

Swimming Pool Water Balance

Part 5: Factors Affecting Precipitation of Calcium Carbonate

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Laboratory tests with clear solutions showed that precipitation of calcium carbonate does not occur in the pH range 7.5 to 8.0 at alkalinities of 80 to 160 ppm and saturation indexes as high as 1.5. However, when the alkalinities are increased to very high levels, i.e., ~460 to ~325 ppm over the same pH range, evidence of precipitation was observed in the 0.5 to 1.1 saturation index (SI) range. At typical swimming pool pH and alkalinity, seed crystals are necessary to initiate precipitation of calcium carbonate supersaturation. Suspended particulate matter can serve as seed crystals.

Results of laboratory studies on precipitation of calcium carbonate in the presence of seed crystals are in general agreement with predictions based on the calcium carbonate precipitation potential (CCPP) model discussed in a previous article (Wojtowicz 1996). The results can be summarized as follows: a) at a given initial pH and alkalinity, the extent of precipitation increases with increasing SI, b) at a given initial pH and SI, the extent of precipitation increases with increasing alkalinity, c) at a given initial alkalinity and SI, the extent of precipitation decreases with increasing pH, and d) at a given initial pH, SI, and carbonate alkalinity, the extent of precipitation increases with increasing cyanuric acid concentration due to increased buffer intensity.

Precipitation of Calcium Carbonate: Theory

In Absence of Seed Crystals

Activation Energy – In the absence of seed

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crystals a positive saturation index (SI) does not result in precipitation of calcium carbonate until a certain degree of supersaturation has been achieved. This is due to the fact that stable nuclei can only form after an activation energy barrier has been surmounted. The activation energy (ΔG_a) is a function of the relative supersaturation or saturation index as shown by the following expression (Stumm and Morgan 1981):

$$\Delta G_a = 16\pi\sigma^3v^2/[3(kT \text{ Ln } S)^2] = B/(SI)^2$$

where: σ is the interfacial energy ($8 \cdot 10^{-6}$ Joules/cm²), v is the molecular volume ($3 \cdot 10^{-23}$ cm³), k is Boltzmann's constant ($1.38 \cdot 10^{-23}$ Joules/kelvin), T is the absolute temperature (kelvins), Ln is the natural logarithm operator, S is the relative supersaturation $S = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_s$, $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ are the concentrations of calcium and carbonate ions, K_s is the concentration solubility product constant of calcium carbonate, and SI is the saturation index. The higher the SI, the lower the activation energy for precipitation.

Rate of Nucleation – The rate of formation ($\text{J cm}^{-3}\text{sec}^{-1}$) of nuclei is a function of the activation energy and is given by (Stumm and Morgan 1981):

$$J = A \exp(-\Delta G_a/kT) = A \exp[-C/(SI)^2]$$

where: A is a constant related to the efficiency of collisions between calcium and carbonate ions [$\sim 10^{30}$ cm⁻³sec⁻¹] and C is also a constant. Since ΔG_a is dependent on SI, the higher the saturation index, the lower the activation energy barrier and the faster the rate of nucleation. Calculated values of the nucleation rate versus saturation index are shown in Table 1.

Table 1 shows that a fairly high relative saturation (~ 7) or saturation index (≥ 0.85) is required to
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Relative Supersaturation S	Saturation Index Log S = SI	Nucleation Rate (J) nuclei/cm ³ /sec
2	0.30	8 • 10 ⁻¹⁶³
3	0.48	3.4 • 10 ⁻⁴⁷
4	0.60	9.5 • 10 ⁻¹⁹
5	0.70	2.3 • 10 ⁻⁶
6	0.78	17.8
7	0.85	4.2 • 10 ⁵
8	0.90	4.5 • 10 ⁸
9	0.95	7.6 • 10 ¹⁰
10	1.00	3.9 • 10 ¹²

Table 1 – Nucleation Rate as a Function of CaCO₃ Saturation Index

attain a high nucleation rate in the absence of seed crystals. At relatively low positive values of SI, water can exist in a supersaturated state almost indefinitely in the absence of seed crystals or rough surfaces that promote heterogeneous precipitation (i.e., scaling).

In Presence of Seed Crystals

Kinetics – In the presence of seed crystals, the rate of precipitation (i.e., crystallization) of calcium carbonate from a supersaturated solution can be represented by the following differential equation (Nancollas and Reddy 1973):

$$dc/dt = -ks(c - c_0)^2$$

where: dc/dt is the instantaneous crystallization rate (mol L⁻¹ mg⁻¹ min⁻¹), k is the rate constant, s is the crystal surface area (expressed as mg/L), c_0 and c are the equilibrium and instantaneous calcium concentrations (mol/L), respectively, and the con-

centration difference $c - c_0$ (i.e., the excess solubility) is the driving force for crystallization. A k value of 5.76 L mol⁻¹ mg⁻¹ min⁻¹ was obtained at 25°C.

