

# Alkalinity Addition Utilizing Carbon Dioxide & Lime: Inexpensive Solution to a Historically Expensive Problem

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Recent research in the drinking water field has re-emphasized the importance of alkalinity in maintaining a stable finished water quality that minimizes corrosion. With the focus on disinfection byproduct precursor removal, the expense of producing a stabilized finished water quality can be difficult to achieve cost-effectively. Low alkalinity waters are particularly challenging because minimal chemical addition of “alkalinity adders” (lime, soda ash) can quickly increase the finished water pH without providing a significant increase in alkalinity; or produce excessively high pHs, which contribute to the formation of THMs; or result in depositing finished waters.

## Defining Alkalinity

Alkalinity is defined as the capacity of water to neutralize acid. The most prevalent form of alkalinity in drinking water systems includes portions of the carbonate system, which consists of the following three species:

- ◆ Carbonic acid ( $H_2CO_3$ )
- ◆ Bicarbonate ion ( $HCO_3^-$ )
- ◆ Carbonate ion ( $CO_3^{2-}$ )

Of these three species, the bicarbonate and the carbonate ions both contribute to the ability of a solution to neutralize acid. When acid is added to a system with bicarbonate or carbonate ion, the solution resists pH change by converting the carbonate to bicarbonate or the bicarbonate to carbonic acid (by protonating each species). It is these conversions that give the water its ability resist pH change.

The total amount of carbonate (including all species of carbonate) in a system does not change (unless a carbonate adding chemical is utilized). The ratio of carbonate species determines the pH of a solution. The higher the amount of total carbonate in a system, the more acid or base is required to change the pH an incremental amount (higher buffering capacity). The more the percentage of the total carbonate shifts to the carbonate ion, the higher the pH.

Based on this discussion, keeping all of the carbonate species shifted to the carbonate ion may seem like a good idea because it also keeps the water as far as possible from acidic conditions, minimizing corrosion problems, which are accelerated under acidic conditions. This approach is typically incorrect because of the potential precipitation of cal-

cium carbonate. Shifting all of the carbonate species to the carbonate ion causes the precipitation of calcium carbonate, which can cause the following problems:

- ◆ Elevated turbidities due to precipitation
- ◆ Reduction of pipe diameter due to the deposition of calcium carbonate
- ◆ Alkalinity reduction due to the precipitation of carbonate

## Alkalinity Effects

To further demonstrate the alkalinity effect on pH adjustment with acid, Table 1 shows the amount of acid required to decrease the pH of water from 8 to 7.

Low alkalinity situations can occur in raw waters across the United States. One area that is not often recognized is the low alkalinity in finished waters that results from softening of alkalinity-limited waters or from permeate of nanofiltration or reverse osmosis membranes.

## Problems Caused by Low Alkalinity

There have been a number of problems that have been attributed to low alkalinity in the distribution system and at water treatment plant facilities. The following lists the potential problems caused by low alkalinity:

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- ◆ Red Water
- ◆ Corrosion
- ◆ Nitrification
- ◆ Pitting and erosion of basins

As discussed in the September 2005 AWWA *Journal* article (Imran, 2005) entitled “Red Water Release in Drinking Water Distribution Systems,” alkalinity was determined to be the only significant variable that can be controlled effectively by chemical addition that reduced the occurrence of red water. This article recommended that an alkalinity of greater than 80 milligrams per liter as  $CaCO_3$  be targeted.

