(Ca(OH)2)   (NaOH)   (Mg(OH)2)

Relationship of Alkalinity and pH:

Origin of Alkalinity, Role of Carbon Dioxide, and Relationship to Alkaline Additives

pH

THE MASTER VARIALBLE

CORROSION OF PIPES
EFFECTIVENESS OF DISINFECTION
RATES OF BIOLOGICAL ACTIVITY

Relationship of Alkalinity and pH: Origin of Alkalinity, Role of Carbon Dioxide, and Relationship to Alkaline Additives

Alkalinity and pH are important measurable parameters in water and wastewater.

Technically, pH is defined as: $\quad$ **pH = -log$_{10}$[H$^+$]** $\;$ where, $\;$ [H$^+$] is in moles/L, M

pH is considered by many to be the "Master Variable" in the environment, and, as such, in water the pH controls the solubility of toxic metals, influences the corrosion rates of metal and cementitious pipes, the effectiveness of disinfection, and the controls the rates of biological reactions, such as Nitrification in aerated bio-processes. In dilute water systems the pH can vary from values of 0 to 14:

Acidic $\qquad$ Neutral $\qquad$ Basic or Alkaline

acid rain

5.6

0.0 $\qquad$ 4.0 $\qquad$ 6.0 $\quad$ 7.0 $\qquad$ 9.0 $\qquad\qquad$ 14
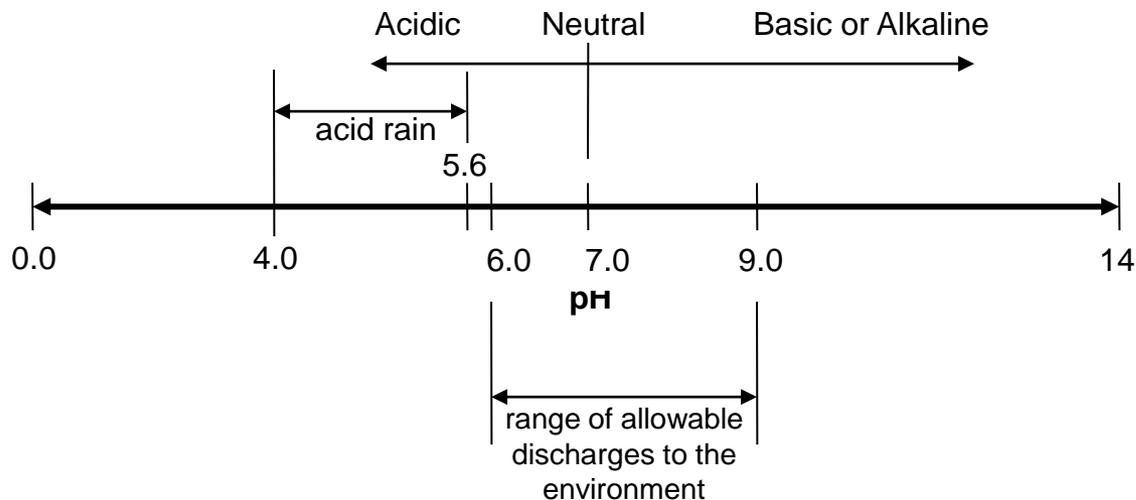
pH

range of allowable discharges to the environment

Figure 1. pH scale in water under dilute conditions at 25°C. Items of environmental significance include the definition of acid rain (pH < 5.6) and the federal regulatory limit on discharges to the environment (6.0 to 9.0).

pH Measurement. The pH can be measured using several techniques, which include pH indicating paper and electrochemical probes. Using either technique, the measurement is fairly quick (minutes), accurate (±0.5 units for pH indicator paper and ±0.2 units for probes), and reproducible.

