentration, and q is the mass adsorbed. If n=1, then a linear relationship will exist between mass adsorbed and the equilibrium concentration.

Plots of SOC of the reactor versus the influent concentration will be linear if the SOC is removed according to a linear isotherm. The SOC of the reactor can be considered as the equilibrium concentration, C; the SOC adsorbed is the same as q, given by Montgomery Consulting Engineers (1982).

(Influent SOC - Effluent SOC) * Flow Rate = SOC Adsorbed

For a constant flow rate,

(Influent SOC - Effluent SOC) =a' * SOC

and SOC versus influent gives a line with a slope of 1/a' and an intercept of -(effluent x 1/a'), where a' is a constant incorporating the flow rate.

Levenspiel (1972) discusses first order reactions, giving and with $r_a = k \times C^1$. The integration indicates that a plot of $-\ln(1-X_a)$ versus time gives a straight line with slope k,

$$- r_a = \frac{-dC_a}{dt}$$

where X_a is the fractional conversion (or removal):

$$X_a = \frac{\textit{Initial Concentration - Remaining Concentration}}{\textit{Initial Concentration}}$$

If one considers daily reactions of the same process then time is a constant, thus $(1-X_a)$ is also a constant, which means the fractional conversion is a constant. In this case a plot of SOC removal versus influent is a straight line, as is a plot of the remaining concentration versus initial concentration. The latter is the same as the reactor SOC versus influent SOC plots in the Figures 5-7, 5-8, 5-9, 6-16, 6-17 and 6-18.

Therefore, what appears to be a first order chemical reaction could be an adsorption process following a linear Freundlich isotherm. Figures 5-7, 5-8, 5-9, 6-16, 6-17 and 6-18 suggest that SOC removal was an absorption phenomenon that is proportional to concentration.

This adsorption hypothesis was the reason for a batch study conducted in November, 1994. A track study was conducted in a batch reactor where a reactor in an anoxic state, endogenously denitrifying, had been spiked with primary effluent and samples were taken to compare soluble organic

carbon (SOC) removal and NO_3 removal. The plot in Figure 6-19 shows that the SOC removal was much faster than NO_3 removal. The SOC removal was essentially complete after 25 minutes whereas the nitrate removal was linear, and after 3 hours, only 50% of the amount of SOC removed could have reacted with the nitrate. There was no oxygen to react with, so SOC removal was by a different phenomenon than reactions with NO_3.

The logical conclusion is that SOC removal in the systems was governed by adsorption. The consequence of this finding is that one must also conclude that SOC removal does not correlate with NO_3 removal, which was one objective of this study.

6.5   TKN and NH_3 Balances

Figures 5-11, 5-12 and 5-13 showed that the slopes of the NH_3:TKN ratio changed from unit to unit. The change in slope is due to different amounts of removal of TKN and NH_3. Some TKN is removed by assimilation, some by nitrification of ammonia, and some is non-degradable TKN. As more ammonia is removed, the non-degradable component forms a larger percentage of the remaining TKN.   Thus, variations in nitrification or in the amount of non-degradable TKN would cause more scatter of the data points at the lower TKN levels. This is reflected by the higher scatter of the effluent data in Figure 5-13 than the scatter of the aerobic reactor data in

101
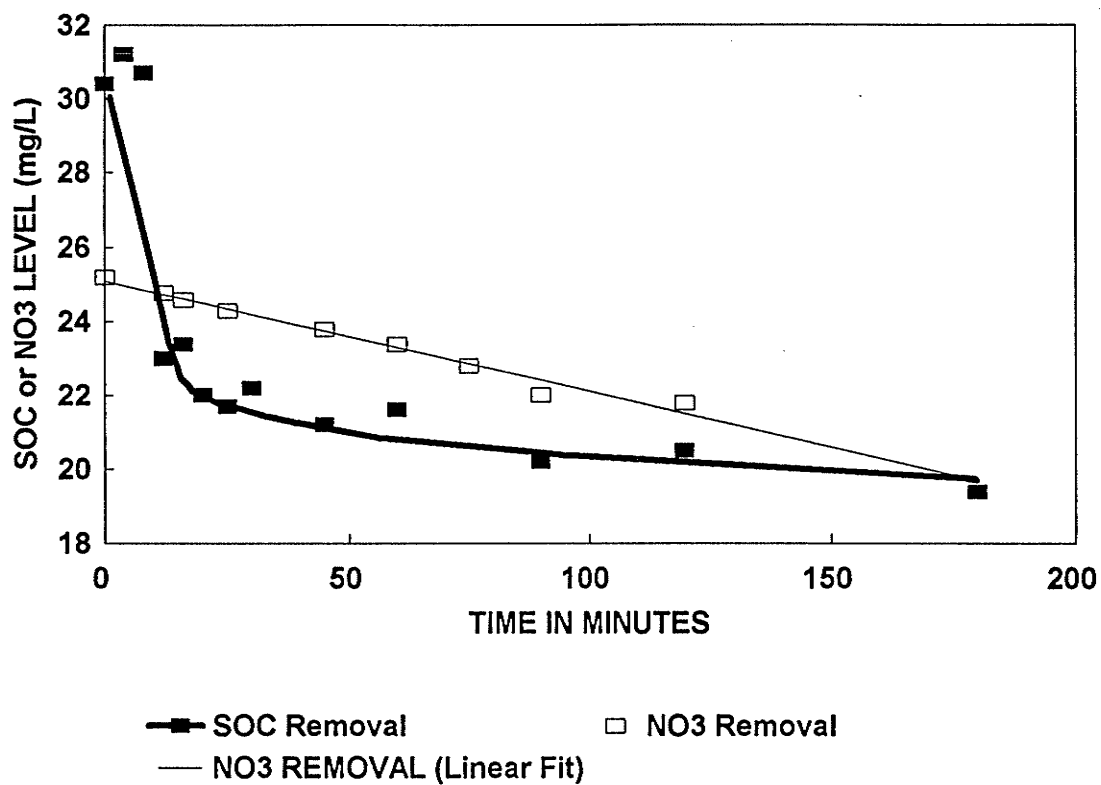
Figure 6-19:   SOC and NO$_3$ Removal vs Time in
              Anoxic Batch Reactor at 22^{0}C

Figure 5-12, which has more scatter than the anoxic reactor data from Figure 5-11.

There should not be any ammonia removal in the anoxic reactor, although there is the possibility of generation of ammonia. However, by assuming that the anoxic reactor simply removes nitrate and carbon without affecting NH_3 or TKN, the NH_3 or TKN values can be used as a tie element for analysis.

The plot of the actual NH_3 versus the calculated NH_3 in Figure 6-20 demonstrates that there is a good fit. Nine points lie above the line, and nine are below the line. Points above the line can reflect two things: ammonia production in the anoxic reactor, or slightly less recycle than assumed in the calculation. Points below the line suggest ammonia removal or higher recycle than assumed in the calculation which would occur if the influent line were plugging, as R/Q would be higher.

The TKN balance should reflect the same thing as the ammonia balance. The TKN balance in Figure 6-21 is a bit more scattered than the NH_3 balance, which is understandable because there is less accuracy in the TKN test than the NH_3 test. However, there are more points below the line than above, which suggests TKN removal. This is significant because ammonia production due to hydrolysis of urea or other

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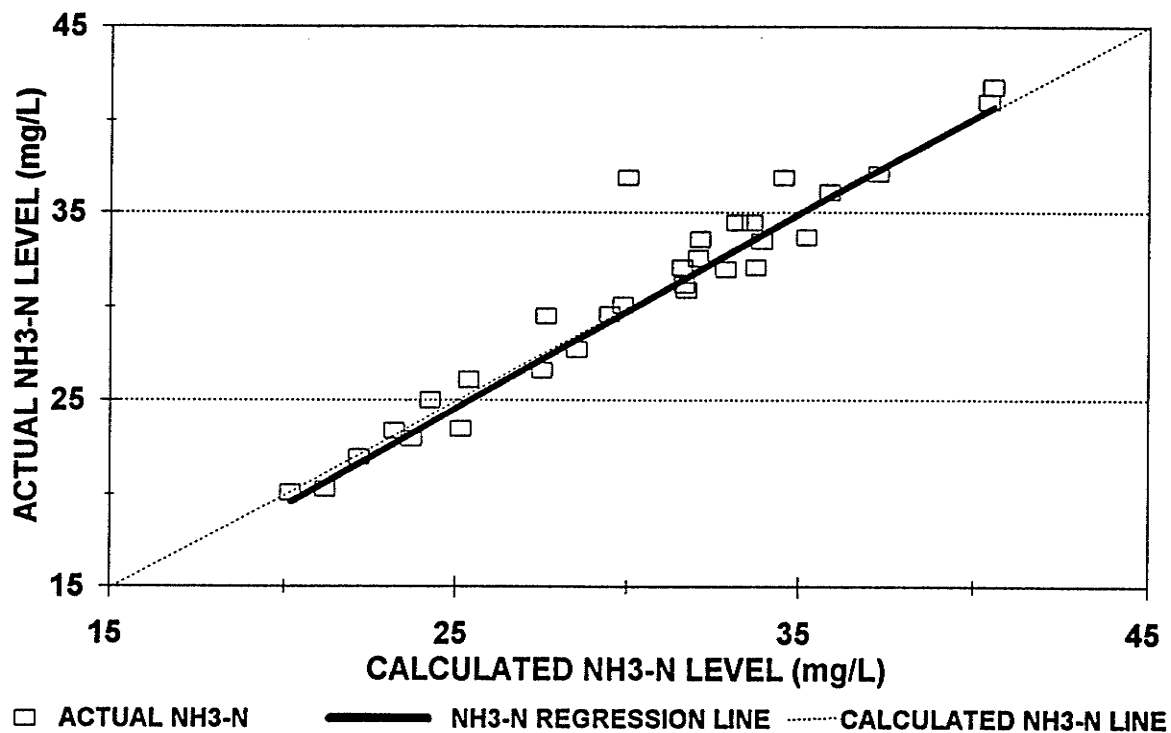
Figure 6-20: Ammonia Balance in Anoxic Unit Using
Recycle, Aerobic Unit, and Effluent
Data in Train A @ 12°C
1.5 h anoxic; 4.5 h aerobic
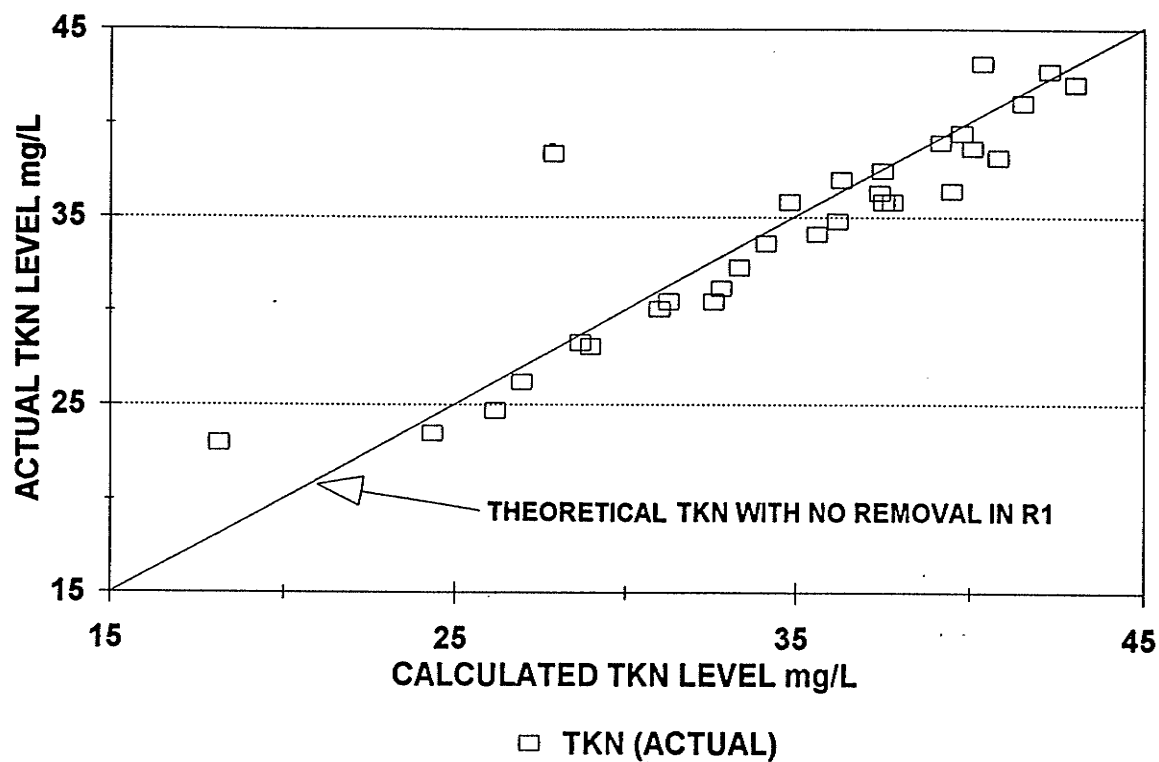
Figure 6-21: TKN Balance in Anoxic Unit Using
              Recycle, Aerobic Unit, and Effluent
              Data in Train A @ 12⁰C
              1.5 h anoxic; 4.5 h aerobic

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compounds was possible. However, the hydrolysis of urea to ammonia would not have affected the TKN, because the ammonia would still have counted as part of the TKN value. Thus the TKN that was removed was not ammonia; it was TKN that was assimilated into cell mass. It may also be concluded that the recycle values and the concentration data used were accurate.

The ammonia and TKN balances are assumed to give the most reliable value for the assumed recycle because the recycle values were determined based on pump RPM, ignoring the possibility that the recycle or RAS lines were plugged or plugging. However, plugging events often caused spills, and sampling would be avoided or delayed after such events.