The reasoning behind alkalinity’s inhibition of red water releases is that poorly buffered waters will cause low localized pH because of acid-producing biofilms such as

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Table 1: Effect of Alkalinity on the Acid Requirements to Decrease the pH from 8 to 7.

| Alkalinity of the water (mg/L as $CaCO_3$ ) | Amount of acid required to lower the pH from 8 to 7 (mg/L of HCl) |
|---|---|
| 20  | 2.3   |
| 50  | 6.0   |
| 80  | 9.3   |
| 100   | 12.0  |
| 200   | 23.0  |
| 300   | 35.0  |

Table 2: Alkalinity Consumption for Common Water Treatment Plant Chemicals

| Chemical         | Alkalinity Consumed (mg/L as $CaCO_3$ per mg/L of chemical) |
|------------------|---|
| Ferric Chloride  | 0.93  |
| Ferric Sulfate   | 0.53  |
| Aluminum Sulfate | 0.51  |
| Chlorine         | 1.41  |
| Fluoride         | 2.08  |
| Carbon Dioxide   | 0   |

Table 3: Alkalinity Added by Common Water Treatment Plant Chemicals

| Chemical                        | Alkalinity Added (mg/L as CaCO <sub>3</sub> per mg/L of chemical) |
|---------------------------------|---|
| Caustic Soda (Sodium Hydroxide) | 1.25  |
| Lime                            | 1.35  |
| Soda Ash                        | 0.94  |
| Sodium Bicarbonate              | 0.6   |
| Sodium Hypochlorite             | 0.67  |

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nitrifiers. The resulting corrosion may form pitting and tubercles that result in increases in surface area for biofilm to perpetuate. Also, the rate of nitrification increases at lower pH.

### How Does Alkalinity Change?

The alkalinity in water changes through a treatment process based on the consumptive nature of the treatment chemicals that are utilized. Table 2 shows common water treatment plant chemicals and their corresponding alkalinity consumption.

It should be noted that carbon dioxide does not decrease the alkalinity. It adds more carbonic acid to the system, which in turn lowers the pH because of the shifting of carbonate species ratios. The addition of carbon dioxide increases the overall carbonate in the system. This increase in the overall carbonate can assist in the overall increase in alkalinity if a shift in the species occurs (towards carbonate ion).

### What Are the Options for Alkalinity Addition?

The alkalinity of a utility's water can be increased by a variety of chemicals that are common to water treatment plants. Table 3 shows common water treatment plant chemicals and how much alkalinity they contribute.

The single most important factor to realize is that sodium hydroxide and lime shift the species but they do not increase the overall carbonate in the system. The addition of sodium bicarbonate and soda ash will both shift the carbonate species and contribute to the overall carbonate in the system. These

two chemicals accomplish both goals, which are desirable when adding alkalinity (especially when the initial alkalinity is very low).

The problem with soda ash is that it adds alkalinity in the form of carbonate ion (CO<sub>3</sub><sup>2-</sup>) and the corresponding increase in pH occurs very quickly before the alkalinity increases significantly (especially in low alkalinity waters). Sodium bicarbonate provides the addition of alkalinity without a significantly raising the pH, but the costs of sodium bicarbonate are significant higher than other alkalinity adding chemicals. Table 4 lists the costs of alkalinity-adding chemicals:

### Practical Uses of a Carbon Dioxide Lime System

The challenge with alkalinity addition is to find a chemical that can shift the carbonate species, add more carbonate to the system, and remain cost effective. All three of these goals can not be accomplished with one chemical, so the use of multiple chemicals was examined. Table 5 lists the chemicals that can add carbonate to the system and the chemicals that can shift the carbonate species.

The approach to the challenge of the alkalinity addition dilemma is to use the two chemicals (one from each list) with the lowest costs simultaneously. For the chemicals listed, carbon dioxide (\$70/ton) and quicklime (\$110/ton) would be the lowest combined chemical cost.

### Advances in Lime & Carbon dioxide Systems

Over the past 10 years, advances in both carbon dioxide and lime feed systems have

created more flexibility in chemical addition and improved feed rate control.

#### Carbon Dioxide

The original carbon dioxide systems utilized gaseous carbon dioxide, which was bubbled up through the water column. These feed systems required a minimum detention time of 30 minutes in order for the gaseous carbon dioxide to dissolve into solution and minimum water depths of 15 feet to provide adequate carbon dioxide transfer efficiency (60-85 percent).

Newer carbon dioxide systems dissolve carbon dioxide into a carrier water solution to be added to the process stream. Dissolved carbon dioxide solutions can be added to pipelines efficiently (>95 percent) and do not require 30 minutes of reaction time.

