CARBONATE CHEMISTRY AFFECTING PRODUCTION OF BEVERAGE STILL WATER

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1.0   SUMMARY

The chemistry of the carbonate equilibrium, including carbon dioxide (CO_2), directly affects the beverage production of still water, which has strict pH and alkalinity standards. CO_2 (g) will pass through a Reverse Osmosis (RO) membrane, which is commonly used in still water production, and end up in the final water.   Unless the CO_2 is removed, adjusting the final pH to specifications will result in high alkalinity concentrations in excess of the specifications. The purpose of this paper is to define the carbonate chemistry, present various treatment options and the impact of CO_2 (gas) on final still water quality.

2.0   REVIEW

Most ground waters have high levels of hardness consisting of calcium and magnesium ions and alkalinity, which are the carbonate ions. These waters, when removed from the ground, increase in temperature and become oversaturated with respect to precipitation of calcium carbonate.   As a result, calcium carbonate scale forms on pipes, valves, heating coils and process equipment.   High levels of calcium and magnesium also impact the sensory qualities of carbonated soft drink products (CSD).

In groundwaters originating from limestone aquifers, the hardness ions calcium and magnesium are normally accompanied with carbonate alkalinity.   The carbonate equilibrium, which includes free CO_2 or carbonic acid, bicarbonate ions and carbonate ions, is highly pH dependent. The CO_2 – bicarbonate equilibrium exists in the pH range of 4.3 to 8.3 and the bicarbonate – carbonate equilibrium dominating at pH 8.3 – 12.3. The concern over carbonate alkalinity is related to the pH buffering of the product, which impacts the sensory qualities of CSDs.

All beverage water treatment plants are designed to remove hardness and alkalinity. For those plants producing only CSD and carbonated water, high CO_2 levels in the final water are not an issue since CO_2 is added to the final product. It is only those plants producing still water that must remove excess CO_2.

A review of the CO2 – Carbonate Chemistry is included in Attachment 1.0. Attachment 2.0 includes a summary of analytical procedures published in *Standard Methods for the Examination of Water and Wastewater*.   Figure 1.0 shows the pH Titration Curve with Sodium Hydroxide.

Table 1.0 - pH Titration Curve with Sodium Hydroxide
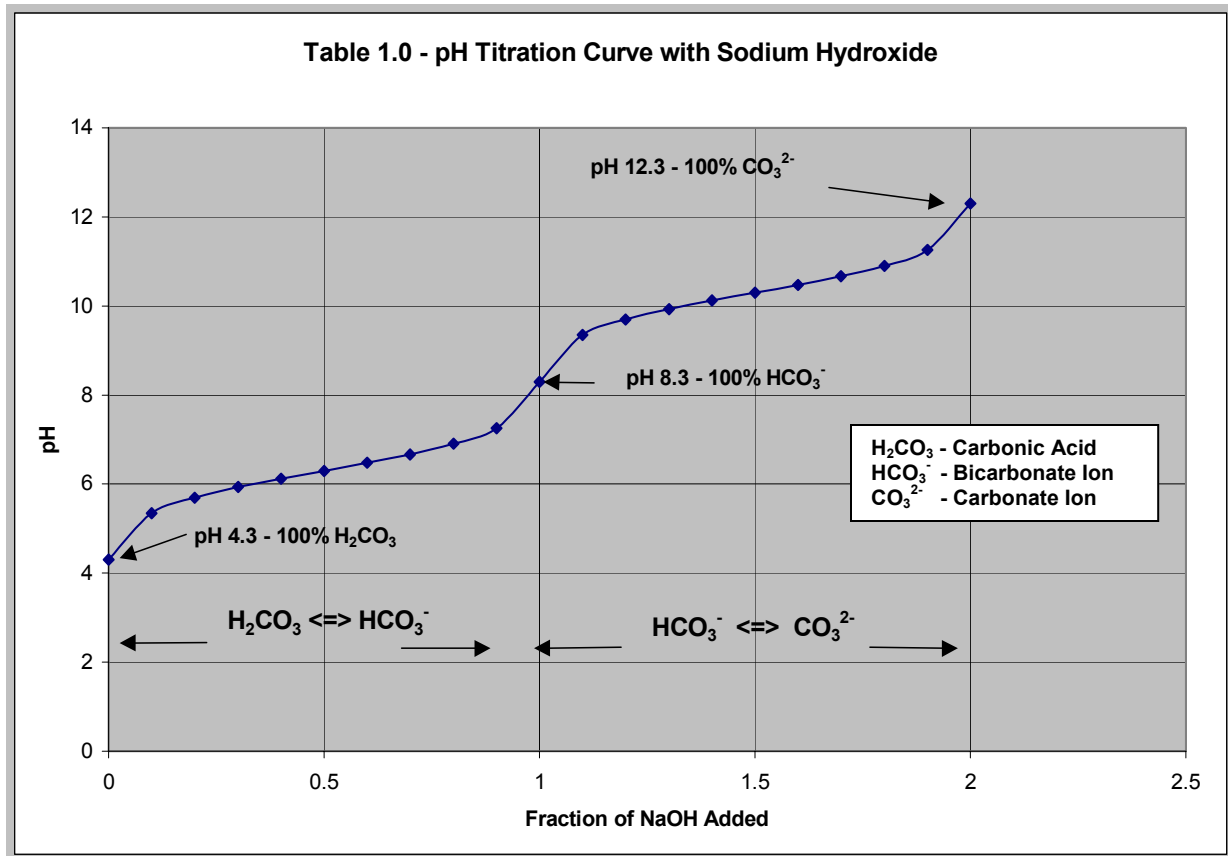
This pH Titration Curve with Sodium Hydroxide shows the pH – Carbonate equilibrium and indicates:

