Alkalinity Profiling in Wastewater Operations

OPS Challenge Laboratory Event 2015
Description and Procedure

The purpose of this competition will be to familiarize participating teams to the definition and concept of alkalinity, and the influences on plant operations related to proper alkalinity levels.

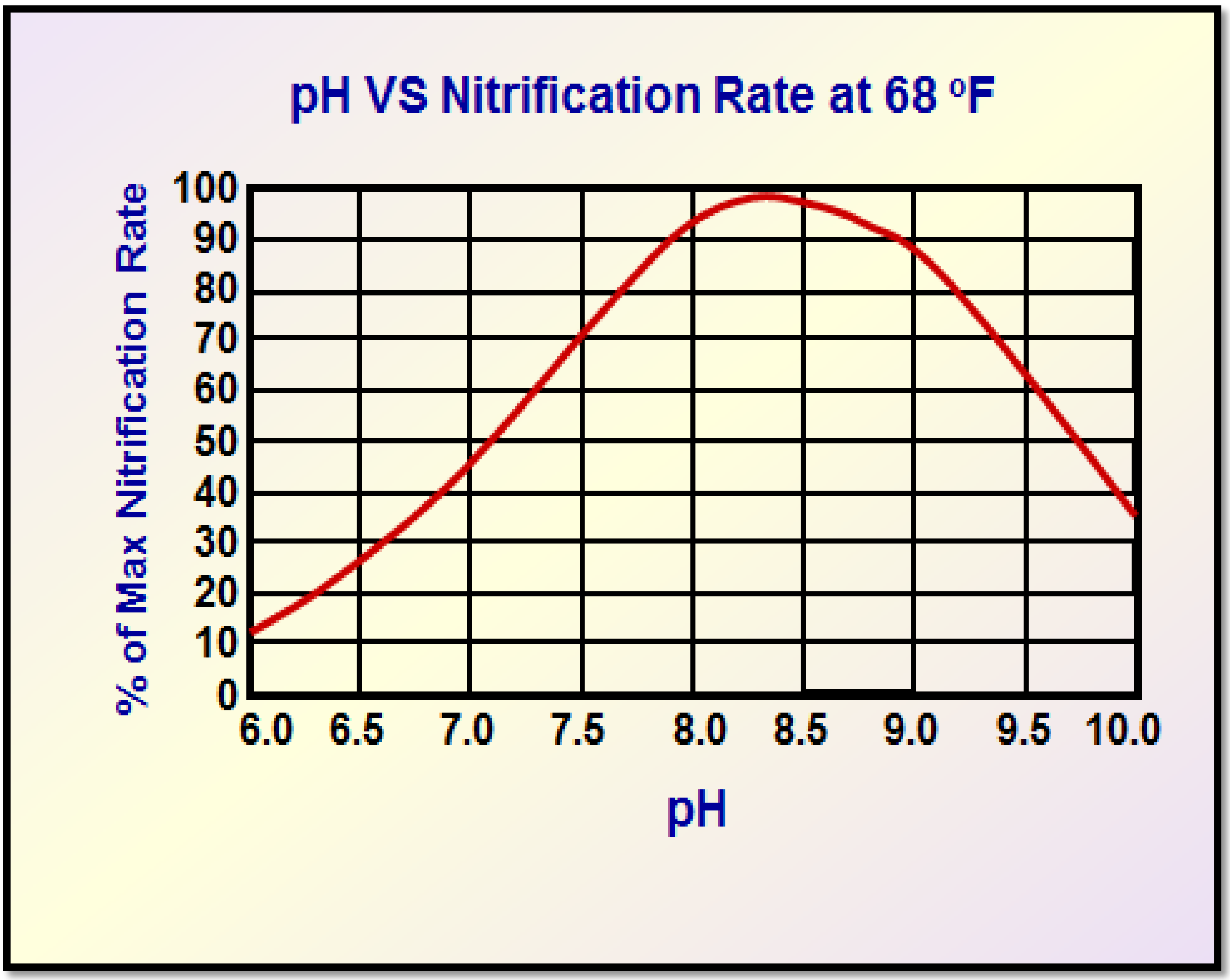
Alkalinity Defined

The alkalinity of water is a measure of its capacity to neutralize acids. It also refers to the buffering capacity, or the capacity to resist a change in pH. For wastewater operations, alkalinity is measured and reported in terms of equivalent calcium carbonate (CaCO3). It is common practice to express alkalinity measured to a certain pH. For wastewater, the measurement is total alkalinity which is measured to a pH of 4.5 SU. Even though pH and alkalinity ARE related, there are distinct differences between these two parameters, and how they can affect your plant operations

