

Softening Pool Water Through Calcium Carbonate Precipitation and Removal

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onBalance

Pool water was softened by reacting dissolved calcium bicarbonate (calcium hardness) in the pool water with added sodium carbonate (soda ash). This formed a filterable precipitate of calcium carbonate. The process had little effect on other dissolved solids, but a marked reduction of calcium hardness.

Swimming pool water chemistry standards commonly call for a maximum calcium hardness level of 1000 ppm. This is primarily intended to facilitate saturation index balancing of the pool water. Once calcium hardness exceeds 1000 ppm, unless the pool is drained either the pH and/or the alkalinity must generally be lowered toward the bottom of the acceptable ranges to compensate.

Draining a pool and replacing some or all of the water with fresh tap water to lower calcium levels is often preferred, since it also lowers other undesirable components of the water, including total dissolved solids, cyanuric acid, accumulated salts, disinfection byproducts, etc.

Unfortunately, there are times when draining a pool may be impractical. Reasons for not draining a pool may include cost, weak

(bond-failed or delaminated) plaster, high ambient temperatures coupled with low humidity, drought restrictions, high water tables, or even particularly conservation-minded pool owners. In these circumstances an alternative to water replacement may be desirable.

Accidental Precipitation

Sodium carbonate (Na_2CO_3 or soda ash) is often added to swimming pool water to raise the pH and alkalinity. Under normal circumstances, the product should be added in such a manner as to distribute the powder evenly across the pool water surface. This method promotes the speed of blending the product (and its effects) throughout the vessel as expeditiously as possible. Even when added carefully, a precipitate may form, momentarily clouding the water. The visible clouding is not soda ash that has not yet gone into solution, but rather a precipitation of calcium carbonate. This is the result of a localized, temporary raising of the pH in the water at least into the mid-10 range, putting a relatively small area of the pool water into extreme over-saturated Langelier Saturation Index (LSI) levels. The clouding fades away as the non-stable precipitate dissolves back into the pool water, and the high-pH products blend throughout the vessel, thereby lowering the pH in the initially affected area while raising the pH of the entire pool from the starting point to the overall target level.

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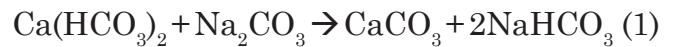
If added incorrectly (in a small, localized area of water rather than spreading it out across the entire surface for proper blending), the correct amount of sodium carbonate to raise, for example, 20,000 gallons from a pH of 7.4 to 7.6 may be able to increase the pH of perhaps a cubic yard of water significantly. At pH 11.5, which is in the pH range of a saturated solution of sodium carbonate, approximately 85% of the carbonate species material in water will be carbonate instead of the bicarbonate form prevalent at normal pool water pH ranges (see Figure 1). When this happens, the cloud of calcium carbonate precipitate takes much longer to dissipate, and sometimes a threshold is achieved at which the formation of a stable precipitate is actually promoted. (For a discussion of this topic, see Wojtowitz 2001 p. 45)

When this happens, the entire pool water becomes white. The precipitate must then be either filtered or re-dissolved through a significant lowering of the pH using acid.

Intentional Precipitation

One method of softening water in water treatment plants is that of “lime softening,” where calcium is removed using this precipitation/filtration process. (See, for example, Lime Softening). In swimming pools, water may also be softened (i.e., calcium ions removed) by precipitation (essentially a process of sodium/calcium ion exchange) and filtration.

Equation 1 shows the reaction of sodium carbonate (added as a powder) and dissolved calcium bicarbonate (hardness in pool water), forming a filterable precipitate of calcium carbonate with a residual of soluble sodium bicarbonate (non-hardness alkalinity).



This process may also be accomplished using sodium hydroxide (NaOH, or caustic soda). Equation 2 shows the same process using sodium hydroxide, which also forms a