One of the oldest, simplest and most portable techniques to determine a water's pH is the use of pH indicating paper. This consists of a set of pH indicating chemicals (change colors in different pH ranges) embedded onto an inert background (paper). The most common type has three sets of indicators that change color according to the pH of the water. The three indicator's blended colors are then matched visually to a color chart and the pH is determined to the nearest pH (±0.5 units)or:

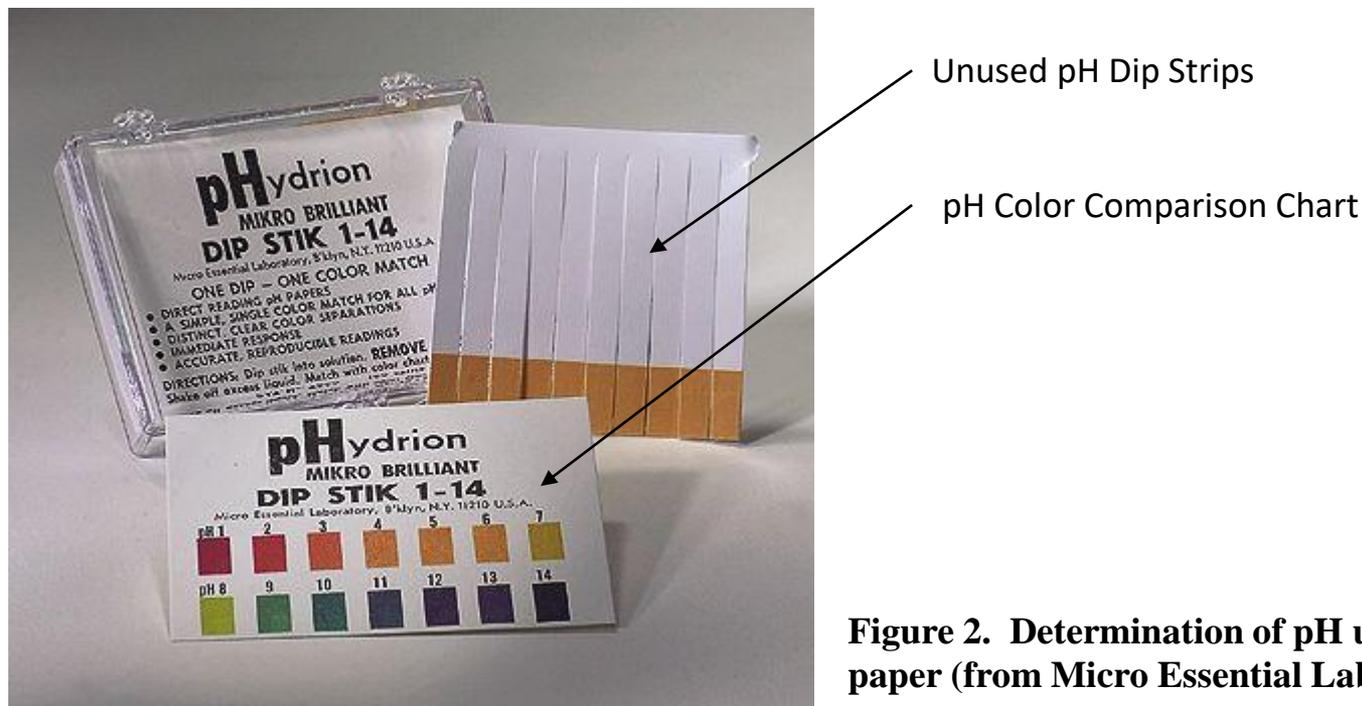Unused pH Dip Strips

pH Color Comparison Chart

Figure 2. Determination of pH using universal pH indicator paper (from Micro Essential Laboratory, Inc.).

More modern techniques of pH measurement involve the use of a specific ion probe (proprietary glass) to determine the H^+ concentration. The probe response (millivolts) is standardized against two standard pH buffer solutions (pH 7.0 and either 4.0 or 10.0) on a daily basis. A probe may be used to take spot measurements (in the field) or immersed at a continuous sampling point to monitor a system in real time.

Figure 3. Simple portable hand-held pH meter with combination glass electrode and standard pH buffers for calibration (red = pH 4.00, green = 7.00, blue = 10.00, all ± 0.02 units at 25ºC)

Note, for samples measured in the lab (batch bottle or beaker) care should be taken to minimize the entrainment of air (stirred so that no vortex forms). This prevents errors and unstable readings due to exchange of CO_2 with the samples.

