Alkalinity 101

A Basic Non-Chemistry approach to understanding how Alkalinity can affect your plant operations
What is Alkalinity?

• 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.
Why is alkalinity important to Wastewater Operations?

• 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 \((\text{NO}_3^-)\),
  • and sulfate ions \((\text{SO}_4^{2-})\).
How Nitrification Affects Alkalinity

- 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.
Wastewater Operations Result in Loss of Alkalinity

- 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.
What Happens When a Treatment Plant Loses Alkalinity?

- 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.
- 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)
pH vs Nitrification Rates

From EPA-625/4-73-004a Revised
Nitrification and Denitrification Facilities
Wastewater Treatment
EPA Technology Transfer Seminar
The Relationship Between pH and Nitrification Rates

- 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).
Nitrification Rates are pH Dependant

<table>
<thead>
<tr>
<th>pH</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2</td>
<td>1.00</td>
</tr>
<tr>
<td>7.0</td>
<td>0.83</td>
</tr>
<tr>
<td>6.8</td>
<td>0.67</td>
</tr>
<tr>
<td>6.6</td>
<td>0.50</td>
</tr>
<tr>
<td>6.4</td>
<td>0.34</td>
</tr>
<tr>
<td>6.2</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Nitrification Activities at pH 7.2 and below
Why Residual Alkalinity?

• 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.
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.
The Importance of Steady State Operations

- 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.
Steady State vs Variable Operating Conditions
Steady State Operations = Good Flock

• If kept in a steady state, good flocculating types of microorganisms will be more numerous
Alkalinity = Steady State Operations

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.

- The theoretical reaction shows that approximately 7.14 mg of alkalinity (as CaCO₃) is consumed for every mg of ammonia oxidized. Therefore, a rule of thumb is an 8 to 1 ratio of alkalinity to ammonia.
What Happens if I Don’t Have Enough Alkalinity?

• This value may be higher for raw wastewaters with higher influent ammonia concentrations than the "normal."

• If adequate alkalinity is not present, this could result in incomplete nitrification and depressed pH values in the plant
A Reminder – pH and Alkalinity

From EPA-625/4-73-004a Revised
Nitrification and Denitrification Facilities
Wastewater Treatment
EPA Technology Transfer Seminar
How Can I Determine How Much Alkalinity I Need for my Plant?

• As a rule of thumb, 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
The Math!

• 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
Calculations for Determining Alkalinity Needs

Plant Influent Ammonia = 36 mg/L

\[36 \text{ mg/L ammonia} \times 7.14 \text{ mg/L alkalinity} = 257 \text{ mg/L alkalinity requirements}\]

257 mg/L is the \textit{minimum} amount of alkalinity needed to nitrify 36 mg/L influent ammonia.
Calculated Alkalinity vs Actual Alkalinity

• 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)

= (257-124)

= 133 mg/L alkalinity deficiency.
I Get It!!

• 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 70 – 80 mg/L as CaC03 (M&E)

• 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.
What is Bio-Available Alkalinity?

• When measuring for 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.
The Experts Speak

• 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 CaCO₃ (M&E).
A Reminder – pH and Alkalinity

From EPA-625/4-73-004a Revised
Nitrification and Denitrification Facilities
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Why Do I Need Alkalinity, and the Treatment Plant Down the Road Doesn’t

Ok, You’ve done the math. Your calculations show that your plant needs alkalinity. Some of the questions you might have include:

• What makes my plant different? Why do I need alkalinity?
  – The answer can be related to sources of drinking water (ground versus surface)
  – Seasonal changes to water including rainfall and potential for I/I
Now What Do I Do?

If you have determined that you need alkalinity, then your next step is to identify which source of alkalinity supplementation that is best for your facility, and the rate of application that you will need to achieve adequate alkalinity residual.
## Summary of Neutralization Reagent Operating Issues