- At pH 4.3, only dissolved CO_2 (gas) or carbonic acid is present; (Please note for the purposes of this paper, free CO_2 and carbonic acid, H_2CO_3, are assumed to be the same.)
- Between pH 4.3 and 8.3, only carbonic acid and bicarbonate ions are present, with the proportion of each species dependent on the pH. At pH 6.3, the concentrations of each are equal;
- At pH 8.3, only bicarbonate ions are present;
- Between pH 8.3 and 12.3, only bicarbonate and carbonate ions are present, with the proportion of each species dependent on the pH;
- At pH 10.3, the concentrations of bicarbonate and carbonate ions are equal;
- At pH 6.3 and pH 10.3, buffers are formed; and
- The pH of a solution of carbonate (say sodium carbonate) is approximately 12.3.

3.0   WATER TREATMENT PROCESSES

3.1   Filtration

The first step in any water treatment plant is filtration to remove suspended solids, normally using a mixed-media filter.   Many plants will add oxidants (chlorine) or aerate to water prior to filtration, to oxidize soluble ferrous iron which precipitates as ferric hydroxide solid. Filtration has no effect on hardness ions or alkalinity.

3.2   Dealkalization

Dealkalization involves the use of a weak acid, cationic ion-exchange resin to remove both hardness and alkalinity. The resin is regenerated using a strong acid, such as hydrochloric acid. After regeneration, the resin is on the "hydrogen ion" cycle.

As water is passed through the resin bed, the hardness ions calcium and magnesium are exchanged by the resin and acidic hydrogen ions are released. The acid then reacts with the alkalinity forming carbonic acid (free CO_2).

$$H^+ \quad + \quad HCO_3^- \quad \Leftrightarrow \quad H_2CO_3$$

$$H_2CO_3 \quad \Leftrightarrow \quad CO_2 \text{ (gas)} \quad + \quad H_2O$$
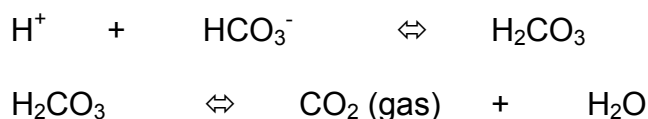
- If you take a sample of water after a dealkalizer, the water is effervescent, releasing small bubbles of CO_2 gas.

- The advantage of a dealkalizer is that both hardness and alkalinity are removed simultaneously.