ALKALINITY

Buffering Capacity

THE SUM OF CARBONATE, CO_3^{-2}, AND BICARBONATE, HCO_3^-, ALKALINTY CONTRIBUTIONS IS NEVER LOST
TOTAL CARBONATE CARBON IS NEVER LOST, C_T
pH $\neq$ ALKALINITY
COVERED SYSTEMS $\neq$ OPEN SYSTEMS

Alkalinity = ability to resist pH change due to acid (H⁺) addition, or, "Buffer Capacity"

Alkalinity is an easy to measure parameter that can be found by a simple titration (generally with 0.16N Sulfuric Acid, H_2SO_4). This can be performed manually, or using a variety of proprietary techniques that automate the process.
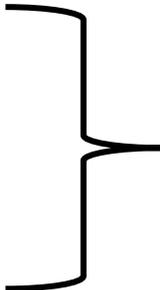
Alkalinity is comprised of all weak acids in water that can consume (react) with H⁺ in the pH range of 4.5 to 12.1 and thus inhibit the decrease in pH associated with acid addition (compared to water). Typical weak acids of importance (those that create Alkalinity) include:

Carbonates: HCO_3^- and CO_3^{-2}
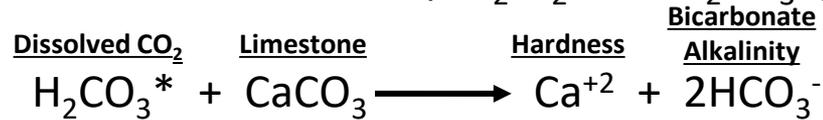
Phosphates: HPO_4^{-2} and PO_4^{-3}

Silicates: $SiO(OH)_3^-$

Borates: $B(OH)_4^-$

While present in water and wastewater, these are typically minor components (< 10% of total) and ignored in Alkalinity calculations/estimates

Alkalinity and pH are related to the fact that Alkalinity arises from Calcium Carbonate and the reaction with dissolved Carbon Dioxide ($CO_2 \cdot H_2O$, or $H_2CO_3^*$), or:

<div align="center">

Dissolved CO_2   **Limestone**   **Hardness**   **Bicarbonate Alkalinity**

$$H_2CO_3^* \ + \ CaCO_3 \longrightarrow \ Ca^{+2} \ + \ 2HCO_3^-$$

</div>

Therefore, Alkalinity is generally expressed as **mg/L $CaCO_3$**.

Consider: Alkalinity = 100 mg/L as $CaCO_3$, and, pH = 7.5

Then, all of the Alkalinity is Bicarbonate, HCO_3^-, by definition **(all Alkalinity is Bicarbonate Alkalinity at pH < 8.3).**

100 mg/L in this example

Example #1: HCO_3^- = Alkalinity as mg/L $CaCO_3$ x (61/100) = **61 mg/L**[a]

and, Alkalinity can be expressed in more technical units (milliequivalents per Liter, meq/L):

      where,   Alkalinity = 100 mg/L/50 = **2.0 meq/L**[a]

a: Note, 61 is the molecular weight of Bicarbonate, and 100 is the molecular weight of $CaCO_3$, and, 50 = equivalent weight of $CaCO_3$

Alkalinity-pH Relationships

Assuming that the carbonates control the relationship between pH and Alkalinity in most wastewaters (this will generally be true unless ortho-phosphates are > 6 mg/L, as P), then, Alkalinity and total carbonate carbon, C_T, are conserved and determine the pH of water, or:

1. Alkalinity and pH are known characteristics of the initial water and determined by direct measurement.
2. C_T is known from the complex equilibrium relationship between Alkalinity, pH, and C_T, or (C_T H^+, and OH^- expressed as millimolar, mM):

$$C_T = H_2CO_3^* + HCO_3^- + CO_3^{-2} \quad \text{(sum of all carbonates)} \qquad [1]$$

and,   Alkalinity, meq/L $= HCO_3^- + 2CO_3^{-2} + OH^- - H^+ = C_T(\alpha_1 + 2\alpha_2) + OH^- - H^+$ [2]