The ammonia balance at 12^0C for Train B in Figure 6-22 shows a good fit with the calculated values. The TKN balance in Figure 6-23 shows, similar to Figure 6-21, both more scatter and also slight TKN removal. The replication of the observations of Train A in Train B supports the conclusions made previously.
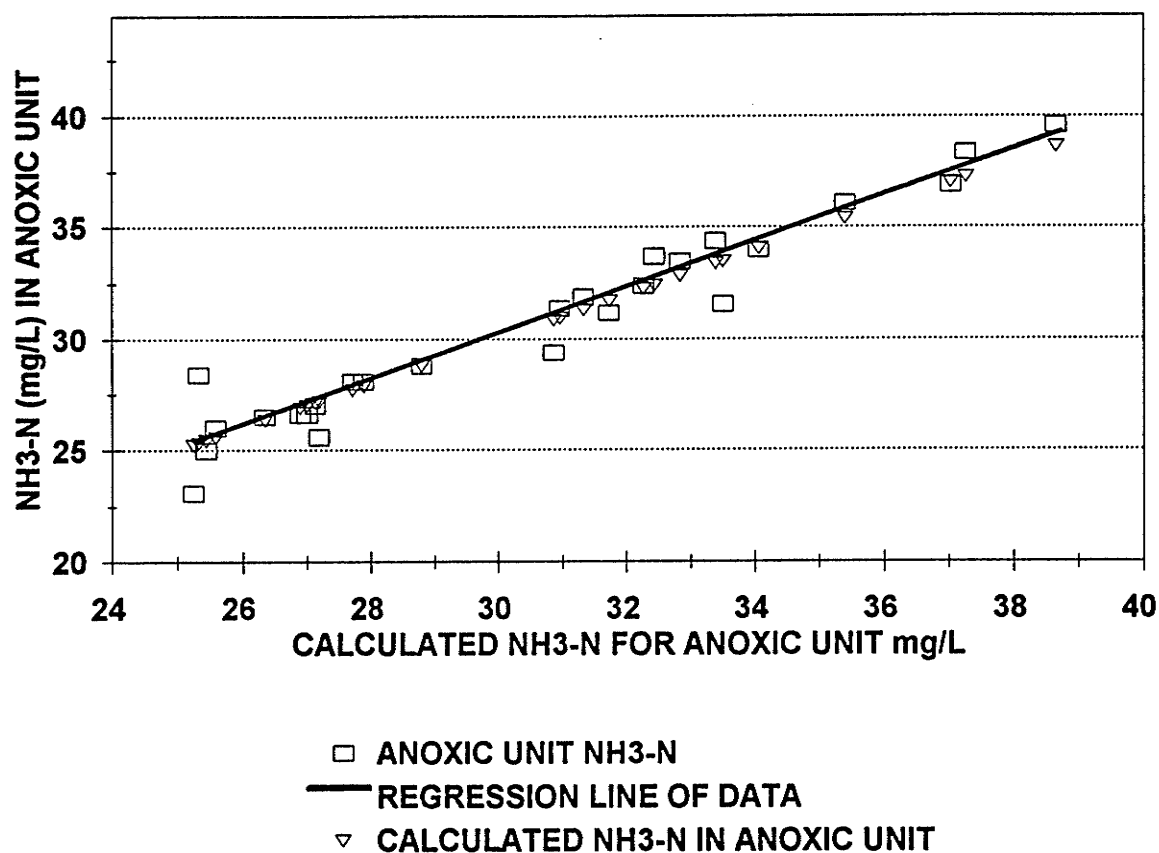
Figure 6-22:   NH₃ Balance in Anoxic Unit Using
Recycle, Aerobic Unit, and Effluent
Data in Train B @ 12⁰C
2.0 h anoxic; 2.0 h aerobic
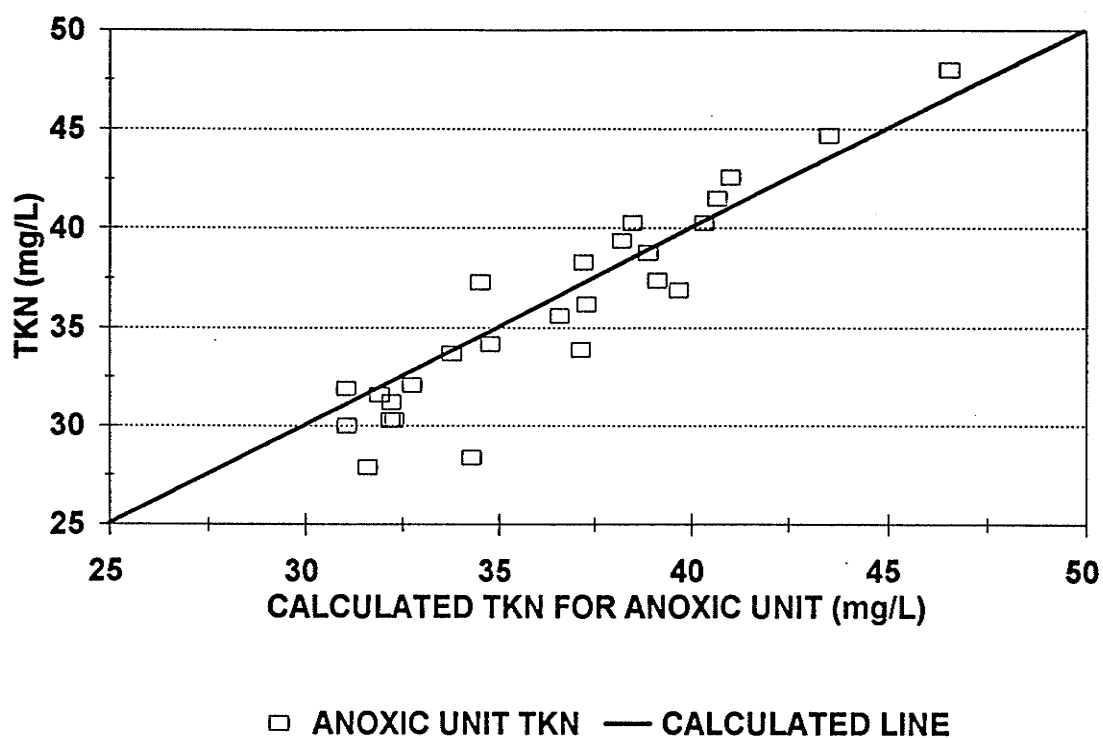
Figure 6-23:   TKN Balance in Anoxic Unit Using
               Recycle, Aerobic Unit, and Effluent
               Data in Train B @ 12°C
               2.0 h anoxic; 2.0 h aerobic

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6.6 % Nitrification and % Denitrification at 12°C

Figure 5-17 showed that the nitrification in Train A increased after February 18, nearing 80% nitrification. The histograph of nitrification and denitrification in Train A at 12°C, starting from November 8, is shown in Figure 6-24. After about January 24 (Day 85 in Figure 6-24), the percentage denitrification rarely exceeded 20% when, if the anoxic reactor were a highly efficient denitrifying reactor, the removals would have been about 70% based on a recycle of 2.11Q. From this it can be concluded that Train A did not denitrify effectively during the period that it began to nitrify. It can also be concluded that Train A did not achieve a steady-state condition.

Figure 5-20 showed that Train B did not nitrify more than 40% of the influent ammonia. Figure 6-25 shows the percent denitrification in Train B at 12°C. A similar conclusion can be made about denitrification effectiveness after Day 95. Denitrification did climb from 30% to about 75% from about Day 20 to Day 70, sustaining more than 50% denitrification for nearly the last thirty days. However, nitrification was less than 40% during this time. It was also noted that SRT control of Train B was affected by solids losses from the clarifier and spills. Therefore, Train B cannot be considered to have achieved steady-state nitrification at any time.
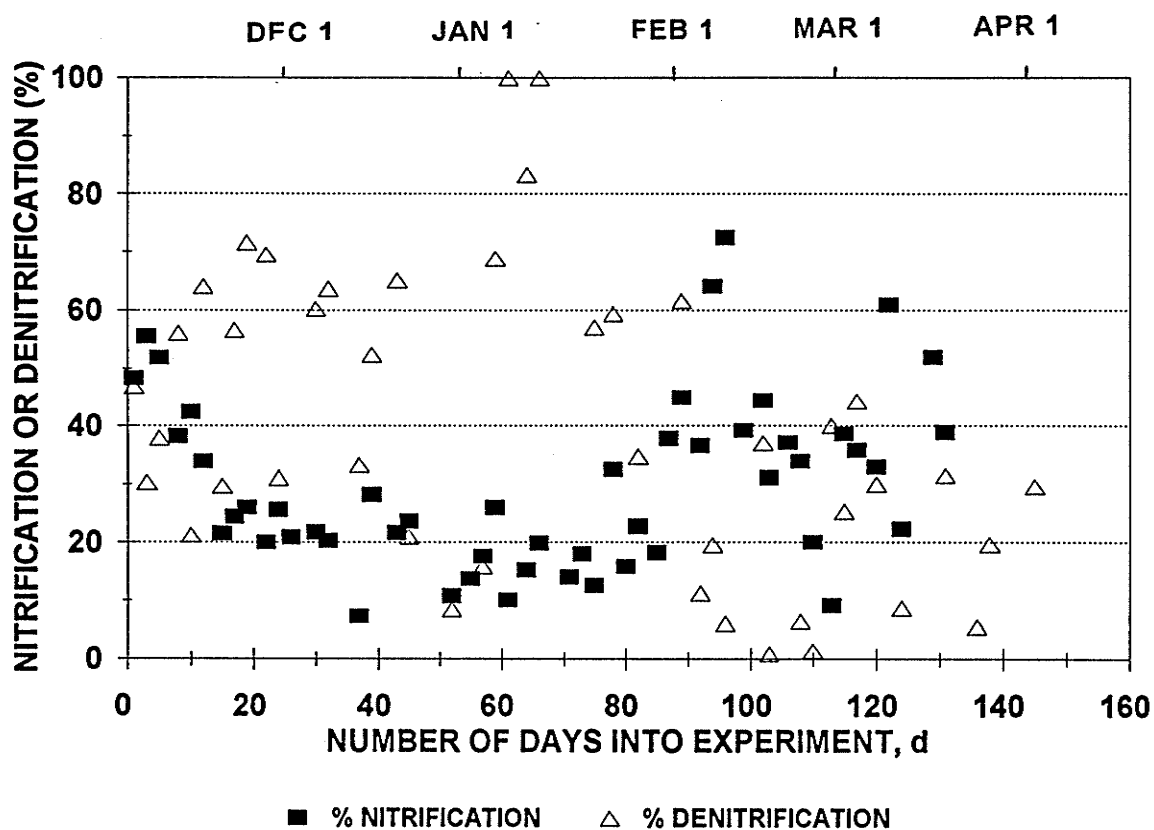
Figure 6-24:   %Nitrification Efficiency (Based on
NH₃ Converted) and %Denitrification
(Based on NH₃ Converted and NO₃
Remaining) in Train A @ 12⁰C
1.5 h anoxic; 4.5 h aerobic
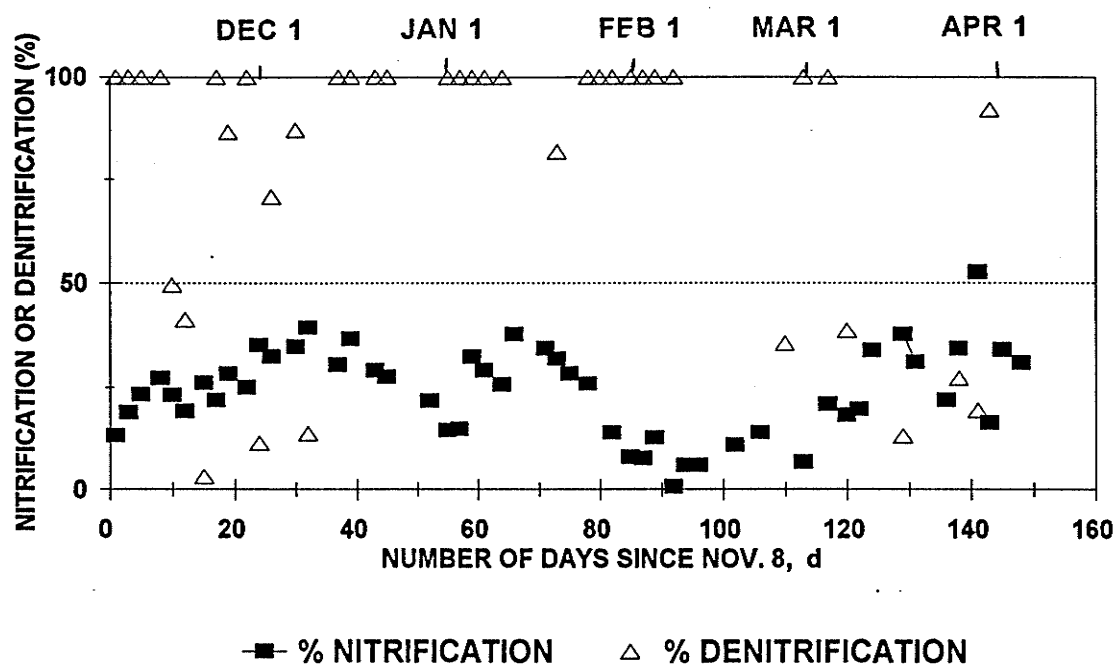
Figure 6-25:   %Denitrification and %Nitrification
Comparison @ 12^0C in Train B
2.0 h anoxic; 2.0 h aerobic

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With only two systems, one not denitrifying very well and the other not nitrifying very well, and neither at steady-state, analysis of nitrification and denitrification is limited. Some analysis of why denitrification was minimal is possible, as is some analysis of the factors that may have improved the nitrification process.

6.7 Hypothesis 1: Denitrification was Limited Due to a Lack of Available Carbon

The first consideration for a lack of denitrification in the 1.5 h anoxic reactor is a lack of carbon. Figure 5-1 showed that the SOC also was low over the summer period. According to Metcalf and Eddy, the amount of SOC required to denitrify 1 mg of nitrate is 0.93 mg. Therefore, the SOC:TKN ratio can be plotted to see if there was enough carbon to denitrify. The SOC:TKN histograph in Figure 5-5 included SOC that was not degradable. Thus, an estimated biodegradable SOC:TKN ratio histograph is presented in Figure 6-26.

There are points where the SOC:TKN ratio is below 0.93, particularly before September 15. For the bulk of the experiment, the degradable SOC:TKN ratio is above 0.93.
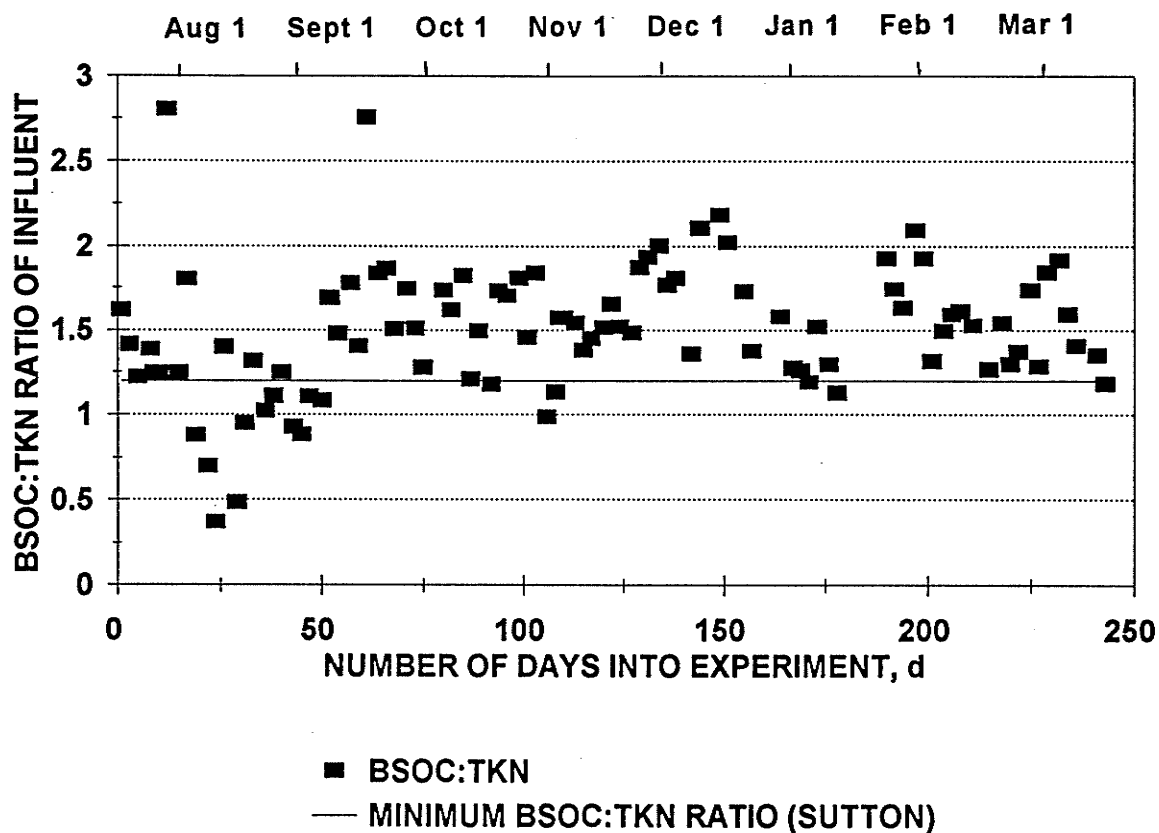
Figure 6-26:   Biodegradable SOC (BSOC) to TKN Ratio
                (BSOC:TKN Ratio), Assuming 14 mg/L
                Nondegradable SOC

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Because the nitrate returned to the anoxic unit could not have been more than about 66% of the TKN, one could conjecture that the critical ratio for these systems should be 0.61. However, McCarty (1969) indicated that using methanol, the actual C/N consumption ratio was 1.3, which boosts the 0.61 ratio based on 66% returned, to 0.8. Mandt and Bell (1982) indicated that maximum denitrification rates can only occur when biodegradable carbon is present in excess, but they did not define the extent of the excess carbon requirement. Based on these authors' findings the critical SOC:TKN ratio should be higher.

Another method of estimating carbon availability is to use COD:TKN ratio in the literature. Carley (1988) reported that a minimum 6.2:1 COD:NO_x ratio was needed, using methanol, and Brannan and Randall (1987) stated that below a COD:TKN ratio of 9.5:1 that the MLE process should be used instead of Bardenpho, which indicates the 9.5:1 ratio would be suitable for denitrification.

Sutton et al. (1978 a,b) conducted practical tests to see what COD to N ratio failed, and concluded that a minimum of 8.6 (a) or 8(b) grams of COD need to be available to reduce 1 gram of NO_3-N. Picard and Faup (1980), using an MLE process with recycles of 4.0Q and RAS of 1.5Q, achieved 85% nitrogen removal with sugar cane wastewater having slightly more than

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a 9.1:1 COD:TKN ratio.