- The disadvantages of the dealkalization process are the storage and handling of an acid, such as hydrochloric, which is dangerous and very corrosive.

- Only the hardness ions equal to alkalinity can be removed.   Unless the released hydrogen ions can be neutralized by alkalinity, the pH drops thus preventing exchange of hardness ions.

- A gas stripper or decarbonator normally follows a dealkalizer to remove the CO_2 gas.

3.3   Membrane Processes

Reverse osmosis membranes do not remove free CO_2 gas from water.   The gas passes through the membrane and ends up in the permeate.

Some descalant additives that rely on acids to prevent scaling due to calcium carbonate and calcium sulfate will convert all or a major fraction of alkalinity to CO_2 gas, which then permeates the membranes (pH 4.5-5.5).

Membrane additives that rely on chelating agents to tie up calcium and magnesium ions are normally used at a neutral pH range (7.0-8.0). At this pH, alkalinity is in the form of bicarbonate ion and associated with calcium, magnesium or sodium ions, which are removed through the membrane.

The membrane permeate water will normally have some free CO_2. Because all total dissolved solids, including alkalinity, has been removed, the permeate water has no buffer. With no buffer, the free CO_2 lowers the pH to 5.0 – 6.0, depending on the concentration. When the permeate water pH is adjusted upwards, the free CO_2 is converted back to bicarbonate alkalinity. Since most still waters have a quality standard of pH >6.5 and < 50 ppm alkalinity, it is possible that when the water is neutralized to a pH > 6.5, the alkalinity exceeds 50 ppm. If this occurs, the CO_2 must be removed from the water prior to adjusting the pH.

3.4   Gas Stripping Processes

Dissolved CO_2 gas can be removed with a simple gas stripping process. For example, passing a water at pH 5.8 with a CO_2 concentration of 120 ppm though a gas stripper can result in a CO_2 concentration of <5ppm and resulting pH of 7.0. The key stripping parameters are air to water ratio, temperature and residence time. The specific design parameters of these processes are beyond the scope of this paper.

There are four basic gas stripping process:

- Submerged Aeration;
- Decarbonators;
- Vacuum Degassers; and
- Membrane Degassers.

3.4.1 Submerged Aeration

Submerged aeration consists of blowing air through dispersed bubble aerators installed on the bottom of a tank. The small bubbles produced by the aerators strip out the dissolved CO_2 gas and transport to the surface.

Lowry Aeration manufacturers a package aeration system on skids, that includes aeration tank, pump, blower and electrical panel. They can be contacted at 800-434-9080 or www.lowryh2o.com

3.4.2 Decarbonators

Decarbonators are basically packed bed (tower) scrubbers where water is introduced at the top of the packing and air is introduced at the bottom. The contercurrent flow of air and water strips the CO_2 from water with the lowest concentration at the bottom of the scrubber. They are normally operated at 0.2 – 0.4 lbs air/lb water.

U.S. Filter offers a wide range of decarbonators, ranging from 15 to 400 gpm, with towers ranging up to 17 feet tall (Models DG-12 to 60). They can be contacted at: Colorado Springs, Standard Products Group.

Additional companies include:

Wesco - http://www.wesco-waterequipment.com/main.htm
GE – Glegg - http://www.glegg.com/products/pr_de_body.htm
Indeck - http://www.indeck.com/h20stats.html

There are many companies that offer decarbonators. Go to the Internet and use the GOGGLE search engine (www.google.com) and seach for "decarbonators".

3.4.3 Vacuum Degassers

Vacuum degassers are pressure vessels operated at - 5 to 8 psi (500 – 346 mm Hg) vacuum. Vacuum degassers are used in the filling operation of CSD to remove dissolved gases, primarily oxygen. Although vacuum degassers have not been used in the soft drink industry to remove CO_2, this is a viable technology.

3.4.4 Membrane Degassers

Gas permeable membranes offer an interesting technology to remove dissolved gases, such as CO_2. Membrana offers a membrane technology can be used to remove oxygen and CO_2. Water is circulated through a shell (looks like heat-exchanger) consisting of fiber membranes. Air, which is circulated through the fiber side, scours the dissolved gases such as CO_2. For more information go to http://www.liqui-cel.com/.