Alkalinity and pH

Alkalinity is often used as an indicator of biological activity. In wastewater operations, there are three forms of oxygen available to bacteria: dissolved oxygen (O_2), nitrate ions (NO_3^-), and sulfate ions (SO_4^{2-}). Aerobic metabolisms use dissolved oxygen to convert food to energy. Certain classes of aerobic bacteria, called nitrifiers, use ammonia (NH_3) for food instead of carbon-based organic compounds. This type of aerobic metabolism, which uses dissolved oxygen to convert ammonia to nitrate, is referred to as nitrification. Nitrifiers are the dominant bacteria when organic food supplies have been consumed. Further processes include denitrification, or anoxic metabolism, which occurs when bacteria utilize nitrate as the source of oxygen and the bacteria use nitrate as the oxygen source. In an anoxic environment, the nitrate ion is converted to nitrogen gas while the bacteria converts the food to energy. Finally, anaerobic conditions will occur when dissolved oxygen and nitrate are no longer present and the bacteria will obtain oxygen from sulfate. The sulfate is converted to hydrogen sulfide and other sulfur related compounds.

Alkalinity is lost in an activated sludge process during nitrification. During nitrification, 7.14 mg of alkalinity as CaCO3 is destroyed for every mg of ammonium ions oxidized. Lack of carbonate alkalinity will stop nitrification. In addition, nitrification is pH-sensitive and rates of nitrification will decline significantly at pH values below 6.8. Therefore, it is important to maintain an adequate alkalinity in the aeration tank to provide pH stability and also to provide inorganic carbon for nitrifiers. At pH values near 5.8 to 6.0, the rates may be 10 to 20 percent of the rate at pH 7.0 (U.S. EPA, 1993). A pH of 7.0 to 7.2 is normally used to maintain reasonable nitrification rates, and for locations with low-alkalinity waters, alkalinity is added at the wastewater treatment plant to maintain acceptable pH values. The amount of alkalinity added depends on the initial alkalinity concentration and amount of NH4-N to be oxidized (M&E). After complete nitrification, a residual alkalinity of 70 to 80 mg/L as CaCO3 in the aeration tank is desirable (M&E). If this alkalinity is not present, then alkalinity should be added to the aeration tank.



From EPA-625/4-73-004a Revised
Nitrification and Denitrification Facilities
Wastewater Treatment
EPA Technology Transfer Seminar

Nitrification Activities at pH 7.2 and below	
pH	**Activity**
7.2	1.00
7.0	0.83
6.8	0.67
6.6	0.50
6.4	0.34
6.2	0.17

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Why is Alkalinity or Buffering Important?

Or: Alkalinity = Capacity

Aerobic wastewater operations are net acid producing. Processes influencing acid formation include, but are not limited to:

- Biological nitrification in aeration tanks, trickling filters and RBC's
- The acid formation stage on anaerobic digestions
- Biological nitrification in aerobic digesters
- Gas chlorination for effluent disinfection
- Chemical addition of aluminum or iron salts

In wastewater treatment, it is critical to maintain pH in a range that is favorable for biological activity. These optimum conditions include a near neutral pH value between 7.0-7.4. Effective and efficient operation of a biological process depends on steady state conditions. The best operations will be carried on without sudden changes in any of the operating variables. If kept in a steady state, good flocculating types of microorganisms will be more numerous. Alkalinity is the key to steady state operations. The more stable the environment for the microorganisms, the more effectively they will be able to work. In other words, a sufficient amount of alkalinity can provide for ***improved performance and expanded treatment capacity***.

How do I know how much alkalinity I need for my system to operate properly?