Taking the average COD of wastewater with the composition from Sawyer and McCarty (1978)of $C_{10}H_{19}O_3N$, and converting Sutton et al's (1978a) 8.6:1 COD:NO_3 ratio to an SOC:NO_3 equivalent gives a biodegradable SOC:NO_3-N (BSOC:NO_3-N)ratio of 2.18:1. By assuming that only 55% of the TKN in the influent becomes NO_3-N that is returned to the anoxic reactor for denitrification, the ratio of biodegradable SOC:TKN becomes 1.2:1. Figure 6-27 shows that in the case of the data before September 15 (approximately day 55), the system was frequently carbon-limited. The BSOC:TKN ratio in Figures 6-26 assumes that 14 mg/L was non-degradable carbon, while 6-27 assumes a minimum of 12 mg/l plus 15% of the SOC above that was non-degradable. Figure 6-28 shows the BSOC:TKN ratio assuming that the BSOC is a minimum of 12 mg/L plus 5% of the remainder, giving:

BSOC = (Influent SOC - 12)*0.95,

where 12 mg/L was the assumed non-degradable carbon.

The value of 12 mg/L was lower than the effluent SOC from Train A at 22°C after it was fed the effluent from the previous day. Caponetto (1994) had effluent BOD's of less than 10 mg/L with effluent SOC's of 20 mg/L, which, with an oxygen demand of 2.67 mg O_2 per mg of degradable SOC, means that the 12 and 14 mg/L assumptions are reasonable. At an influent SOC of 60, the non-degradable component is 14.4 mg/L.

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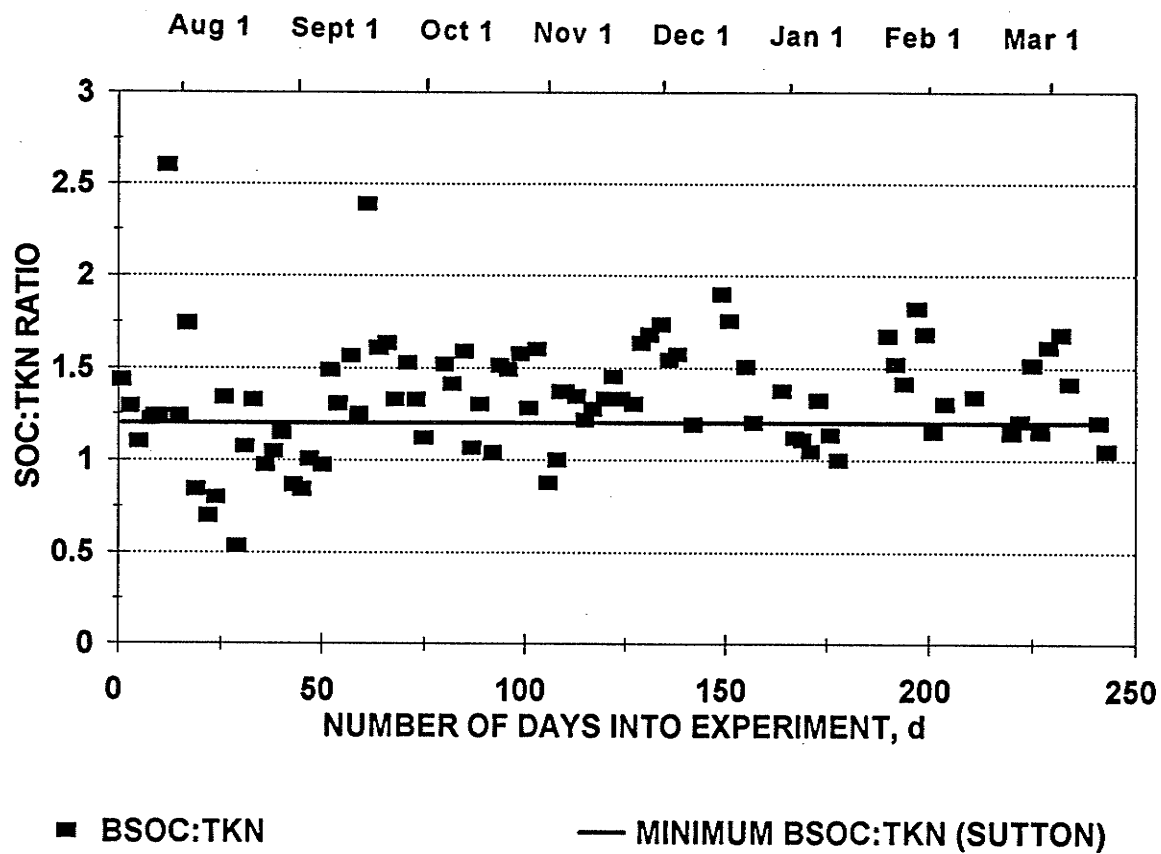
Figure 6-27:   Biodegradable SOC (BSOC) to TKN Ratio
(BSOC:TKN Ratio) Assuming 12 mg/L
+ 15% of Remaining SOC as
Nondegradable SOC
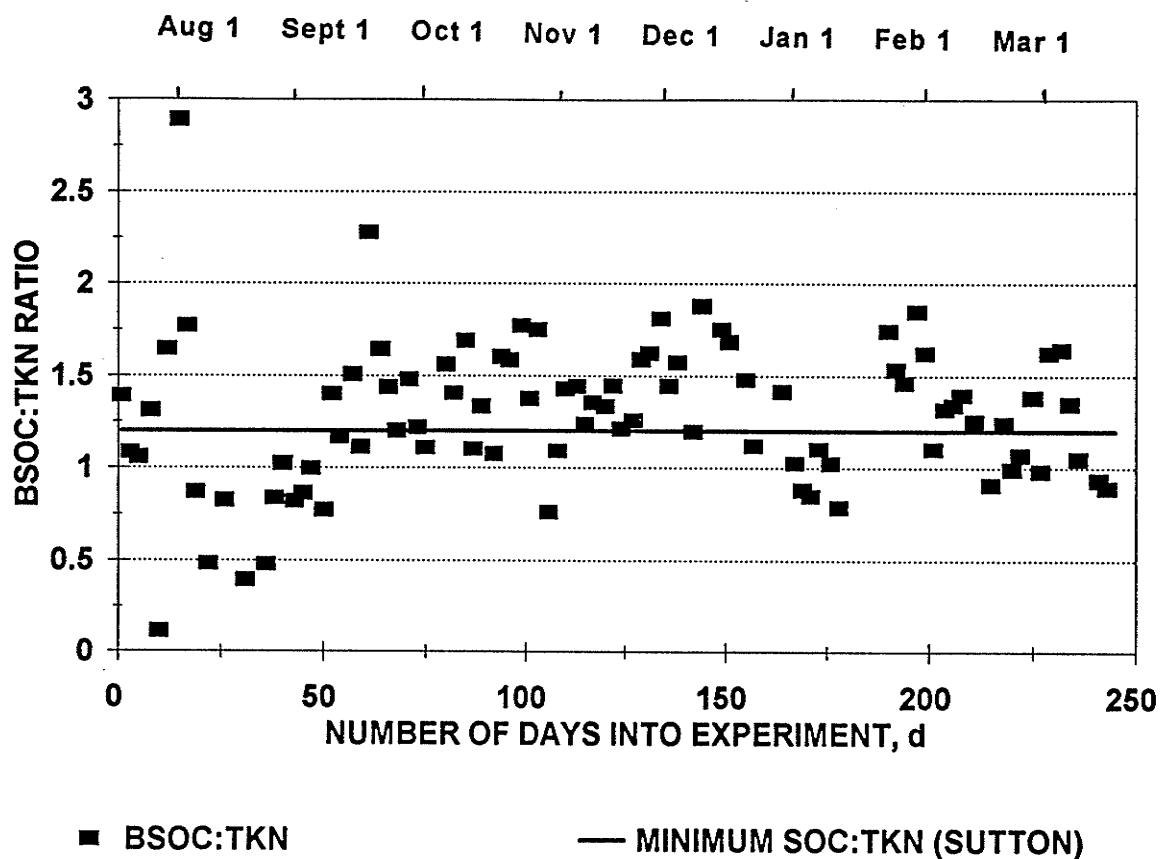
Figure 6-28: Biodegradable SOC (BSOC) to TKN Ratio (BSOC:TKN Ratio) Assuming 5% of Remaining SOC is Nondegradable SOC

Figure 6-28 shows the BSOC:TKN ratios assuming that the system data of the actual SOC removed represented 95% BSOC removal. It is apparent from Figures 6-26 through 6-28 that any conclusion regarding carbon availability depends upon the assumptions made about the BSOC value. Figure 6-28 is the worst case from the perspective of denitrification potential, and, if correct, points to a serious limitation for the MLE process at recycles that aren't even at the maximum economic level of 4Q. Therefore, it is important to determine whether the assumptions made calculating BSOC in Figure 6-28 are valid.

Therefore, the data analysis of the influent wastewater characteristics indicates that any design of an MLE system at 20^0C must overcome carbon availability problems; otherwise, predenitrification is not feasible at recycles approaching 300% or more.

6.8 Hypothesis 2: Denitrification was Low Due to Kinetic or HRT Limitations

Thermodynamics indicate when a reaction is possible, but not when the reaction will be complete. The kinetics of denitrification have to be considered as a potential reason for incomplete denitrification in the 1.5 h anoxic reactor. Stated from the operational perspective, perhaps the HRT was too small.

Sutton et al. (1973) indicated that in excess carbon conditions, the denitrification rate can be considered a constant, with a rate of 0.06-0.145 gN/gMLVSS.d at 22^0C. Using the experimental and operating data to calculate a general kinetic rate provides a performance target. The 1.5 h anoxic reactor, having 2000 mg/L MLVSS, and 67% return of the approximately 27 mg/L NO_3 that form at full nitrification, has to denitrify at a rate of 0.145 gN/gMLVSS.d, which is at the upper end of Sutton's data. This calculation suggests that the 1.5 h anoxic reactor may have been too small.

The operating recycle was about 2:1, which means that about 67% of the nitrate was returned, and the average MLSS at 22^0C was about 2500, which yields an average MLVSS of about 2000 at 80% VSS. This indicates that the data used in the calculation are reasonable. Therefore, there is a definite possibility

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that even at excess carbon conditions, the HRT of the anoxic reactor was too low for complete denitrification at 22^0C.

At 12^0C, the same kinetic rate is required for the same amount of biomass, which is not possible. The need to increase the SRT at colder temperatures for nitrification would result in a higher amount of biomass in the system. A doubling of the biomass would cut the rate requirement in half, which would still require denitrification rates higher than the denitrification rates (0.02-0.05 gN/gMLVSS.d) found by Sutton et al. (1973) at 12^0C. Raising the SRT to nitrify would mean an increase in the anoxic SRT, but that would decrease the denitrification rate, meaning that even by tripling the biomass, the maximum denitrification rate could not be sustained at 12^0C. Thus it appears that the system design has a kinetic limitation at 12^0C irrespective of any other factors limiting denitrification.

Therefore the MLE system requires a design HRT for the anoxic reactor greater than 1.5 hours with wastewater having the influent characteristics of the NEWPCC.

6.9 Hypothesis 3: Oxygen Inhibited Denitrification

With oxygen present in the recycle, there is ample reason to doubt that the 1.5 h anoxic reactor could have been 100% efficient, especially since the reaction kinetics would have to be at the upper range of researchers' findings and the system had a low amount of carbon.

The presence of oxygen in the anoxic reactor would inhibit denitrification and is considered one reason why denitrification failed to occur in System A. The difficulty is to prove that inhibition due to oxygen occurred, when the above factors could also explain the lack of denitrification.

In order to support the case for oxygen inhibition of denitrification, it is necessary to examine the behaviour of both the nitrification and denitrification processes and see if oxygen effects can be detected, or the other factors such as insufficient carbon were not present during certain periods. This means that one must look at several possible sources of oxygen and evidence that indicate the presence of oxygen.

6.9.1 Possible Sources of Oxygen

The first source of oxygen would be the influent itself. The primary effluent should not have contained much oxygen initially, although some may have dissolved in the feed bucket, since it was at 4^0C. Tests done on the influent by Takach (1995) showed that the feed did have trace amounts of oxygen when mixed, but levels were on the order of 0.2 mg/L.

The recycle lines from the reactors would not only pump sludge back, they would also pump gas, which would have the headspace composition. Given the high input of pure oxygen, it is certain that the gas had at least 20% oxygen, and this gas would form part of the headspace in the anoxic reactor. Furthermore, the fluids going into the reactor fell through this headspace for a distance of about 3 cm, which gave a pathway for oxygen to dissolve into the mixed liquor in the anoxic reactor.

The anoxic reactor was mixed with a magnetic stirrer. The minimum speed required to sustain mixing was above 100 rpm. During the batch study of November 1994, it was observed that a mixing paddle of similar diameter to the magnetic stirrer could retain a dissolved oxygen level above 1 mg/L with over 1000 mg/L VSS at 90 rpm having started under anoxic conditions. Therefore, a certain amount of oxygen could be

dissolved into the reactor due to mixing; the amount would have been influenced by the concentration of oxygen in the headspace of the anoxic reactor.

These sources of oxygen have to be considered fairly minor compared to the amount that was returned to the anoxic reactor in the recycle from the aerobic reactor. At a recycle flow rate of 2Q and a DO of 4 mg/L, the input is over twenty times that in the influent, and about ten times that from the mixer. In addition, the oxygen inputs from the influent and the mixer could be considered essentially constant over the duration of the experiment. Thus the only true variable source of oxygen would have been in the recycle streams, so this is the only source that could be considered to cause performance changes.

Previously it was shown that some ammonia removal occurred in the clarifier. From this, there is a corollary that the clarifier was aerobic, resulting in the conclusion that the RAS not only contained NO_3 but also O_2. The key question is whether or not there was enough O_2 returned to inhibit denitrification.

6.9.2   Nitrate Removal and ORP Behaviour in Train A

The data in Figure 6-20 which showed the ammonia and TKN data fitting the line calculated from mass balances allows the NO_3 calculations to be made with more certainty. The NO_3 balances in Figure 6-15 showed that little nitrate was removed in most cases. Points above the line suggest nitrification in the anoxic reactor, or higher recycle than assumed. The latter would happen if the influent line were plugging, so R/Q would be higher than that assumed in the calculation.

The total nitrogen balance in Figure 5-19 showed that nitrogen was removed in relation to ORP. Figure 5-19 clearly demonstrates that as the ORP in the anoxic reactor goes down, nitrogen removal increases; and as the ORP increases, the nitrogen removal decreases. These deductions agree with denitrification theory, and the correlation makes sense.

6.9.3   Examination of Factors that could Influence the Anoxic Reactor ORP

Figure 5-21 also showed that in Train B, as the ORP increased, nitrogen removal decreased. This leads to the question: why did the ORP increase? The first possibility that must be evaluated is the effect of the influent carbon. This would imply a relationship between ORP and influent carbon. Not

only that, it would imply an ORP-influent SOC relationship similar between Trains A and B, because the systems were fed the same influent. Figure 6-29 shows that the regressions of the ORP-influent SOC data from Trains A and B at $22^{0}C$ are nearly parallel. However the data also are scattered enough to indicate that other influences are responsible for the variations in ORP, and the linear fits in both cases do not appear to be very good.

Theoretically, the ORP's should correlate to the influent carbon, but would differ due to other factors affecting ORP such as pH, different biomass levels, dilution from different recycles, NO_3 and O_2 in the recycle. Attempting to separate all of these factors was not part of the design of the experiment. However, these results showing nearly parallel regression lines may not have been a coincidence, but may reflect the contribution of the influent carbon on ORP.

Another possible reason for increases in ORP is that the recycle increased, leading to maximum dilution of the feed. However, dilution would not influence other parameters in the system, other than having an equivalent dilution effect.