The advantages of vacuum and membrane degassers are:

- Compact systems, requiring relatively small space; and
- Do not require an additional transfer pump.

4.0   SODIUM HYDROXIDE NEUTRALIZATION

After the CO_2 has been removed, the pH should be in the range of 6 to 7.   However, if the pH is too low and does not comply with specifications, the addition of sodium hydroxide may be required.

Additional of a strong base, such as sodium hydroxide, to water with low buffer capacity may be difficult to control.   Adding too much sodium hydroxide results in high pH and too little results in low pH. To minimize wide pH swings, it is important to measure system parameters and to actually design the system.

To design a sodium hydroxide pH neutralization system, it is important to:

- Match up the feed of sodium hydroxide to the input of acidity. To determine the acidity, you must determine the amount of alkalinity required to raise the water to the desired pH (say pH 7.0).   Titrate the water with a pH electrode and stirrer with sodium hydroxide to pH 7.0 and calculate the amount of alkalinity added.

    For example, to neutralize 200 gpm of 10 ppm of acidity (as $CaCO_3$), you must calculate the input of acidity in terms of lbs/hour:

    12,000 gph/1E-6 * 10 mg/L * 8.34 lbs/gal = 1.00 lbs acidity / hour

    Assume 10% NaOH (1.25 lbs alkalinity/lb NaOH).

    0.1 lbs NaOH / lb solution * 1.25 = 0.125 lbs alkalinity / lb solution

    Will require 1.00 lbs acidity / 0.125 lbs alkalinity = 8.0 lbs 10% NaOH solution

    Assume the sodium hydroxide solution has a density of 1.1;

    8.0 lbs / (1.1 * 8.34 lbs/gal) = 0.87 gph of sodium hydroxide

    The last very important parameter is to locate the pH meter and controller in a position where there is good mixing.

Attachment 1 – Carbonate Equilibrium Theory

Carbon dioxide (CO_2) in the air phase is in equilibrium with CO_2 dissolved in the water phase, with the distribution in each phase controlled by the Henry's Law Constant.

$$CO_2 \text{ (gas)} \quad \Leftrightarrow \quad CO_2 \text{ (water)} \tag{1}$$

Henry's Law Equation

$$P_p \quad = \quad K_h * C_{molar} \tag{2}$$

Where:

P_p Partial pressure of CO_2 in the gas phase
K_h Henry Law Constant = 29.76
C_{molar} Molar concentration of CO_2 in the water phase

If you assume various concentrations of CO_2 in equilibrium with pure water, the distribution will be as indicated in Table 1.0

Table A1.0   Distribution of CO_2 @ 25°C

| CO₂ Gas Concentration		Water Concentration as CO₂	
Partial Pressure	ppm (v/v)	Molar	ppm
0.000350[a]	350	0.000012	0.5
0.001	1000	0.000034	1.5
0.01	10,000	0.000336	14.8
0.1	100,000	0.00336	147.
1.0[b]	1,000,000	0.0336	1478.

     [a] = ambient CO_2 concentration
     [b] = 100% CO_2

Note: The solubility of CO_2 increases with decreasing temperature. For example at 0°C, the solubility of pure CO_2 in water is 3,480 ppm, approximately 2.4 times the solubility at 25°C.

The CO_2 in the water phase reacts with water to form carbonic acid.

$$CO_2 \text{ (water)} \quad + \quad H_2O \quad \Leftrightarrow \quad H_2CO_3 \text{ (carbonic acid)} \tag{3}$$

For all practical purpose, CO_2 dissolved in water behaves the same as carbonic acid, so we do not consider both forms of CO_2 in our calculations. Carbonic Acid then dissociates forming bicarbonate ion and releasing a hydrogen ion.

$$H_2CO_3 \text{ (carbonic acid)} \quad \Leftrightarrow \quad HCO_3^- \text{ (bicarbonate ion)} \quad + \quad H^+ \qquad (4)$$
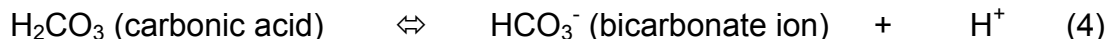
As indicated by Equation 4, the distribution between carbonic acid and bicarbonate acid is pH dependent and is represented by:

$$K_{a1} \quad = \quad \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \qquad (5)$$

$$K_{a1} \quad = \quad 10^{-6.36}$$

Note: Brackets [ ] normally indicate the molar activity of the species. For the purposes of this discussion, assume that brackets indicate the molar concentration in moles per liter.