When carbon dioxide solution is added to water with moderate pH changes (i.e. shifting the pH from 9.5 to 8.0) the required reaction time is approximately 1.5 minutes. When carbon dioxide solution is added to water with significant pH changes (i.e. shifting from pH 11.0 to 8.0), the required reaction time is three minutes. The carbon dioxide solution system provides increased treatment flexibility by eliminating detention time requirements and basin depth (transfer efficiency) requirements.

#### Lime Systems

Advances in lime systems (both quicklime and hydrated lime) have improved the flexibility and control of lime addition. The quicklime slaking technology 15 years ago was difficult to control based on the lack of slaking temperature control. Changes in the quality of lime or the temperature of the water used in the slaking process would affect the slaking temperature of traditional slakers.

The reactivity of slaked lime depends on the surface area of the lime. The surface area of the slaked lime is almost completely dependent upon the slaking temperature of the lime slaking reaction. The optimal (and practical) slaking temperature is 185 degrees Fahrenheit.

New lime slaking systems can maintain a constant slaking temperature despite the changing of other variables. This constant slaking temperature allows these systems to

Table 4: Cost of Common Water Treatment Plant Alkalinity-Adding Chemicals

| Chemical                                    | Cost (\$/ton) 2003 dollars | Cost (\$/ton) 2007 dollars |
|---|----------------------------|----------------------------|
| Quicklime (CaO)                             | 97                         | 110                        |
| Hydrated Lime [Ca(OH) <sub>2</sub> ]        | 195                        | 261                        |
| Sodium Hydroxide (NaOH)                     | 427                        | 713                        |
| Soda Ash (Na <sub>2</sub> CO <sub>3</sub> ) | 378                        | 539                        |
| Sodium Bicarbonate (NaHCO <sub>3</sub> )    | 760                        | 900                        |

produce lime slurries with hydrated lime surface areas of 50,000-75,000 square centimeters per gram of lime. This produces lime slurry that is consistent and reactive, allowing for much better control of lime dosing.

Improvements have also been made with hydrated lime systems that utilize higher-quality (more surface area) hydrated lime, as well as higher concentration feed solutions (30-35 percent). Higher-quality hydrated lime can have surface areas as high as 220,000 square centimeters per gram of lime. This lime feed system also provides lime slurry that is consistent and reactive. High-quality hydrated lime also has the advantages of reduced scaling and minimal grit.

### **Enhanced Coagulation**

There are a number of different treatment scenarios for a combination alkalinity (lime/CO<sub>2</sub>) addition system. Staggering the addition of the two chemicals used in this process can provide value in addition to the original goal of alkalinity addition.

Enhanced coagulation regulations require increased removals of organics for low alkalinity waters. It is well known that a lower pH increases the removal of organics because the organics are less soluble and are easier to remove with coagulation. The combined use of carbon dioxide and lime afford a treatment scenario that is beneficial for low-alkalinity water when enhanced coagulation is required.

Carbon dioxide can be added to the front of the treatment process in order to reduce the pH (and also add more carbonate to the system), providing a low coagulation pH for the coagulation process. After sedimentation, lime can be added to raise the pH and shift the carbonate species. Lime can also be added with carbon dioxide at the front of the process if the addition of carbon dioxide would result in an excessively low coagulation pH.

Similarly, additional carbon dioxide can be added with lime after coagulation to supplement the total carbonate to achieve the desired finished-water alkalinity. This chemical addition configuration provides an incredible amount of treatment flexibility for waters with varying pH and alkalinity because the combination system can “dial in” the exact finished water quality parameters (both pH and alkalinity). Meeting both pH and alkalinity goals in the finished water is typically mutually exclusive if only one chemical is utilized.