A higher return of oxygen would increase the ORP. It is also true that at higher recycles more nitrate is returned and increases the ORP. However, recycled nitrate's influence on
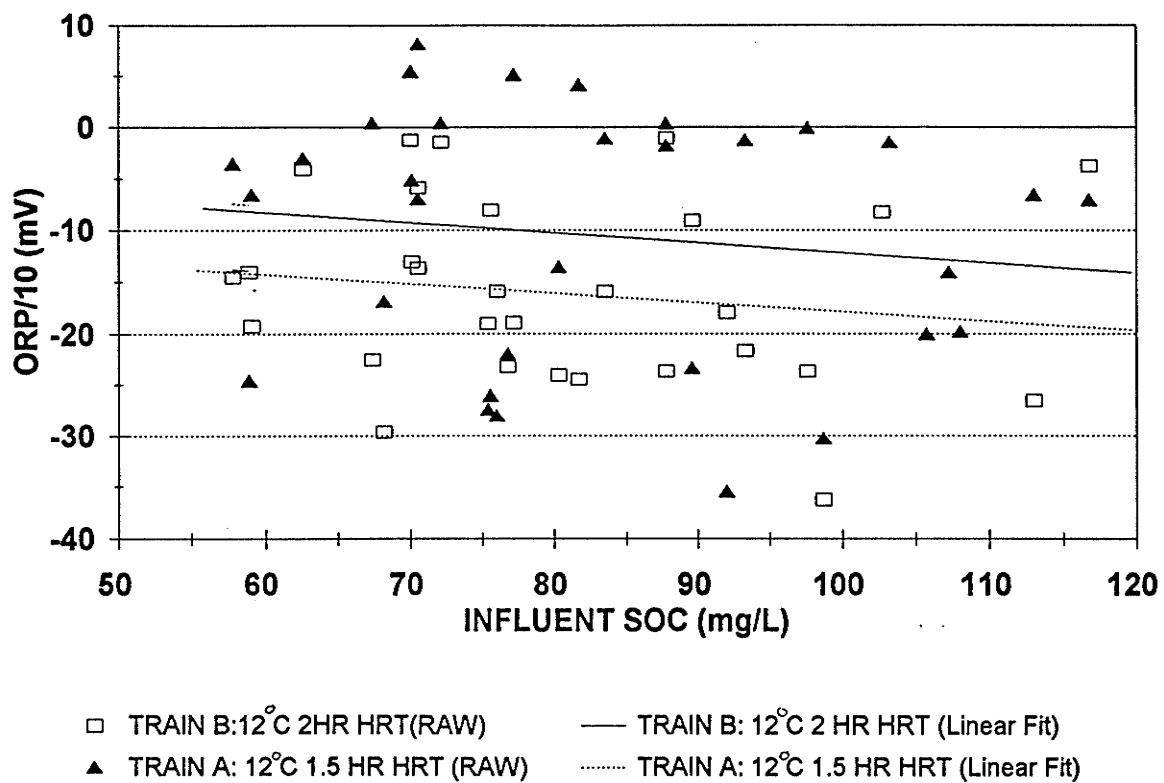
Figure 6-29:   ORP vs Influent SOC for Trains A
and B @ 12⁰C

nitrification depends on the denitrification of that nitrate. Denitrification of that nitrate did not occur in the anoxic reactor of Train A since several graphs have shown that nitrogen removal (a measurement of denitrification) at high ORP was low. Oxygen in the recycle is the only factor that can increase the anoxic reactor ORP and help the nitrification process independently of carbon. The effect of oxygen can be identified by looking at the nitrification percentage versus ORP: Dilution due to higher recycle would not affect nitrification, but oxygen would, and only oxygen would inhibit denitrification.

The graph of the percentage nitrification versus ORP in Figure 5-18 showed that the increase in the ORP in R1 corresponds to a subsequent increase in nitrification: providing the evidence that it is oxygen in the recycle that increases nitrification; and, more importantly, inhibiting denitrification.

6.9.4   Proving Inhibition of Denitrification

Figure 6-29 showed a weak correlation between ORP and influent SOC in Train B at $12^{0}C$. Train B had less NO_3 returned, a more stable pH, and usually lower dissolved oxygen levels than Train A, so it would appear to be the better system to try to analyse for some relationships involving ORP, because of slightly lower influence of these parameters.

One could speculate that denitrification reactions might affect SOC removal, and the relationship one would expect is that high nitrate removals would coincide with high SOC removals. Given the previously established linear relationship between influent and SOC removals, higher influent SOC's should be points of high SOC removal, and thus better conditions that should lead to higher NO_3 removal. Figure 6-30 shows a plot of SOC removal versus NO_3 removal, but the correlation between SOC removal and NO_3 removal is an inverse one, with a better fit than either influent SOC versus ORP in Figure 6-29 or R1 SOC versus ORP in Figure 6-31.

If high SOC removals are correlated to the biomass present (which is what adsorbs the SOC), high SOC removal would imply that recycle lines were not plugged. This would mean that the nitrate from the recycle should have been present in the reactor, and that there also was biomass available to denitrify it. Furthermore, the high SOC removals imply that the influent carbon was high. However, Figure 6-31 indicates that in these high SOC removal conditions, there was less nitrate removal, despite having the nitrate, carbon and biomass to accomplish the removal – which would be defined as an inhibited condition.
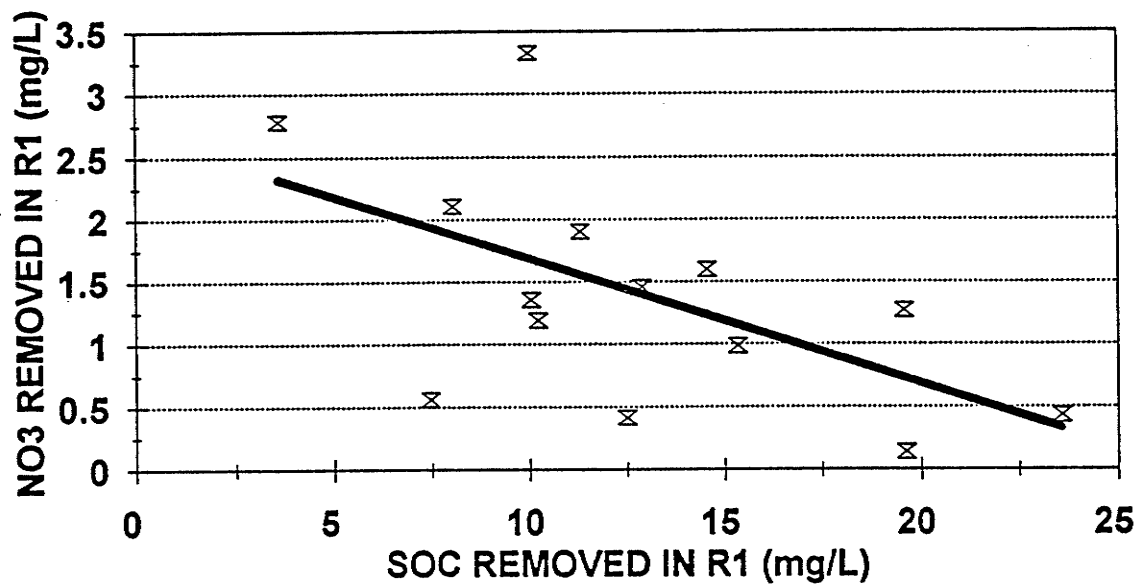
Figure 6-30:   NO$_3$ Removed vs SOC Removed from
                Anoxic Reactor of Train B @ 12^{0}C
                2.0 h anoxic; 2.0 h aerobic
                NO3 is reported as NO3-N
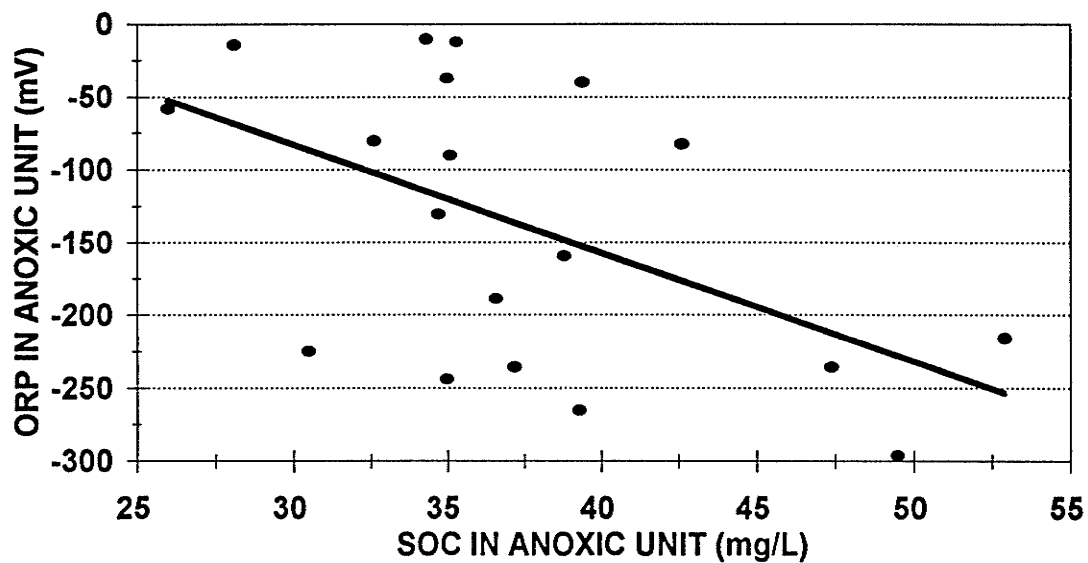
Figure 6-31:   ORP vs Anoxic Reactor SOC
               for Train B @ 12^0C
               2.0 h anoxic; 2.0 h aerobic

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It is possible that the high SOC removals coincided with high carbon levels and limited denitrification because nitrification was reduced because of the high amount of carbon, so Figure 6-30 doesn't necessarily prove that there was an inhibited condition. However, Figure 6-32 shows the percentage denitrification versus SOC removal, and it is clear that several points of high SOC removal simply did not have denitrification, and that there was inhibition.

Figure 6-33 shows that denitrification in Train B was limited to no more than about 3 mg/L. In the nitrate balance for Train B, five out of the six leftmost points in Figure 6-34 have actual nitrate levels close to or higher than the calculated value. Thus the points of high nitrification in Train B were limited, but points where nitrification was high correspond to points where denitrification was lower than other times, leading to the conclusion that the reason for the high nitrification was that oxygen was making the anoxic reactor somewhat aerobic.

If the returning nitrate were a significant cause for improvements in nitrification and high ORP, there not would be an inverse relation between the ORP and SOC removal, which was the case in Figure 6-31. Instead Figures 6-31 and 6-33 prove that there was inhibition of denitrification when there was a reasonable amount of carbon available.
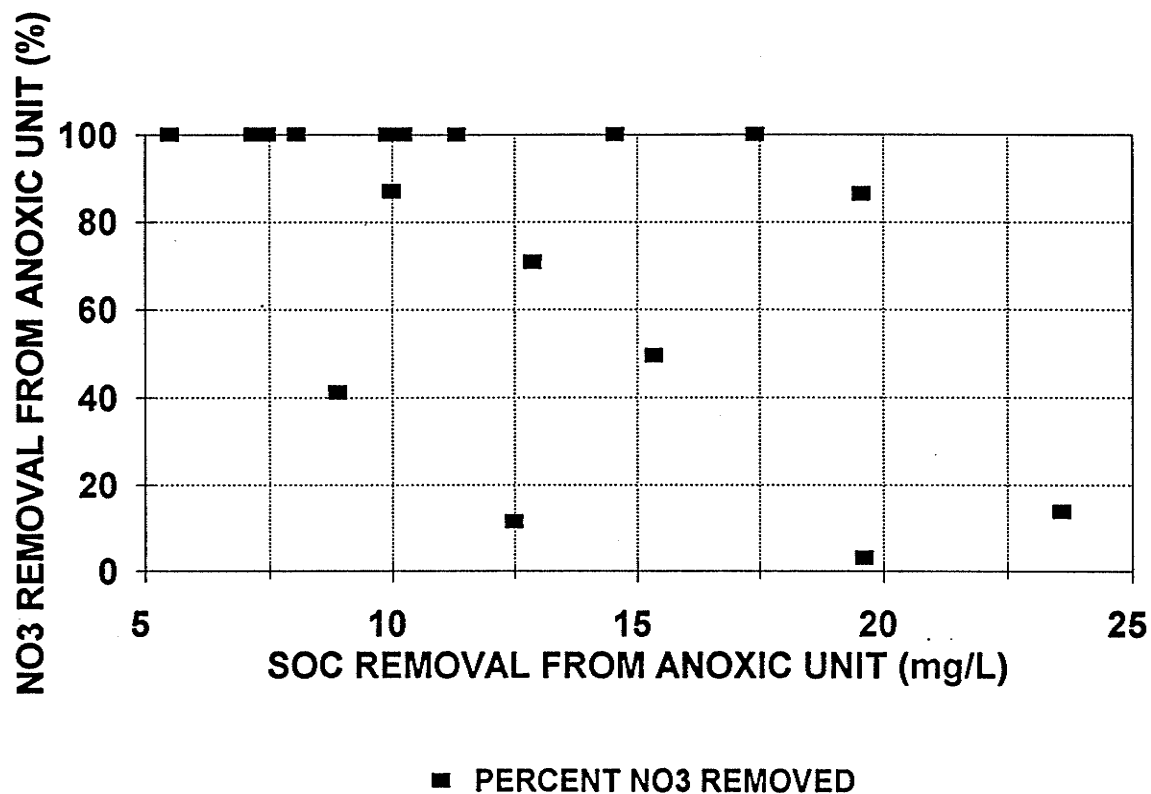
Figure 6-32:   %NO$_3$ Removed vs SOC Removed from
Anoxic Reactor of Train B at 12^{0}C
2.0 h anoxic; 2.0 h aerobic
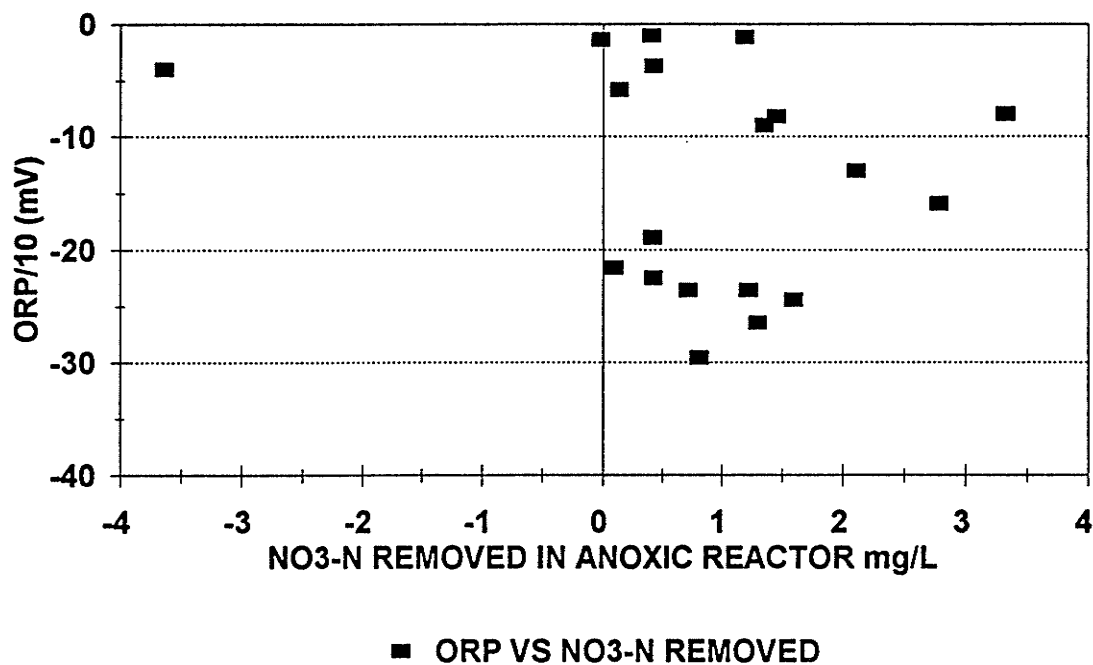
Figure 6-33:   ORP vs. NO$_3$ Removed in Anoxic Reactor
                in Train B @ 12^{0}C
                2.0 h anoxic; 2.0 h aerobic

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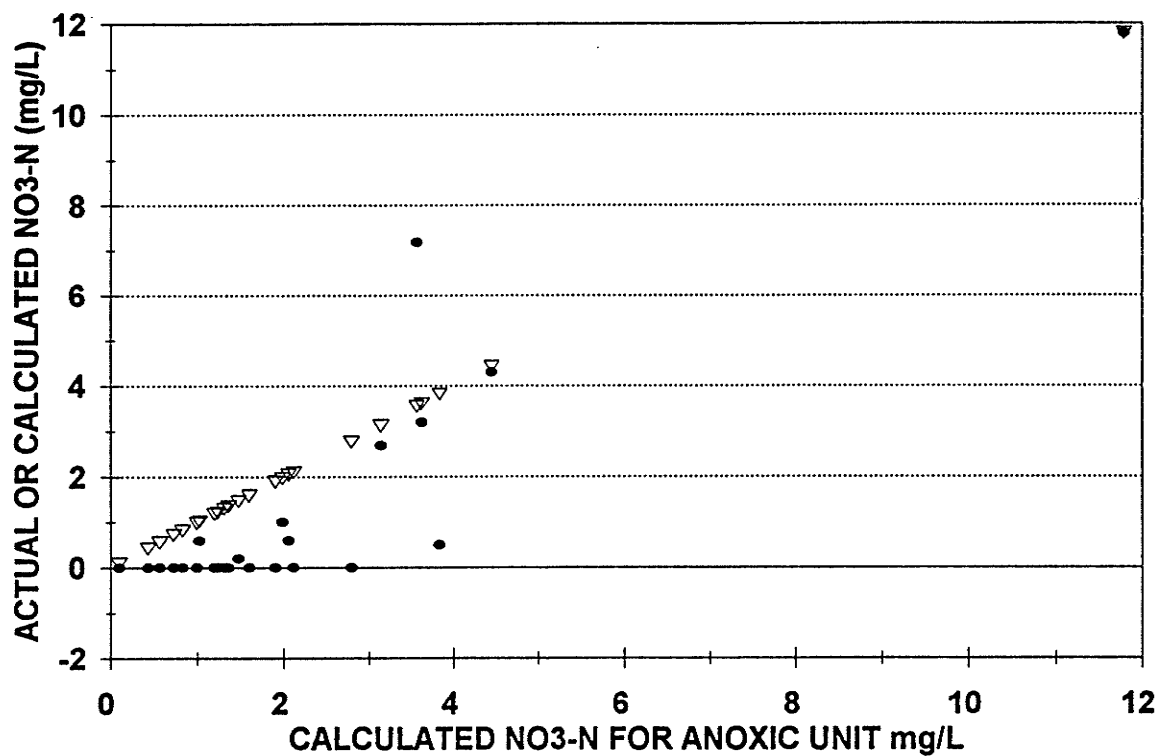
Figure 6-34: NO₃ Balance for Anoxic Reactor
in Train B @ 12⁰C
2.0 h anoxic; 2.0 h aerobic

Figure 5-19 reflected inhibition of denitrification at high ORP, and the cause of the high ORP due to the presence of oxygen was indicated by the relationship between ORP and nitrification in Figure 5-18.