To nitrify, alkalinity levels should be at least eight times the concentration of ammonia present in the wastewater. This value may be higher for raw wastewaters with higher influent ammonia concentrations than the "normal." The theoretical reaction shows that approximately 7.14 mg of alkalinity (as $CaCO3$) is consumed for every mg of ammonia oxidized. Rule of thumb is an 8 to 1 ratio of alkalinity to ammonia. If adequate alkalinity is not present, this could result in incomplete nitrification and depressed pH values in the plant. Plants with the ability to denitrify are able to add back valuable alkalinity to the process, and those values should be taken into consideration when doing mass balancing. For purposes of the OPS competition, the decision has been made to not incorporate the denitrification step in process profiling. To determine alkalinity requirements for plant operations, it is critical to know:

- influent ammonia in mg/L
- influent total alkalinity in mg/L
- effluent total alkalinity in mg/L

For every mg/L of converted ammonia, alkalinity will decrease by 7.14 mg/L. Therefore, to calculate theoretical ammonia removal, multiply the influent (or raw) ammonia mg/L X 7.14 mg/L alkalinity to determine a minimum amount of alkalinity needed for ammonia removal through nitrification.

EXAMPLE
Influent Ammonia = 36 mg/L
36 mg/L ammonia X 7.14 mg/L alkalinity to nitrify = 257 mg/L alkalinity requirements
257 mg/L is the ***minimum*** amount of alkalinity needed to nitrify 36 mg/L influent ammonia.

Once you have calculated the minimum amount of alkalinity needed to nitrify the ammonia present in the wastewater, it is then critical to compare this value against your actual measured available influent alkalinity to determine if you have enough for complete ammonia removal, and how much (if any) additional alkalinity is needed to complete the nitrification process.

Example

Influent Ammonia Alkalinity needs for nitrification = 257 mg/L

Actual Influent Alkalinity = 124 mg/L

Influent Ammonia Alkalinity needs (257 mg/L) – Influent Alkalinity (124 mg/L) = 133 mg/L alkalinity deficiency.

In other words, in this example, sufficient alkalinity is not available to completely nitrify the influent ammonia, and supplementation through denitrification and/or chemical addition will be required. Remember that this is a minimum — you still need some for acid buffering in downstream processes, like disinfection.

Alkalinity 101, or: Bio-Available Alkalinity

Most experts recommend an alkalinity residual (effluent residual) to be between 75-150 mg/L alkalinity. As previously identified, total alkalinity is measured to a pH endpoint of 4.5 standard units (su). For typical wastewater treatment applications, operational pH never goes that low. When measuring total alkalinity, the endpoint reflects how much alkalinity would be available at a pH of 4.5. At higher pH values of 7.0-7.4 su, where wastewater operations are typically conducted, not all of a total alkalinity measured to a pH of 4.5 su is available for use. This is a critical distinction for available alkalinity or the “Bio-availability” of alkalinity. Therefore, in addition to the alkalinity required for nitrification, additional alkalinity must be available to maintain the pH in the range from 7.0 to 7.4 standard units. Typically the amount of residual alkalinity required to maintain pH near a neutral point is between 70 and 80 mg/L as $CaCO_3$ (M&E).

Proper levels of alkalinity in treatment processes:

- Provides for optimum microscopic organisms whose primary function is to reduce waste. When not provided with adequate alkalinity, the ability of these microorganisms to settle is greatly impaired.
- In activated sludge, the good microorganisms are the type of floc forming organisms that have the capability, under the right conditions, to clump together and form a gelatinous floc which is heavy enough to settle. The formed floc or sludge can be then

characterized as having a SVI

- The optimum pH range for good plant operations is between 7.0-7.4. *Although growth can and does occur at pH values of 6-9, it does so at much reduced rates (See above charts). It is also quite likely that undesirable forms of organisms will form at these outside ranges and cause bulking problems.* The optimal pH for nitrification is 8.0; with nitrification limited below pH 6.0.
- Oxygen uptake is optimum a pH's between 7.0 and 7.4 and shows a reduction as pH goes outside this range. BOD removal efficiency also decreases as the pH moves outside the optimum range.

In conclusion, Alkalinity is a major chemical requirement for nitrification, and can be a useful and beneficial tool for use in process control.

References and Sources of Additional Information

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