### **Softening Process**

In the past, carbonate-limited waters required soda ash in order to optimize the softening process. Carbonate-limited water, when softened, results in finished water with extremely low alkalinities. With the introduction of the carbon dioxide solution feed sys-

Table 5: Common WTP Chemicals that Add Carbonate or Shift Carbonate Species

| Chemicals that add Carbonate to the System | Chemicals that shift the carbonate species |
|--|--|
| Sodium Bicarbonate                         | Quicklime                                  |
| Sodium Carbonate (Soda Ash)                | Hydrated Lime                              |
| Carbon Dioxide                             | Caustic Soda                               |
|  | Sodium Carbonate (Soda Ash)                |
|  | Sodium Hypochlorite*                       |

\* Sodium hypochlorite would not be used for shifting carbonate species because of limits on chlorine addition, but it should be realized that its addition would shift the carbonate species.

tems, adding carbon dioxide prior to softening is a viable alternative for improving both the precipitation process and providing additional carbonate, which results in higher finished-water alkalinities. Improving the softening process results in lower effluent hardness from the softening process, which can also allow for high bypass flows, resulting in higher finished-water alkalinities and lower treatment costs.

### **Nanofiltration/Reverse Osmosis Permeate (NF/RO)**

Membrane processes (NF/RO) will remove bicarbonate and carbonate, greatly reducing the alkalinity of the permeate water. The use of a combination chemical system can provide advantages in a membrane treatment process. When carbon dioxide is added in front of the membrane process, more carbonic acid is present in the feed water to the membranes. Carbonic acid is not removed by the membranes and can be converted to bicarbonate and carbonate in permeate by the addition of lime.

The addition of carbon dioxide prior to the membrane also depresses the pH of the feed water, which reduces/eliminates the need for proprietary antiscalants because of the increased solubility of salts in lower pH waters. The addition of carbon dioxide for this purpose also is advantageous because excessive amounts of carbon dioxide will reduce the pH by only small incremental levels below traditional enhanced coagulation pH (6.0).

Utilities should be sensitive to the impact of lime addition on the downstream turbidity of the finished water. It is recommended that lime addition occur in the permeate water before blending occurs. The permeate water will be the most aggressive water that corresponds to a much quicker dissolution of lime particles and correspondingly a lower impact on the finished water turbidity.

Fort Collins, Colorado, found that immediately after the addition of lime (post filtration), the turbidity of the finished water increased from 0.05 NTU to 0.25 NTU. Because of the aggressive nature of the fil-

tered water (low alkalinity - similar to membrane permeate) at this facility, the turbidity would decrease to 0.1 NTU by the time the water left the clearwell. If the water quality is not aggressive enough to eliminate turbidity concerns, the utility should consider sodium hydroxide in lieu of lime addition.

### **Conclusions**

Advances in chemical feed equipment provide options for cost-effective alkalinity addition that were previously unavailable. In the past, carbon dioxide systems required deep basins and a significant amount of reaction time to achieve stable water. Solution carbon dioxide feed systems allow for instantaneous dissolution of “liquid” carbon dioxide and provide a means for depressing the pH in an inexpensive, safe method that, when used in combination with lime addition, can allow utilities to “dial-in” the optimal pH for coagulation and significantly increase pre-softened, coagulated, and finished-water alkalinity.

Carbon dioxide addition in combination with lime prior to coagulation allows additional buffering capacity in the coagulation process to minimize basin corrosion, while providing an optimal enhanced coagulation pH. Lime or caustic addition prior to media filtration or after membrane filtration allows the shift in the carbonate species and stabilizes the water quality. Improved technology, which provides faster reacting lime slurry, allows for addition of lime after filtration, without significantly impacting the turbidity of the finished water (depending on the water quality).

### **Acknowledgements**

- **Coauthors:** Thomas Crowley, Carollo Engineers, Overland Park, Kansas; and Sam Samandi, city of Oklahoma City, Oklahoma.
- **References:** S. Imran, J. Dietz, G. Mutoti, J. Taylor, A. Randall, and C. Cooper (2005) Red Water Release in Drinking Water Distribution Systems. *Journal AWWA*, September 2005. ◊