It must be concluded that oxygen in the recycle was a factor in the experiment because it is the only explanation for all the relationships of Figures 6-30, 6-32, 6-33, and 6-34.

6.10 Comparison of Mass Balances of Anoxic Reactor Denitrification to Establish ORP Relationships

Figure 6-34 showed the ORP and the corresponding amount of nitrate removed based on mass balances for the anoxic reactor in Train B at 12°C. There was no strong correlation evident. However, converting the mass conversions to percentage removals as in Figure 6-35, it is more apparent that the points of low ORP were largely at 100% denitrification, and that there is a better indication that the denitrification efficiency was lower at high ORP.
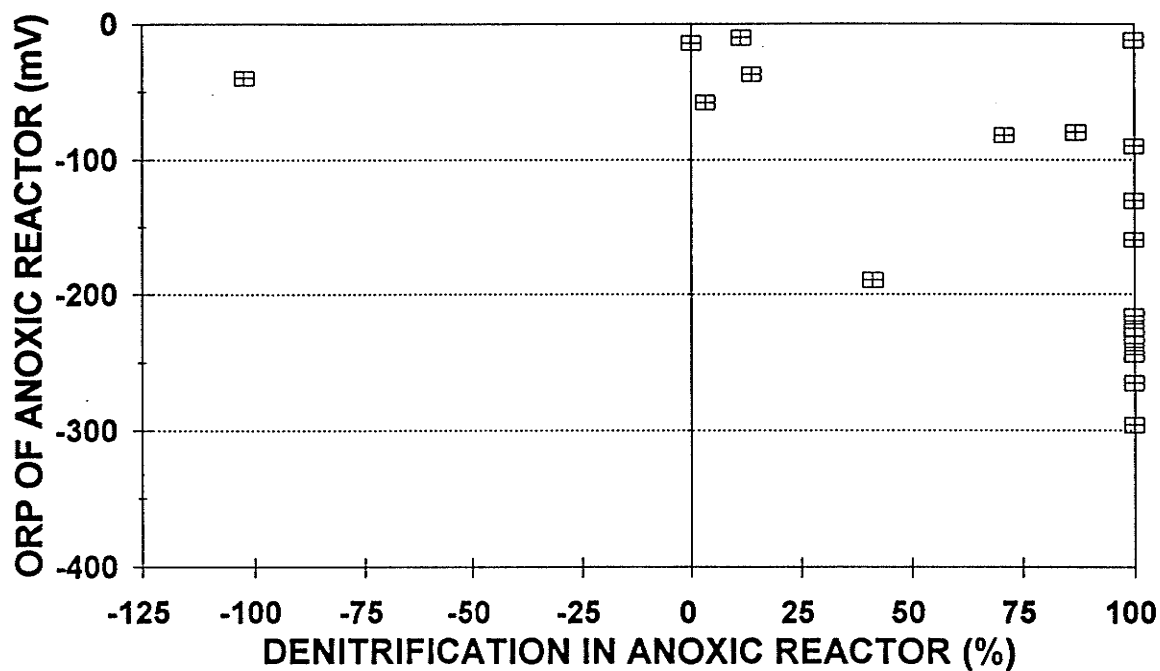
Figure 6-35:   ORP vs %Denitrification in Anoxic
                Reactor in Train B @ 12^{0}C
                2.0 h anoxic; 2.0 h aerobic

6.11 Kinetic Rate Data

One objective was to obtain denitrification rates for the systems. However, the factors of oxygen inhibition in Train A and limited nitrification in Train B confound the analysis of reaction kinetics.

The literature has indicated that the nitrate concentration is a rate limiting factor only at nitrate levels of about 1 mg/L or lower. Figure 6-36 shows the denitrification rates at 12^0C for the anoxic reactor in Train A, versus the amount of nitrification for the system as indicated by the effluent NH_3 data.

Figure 6-36 shows the denitrification rates versus the amount of nitrification, and appears that the denitrification rate is a function of the amount of nitrification-which had not reached steady-state. Thus the denitrification rates from the study cannot be accepted as indicative of the steady state condition.
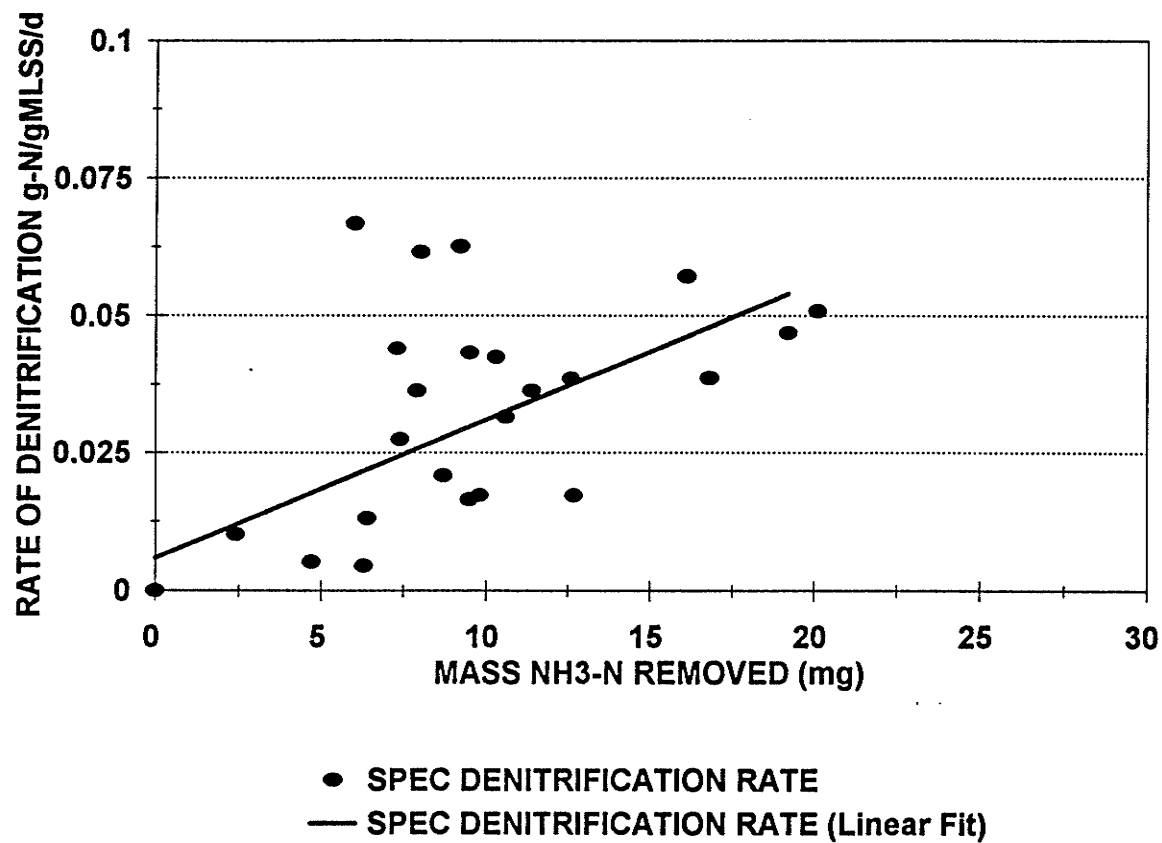
Figure 6-36:   Rate of Denitrification vs Mass of
                NH_3 Nitrified in Train A at 12^0C
                1.5 h anoxic; 4.5 h aerobic

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6.12 Hypothesis 4: Denitrification Occurred Outside of the
  Anoxic Reactor

Figure 6-36 showed that as the nitrification increased, the
rate of denitrification increased. This contradicts the
indications that as nitrification increased, denitrification
decreased. Mass balances are needed to resolve the
contradiction.

Figure 6-37 plots the denitrification rate data for Train A,
with the y axis being the anoxic reactor denitrification rate
based on the nitrate mass balance for the anoxic reactor but
using the R2 values rather than the effluent values, and the
x axis is the denitrification rate based on the ammonia
balance. Figure 6-37 demonstrates that the points showing
higher rates of denitrification in the anoxic reactor than in
the system lie too far away from the 45^0 line to be resolved
by slight errors in the values or recycle values. Instead, it
must be concluded that the effluent values are the more
reasonable values to use for these outliers. Furthermore,
without having used the effluent data, Figure 6-37 suggests
that the system denitrification was a major source of
denitrification.

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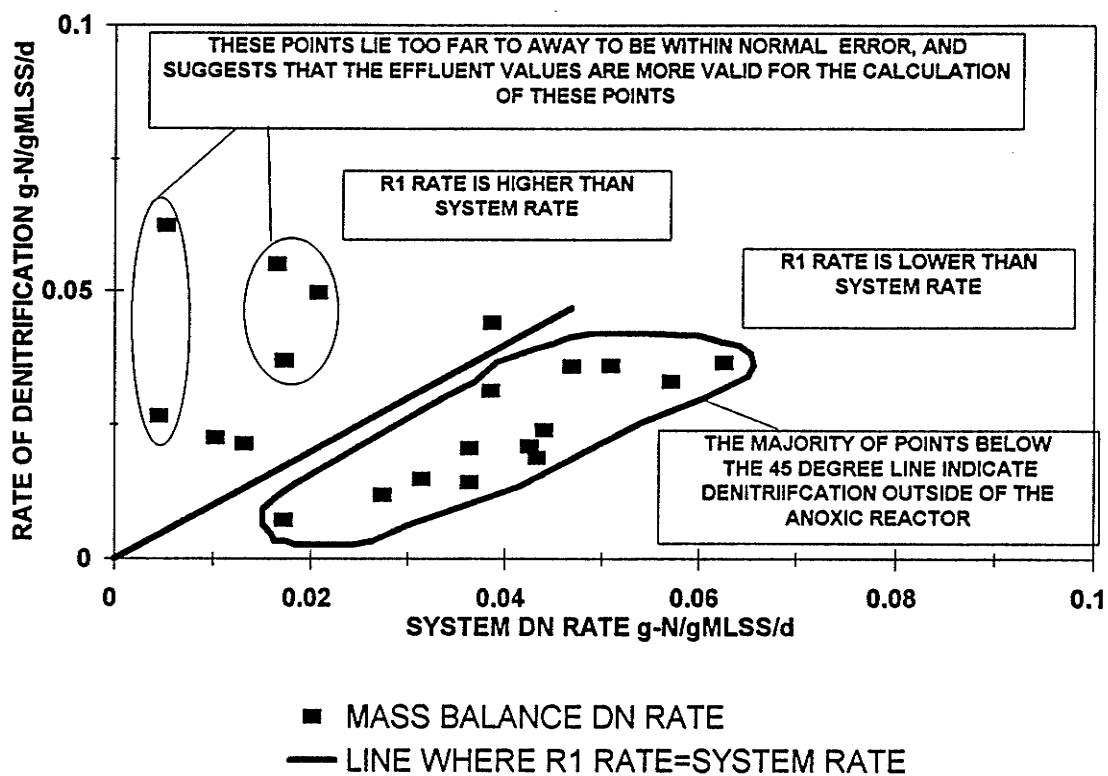
Figure 6-37:   Denitrification Rate in Anoxic Reactor
                vs System Rate From Mass Balances
                Using Aerobic Reactor Values in RAS
                Recycle for Train A @ 12°C
                2.0 h anoxic; 2.0 h aerobic

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Figure 6-38 uses the effluent data, and gives the same result that the system denitrified nitrate. Both graphs suggest that there was significant denitrification outside the anoxic reactor.

Even though the mass balances show that the anoxic reactor does not account for all the denitrification, the proportionality to the amount of nitrification is significant. The amount of nitrate recycled is proportional to the amount nitrified, and Figure 6-37 showed that the amount of denitrification was also dependent upon the amount nitrified. This suggests that the system denitrified more than the anoxic reactor, and the recycle may be a very important factor in explaining why.