where, $\alpha_1, \alpha_2, OH^-, H^+$ are all defined by the pH, or (in units of mM):

$$H^+ = 1000 \times 10^{-pH} \text{ and, } OH^- = 1000 \times 10^{-(14-pH)} \qquad [3]$$

and, $\alpha_1 = HCO_3^-/C_T = K_{a1}[H^+]/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2})$ [4]

$$\alpha_2 = CO_3^{-2}/C_T = K_{a1}K_{a2}/([H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}) \qquad [5]$$

where, $K_{a1} = 5.01 \times 10^{-7}$ and $K_{a2} = 5.01 \times 10^{-11}$

3. Alkalinity and C_T are conserved meaning **they do not change without the addition of Alkaline components** (such as acids or bases) or carbonates (such as Na_2CO_3 or $NaHCO_3$)

Common Alkaline Agents

To manipulate the Alkalinity (and thus the pH) of water and wastewater, common Alkaline agents, such as NaOH (Caustic), CaO or $Ca(OH)_2$ (Lime), or MgO or $Mg(OH)_2$ (Thioguard) can be added.   Generally, a limited amount of Alkalinity can be provided on a per gallon basis (based on composition of the product supplied), or, based on manufacturers data:

Alkaline Agent	lb Alkalinity/gallon (as $CaCO_3$)
Thioguard ($Mg(OH)_2$)	13.4
50% NaOH	7.43
40% $Ca(OH)_2$	3.6

Example #2:   Add 20 gallons Thioguard per MGD of wastewater

$$\text{Alkalinity Added} = \frac{20 \text{ gallons x } 13.4 \text{ lb Alkalinity/gallon/MGD}}{8.34^a} = \textbf{32.1 mg/L, as } \textbf{CaCO}_3$$

a: Note, 8.34 is a conversion factor from mg/L/MGD to lb/day, or, mg/L x MGD x 8.34 = lb/day

Open vs Closed Systems

In most water and wastewater systems the pH and Alkalinity are controlled by the dissolved CO_2 (HCO_3^- and CO_3^{-2}) in the aqueous system. Since CO_2 is an atmospheric gas, the system can be divided into 2 cases:

1. Open – System is free to exchange CO_2 with the atmosphere (in equilibrium Dissolved CO_2, i.e., H_2CO_3* is constant at about 1.39×10^{-5} M).

2. Closed – System does not exchange CO_2 with the overlying atmosphere and so CO_2, is independent of the equilibrium with air, and therefore total carbon, $C_T = H_2CO_3$* $+ HCO_3^- + CO_3^{-2}$.
This simplifies the system, and then Alkalinity and C_T are conserved and any two of pH, Alkalinity, and C_T define the third parameter.
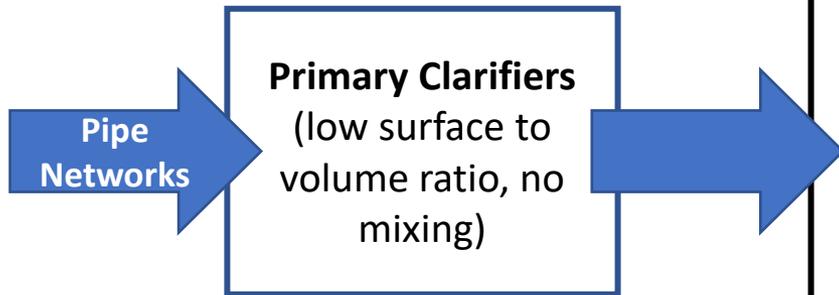
For purposes of estimating the Alkalinity requirement to achieve a desired pH from an set of initial conditions, the closed system most closely represents the real world, and the relationship between pH and Alkalinity is well understood[1]. These systems (Closed) are easily predicted. However, some wastewater systems (such as aeration basins) are highly aerated, and, CO_2 may be produced from organic degradation making the system unknown (Open, but not in equilibrium with the atmosphere). These systems (Open, but not in equilibrium) are not well understood, and accurate predictions are difficult.

[1.] Stumm, W., and J.J. Morgan, 1993, *Aquatic Chemistry*, 3rd edition, Wiley and Sons, Inc., New York.

