General Information on Nitrogen

What is nitrogen?

- Nitrogen was discovered in 1772 by Daniel Rutherford in Scotland
- Nitrogen gas makes up nearly 80% of the air we breathe
- Nitrogen gas is not toxic
- Nitrogen compounds such as ammonia (NH_3) are toxic in high concentration
- Nitrogen containing compounds like cyanide (CN^-) are lethal in very small amounts

Forms of nitrogen in water

- Ammonia (NH_3 as a gas or NH_4^+ ions)
- Organic nitrogen (urea, fecal material)
- Nitrate (NO_3^-) and nitrite (NO_2^-)
- Total Kjeldahl Nitrogen (TKN) is the combination of ammonia and organic nitrogen

Why remove nitrogen from wastewater?

In its various forms, nitrogen can deplete dissolved oxygen in receiving waters, stimulate aquatic plant growth, exhibit toxicity toward aquatic life, present a public health hazard, and affect the suitability of wastewater for reuse purposes. Wastewater effluents containing nutrients such as nitrogen and phosphorus can cause eutrophication, the excessive growth of plant and/or algae blooms in lakes, streams and rivers.

Nitrate is a primary contaminant in drinking water and can cause a human heath condition called Methemoglobinemia (blue babies). This is due to the conversion of nitrate to nitrite by nitrate reducing bacteria in the gastrointestinal tract. Oxidation by nitrite of iron in hemoglobin forms methemoglobin. Since methemoglobin is incapable of binding molecular oxygen, the result is a bluish tinge to the skin and suffocation or death may occur if left untreated. The maximum contaminant level (MCL) for nitrate in drinking water is 10.0 mg/L.

Typical effluent permit limits for nitrogen compounds in wastewater effluent vary, but all are based on location of final effluent discharge. A wastewater plant that discharges to a spray field may not have a limit on nitrogen while a plant that discharges to percolation ponds may have an effluent nitrate limit of 12 mg/L. A treatment plant that discharges to a nearby stream or river may have a total nitrogen limit of 3 mg/L, or a unionized ammonia limit of 0.2 mg/L.

In order to achieve these limits, we must operate treatment plants to not only remove CBOD and TSS, but to convert nitrogen compounds to less noxious forms. This requires operators to use processes that they may not be entirely familiar with. Many new package plants are being built with anoxic tanks, which require different process control methods than a basic extended aeration treatment plant. If a wastewater treatment plant does not have an anoxic tank, cycling the aeration blowers on and off may be needed to create an anoxic zone or time to denitrify in the aeration tank. These concepts will be discussed further in the following sections.

Nitrogen in Wastewater Treatment

Depending on environmental variables such as temperature and pH, nitrogen enters a treatment plant in various forms.

Ammonification

Beginning at the house connection to the main sewer line, nitrogen is mostly in the form of organic nitrogen. Through a process called hydrolysis, organic nitrogen begins conversion to ammonia or ammonium. The form of nitrogen depends on pH and temperature. When the pH of the wastewater is acidic (<6.9) or neutral (7.0), the majority of the nitrogen is ammonium (NH_4^+). When the pH increases over 8.0, the nitrogen is mostly ammonia (NH_3). Typically by the time the wastewater enters the treatment plant, most of the organic nitrogen has been converted to ammonium.

Nitrification

Nitrification is the biological conversion of ammonium to nitrate nitrogen, and is a two-step process. First, bacteria known as *Nitrosomonas* convert ammonia and ammonium to nitrite. Next, bacteria called *Nitrobacter* finish the conversion of nitrite to nitrate. The reactions are generally coupled and proceed rapidly to the nitrate form; therefore nitrite levels at any given time are usually low.

These bacteria known as "Nitrifiers" are strict aerobes, which means they must have free dissolved oxygen to perform their work, and are only active under aerobic conditions. It requires approximately 4.6 pounds of oxygen for every pound of ammonia converted to nitrate. The growth rate of nitrifiers is affected by the concentration of dissolved oxygen (DO), and at DO less than 0.5 mg/L the growth rate is minimal. Typical operational guidelines call for a minimum DO concentration of 1.0 mg/L at peak flow and an average daily DO concentration of 2.0 mg/L. For nitrification to proceed the oxygen should be well distributed throughout the aeration tank and its level should not be below 2.0 mg/L.