*Source: Charles River Associates, 1993*

<table>
<thead>
<tr>
<th>SAFETY</th>
<th>LIME</th>
<th>CAUSTIC SODA</th>
<th>SODA ASH</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PH and Dissolved Solids Effluent</strong></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Primary compound (or derivatives) in “Milk of Magnesia”, antacids, foodstuffs, etc.</td>
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<tr>
<td></td>
<td>Hazardous to handle. Contact with eyes can cause permanent loss of vision. Repeated and prolonged contact with skin may cause severe irritation, mild burns and, in extreme cases, systemic injuries due to absorption. Breathing dust or mist may cause intolerable discomfort to nose and throat.</td>
<td>Extremely hazardous to handle. Contact with eyes can cause permanent loss of vision. Contact with skin may cause severe burns. Breathing vapor may cause damage to the upper respiratory tract and the lungs.</td>
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<tr>
<td></td>
<td>Limestone (CaCO₃) is a naturally occurring mineral that poses no threat to the environment. Lime (CaO) and hydrated lime (Ca(OH)₂), however, are highly caustic and can cause immediate damage to the environment.</td>
<td>Because caustic soda is highly corrosive, it can cause severe physical injury to plant and animal life if it escapes.</td>
<td></td>
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<tr>
<td></td>
<td>Supplied as a ready-to-use slurry or powder. Requires no special equipment except possibly an agitator in the slurry storage tank to prevent settling. Low temperatures create no special problems, because the slurry freezes at the same temperature as the water being treated, i.e. 32°F.</td>
<td>Requires elaborate safety equipment and rigorous, time-consuming safety procedures. Workers must be trained in safety and wear special clothing and goggles.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Less than for caustic soda, lime, and soda ash, even with an agitator to prevent slurry settling in storage. May be used in powdered form (MgO, Mg(OH)₂) with minor modifications to installed feed systems.</td>
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<tr>
<td></td>
<td>With heavy metals and sulfuric acid, lime creates large quantities of calcium sulfate dehydrate, a sludge that settles very slowly and is difficult to filter and dewater.</td>
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<td></td>
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<tr>
<td></td>
<td>With a wide range of acids and metals, creates a sludge that is more fast-settling and easily filtered and dewatered. Sludge less, sludge cost.</td>
<td>If effluent contains heavy metals, creates large quantities of gel-like, slow settling sludge that is difficult to filter and dewater.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Equipment costs higher than for magnesium hydroxide. Equipment maintenance is also higher because lime is abrasive.</td>
<td>Greater than for magnesium hydroxide because of need for heated system and safety equipment. Corrosive.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Magnesium hydroxide</td>
<td></td>
<td></td>
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<td></td>
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</tbody>
</table>
The addition of treatment chemicals, especially lime, may increase the volume of waste sludge up to 50 percent.
NEUTRALIZATION OF SULFURIC ACID (H₂SO₄)

For one mole (98 lbs) of 100% (H₂SO₄ – Sulfuric Acid) to be neutralized, the following chemical reactions occur:

**Magnesium Hydroxide**

\[
\text{Mg(OH)₂ + H₂SO₄} \rightarrow \text{MgSO₄ + 2H₂O}
\]

\[
\text{58.3 lbs} \quad \text{(58.3 lbs)} \quad \text{120.3 lbs} \quad \text{(36 lbs)}
\]

**Hydrated Lime**

\[
\text{Ca(OH)₂ + H₂SO₄} \rightarrow \text{CaSO₄-2H₂O}
\]

\[
\text{74 lbs} \quad \text{(74 lbs)} \quad \text{172 lbs}
\]

**Caustic Soda**

\[
2\text{NaOH + H₂SO₄} \rightarrow \text{Na₂SO₄ + 2H₂O}
\]

\[
\text{80 lbs} \quad \text{(80 lbs)} \quad \text{142 lbs} \quad \text{(36 lbs)}
\]

**Soda Ash**

\[
\text{Na₂CO₃ + H₂SO₄} \rightarrow \text{Na₂SO₄ + CO₂ + H₂O}
\]

\[
\text{106 lbs} \quad \text{(106 lbs)} \quad \text{142 lbs} \quad \text{(44 lbs)} \quad \text{(18 lbs)}
\]

**Caustic Potash**

\[
2\text{KOH + H₂SO₄} \rightarrow \text{K₂SO₄ + 2H₂O}
\]

\[
\text{112 lbs} \quad \text{(112 lbs)} \quad \text{174 lbs} \quad \text{(36 lbs)}
\]

These equations can be used to calculate the amount of alkali needed to neutralize one ton of sulfuric acid and the resultant amount of salt formed:

<table>
<thead>
<tr>
<th>Neutralizing Agent</th>
<th>Lbs Required To Neutralize 1 Ton H₂SO₄</th>
<th>Ratio To Mg(OH)₂</th>
<th>Total Dissolved Solids In Effluent (100% Basis) Per Ton of Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium Hydroxide</td>
<td>Mg(OH)₂</td>
<td>1190</td>
<td>1.00</td>
</tr>
<tr>
<td>Hydrated Lime</td>
<td>Ca(OH)₂</td>
<td>1510</td>
<td>1.27</td>
</tr>
<tr>
<td>Caustic Soda</td>
<td>NaOH</td>
<td>1630</td>
<td>1.37</td>
</tr>
<tr>
<td>Soda Ash</td>
<td>Na₂CO₃</td>
<td>2160</td>
<td>1.82</td>
</tr>
<tr>
<td>Caustic Potash</td>
<td>KOH</td>
<td>2290</td>
<td>1.92</td>
</tr>
</tbody>
</table>

**The CaSO₄-2H₂O will precipitate as a sludge.**
Sources of Alkalinity and lbs/Alkalinity per Gallon

Lbs. Alkalinity per Gallon

- Mg(OH)\textsubscript{2} 60%
- NaOH 50%
- Ca(OH)\textsubscript{2} 30%

Lbs Alkalinity / Gallon

- 13.38 lbs
- 7.43 lbs
- 3.6 lbs
How to Evaluate the Data

When reviewing the lbs/alkalinity per gallon in the previous chart, each of the products identified have specific chemical properties which determine the amount of alkalinity present.

It is important to be aware that these estimates are based on specific concentrations of product, and that different concentrations provide different volumes of alkalinity.
What you need to know

To evaluate the best option for your facility, it is important to determine the following facts:

– How much alkalinity is present in each product under consideration (lbs alkalinity per gallon)
– Rate of application
– Cost/Budget
## How Much Alkalinity Do I Need per MGD?

<table>
<thead>
<tr>
<th>Plant Influent Alkalinity mg/L</th>
<th>Plant Influent NH3-N in mg/L</th>
<th>What is the Calculated Amount of Alkalinity needed for nitrification in mg/L?</th>
<th>What is amount of available Alkalinity in mg/L?</th>
<th>Is there sufficient alkalinity present to nitrify?</th>
<th>If not, how much additional alkalinity is needed to nitrify?</th>
<th>If yes, is there sufficient alkalinity to provide an effluent residual of 80 mg/L?</th>
<th>How much additional alkalinity (if any) is needed to achieve 80 mg/L effluent residual?</th>
</tr>
</thead>
<tbody>
<tr>
<td>212</td>
<td>33</td>
<td>235.6</td>
<td>212</td>
<td>no</td>
<td>23.6</td>
<td>no</td>
<td>104</td>
</tr>
</tbody>
</table>
If the plant needs an additional 104 mg/L of alkalinity per MGD per day, we then calculate the different options in this manner:

<table>
<thead>
<tr>
<th>Product</th>
<th>Alkalinity Deficiency mg/L</th>
<th>Pounds of Alkalinity per Gallon of Product</th>
<th>Calculated GPD of Product per MGD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lime Slurry</td>
<td>104</td>
<td>3.6</td>
<td>241</td>
</tr>
<tr>
<td>Caustic Soda</td>
<td>104</td>
<td>7.43</td>
<td>117</td>
</tr>
<tr>
<td>Magnesium Hydroxide</td>
<td>104</td>
<td>13.38</td>
<td>65</td>
</tr>
</tbody>
</table>
Once you know what your alkalinity needs are, you can then calculate your costs per gallon or ton based on quotes you receive from a supplier.
Product Quality is Critical

• It is important to recognize that there are superior and inferior sources of product on the market.

• It is critical for you to be knowledgeable about your product and specify products that meet stringent industry standards.

• You should maintain a strict quality control check on any product you receive
With Proper Alkalinity.....

• A treatment plant experiences 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.
Additional Benefits of Good Alkalinity

• 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
Alkalinity = Capacity

• 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.
Optimum Oxygen Uptake

• Oxygen uptake is optimum at 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.
Denitrification Can Add Alkalinity

- 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. On an average, you should expect approximately 4.2 mg/L.
Conclusion

• 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

2. USEPA Advanced Waste Treatment, A Field Study Training Program, California State University Department of Civil Engineering and the California Water Pollution Control Association, 1989
3. USEPA Process Control Manual for Aerobic Biological Wastewater Treatment Facilities, March 1977
5. USEPA Nitrification and Denitrification Facilities, Wastewater Treatment, EPA Technology Transfer Seminar Publication EPA-625/4-73-004a Revised
7. USEPA Manual of Nitrogen Control, Office of Research and Development Center for Environmental Research Information Risk Reduction Engineering Laboratory, Cincinnati, OH, September 1993 EPA/625/R-93/010