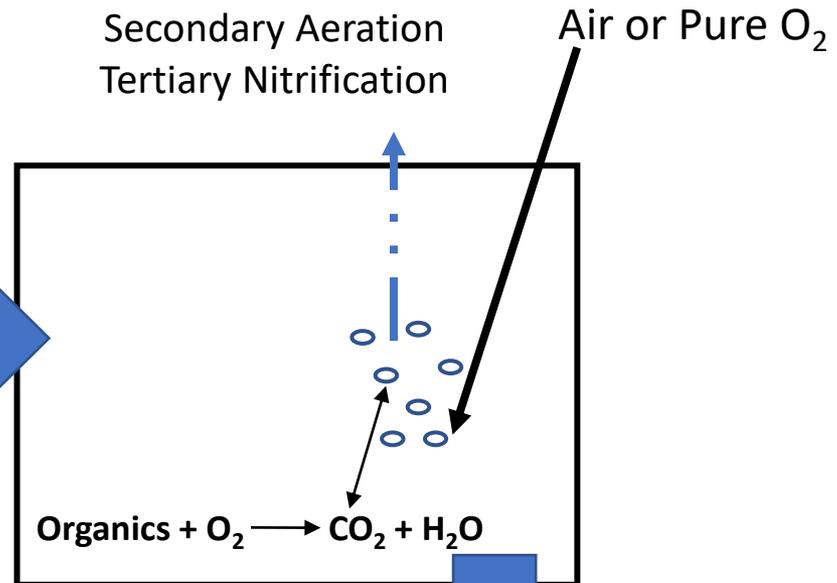# Examples of Open and Closed Systems in Water and Wastewater

Closed Systems (approximate)

Flow in Closed Conduits
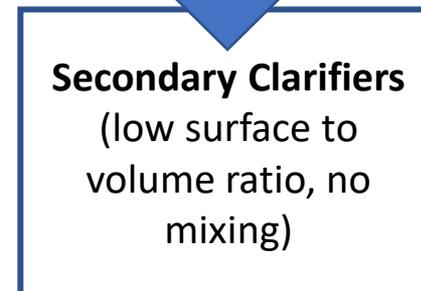Unaerated Tanks
Sewer Pipes

Open Systems (not in equilibrium)

Secondary Aeration
Tertiary Nitrification

Air or Pure O_2

Pipe Networks

Primary Clarifiers (low surface to volume ratio, no mixing)

Organics + O_2 $\longrightarrow$ CO_2 + H_2O

Closed System (approximate)

Secondary Clarifiers (low surface to volume ratio, no mixing)

ALKALINITY AND THE BIOLOGICAL SYSTEM

Closed System

Now, for example, **with the addition of an Alkaline agent, such as Thioguard, Mg(OH)$_2$,** for each unit of Alkalinity added (Alk, meq/L = Alk, mg/L as CaCO$_3$/50), then the **Alkalinity is increased by the amount added (see example 2)**, and **C$_T$ is unchanged** (no significant carbonates present in NaOH, Ca(OH)$_2$ or Mg(OH)$_2$). We can find the new pH by solving for C$_T$ in the initial known wastewater (calculated) and then we know the final Alkalinity (initial + added) and final C$_T$ (unchanged = initial calculated C$_T$). Considering a Practical Field Case:

Example 3: Add 20 mg/L Alkalinity to the given system, pH = 6.8, Alkalinity = 200 mg/L.

Initial Wastewater	**20 mg/L Alkalinity Added**
Alkalinity = 200 mg/L	Final Alkalinity = 200 + 20 = 220 mg/L
pH = 6.80	pH > 6.80 (to be calculated)
Alk$_o$ = 200 mg/L/50 = 4.0 meq/L	**Alk$_f$ = 220/50 = 4.4 meq/L**