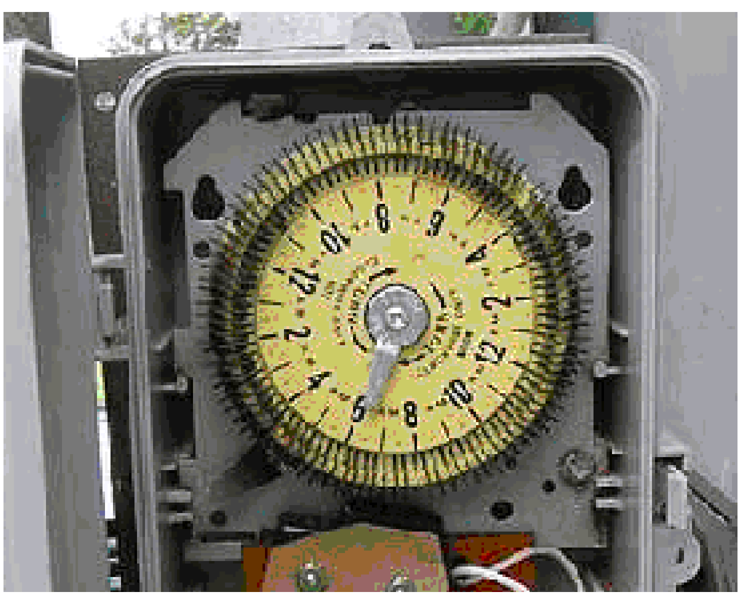
The process of nitrification produces acid. This acid formation lowers the pH of the MLSS and can cause a reduction of the growth rate of nitrifying bacteria. The optimum pH for *Nitrosomonas* and *Nitrobacter* is between 7.5 and 8.5 and nitrification stops at pH at or below 6.0. Approximately 7.14 pounds of alkalinity (as $CaCO_3$) are destroyed per pound of ammonia oxidized to nitrate.

Water temperature also affects the rate of nitrification. Nitrification reaches a maximum rate at temperatures between 30 and 35 degrees C (86ºF and 95ºF). At temperatures of 40ºC (104ºF) and higher, nitrification rates fall to near zero.

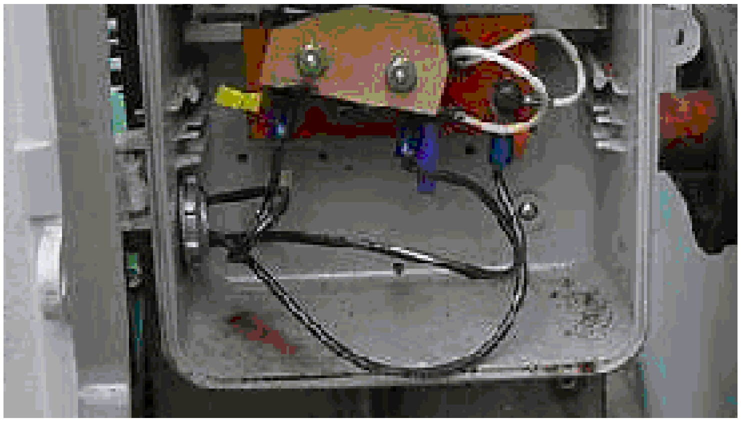
Sludge Age and Mixed Liquor levels are also integral components in the nitrification process. When performing sludge age calculations (MCRT or SRT) to determine the detention time required for nitrification, the capacity of the oxic (aerated) portion of the plant should be used. Since anoxic or fermentation basins are not aerated and nitrifying organisms are strict aerobes, the capacity of these basins should not be included in calculations for oxic SRT. Extended aeration (package type) wastewater plants are more capable of nitrification than contact-stabilization and other activated sludge systems due to the high sludge age and long periods of aeration.

Toxicity and sources of inhibition to microorganisms present problems to operators and nitrifying organisms. Some of the most toxic compounds to nitrifiers include cyanide, thiourea, phenol and heavy metals such as silver, mercury, nickel, chromium, copper and zinc. Some of these compounds can enter a wastewater treatment plant from landfill leachate and septage. Nitrifying bacteria can also be inhibited by free forms of their own substrate. Nitrite oxidizing bacteria are sensitive to free nitrous acid, and ammonia oxidizing bacteria are sensitive to free ammonia. Increased levels of free ammonia can decrease nitrifier growth rates. Some treatment plants that may have increased influent organic nitrogen and ammonia levels include plants that serve Department of Transportation highway rest areas and wastewater plants serving schools.