Figure 6-39 shows that the theoretical alkalinity consumption of Train B, assuming that nitrification consumed 7.1 mg/L, with the actual data. The shaded area between the two curves represents the alkalinity produced by denitrification. Figure 6-40 is another comparison of theoretical alkalinity consumption to the actual consumption. However, in this figure, the theoretical consumption was calculated by assuming that 70% of the nitrate formed returned to the anoxic reactor for denitrification, where the 70% corresponds to the system recycle rate. The actual and theoretical curves compare very well. This means that the recycle assumption was valid. The

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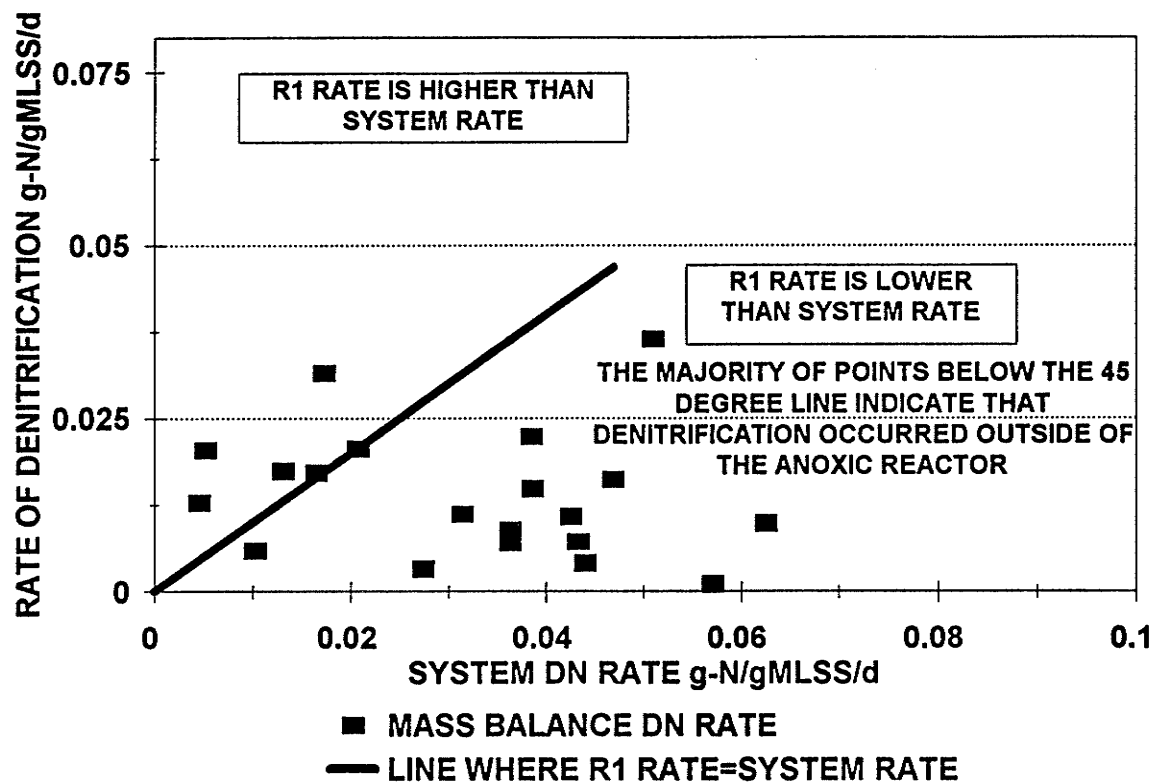
Figure 6-38:   Denitrification Rate in Anoxic
                 Reactor vs Rate from Mass Balances
                 Using System Data for Train A @ 12°C
                 2.0 h anoxic; 2.0 h aerobic

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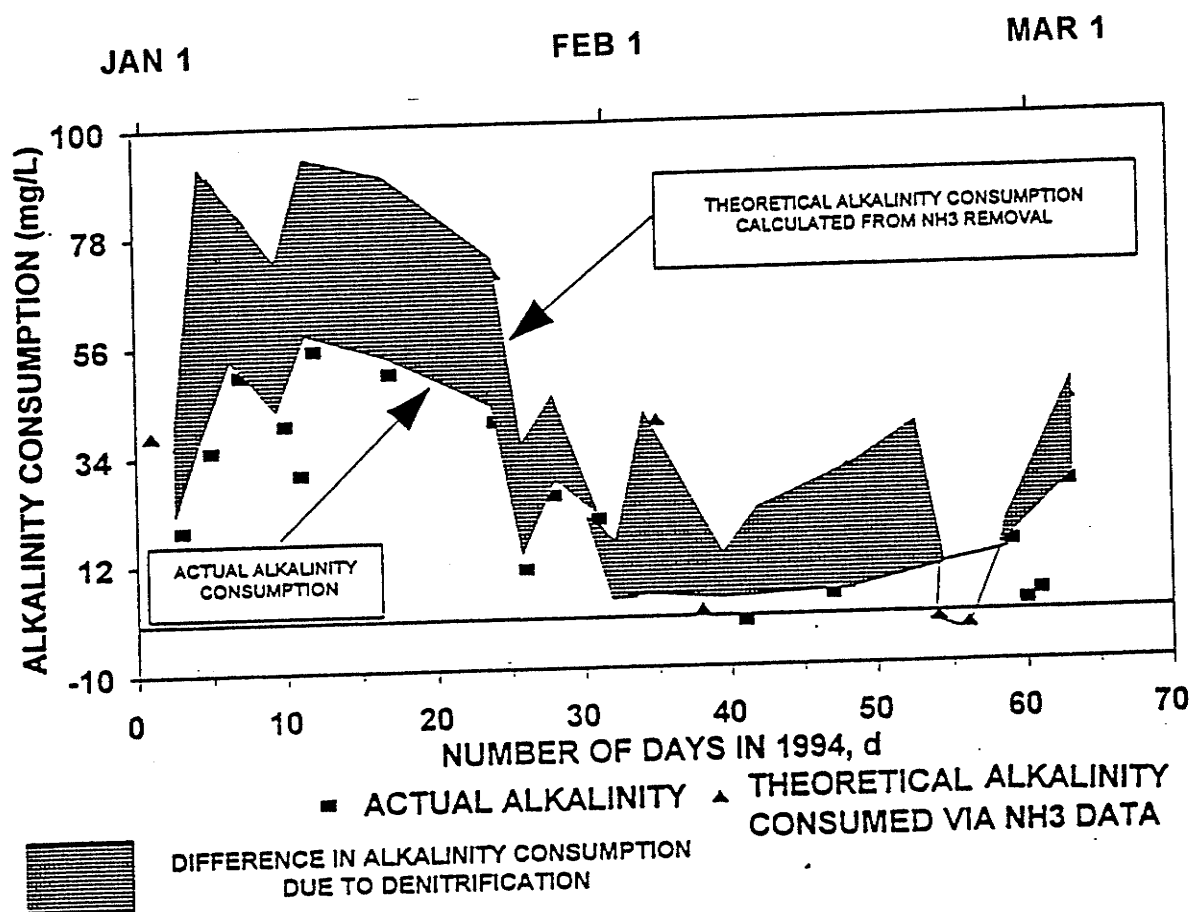
Figure 6-39: Theoretical Alkalinity Consumption Using NH_3 Consumption Data, and Actual Alkalinity Consumption in Train B @ 12^0C 2.0 h anoxic; 2.0 h aerobic from January 1, 1994 to March 8, 1994

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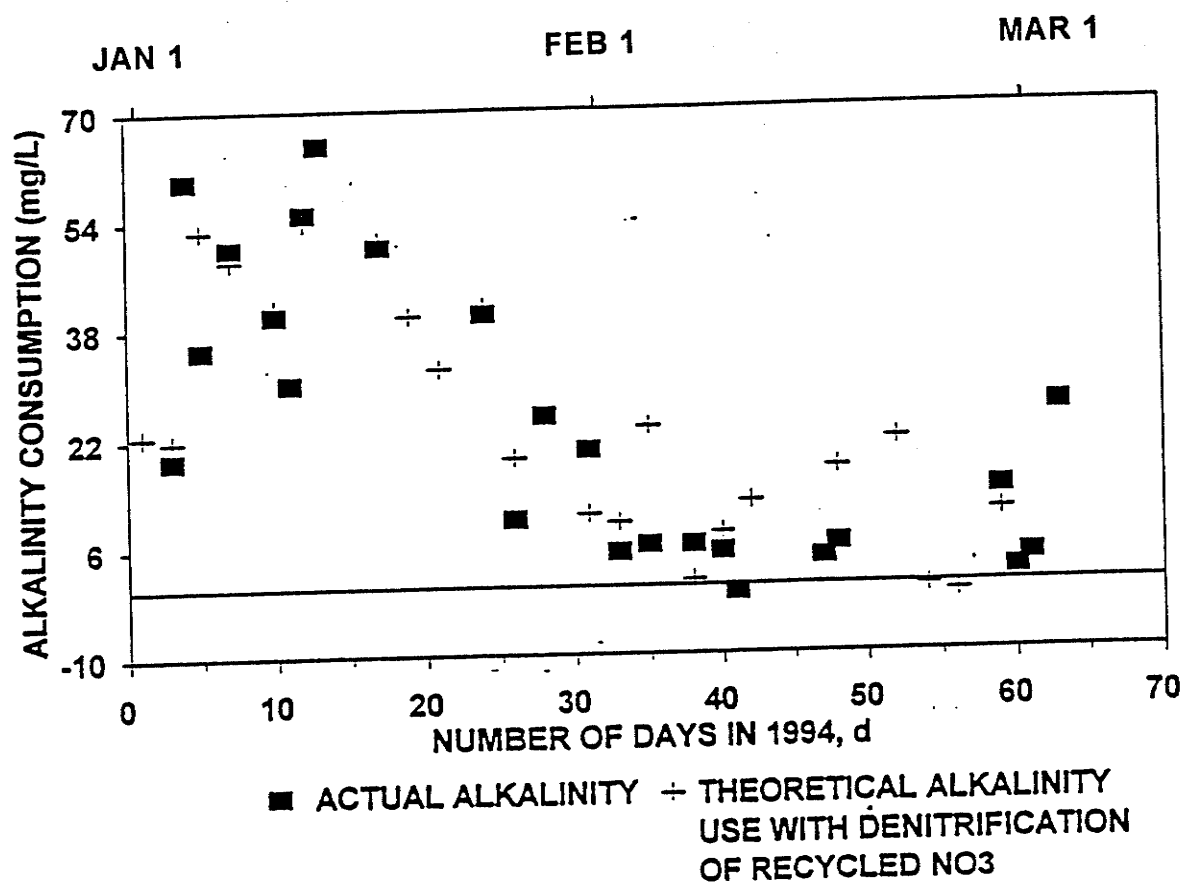
Figure 6-40:   Theoretical Alkalinity Consumption
Using NH_3 Consumption Data, and
Actual Alkalinity Consumption in
Train B @ 12^0C
2.0 h anoxic; 2.0 h aerobic
from January 1, 1994 to March 8, 1994

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anoxic reactor in Train B did denitrify 100% of the nitrate in many of the mass balances, but the alkalinity produced by denitrification in the first twenty days appears to be greater than the 3-4 mg/L indicated by Figures 6-34 and 6-35. This also leads to the hypothesis that some denitrification occurred in the aerobic reactor, where the nitrate removed would be hidden from analysis.

The anoxic reactor for Train A did not denitrify as efficiently on a percentage basis as the anoxic reactor for Train B. Thus, the alkalinity data for Train A could be expected to have a closer match to the theoretical alkalinity consumption based solely on nitrification than it should to the theoretical alkalinity consumption assuming denitrification based on the recycle of nitrate and assuming 100% denitrification of the nitrate that was recycled.

Figure 6-41 shows the two different theoretical alkalinities and the actual alkalinity data. Figure 6-41 clearly shows the actual alkalinity data agrees much better with the denitrification assumption than with the calculation that just assumes nitrification. The percent removal efficiency has to be considered fairly high, which contradicts the efficiencies determined by the mass balances around the anoxic reactor. Since the recycle of the nitrate was important to the denitrification rates, it must be concluded that

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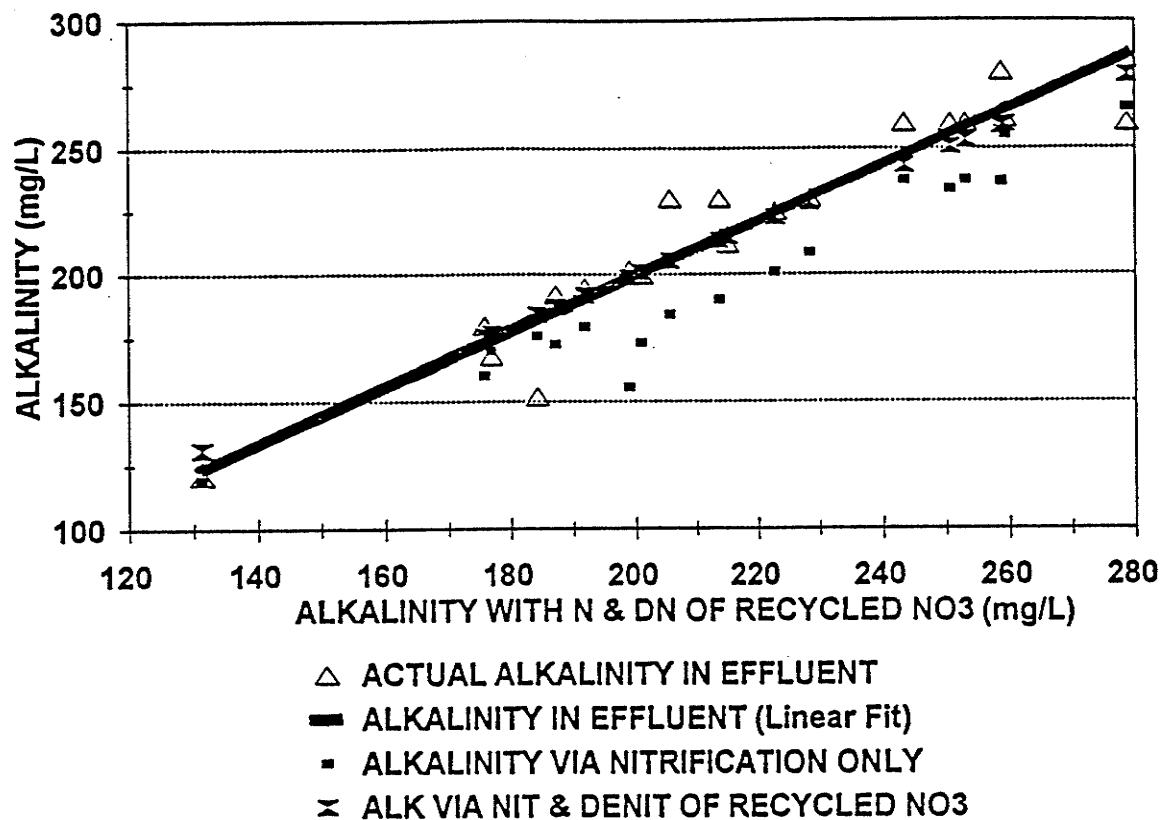
Figure 6-41:   Theoretical Alkalinity Consumptions
                Using NH₃ Consumption Data but
                Assuming Nitrification Only or
                Assuming Denitrification of the
                Recycled Nitrate and the Actual
                Alkalinity Consumption
                in Train A @ 12°C
                1.5 h anoxic; 4.5 h aerobic

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denitrification occurs in an anoxic part of the floc -- in the aerobic reactor!

The clarifier must be considered a less likely point of denitrification because it was shown in Section 6.3 that nitrification occurred in the clarifier, even though a full scale clarifier could denitrify, and Sears (1995a) also experienced some denitrification in the clarifier in his bench -scale tests. First, denitrification in the clarifier would not be related to recycle, and secondly, the carbon for denitrification (which was limited in availability) has a better opportunity to react in the aerobic reactor at the floc level than in the clarifier. The recycled biomass would have some spaces in the floc filled with the anoxic wastewater containing carbon and nitrate. The carbon would have been rapidly adsorbed into the biomass, so the tests might still have detected nitrate from the recycle, but not carbon. The mixture of raw wastewater and nitrified recycle would form an exterior core around the biomass, and remain anoxic even after being dumped into the aerobic reactor. Diffusion of nitrate in this anoxic zone into the biomass would occur until oxygen could be transferred to those points.

The denitrification that occurred in the aerobic reactor should be attributed to some effect from the anoxic reactor. Without recycle to the anoxic reactor, there would not be the

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opportunity to combine the carbon source with nitrate in a more oxygen deficient environment that could result in much denitrification. Meanwhile, the oxygen that was returned with the nitrate would have been preferentially used.

Since inhibition was shown for the anoxic reactor of Train B, it is certain that the aerobic reactor, having much more oxygen, would have to be considered even more inhibitory to denitrification. Because the system balances indicate significant denitrification outside of the anoxic reactor while there was simultaneous inhibition in the anoxic reactor itself, it must be concluded that the recycle of biomass into the anoxic reactor created a microenvironment that was anoxic, but the denitrification reactions were largely completed outside the anoxic reactor. It must be concluded that these denitrification reactions occurred in the aerobic reactor.

7.0 CONCLUSIONS

The influent wastewater varied in quality over time. In particular, the carbon load increased in the colder months and fell during warmer months. Part of this variability is linked to centrate returned from the centrifuge, which dewaters sludge from the anaerobic digesters.

There was a correlation between the influent SOC and influent TKN, where SOC in mg/l was roughly double the TKN in mg/l. There was an excellent correlation between the influent TKN and NH_3, indicating that approximately 80% of the TKN in the primary effluent was ammonia.

Some of the inability to denitrify could be attributed to insufficient carbon in the wastewater.

Analysis of the influent showed that carbon availability limits the maximum denitrification to a recycle ratio of approximately 2.7Q, which corresponds to approximately 70% nitrate removal. It is not feasible to reliably denitrify using the MLE configuration at NEWPCC at a recycle of 3Q (75% nitrate removal) without another carbon source, whether it is generated internally via fermentation or externally supplied.

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The 1.5 h anoxic HRT was too short for complete denitrification within the reactor.

The maximum anoxic reactor HRT that can be considered is about 2.5 h, (because a larger HRT forces the aerobic HRT or system SRT, or both, to be increased in order to maintain a nitrifying population). The 2.5 h anoxic HRT allows complete denitrification using average kinetic denitrification rates from the literature using wastewater carbon.

The clarifiers exhibited some reactor behaviour, particularly nitrification. The aerobic reactor-like behaviour indicated that the activated sludge recycled to the anoxic reactor contained oxygen in this laboratory work at both 12^0C and 22^0C.

Nitrification of 20 mg/L NH_3 at 12^0C (about 70% of the influent NH_3) was possible at a 15 day aerobic SRT and HRT OF 4.5 h. This system showed a trend towards higher nitrification, before the experiment was terminated.