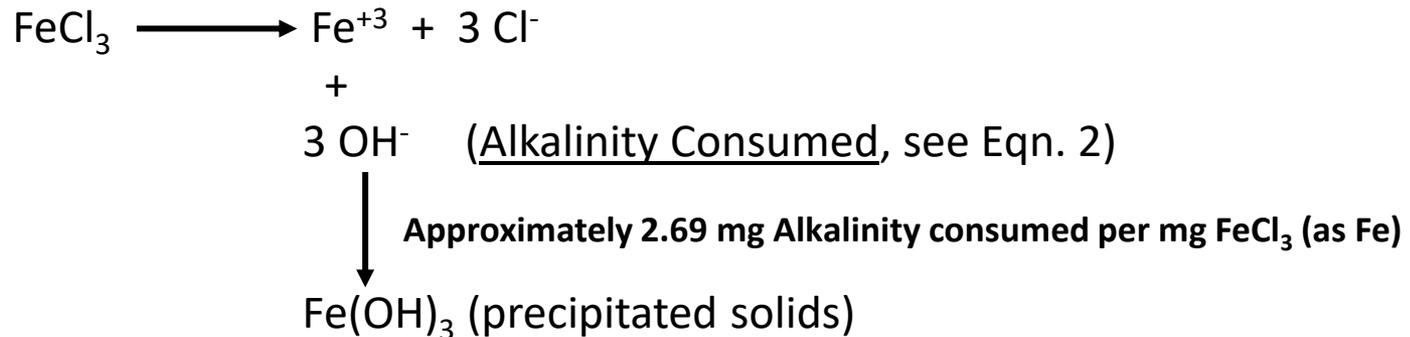C$_T$ is Calculated from the initial Alkalinity (equations 1, 2, 3, 4, and 5) and pH, or **C$_T$ = 5.26 mM**

Now, the new pH can be calculated by solving for the pH so that C$_T$ = 5.26 mM now yields the final Alkalinity of 4.4 meq/L, or **final pH = 7.006** (solving equations 2, 3, 4, and 5) , compared to 6.80 initially.   Also, since the original measurements (Alkalinity and pH) are not exact, we would round the Alkalinity and C$_T$ (as meq/L and mM, respectively) to the nearest hundredth and the final pH would be rounded to 7.01.

Note: Alkalinity added increases the Alkalinity, C$_T$ doesn't change, and pH is increased

Alkalinity consumption due to chemical addition and Biological Processes

Alkalinity is influenced by chemical addition and by Bio-Processes that can result in a pH change that is undesirable and requires <u>Alkalinity addition</u>:

1. Addition of coagulating/precipitating agents, such as $FeCl_3$ or $Al_2(SO_4)_3$:

$$FeCl_3 \longrightarrow Fe^{+3} + 3\ Cl^-$$
$$+$$
$$3\ OH^- \quad (\underline{Alkalinity\ Consumed},\ see\ Eqn.\ 2)$$

Approximately 2.69 mg Alkalinity consumed per mg $FeCl_3$ (as Fe)

$$Fe(OH)_3 \text{ (precipitated solids)}$$

2. Biological Processes, such as Nitrification can produce acids:

$$NH_4^+ + 2\ O_2 \longrightarrow NO_3^- + H^+ \text{ (unbalanced)}$$

<u>Nitrification consumes 7.12 mg Alkalinity (as $CaCO_3$) per mg Ammonia (as N)</u>

3. In addition, where CO_2 is produced (BOD + $O_2 \longrightarrow CO_2 + H_2O$), acidity can be increased, and pH can go down (note: CO_2 does not change Alkalinity but increases C_T and pH decreases). This is difficult to quantify because it takes place in an aeration basin that is an open system (not in equilibrium with air)

Example 4: Consider a wastewater contains 20 mg/L Ammonia, as N. How much Alkalinity is consumed and needs to be replaced to maintain the pH (also note, that the optimal pH for Nitrification is about 7.8). Consider that about 90% of the Ammonia will be converted to Nitrate:

Alkalinity Consumed, mg/L = 20 mg/L x 0.9 x 7.12 mg/mg = **128 mg/L (as CaCO$_3$)**

Example 5. How much 50% NaOH would be required to maintain the original Alkalinity (on a MGD basis):