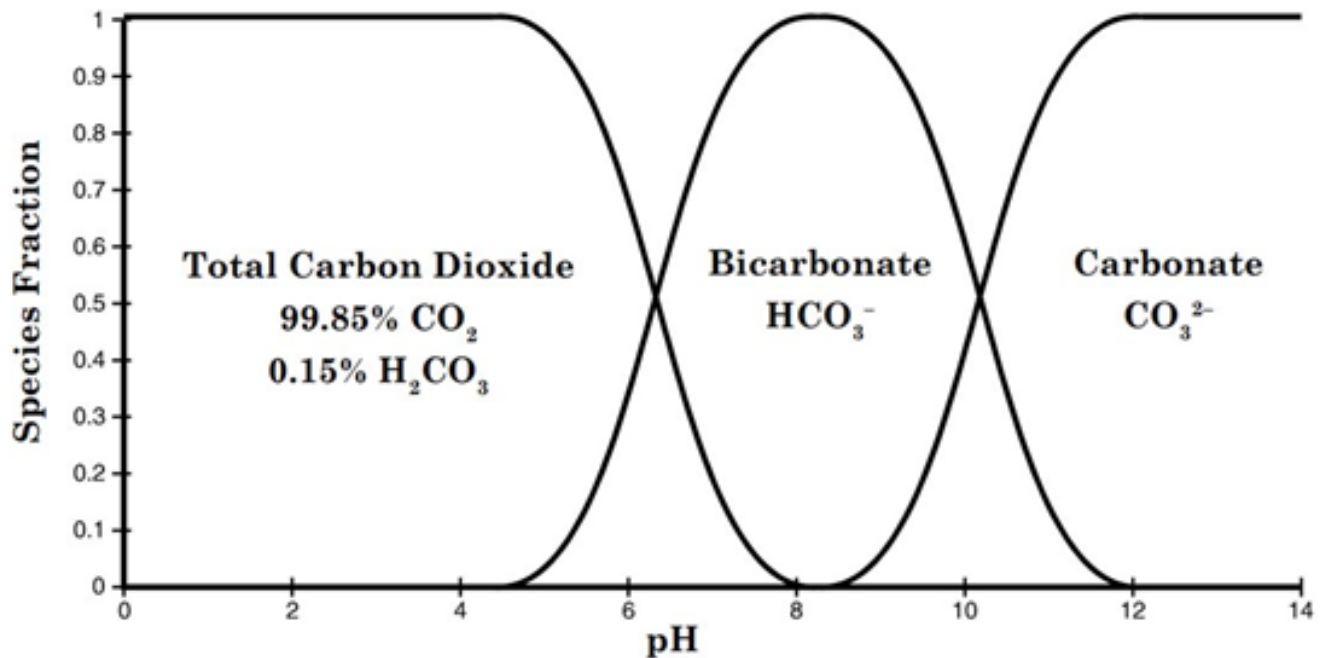


Figure 1 – Distribution of Total Carbon Dioxide, Bicarbonate, and Carbonate vs. pH

filterable precipitate of calcium carbonate, along with water and sodium bicarbonate alkalinity.



Sodium hydroxide (caustic soda) is generally not favored in the pool water treatment industry because it must be handled under hazardous materials precautions, is less available to the pool service technician, and is more dangerous to use.

Dosage

The potential amount of filterable precipitate that could be generated may be estimated by taking into consideration the following: The molecular weight of sodium carbonate is 105.98 and the molecular weight of calcium carbonate is 100.08. Therefore, one pound of added soda ash reacting with calcium bicarbonate in the pool water can potentially yield 0.944 lbs. of calcium carbonate precipitate. Or, 1.06 pounds of soda ash reacting with calcium bicarbonate can yield up to 1.0 lbs. of calcium carbonate. One pound of calcium carbonate precipitate translates to about 12 ppm of calcium hardness reduction in 10,000 gallons of water.

Variables

It is important to note that there are a number of variables to how much calcium carbonate precipitate will actually be formed and filtered when this process is utilized in a swimming pool. These variables include the method of addition (localizing and raising pH as much as possible), existing buffers in the pool water, the temperature of the water, the speed and efficiency of the filtration process (inhibiting re-dissolving of any precipitate), etc.

An In-field Example

A swimming pool was treated with the Soda Ash / Calcium Hardness precipitation technique. The water had a beginning calcium hardness level of roughly 1200 ppm, and the pool owner did not wish to drain the pool due to the cost of water replacement and the weather (very hot temperature).

The water was pre-tested, and the initial readings are given in the “Before” column of the accompanying Table.

The pool was dosed twice, the first time with 20 pounds of sodium carbonate and then a follow-up dose a few days later (after the pool cleared) of 50 pounds.

	Before	After 20 Pounds Soda Ash	After 50 More Pounds Soda Ash
pH	8.2	7.8	7.5
Total Alkalinity	180	154	158
Calcium Hardness	1196	972	598

- The pH was determined using a calibrated Kruger and Eckels Model 100 pH meter using a wide-range combination electrode with a silver/silver chloride reference. The instrument precision is 0.1 pH units.
- Total Alkalinity was determined using a 0.02 N HCl buret titration to a 4.6 pH endpoint and a temperature of 20°C, with a precision of 2 ppm [Standard Methods 2320 - Alkalinity].
- The method used to determine calcium hardness was a 0.1 Molar EDTA buret titration utilizing murexide as an indicator and an NaOH solution for magnesium precipitation. The precision is 2 ppm [Standard Methods 3500-Ca – Calcium].



**Illustration 1 –
Setting Up the
Filter at a Hard
Water Pool**



**Illustration 2 –
Adding the Soda
Ash in a Local
Area to Create
the Cloud**



**Illustration 3 –
“Milking” the Pool
so it Precipitates
the Calcium**



**Illustration
4 – Brushing
the Pool and
Cleaning the
Filter Each Day**



**Illustration
5 – Residue
on the Bottom
is Removed
By Adding a
Suction-side
Cleaner to the
Filter**



**Illustration 6 –
Result, a Clear
Pool With Half
the Hardness**

Follow-up Readings

The results after the 20 pound and 50 pound additions are given in the Table. The result was not only a decrease in calcium hardness of nearly 600 ppm from the 70 pounds of soda ash added, but also a decrease in alkalinity of about 20 ppm and a decrease in pH of 0.7 pH units. The LSI went from roughly +1.4 to +0.4.

The slight lowering of pH and TA by the addition of soda ash and the precipitation of calcium carbonate was one of the interesting side notes of the process. One may intuit a large rise in alkalinity and pH when adding such a large dose of sodium carbonate, but instead the consequent loss of calcium carbonate offset that effect.

The filter available for precipitate removal was a Sta-rite System 3 unit with a DE cartridge. No DE was added, and the filter was opened and cleaned once per day for three days, resulting in a removal of approximately 70 pounds of precipitated calcium carbonate. A suction cleaner was attached to the filter to remove precipitate that had settled to the bottom of the pool.

The precipitate was not in the pool long enough to adhere to the interior surfaces. One caution to observe if trying this technique is that the process could potentially precipitate heavy metals such as copper or iron if they are present in significant concentrations.

References

Lime Softening. National Drinking Water Clearinghouse Fact Sheet. See <https://water-research.net/Waterlibrary/>

privatewell/limesoftening.pdf

Wojtowicz, John A. "Factors Affecting Precipitation of Calcium Carbonate" *Journal of the Swimming Pool and Spa Industry* 3:1(2001):18-23. See http://www.poolhelp.com/wp-content/uploads/2017/05/JSPSI_V3N1_pp18-23.pdf (internal pagination follows the compiled works publication of Wojtowicz's articles)

About the Authors

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