Denitrification



Denitrification is an anaerobic respiration process in which nitrate serves as the electron acceptor. In simpler terms, denitrification occurs when oxygen levels are depleted and nitrate becomes the primary oxygen source for microorganisms. When bacteria break apart nitrate (NO_3^-) to gain the oxygen (O_2), the nitrate is reduced to nitrous oxide (N_2O), and nitrogen gas (N_2). Since nitrogen gas has low water solubility, it tends to escape as gas bubbles. These gas bubbles can become bound in the settled



sludge in clarifiers and cause the sludge to rise to the surface.

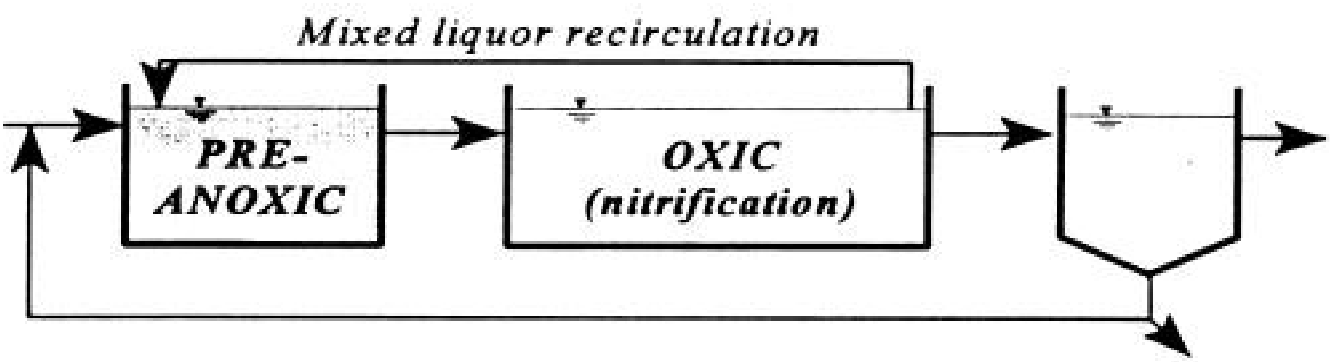
Denitrification Process Description

There are several ways to force bacteria to perform the work of denitrification. The processes may be designed specifically for nitrification/denitrification using anoxic tanks (selectors) or may use timers (Figure 1) controlling aeration blowers to turn blowers on and off.

Figure 1 Blower Control Timer

The Modified Ludzack-Ettinger process (Figure 2) is designed to use nitrate produced by the aeration zone as an oxygen source for facultative bacteria in the breakdown of raw wastewater in the anoxic basin. The first process in the treatment train is a pre-anoxic basin where influent wastewater, return sludge from the clarifier, and nitrate-rich mixed liquor pumped from the effluent end of the aeration tanks are mixed together. The influent wastewater serves as the carbon source for bacteria, return activated sludge from the clarifier provides microorganisms, and the anoxic recycle pumps provide nitrate as an oxygen source.

Figure 2 Modified Ludzack-Ettinger process



The anoxic basin is mixed, but not aerated. Mixers can be floating mechanical type or submersible motors fitted with propeller type mixers.

The Wurhman Process places the anoxic basin after the nitrification zone (Figure 3). This process relies on nitrate produced in the preceding aeration tank as the oxygen source. Facultative bacteria that make up a majority of the MLSS perform the work of denitrification.