NaOH Required (gallons as 50% NaOH) = 128 mg/L x 8.34 x 1 MGD/7.43 lb Alk/gal
= **144 gallons/day of 50% NaOH per MGD**
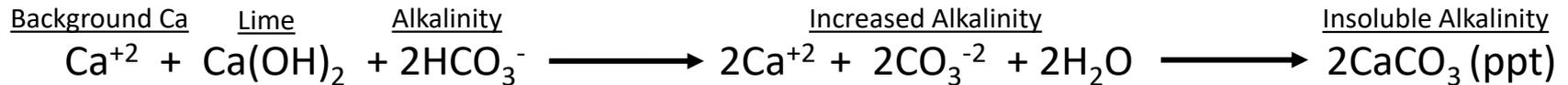
CONSIDER THE SOURCE

DOWNSTREAM EFFECTS
SYSTEM WIDE COSTS
UNIT PRICE VS UNINTENDED COST

Lime Considerations

Lime, CaO or Ca(OH)$_2$, is a special consideration due to the circumstances surrounding CaCO$_3$ precipitation (lime is used to remove harness, Ca^{+2}, in water softening processes). When lime is added to water containing Calcium (temporary hardness) or if added to water that contains no Calcium, the combination of Ca^{+2} from lime, and the elevated pH results in CaCO$_3$ that builds up as nuisance scale and/or additional solids that ends up as additional sludge to process and dispose, or (with Ca present initially):

$$\underset{\text{Background Ca}}{Ca^{+2}} + \underset{\text{Lime}}{Ca(OH)_2} + \underset{\text{Alkalinity}}{2HCO_3^-} \longrightarrow \underset{\text{Increased Alkalinity}}{2Ca^{+2} + 2CO_3^{-2} + 2H_2O} \longrightarrow \underset{\text{Insoluble Alkalinity}}{2CaCO_3 \, (ppt)}$$

In this case, the end result is that Alkalinity added is precipitated out and not available in water to elevate the pH, i.e., the Alkalinity added is lost and not available. Simultaneously, Lime has created nuisance solids that require maintenance and/or additional disposal costs. This reaction is not quantitative and will not result in the loss of all the Alkalinity as show here. However, depending on the initial Calcium in the water, and the final pH desired, many times, 2 to 4 x (or more) the equivalent amount of lime may be required to replace Alkalinity as would be required using NaOH or Mg(OH)$_2$ for Alkalinity addition.

When Using Lime, all of the Costs must be considered, one cannot compare the true costs of Lime addition without considering the loss of Alkalinity in the system.

Example 6: Consider a wastewater with a pH of 6.8 and Alkalinity = 200 mg/L (as $CaCO_3$), and, there is no initial Calcium (Ca = 0). How much Alkalinity must be added to raise the pH to 8.0 using Lime compared to NaOH or $Mg(OH)_2$?
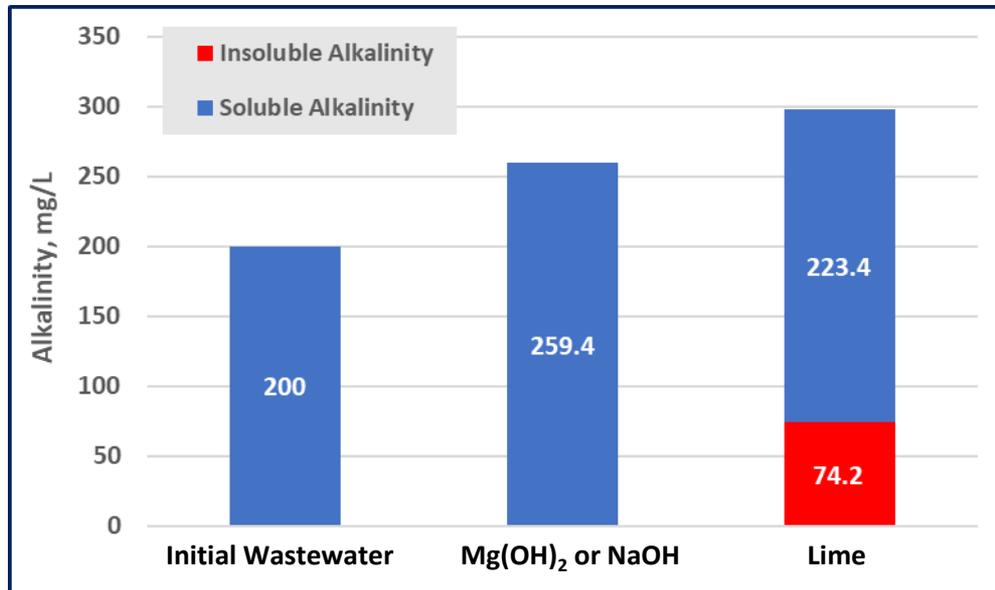
1. Lime:
- 97.6 mg/L Alkalinity Required
- $CaCO_3$ precipitation begins at pH 7.59
- 1.64 x as much Lime required
- 619 lb excess solids produced /MGD