The anoxic reactors commonly showed removals of biodegradable SOC that were greater than accountable by reactions with returned nitrates and oxygen both at 12^0C and 22^0C. Batch studies confirmed that SOC removal rates exceeded nitrate removal rates. SOC removal was a first order process, and considered an absorption phenomenon. SOC removal was not

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correlated to the nitrate removal.

The 1.5 h anoxic reactor failed to denitrify effectively according to mass balances around the reactor. However, the system mass balances indicated denitrification inside the aerobic reactor. The denitrification that occurred in the aerobic reactor was correlated to the recycle, indicating that recycle to the anoxic reactor was necessary for denitrification to occur.

Total N removal in both trains showed an inverse type of relationship with ORP of the anoxic reactor, while nitrification showed a direct type of relationship to ORP.

Oxygen was consumed in the anoxic reactor in lieu of NO_3. Most of the oxygen in the anoxic reactor came in the recycle or RAS lines.

Calculations showed that the anoxic reactor had a potential of 70% nitrate removal based on recycle. Total N removal was usually less than 30%.

8.0 RECOMMENDATIONS

The variability of the influent data suggest that the influent wastewater characteristics should be analysed so that the design load coincides with the design temperature.

The problem with increasing the HRT of the anoxic reactor is that an increase in the size of the anoxic reactor reduces the aerobic SRT, which could lead to a loss of nitrification. An increase in HRT should be done with consideration to the aerobic SRT, which should be at least 10 days at 12^0C. This limits the anoxic reactor HRT to 2.5 hours or less. The kinetic data indicated that a 1.5 h HRT was the minimum HRT that could be used at a recycle of 2.5Q or more.

In order to achieve the denitrification potential, the oxygen in the recycle streams has to be reduced. Oxygen levels can be reduced by reducing and controlling the aerobic reactor DO at 3 mg/L. The solids in the clarifier also should be sufficient to allow the oxygen to be consumed by the time it is to be returned as RAS.

Higher MLSS levels take time to build up, and a spill can result in significant solids losses that waste a lot of time. Spill containment vessels allow spilled biomass to be returned to the system. Another way of increasing system biomass is to

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decant the effluent and return the effluent solids to the system. These efforts may result in a system with an MLSS that may not be practical or sustainable for the operation. An effort must be made to ensure that the settling characteristics obtained in the research are also feasible in practice.

Larger tubing that would not plug so easily would eliminate the cause of most spills. Larger tubing in further research is essential.

The relationship between the COD or BOD removed and the nitrate + oxygen removed should be studied. The continuous system allows mass balance calculations, but tend to yield a single point or very narrow range of kinetic data. Batch studies allow the researcher to observe behaviour over time. This is very important because batch studies can be conducted using different substrates within a short period of time.

Batch studies should be done to compare the kinetics of primary effluent to prefermented wastewater. The kinetic rates dictate the size of the anoxic reactor, so knowledge of the best way to achieve higher rates may lead to more compact and cost effective designs.

Further studies should be done to compare a phosphorous and nitrogen removal system to the nitrogen removal system.

It appeared that there was some improvement in settling at higher nitrification rates. The settleability of sludge under fully nitrifying conditions warrants further study.

9.0 ENGINEERING SIGNIFICANCE

There was a replicable symmetry between nitrogen removal and ORP. This is significant because this indicates some potential for ORP as a prospective control parameter in complex systems where reactors have different environments.

The system at 12^0C with an aerobic SRT of 15 days and 4.5 h HRT showed a trend towards complete nitrification with a pH approaching 6.0. This supports the findings of Sears (1995) and Stankewich (1972), whose systems fully nitrified at lower pH's with systems not having pre-denitrification. These findings contradict the general consensus among the engineering community that low pH nitrification is not likely, and low temperature & low pH nitrification is even less likely.

Just as the trend towards full nitrification (in 4.5 hours @ 12^0C & pH of 6.1) does not mean a full scale system will perform identically to the lab scale reactors, the failure of the anoxic reactor to denitrify does not mean that the MLE system would fail in a full scale situation. The problem of inadvertently high oxygen levels in recycle lines can be reduced in further research, and further research is necessary to give a fair evaluation of the MLE system.

The failure in this research to denitrify efficiently in the anoxic reactor emphasizes the importance of control of dissolved oxygen levels, and the considerable impact dissolved oxygen in the recycle can have on anoxic reactor performance. This not only applies to MLE systems, but also phosphorous removal systems such as the Bardenpho or VIP processes.

Another significant finding was that the lab scale reactors exhibited reactor behaviour, whereas design assumptions give clarifiers no performance. This may be due to the fact that it was a lab scale. However this behaviour, also noted by Sears (1995) whose reactors behaved differently at 22°C and 12°C, suggest that at low temperatures, where HRT's and consequently capital costs become very large, some cost savings could be realized if the reactor-like behaviour of clarifiers were taken into account.

The work showed difficulties in operation that need to be overcome in further research, or full scale operation. If further research can confirm that this approach will work at the HRTs used in this research, then future designs can be more cost effective for the taxpayer or user. Likewise, it would also indicate a more cost effective means of retrofitting existing plants for nutrient removal. Figure 9-1 shows a graph of the capital costs of nitrification versus design temperature based on the consultants data, but for

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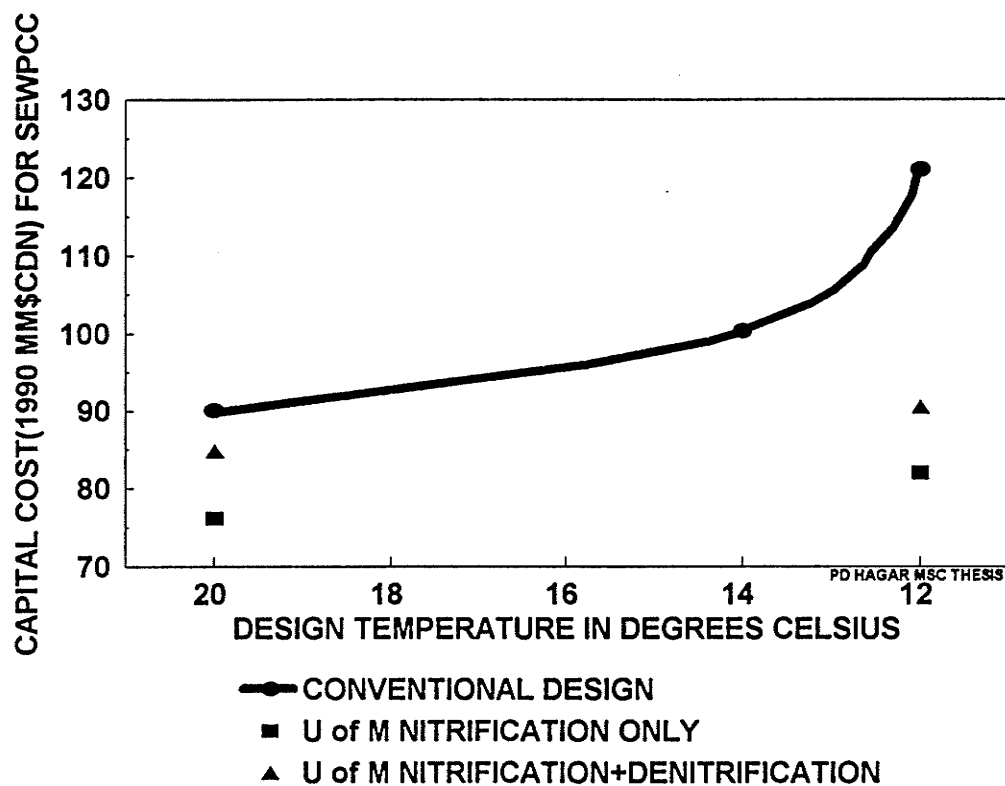
Figure 9-1:   Capital Cost Projections from
              Conventional Design and Implied from
              Lab-scale Research Conducted at
              University of Manitoba

three conditions: the consultants report, the costs implied for a nitrification system, and the costs implied for a system with nitrification & denitrification based on the results noted from this work and other work done at the University of Manitoba.

The cost estimates are given in Appendix 2, but it must be noted that the nitrification & denitrification system assumes the maximum anoxic HRT that would be designed is 2.5 hours. There is no proof that such an HRT would be feasible at the lower temperatures, nor did this work demonstrate that it would work at 22°C. However, due to the effect of the anoxic reactor HRT on the aerobic SRT, an HRT> 2.5 with an aerobic HRT <5 would keep the 12°C aerobic SRT above the critical SRT for nitrifiers. An anoxic HRT >2.5 h would jeopardize the maintenance of the critical SRT for nitrifiers at the lower aerobic HRT. Thus an HRT >2.5 h does not appear feasible if the system is to denitrify using the lower HRT's suggested by this research.

The analysis of the carbon availability suggests that there would be enough carbon to denitrify nitrate up to a recycle approaching 300%, and the kinetic calculations for that amount of denitrification in a 2.5 h HRT are close to the average denitrification rates at 22°C and 12°C found by Sutton et al. (1978). Takach's research may prove that a smaller HRT at

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22^0C could be used for 300% recycle, further reducing the implied costs.

Nonetheless, the potential benefits of the research can be deduced from Figure 9-1: the cost of designing a nitrification or nitrification & denitrification system may be lower than is currently thought. This would be especially true of systems requiring nitrification and denitrification plants with wastewaters at lower temperatures. A number of such plants would be in the Great Lakes regions of Canada and the United States, where a great many people reside. Theoretically the savings implied for just the NEWPCC in Winnipeg, for the 12^0C temperature is several million dollars. Therefore, this and the other research conducted at the University of Manitoba using small laboratory reactors has shown enough potential benefit to their own local taxpayers to warrant further research at the pilot scale.

The current consensus that high HRTs are essential to achieve performance goals leads to conservative designs at tremendous cost. Despite the difficulties encountered, this research is a step towards changing that view.

10.0 FURTHER RESEARCH

The immediate follow-up of this research was well underway by October, 1994. Larger reactors were used, gas recovery lines were put in, and glass plates were placed at the bottoms of the reactors, resulting in very few stirrer failures. The most significant improvement came as a direct result of using larger tubing. Plugged lines and reactor spills were virtually eliminated.

Due to concerns about pH, there is interest in the benefits of stripping CO_2 in one of the plug flow aerobic reactors. This can be investigated.

The parameters that need to be correlated to nitrate removal are BOD and COD removals. BOD/COD balances give the amount of oxidizing agents consumed, which would be NO_3 and O_2. These balances would further determine the impact of dissolved oxygen upon the anoxic reactor performance.

Batch studies should be done to compare the kinetics of primary effluent to prefermented wastewater and other substrates. Knowing the best way to achieve higher rates will lead to more compact and cost effective designs.

An investigation should be done with the goal of showing *when* it is more reasonable to try to accomplish nitrogen & phosphorous removal in one step rather than work on one retrofit for nitrogen, with the risk of second one for phosphorous.

The relationship between ORP and nitrification/denitrification suggests further research into ORP as a control parameter. The settleability of sludge under fully nitrifying conditions warrants further study.

Another issue to study is the possible exportation from the anoxic reactor of floc with anoxic zones that denitrify in the aerobic reactor. Similarly, there is need to study the issue of possible exportation of floc with aerobic zones when returned to the anoxic unit.

Calculations show that a predenitrifying reactor that denitrifies 25 mg/L of nitrate will generate about 18 mg/L of CO_2, which is otherwise produced and concentrated in the aerobic reactor. This outside production is not much of an advantage however, because that carbon dioxide is not going to leave solution since the anoxic reactor has minimal mixing. However, if a plant generates its own oxygen, that plant has the option of using the pressurized nitrogen to both mix the solids in the anoxic reactor and simultaneously strip the CO_2

formed as well as the excess CO_2 that returned from recycle. This option should be evaluated, especially in the case of a predenitrification system that would have a pseudo-plug flow arrangement, where the recycle from the aerobic reactor could be returned to a second stage which, if mixed with the nitrogen gas that has some oxygen, would strip the carbon dioxide while allowing the first anoxic stage to be oxygen free, ensuring maximum kinetic denitrification rates in the first stage.

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APPENDIX 1

Statistical Analysis of Figures 6.5 to 6.12

To test whether the slopes are significantly less than one, linear regressions forced through the origin were fitted for the data shown in Figures 6.5 to 6.12. A one-tailed t-test was used to test whether the slope of the fitted regression was significantly less than one.

Let:

β_1	=	Slope of the regression under the null hypothesis
	=	1
b_1	=	Slope of the fitted regression
$s(b_1)$	=	Standard error of b_1
α	=	Significance level of the test
	=	0.05 (1-tailed)
df	=	degrees of freedom
	=	39 to 47
$t_{\alpha,df}$	=	t-value from the table
	=	1.68 (for α=0.05, df=39 to 47)

Null Hypothesis: H_o: $\beta_1 = 1$
Alternate Hypothesis: H_a: $\beta_1 < 1$

Test statistic: $t^* = (b_1 - \beta_1) / s(b_1)$

If $|t^*| < t_{\alpha,df}$, then fail to reject H_o (b_1 not less than 1)
If $|t^*| \geq t_{\alpha,df}$, then reject H_o (b_1 less than 1)

Figure	b_1	$s(b_1)$	t^*	Conclude
6.5	0.979	0.0174	-1.23	slope = 1
6.6	0.767	0.0504	-4.62	slope < 1
6.7	0.924	0.0134	-5.69	slope < 1
6.8	0.877	0.0237	-5.19	slope < 1
6.9	0.923	0.0284	-2.71	slope < 1
6.10	0.928	0.0107	-6.77	slope < 1
6.11	0.686	0.0311	-10.08	slope < 1
6.12	0.749	0.0525	-4.77	slope < 1

APPENDIX 1: STATISTICAL DATA FOR FIGURES 5-7 TO 5-9
AND FOR FIGURES 6-5 TO 6-12

SOLUBLE ORGANIC CARBON INFLUEN MG/L	SOC REACTOR ONE MG/L	SOC REACTOR TWO MG/L	SOC IN EFFLUENT MG/L
117.8	39.2	34.6	36.4
99.4	33	25.1	22.3
96.1	34.5	26.6	26.5
95.7	38.4	25	23.7
90.1	30.2	24.4	23.2
88.3	29.7	26.2	24.1
85.9	26.8	24	26.6
82.8	25.4	22.1	24.1
82.3	27.8	25	25.1
81.2	26.7	21.2	21.8
81	31.8	28.7	31.9
81	32.5	34.2	26.9
80.9	24.9	24.1	24
74.2	30.1	25.5	24.5
72.2	25.3	27.5	25.3
70.5	25.7	24.3	19.7
68.3	30.8	25.2	25.5
68.3	27.5	23.2	21.2
68.3	27.5	23.2	21.2
66.8	22.2	19.7	18.5
66	29.5	21.9	26.9
64.5	31.5	20.3	19
63.5	27	24	25.9
59.3	27.9	23.2	26.1
58	25	22	22
56.5	31.6	22.4	24.5
48.3	21.7	29	25
48	25	25	20
43.3	20.1	17.8	18.2
40	24	21	21
38.9	20.1	19	19.5
35.9	22.9	20.3	23.7
34.4	23.6	17	17.3
32.6	23.5	20.1	19.3
30.6	20.1	22.1	23.2
30.5	21.4	17.1	15.2
30	25	23	15
28.8	15.5	13.7	15
25.6	17.7	26	24.6
25.3	16.6	15.7	17.9
20.8	15.4	19.1	23
20.1	13.9	18.8	17.7
15.3	13.9	12	26.1
24.8	17.4	23	NA
93.1	20.4	23.6	19.5
75.7	35.8	28.3	28.4
48.4	16.9	15.1	16.5
29.7	28.3	17.5	20.9

STATISISTICS FOR FIGURE 5-7

Regression Output:
Constant	14.2687
Std Err of Y Est	3.88098
R Squared	0.61945
No. of Observations	48
Degrees of Freedom	46

X Coefficient(s)	0.18908
Std Err of Coef.	0.02185

STATISTICS FOR FIGURE 5-8

Regression Output:
Constant	15.5668
Std Err of Y Est	3.39381
R Squared	0.46148
No. of Observations	48
Degrees of Freedom	46

X Coefficient(s)	0.11997
Std Err of Coef.	0.01911

STATISTICS FOR FIGURE 5-9

Regression Output:
Constant	17.1076
Std Err of Y Est	3.62294
R Squared	0.30456
No. of Observations	47
Degrees of Freedom	45