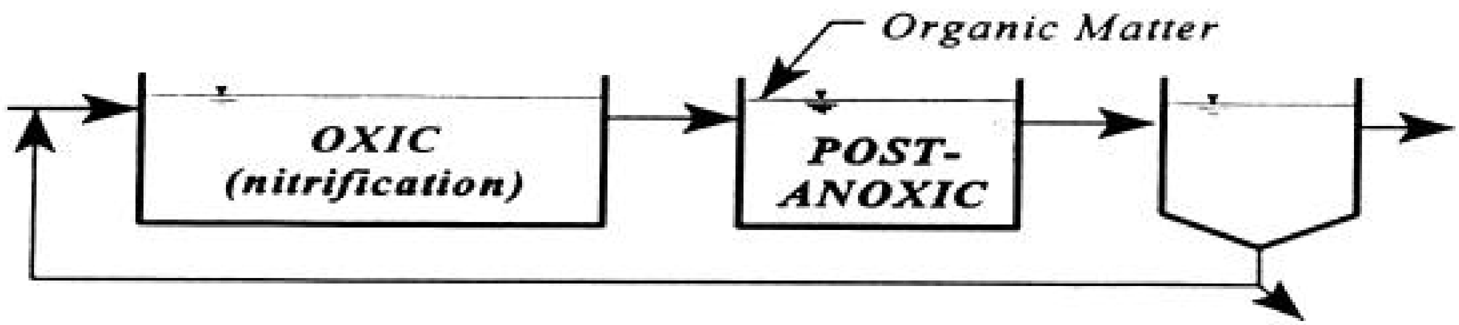


Figure 3 Wurhman Process

In order to drive the denitrification process, organic matter is added to the anoxic basin. Since most of the organic matter present in raw wastewater has been consumed through the aeration tank by aerobic and facultative bacteria, a supplement must be added to the anoxic basin. Sources of organic matter are discussed in following sections. The anoxic basin is mixed, but not aerated. Many facilities employ a reaeration zone after the anoxic basin to release nitrogen gas bound in the sludge, and freshen the mixed liquor before it enters the clarifier.

When a small plant is required to meet nitrate limitations according to the operating permit, but was not originally designed to meet these limits, an alternative method must be employed. These methods may require cycling the aeration blowers on and off to provide a time for bacteria to enter an anoxic period. This time period can be monitored and blower run times (Figure 1) are set using process control methods discussed in later sections of this manual.

Conditions Required for Effective Denitrification

Conditions that affect the efficiency of denitrification include nitrate concentration, anoxic conditions, presence of organic matter, pH, temperature, alkalinity and the effects of trace metals.

Since denitrifying bacteria are facultative organisms, they can use either dissolved oxygen or nitrate as an oxygen source for metabolism and oxidation of organic matter. If dissolved oxygen and nitrate are present, bacteria will use the dissolved oxygen first. This will occur since dissolved oxygen is readily available and yields more energy to the organisms. Therefore it is imperative to keep dissolved oxygen levels as low as possible in anoxic basins or timed anoxic cycles. Excessive aeration in basins designed as anoxic is possible through aerated return sludge (air lift type RAS), excessive splashing of liquid streams into anoxic basins, and air diffusion being used for tank mixing instead of using mixing pumps or mixing devices.

Another important aspect of denitrification is the presence of organic matter to drive the denitrification reaction. Organic matter may be in the form of raw wastewater, food-processing wastes, or chemical sources such as methanol, ethanol, acetic or citric acid. When these sources are not present, bacteria may depend on internal (endogenous) carbon reserves as the organic matter. This matter is released during the death phase of organisms, and may not be a consistent enough source of carbon to drive the denitrification to completion. Whatever organic source is used to drive the denitrification reaction, it should be fed consistently and at a rate to keep denitrification levels maximized. Conversely, it is important to avoid raising effluent CBOD values and avoid spending excessive money on organic sources such as methanol.

An advantage of denitrification is the production of alkalinity and an increase of pH. Approximately 3.0 to 3.6 mg of alkalinity (as CaCO3) is produced per milligram of nitrate reduced to nitrogen gas. Optimum pH values for denitrification are between 7.0 to 8.5.

Temperature affects the growth rate of denitrifying organisms, with greater growth rate at higher temperatures. Denitrification can occur between 5 to 30^{o}C (41^{o}F to 86^{o}F), and these rates increase with temperature and type of organic source present. The highest growth rate can be found when using methanol or acetic acid. A slightly lower rate using raw wastewater will occur, and the lowest growth rates are found when relying on endogenous carbon sources at low water temperatures.

Denitrifying organisms are generally less sensitive to toxic chemicals than nitrifiers, and recover from toxic shock loads quicker than nitrifiers.