2. NaOH or $Mg(OH)_2$:
- 59.4 mg/L Alkalinity Required
- No Excess Solids Produced

Note, with Ca in background water, more $CaCO_3$ would precipitate.

Note, All calculations (theoretical estimates) performed using the equations for Alkalinity and C_T as a function of pH, assuming a solubility product of 5.01 x 10^{-9} for $CaCO_3$, and using mass balances on C_T, and Ca including soluble and insoluble fractions as $CaCO_3$.

KEY TAKEAWAYS

USE CAUTION ADDING CHEMISTRY

ADDITIVES CAN CONSUME ALKALINITY
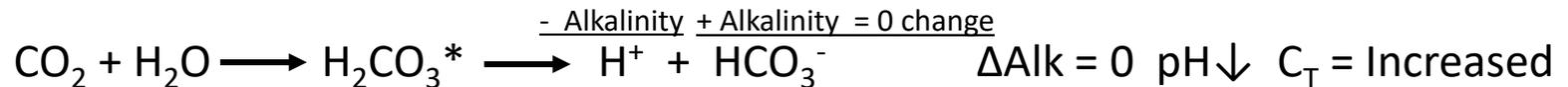LIME CAN DROP OUT ALKALINITY
CO_2 CAN REDUCE pH

Alkalinity, C_T, and pH are entwined in a complex set of equilibrium equations. However, qualitatively, there are some points that are easily understood based on the definition of Alkalinity, or:

$$Alkalinity = HCO_3^- + 2CO_3^{-2} + OH^- - H^+$$

1. Acids such as HCl, H_2SO_4, acetic acid, etc. reduced Alkalinity and decrease pH ,or:

$$HCl \xrightarrow{\text{Negative Alkalinity}} H^+ + Cl^- \qquad Alk\downarrow \ pH\downarrow \ C_T = Unchanged$$

2. Biodegradation produces CO_2 that does not change Alkalinity but increases C_T and reduces pH:

$$CO_2 + H_2O \longrightarrow H_2CO_3^* \xrightarrow{\text{- Alkalinity + Alkalinity = 0 change}} H^+ + HCO_3^- \qquad \Delta Alk = 0 \ pH\downarrow \ C_T = Increased$$

3. Many Coagulants, such as $FeCl_3$ or $Al_2(SO_4)_3$ decrease Alkalinity and Result in a lower pH that requires the addition of supplemental Alkalinity:

$$FeCl_3 + 3H_2O \xrightarrow{\text{Negative Alkalinity}} Fe(OH)_3 + 3H^+ \qquad Alk\downarrow \ pH\downarrow \ C_T = Unchanged$$
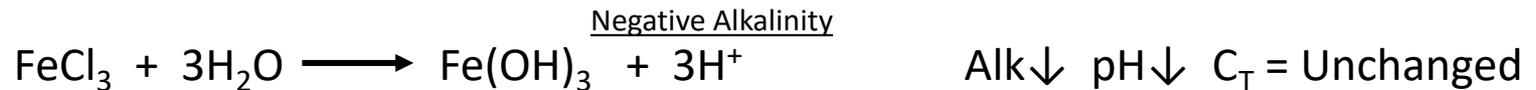
4. Alkaline Additives must be chosen based on the total cost, including side reactions that consume Alkalinity and/or **create nuisance solids, such as $CaCO_3$ from Lime**