Taking logarithms and rearranging the equation becomes:

$$pH \quad = \quad 6.3 \quad - \quad Log \, [H_2CO_3] / [HCO_3^-] \qquad (6)$$

What does this equation tell us?

- The ratio of $[H_2CO_3] / [HCO_3^-]$ will determine the pH, which is not concentration dependent.
- We can calculate the pH if we know this ratio, and we can calculate the ratio if we know the pH.
- When the concentrations of $[H_2CO_3]$ and $[HCO_3^-]$ are equal, the logarithm is zero, therefore the pH = 6.3. This is also the pH of maximum buffer.
- How do we determine the concentrations of CO_2 and $[HCO_3^-]$. You can follow the procedures in *Standard Methods for the Examination of Water and Wastewater* for analysis of Alkalinity and free CO_2. You titrate the water sample to methyl orange endpoint (pH 4.3) to determine Alkalinity (Method 2320 B) and titrate to phenolpthalein endpoint (pH 8.3) to determine free CO_2 concentration (Method 4500-CO_2 C).
- You can also calculate the free CO_2 concentration if you know the Alkalinity and pH (Method 4500-CO_2 D).

$$CO_2 \text{ (ppm)} \quad = \quad Alkalinity * 44/50 * 10^{(6.36-pH)} \qquad (7)$$

How do we calculate the pH of CO_2 dissolved in pure water, with no alkalinity.

a. First the concentration of CO_2 is dependent on the partial pressure of CO_2 in the gas phase. Assume the partial pressure is 0.01 atmospheres (10,000 ppm). Table 1.0 indicates the molar concentration in the water phase is 0.00336 M.

b. Referring to Equation 4, assume carbonic acid has equally disassociated into bicarbonate and hydrogen ion, the formula becomes:

$$K_{a1} = \frac{X * X}{(1 - X) * C_{CO2}} \qquad (8)$$

Assume that X <<1, then

$$X = SQRT (K1 * C_{CO2})$$

$$X = SQRT (10^{-6.36} * 0.00336)$$

$$X = [H^+] = 3.83 \times 10^{-5} \text{ Molar}$$

$$pH = -Log [H^+] = 4.41$$

If you combine this equation with Henry's Law, you can calculate the pH of water in equilibrium with different concentrations of CO_2 (gas).
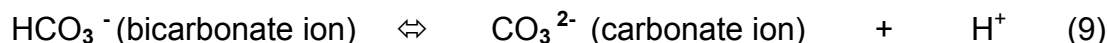
$$X = SQRT (10^{-6.36} * P_p / K_h)$$

Assuming a CO_2 (gas) concentration of 1,000 ppm, the pH would be:

$$X = SQRT (10^{-6.36} * 0.001 / 29.76)$$

$$pH = 5.4$$

Total Alkalinity also includes the bicarbonate – carbonate equilibrium.

$$HCO_3^- \text{(bicarbonate ion)} \Leftrightarrow CO_3^{2-} \text{(carbonate ion)} + H^+ \qquad (9)$$

$$K_{a2} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \qquad (10)$$

$$K_{a2} = 10^{-10.36}$$

Taking logarithms and rearranging the equation becomes:

$$pH \quad = \quad 10.36 \quad - \quad Log \; [HCO_3^-] \, / \, [CO_3^{2-}] \tag{11}$$

How do we calculate the pH of HCO_3^- dissolved in pure water, with no alkalinity.