X Coefficient(s)	0.09233
Std Err of Coef.	0.0208

STATISTICS FOR FIGURE 5-7
TOSSING BOTTOM FOUR POINTS

Regression Output:
Constant	13.4157
Std Err of Y Est	3.04249
R Squared	0.75804
No. of Observations	44
Degrees of Freedom	42

X Coefficient(s)	0.20447
Std Err of Coef.	0.01783

STATISTICS FOR FIGURE 5-8
WITHOUT BOTTOM FOUR POINTS

Regression Output:
Constant	15.8715
Std Err of Y Est	3.32111
R Squared	0.46537
No. of Observations	44
Degrees of Freedom	42

X Coefficient(s)	0.11765
Std Err of Coef.	0.01946

STATISTICS FOR FIGURE 5-9
WITHOUT LAST FIVE POINTS

Regression Output:
Constant	17.0051
Std Err of Y Est	3.51135
R Squared	0.33917
No. of Observations	43
Degrees of Freedom	41

X Coefficient(s)	0.09636
Std Err of Coef.	0.02101

STATISTICS FOR FIGURE 6-6

NH3-N REACT TWO MG/L	NH3-N IN EFFLUENT MG/L
31	24.2
25.5	24.5
24	13.8
23.5	20.9
22.5	15.6
20.6	9.5
18.4	15.3
14.9	12.8
11.6	8.9
11.4	7.1
10.5	5.5
10.1	9.5
9	2.9
8.5	5.2
8.4	8.7
7.8	6
7.5	1.8
6.9	1.7
6.1	1.9
5.8	4
5.8	2.6
5.6	3.7
5.3	2.9
5.2	1.7
4.9	2
4.9	0.7
4.5	2.2
4.4	3
3.5	1
2.8	1.4
2.5	0.2
2.5	0.3
2.3	0
2.2	0
1.8	12.8
1.4	0.8
1.4	0
1.3	0.3
1.2	0.5
0.4	0
0.4	0
0.3	0.2
0.2	0
0.2	0.5
0.1	0.4
0.1	0
0.1	0
0	0

Regression Output ALL POINTS, FORCED THROUGH (0,0)

Constant	0
Std Err of Y Est	2.69454
R Squared	0.83226
No. of Observations	47
Degrees of Freedom	46

X Coefficient(s)	0.72487	
Std Err of Coef.	0.03657	

Regression Output ALL POINTS, NOT FORCED THROUGH (0,0)

Constant	-0.6605
Std Err of Y Est	2.68032
R Squared	0.83763
No. of Observations	47
Degrees of Freedom	45

X Coefficient(s)	0.76738	
Std Err of Coef.	0.05037	

STATISTICS FOR FIGURE 6-7

mg/l NH3-N R R2NH3	mg/l NH3-NEffl. NH3EFF	Regression Output	
33.4	34.7	Constant	0
21.4	18.4	Std Err of Y Est	2.34391
42.6	36.3	R Squared	0.88883
32.8	33.2	No. of Observations	40
30.3	29.4	Degrees of Freedom	39
32.9	30.3		
19.9	17.2	X Coefficient(s)	0.92389
23.5	20.7	Std Err of Coef.	0.0134
30.7	27		
24.5	29.9		
24.2	21.3		
36.2	33.2		
22.1	19		
31.4	26.7		
26.5	26.1		
24.4	19.5		
28.9	24.6		
31.6	31.5		
20	18.9		
31	26.2		
28.7	27.5		
24.4	26.4		
13.4	13.4		
23.7	22.9		
26.9	25.2		
34.7	32.5		
27.2	20.5		
39.7	38.5		
29.4	26.2		
19.9	18.3		
23.4	20.9		
21.9	23.2		
35.6	30.6		
31.5	30.7		
12.7	8.1		
15.5	13.8		
17.9	14.9		
32.1	29.4		
16.9	13.4		
28.4	27.8		

STATISTICS FOR FIGURE 6-8

mg/l SOC R2 R2SOC	mg/l SOC Effl. SOCEFF	Regression Output	
34.5	33	Constant	0
38	23.1	Std Err of Y Est	4.862
34.4	37.5	R Squared	-0.78891
33.8	29.5	No. of Observations	42
41	32.2	Degrees of Freedom	41
34.5	29.5		
40.1	24.7	X Coefficient(s)	0.87689
31.6	29.3	Std Err of Coef.	0.02369
34	32.2		
58.5	35.4		
30.6	30.7		
31.6	29.6		
25.5	24.8		
33.5	33.7		
32.2	26.3		
31.2	26.7		
27.9	26.6		
25.4	27.8		
29.9	28.2		
30.6	27		
27.2	26.9		
26.8	28.6		
28.4	28.1		
33.1	29		
29.9	28.3		
28.1	30.4		
32.6	27.9		
26.4	22.8		
29	26.6		
26.1	24.1		
26.5	25.6		
27.3	27.4		
40.4	24.9		
31.5	29.3		
26.7	27.1		
27.9	27.9		
26.3	22.8		
23.2	23.7		
27.6	20.4		
32.2	32.2		
21.4	21.9		
27.8	30.5		

STATISTICS FOR FIGURE 6-9

SOC R2 mg/l	SOC Effl. mg/l	Regression Output	
		Constant	0
		Std Err of Y Est	5.72541
33.6	29.4	R Squared	-0.6548
25	26.5	No. of Observations	40
35	34.8	Degrees of Freedom	39
49.4	15.3		
31.8	31.7	X Coefficient(s)	0.92294
33.7	42.5	Std Err of Coef.	0.02839
29.5	30.6		
32.1	27.6		
32.9	30.6		
29.3	29		
35.3	34.8		
28.2	30.3		
34.3	30.1		
36.2	35.7		
36.4	32.4		
34.1	31.8		
29.7	28.5		
33.4	31.1		
37.5	31.6		
31	30.5		
26.2	26.4		
28.9	27.9		
27.3	28.1		
25.9	29.3		
37	37.6		
30.3	30.1		
39.4	33.8		
33.1	31.8		
29.4	27.8		
40	31		
32.7	31.8		
26.4	26		
28.6	25.8		
28.3	27.8		
32.5	31.6		
24.6	24.2		
23.3	24.6		
23	24.5		
24.5	23.6		
28.8	27.3		
NA	NA		
NA	NA		
NA	NA		
NA	NA		

STATISTICS FOR FIGURE 6-10

NH3-N R mg/l	NH3-NEffl. mg/l	Regression Output	
		Constant	0
		Std Err of Y Est	2.10523
36.5	34.4	R Squared	0.88169
25.7	24.5	No. of Observations	46
25.8	23.8	Degrees of Freedom	45
24.1	21.7		
25.1	23	X Coefficient(s)	0.92774
28.1	25.3	Std Err of Coef.	0.01068
23.6	21.9		
25.9	23.7		
29	26.2		
31.2	29.6		
24.7	22		
29.6	25.7		
26.1	21.9		
27.9	23.8		
22.5	22.5		
29.7	23.6		
35.5	30.1		
31.9	29.1		
37.2	33.8		
34.8	32.2		
31.8	30.4		
29.4	26.9		
30.7	28.7		
29.8	29.2		
21.5	21.6		
24.8	23.7		
20.4	20.8		
32.6	28.8		
32.2	31.9		
43	36.9		
28.9	29.7		
24.5	27.3		
43.3	39		
39.7	40.9		
33.7	32		
34.9	34.7		
35.6	35.6		
26.3	23.4		
23.1	22.3		
17.7	16.7		
18.2	17.4		
24	22		
17.4	17.9		
18.7	17.1		
22.7	13.1		
26	25.6		

STATISTICS FOR FIGURE 6-11

mg/l NO3-NR R2NO3	mg/l NO3-NEffl. NO3EFF
2.1	2.1
2.1	5
0	0
1.4	1
1.6	5.3
8	10
2.8	3.8
0.5	2.7
0	1.6
7.5	10.7
0	3.2
1.9	5.9
1.2	5
10.9	13.4
4.8	6.4
3.8	8.5
7.8	7.7
1.4	2.4
8.6	14.3
2.3	5.1
5.3	6.8
9.6	9
13.5	14.6
1.6	3.2
1.4	6
2.7	5.9
5.6	10.2
0.4	4.3
0.5	2.9
4.4	6.3
6.8	10
3.8	4.5
1.8	7.5
8.3	8.3
7.9	15.4
4.4	6.5
6	10
1.1	3.2
7.2	11.7
2.8	0
1.7	1.7
7.3	10.6
7.7	11
8.6	8.6
4.6	9.9
13.4	16
10.3	12.7
3.9	4.4

Regression Output:

Constant	0
Std Err of Y Est	1.75225
R Squared	0.76464
No. of Observations	48
Degrees of Freedom	47
X Coefficient(s)	0.68598
Std Err of Coef.	0.03115

STATISTICS FOR FIGURE 6-12

NO3-NR mg/l	NO3-NEffl. mg/l
0	0.4
0	0.3
0	0.4
0	1
0.3	2.2
0.5	1
0.6	3.6
0.7	1.4
0.8	1.2
1	3.3
1.1	3.8
1.1	1.6
1.1	1.7
1.2	5.1
1.2	2.5
1.4	3.9
1.4	4.7
1.5	3
1.5	5.7
1.8	5
1.8	2.7
1.8	5.2
1.9	2.9
2.1	2.8
2.2	5.8
2.3	2.5
2.4	6.2
2.5	5
2.9	3.2
2.9	3.8
3.7	3
4	7.3
4.2	2.7
4.7	7.9
5.2	7
5.4	3.3
5.7	8.3
5.9	8.3
6.4	6.1
6.6	6.4
6.9	4.6
8.5	8.9
12.3	6.8
15.5	18.6

Regression Output:

Constant	0
Std Err of Y Est	1.8706
R Squared	0.66496
No. of Observations	44
Degrees of Freedom	43
X Coefficient(s)	0.74936
Std Err of Coef.	0.0525

APPENDIX 2

Cost Estimate Calculations

Data from Consultants' Report to City of Winnipeg:

Expansion for nitrification at 2011 flows:

@ 20^{0}C, needs **6** oxygen reactors and **3** clarifiers (Table 7-3)
@ 14^{0}C, needs **8** oxygen reactors and **3** clarifiers (Table 7-3)
@ 12^{0}C, needs **12** oxygen reactors and (presumably)
    3 clarifiers (Page 7-5)

Page 7-5 notes a model was used for 12^{0}C
Page 7-6 notes a model was used for cost estimates

Page 7-6 notes capital cost for nitrification for the South
End Water Pollution Control Centre (SEWPCC) is **$90 million**,
emphasizing that this was for a design temperature of **20^{0}C**.

Table 7-4 gives:

SEWPCC	$ millions (1990$)
Reactor Tanks	31
Oxygen Supply	23
Clarifiers	<u>36</u>
Total	90

∴ 31 reactors ÷ 6   => $5.2 million / reactor
∴ **cost @ 14^{0}C**   => $90 + 2*$5.2
                = **$100 million**
∴ **cost @ 12^{0}C**   => $90 + 6*$5.2
                = **$121 million**

These three costs for the basis for the graph in Section
9.1.

From the U. of Manitoba work, we can nitrify at 3 h HRTs if
acclimated (Sears). My 4.5 h data nitrified completely at
22^{0}C with low solids, suggesting smaller HRT would work.
Furthermore, the report design had the luxury of modelling
the pseudo-plug flow of the SEWPCC, whereas our lab reactors
were a single completely mixed reactor, which would give
worse performance.

Using design flow of 88 mL/d (Tables 7.1 and 7.2) and
reactor volume of 19,680 m^3 (Table 7.3), we get a 5.4 h HRT
@ 20^{0}C, from the report.

At 12^0C, Sears nitrified in 2.5 h and 4.0 h. My 4.5 h had the trend to nitrification as well. Thus, a 4 h HRT at 12^0C could be implied.

Reactor Cost$_{UM}$ (in \$ millions) = (HRT$_{UM}$/5.4 h)*\$31

Total Cost$_{UM}$ (in \$ millions) = Reactor Cost$_{UM}$ + \$23$_{O2}$ + \$36$_{Clarifiers}$

∴ **Total Cost$_{UM}$ @ 20^0C = \$76.2 million (nitrify only)**
∴ **Total Cost$_{UM}$ @ 12^0C = \$82 million (nitrify only)**

Denitrification adds HRT and cost, but some savings occur due to a reduction in O_2 requirements.

For the anoxic reactor, I have found no reason to exceed a 2.5 h HRT. Rather, there is a reason not to exceed 2.5 h as a higher anoxic HRT decreases the aerobic SRT, which must be maintained in order to nitrify. Therefore, a 2.5 h HRT is all that should be added.
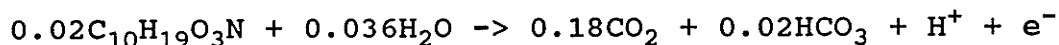
∴ Reactor Cost$_{DN}$ = (5.5/5.4)*31 = \$31.6 million
Add \$36 million for clarifiers, but because of reduced O_2 requirements need, start @ \$23 million

Assume we treat 30 mg/L NH_3 and 75 mg/L SOC via:
    SOC ≈ 2*TKN = (2*NH_3) / 0.8

Carbonaceous oxygen demand = ?

$0.02C_{10}H_{19}O_3N + 0.036H_2O \rightarrow 0.18CO_2 + 0.02HCO_3 + H^+ + e^-$

SOC = 0.02 mol*(12 mg SOC/mol) = 0.24 mg

Oxygen demand = 0.036 mol*(16 mg O/mol) = 0.576 mg

∴ Carbonaceous oxygen demand = 2.4 mg O/mg SOC

∴75 mg * 2.4 mg O/mg SOC = 180 mg oxygen demand

$NH_4^+ + 1.83O_2 + 198HCO_3 \rightarrow 0.021C_5H_7NO_3 + 1.041H_2O + 0.98NO_3 + 1.88H_2CO_3$
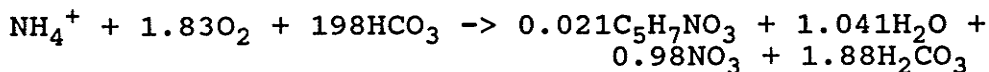
NH_3N = 1 mg*(14 mg/mol) = 14 mg

Oxygen demand = 1.83 mol*(32 mg O/mol) = 58.56 mg

@ 20^0C:

Oxygen demand   = 58.56 mg O/14 mg NH_3N
                 = 4.18 mg O_2/mg NH_3N

$\therefore$ Nitrogenous oxygen demand
$$= 30 \text{ mg } NH_3 * 4.18 \text{ mg } O/14 \text{ mg } NH_3N$$
$$= 125.5 \text{ mg } OD$$

Total = 305.5 mg

Oxygen returned
$$= (30 \text{ mg } NO_3\text{-N formed}) * (48 \text{ mg } O/14 \text{ mg } NO_3\text{-N}) * R/(R+1)$$
$$= 30 * (48/14) * 3.0/(3.0+1) \qquad (with\ R \approx 3.0)$$
$$= 77.14 \text{ mg } O$$

$100\% * 77.14/305.5 = 25.25\%$

==> Oxygen required is 75% of that to nitrify

$\therefore$ Oxygen cost = 0.75*$23 million = $17.2 million

$\therefore$ **Total cost** = $31.6 + $36 + 17.2 = **$84.8 million (@ 20^{0}C)**

@ 12^{0}C:

4 h aerobic + 2.5 h anoxic adds 1 h HRT
We assume O_2 savings are the same as for 20^{0}C.

$\therefore$ **Total cost** = $84.8 + ($31/5.4) = **$90.5 million (@ 12^{0}C)**

Note: The 2.5 h is a "high" anoxic HRT. While our
       nitrification assumptions are optimistic, the anoxic
       HRT counters that assumption.

Our winter design could focus more on nitrification and less
on denitrification, because NO_3 in winter is not much of a
problem. Thus a design shrinking the anoxic reactor in
winter to (say) 1.75 h, and aerating that 0.75 h HRT space,
would give a winter HRT the same as summer. O_2 savings
would not be 25%, but about:

   $(1.75/2.5) * 25\% = 17.5\%.$

Then the cost is:

   $84.8 + $23 * (25-17.5)/100 = $86.5 million.

However, the $90.5 million still tells us that the U. of
Manitoba cost, due to **implied lower HRTs** is well below the
computer design cost at 12^{0}C of $121 million.