If you have a solution of bicarbonate, you have to consider both carbonate reactions.

$$K_{a1} \quad = \quad \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \tag{12}$$

$$[HCO_3^-] \quad = \quad \frac{K_{a1} \; * \; [H_2CO_3]}{[H^+]} \tag{13}$$

Substituting into Equation:

$$K_{a2} \quad = \quad \frac{[CO_3^{2-}] \; * \; [H^+]^2}{K_{a1} * [H_2CO_3]} \tag{14}$$

Making the assumption that $[CO_3^{2-}] = [H_2CO_3]$, the equation becomes:

$$[H^+] \quad = \quad SQRT \, (\, K_{a1} * K_{a2})$$

$$pH \quad = \quad (pK_{a1} \; + \; pK_{a2})/2$$

$$pH \quad = \quad (6.36 + \; 10.36)/2$$

$$pH \quad = \quad 8.36$$

Therefore, the pH of a bicarbonate solution is independent of pH and is equal to 8.36.

What would be the pH of a solution of carbonate?

$$CO_3^{2-} \; \text{(carbonate ion)} \quad \Leftrightarrow \quad HCO_3^- \text{(bicarbonate ion)} \quad + \quad OH^- \tag{15}$$
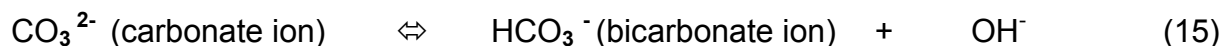
If can be shown that:

$$K_{b1} \quad = \quad K_w/K_{a2} \tag{16}$$

$$= \quad 10^{-14} / 10^{-10.36}$$

$$= \quad 10^{-3.64}$$

$$K_{b1} = \frac{[HCO_3^-]\ [OH^-]}{[CO_3^{2-}]} \tag{17}$$

Assuming the $[OH^-]$ and $[HCO_3^-]$ come from the dissociation the carbonate ion, then using the same approach as Equation 8;

$$K_{b1} = \frac{X * X}{(1 - X) * C_{CO3}^{2-}} \tag{18}$$

Assume that $X \ll 1$, then

$$X = SQRT\ (K_{b1} * C\ C_{CO3}^{2-})$$

Assuming the carbonate concentration is 10 % by weight, as sodium carbonate (1.2 Molar);

$$X = SQRT\ (10^{-3.64} * 1.2)$$

$$X = [OH^-] = 1.66 \times 10^{-2}\ Molar$$

$$pOH = -log\ [1.66 \times 10^{-2}\ Molar] = 1.78$$

$$pH = 14 - pOH$$

$$= 12.22$$

Attachment 2 – Summary of Alkalinity Test Procedures

The bible of water chemistry tests procedures is the latest version of *Standard Methods for the Analysis of Water and Wastewater*, a joint publication of the American Public Health Association, American Water Works Association and Water Environment Federation.

Alkalinity

The test consists of titrating a sample of water with sulfuric acid to a pH 8.3 and to pH 4.3 (Table 1.0). These pH values reflect the inflections in the pH titration curve where 100% bicarbonate and 100% carbonic acid are present.   If the water pH exceeds 8.3, then the alkalinity tests indicates the amount of carbonate and hydroxide present. Titrating to pH 4.3 indicates the amount of bicarbonate present.

To simplify the test, phenolphthalein indicator is used to indicate pH 8.3; and a mixed indicator consisting of bromcresol green-methyl red dyes are used to indicate pH 4.3. In the past methyl orange was used at pH 4.3.

Water treatment people sometimes refer to alkalinity as M & P, to indicate the concentrations obtained titrating to phenolphthalein (P) and methyl orange (M) endpoints.

The alkalinity titration test is listed in Method 2320 B.

Carbon Dioxide (CO_2)

Carbon Dioxide can only be present at pH values below 8.3. To determine CO_2 concentration, a sample of water is titrated to pH 8.3 using phenophthalein indicator.

The CO_2 titration test is listed in Method 4500- CO_2 C.

If you know the alkalinity, the CO_2 concentration can be estimated according to the following equation.

ppm CO_2 = 2 * bicarbonate aklalinity * (10^{6-pH})

If you do not have access to these methods, send an E-Mail to Phil Hayden @ philh@heg.com and I will send you a copy.