Laboratory Studies on Precipitation of CaCO₃

In Absence of Seed Crystals

Threshold SI for Precipitation of CaCO₃ – A series of tests was carried out in 100-ml glass volumetric flasks at 80 and 160 ppm alkalinity at pH 7.5 and 8.0 at saturation indexes of 0.5, 1.0, and 1.5. Only the data for SI = 1.5 are shown in Table 2. No precipitation was observed after 2 weeks (at all SI values) even though the pH had increased by a few tenths of a unit due to CO₂ loss. The presence of cyanuric acid had no effect.

A second series of tests was carried out in 8-L polycarbonate tanks at various pH's and constant hardness (added as calcium chloride). The alkalinity was increased with sodium bicarbonate while

pH	Carbonate Alkalinity (ppm)	Calcium Hardness (ppm)	Precipitation
7.5	80	9929*	none after 2 weeks
7.5	160	4965	"
8.0	80	3140	"
8.0	160	1570	"

*Addition of 80 ppm cyanuric acid had no effect.

Table 2 – Precipitation of CaCO₃ in Absence of Seed Crystals (Temperature 75°F, SI 1.5)

holding the pH constant until evidence of precipitation was observed. The data in Table 3 show that the threshold SI for perceptible precipitation of calcium carbonate increases with pH. In contrast to the data in Table 2, a very high alkalinity was required to initiate precipitation of calcium carbonate.

pH	Carbonate Alkalinity (ppm)	SI
7.2	554	0.5
7.6	429	0.8
8.0	323	1.1
8.4	242	1.4

**Table 3 – Threshold Alkalinity and SI for Precipitation of CaCO₃
(Temperature 75°F, Calcium Hardness 300 ppm)**

In Presence of Seed Crystals

Preliminary Tests – Tests were carried-out in 8-L polycarbonate tanks starting with distilled water and adding sodium bicarbonate for alkalinity and calcium chloride for hardness. The pH was adjusted with 0.1 N HCl or 0.1 N NaOH solution. A suitable volume of a dilute calcium carbonate slurry was added and the solution stirred to disperse the seed crystals. In initial experiments, freshly precipitated calcium carbonate (Na₂CO₃ + CaCl₂) completely redissolved when added to the test solutions, indicating that the particle size was too small. Use of aged calcium carbonate crystals circumvented this problem.

Effect of pH and Alkalinity on Precipitation of CaCO₃ – The total dissolved solids was adjusted to 3000 ppm with NaCl. Hardness was adjusted with calcium chloride to provide the required saturation indexes. Ten ml of a 0.05% calcium carbonate slurry was added to each tank and stirred to homogeneously disperse the seed crystals. The solutions were analyzed for alkalinity after one day. The data are shown in Table 4.

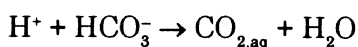
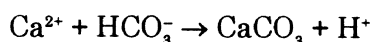
SI	Calcium Carbonate Precipitated (ppm)			
	pH 7.6		pH 8.2	
	Alkalinity 50	Alkalinity 150	Alkalinity 50	Alkalinity 150
0.45	1.2	2.4	0	0
0.70	9.6	17.4	2.0	4.7

**Table 4 – Effect of pH, Alkalinity, and SI on Precipitation of CaCO₃
(Temp. 75°F, Time 1 day, 0.6 ppm Seed Crystals, TDS 3000 ppm)**

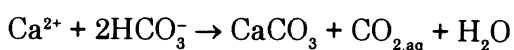
The data show that CaCO₃ precipitation increases with increasing alkalinity at a given SI and decreases with increasing pH. The change in precipitation with alkalinity and pH is due to a change in buffer intensity which varies directly with alkalinity and inversely with pH, in agreement with calcium carbonate precipitation potential (CCPP) theory (Wojtowicz 1996).

Effect of pH, Alkalinity, and Time on Precipitation of CaCO₃ – In another test series, both pH and alkalinity, which were monitored on a daily basis over a period of 11 days, decreased with time. The data are summarized in Table 5. Plots of pH and alkalinity versus time are shown in Figures 1 and 2.

The decrease in alkalinity, pH, and saturation index associated with precipitation of calcium carbonate can be explained by the following reactions:



Overall:



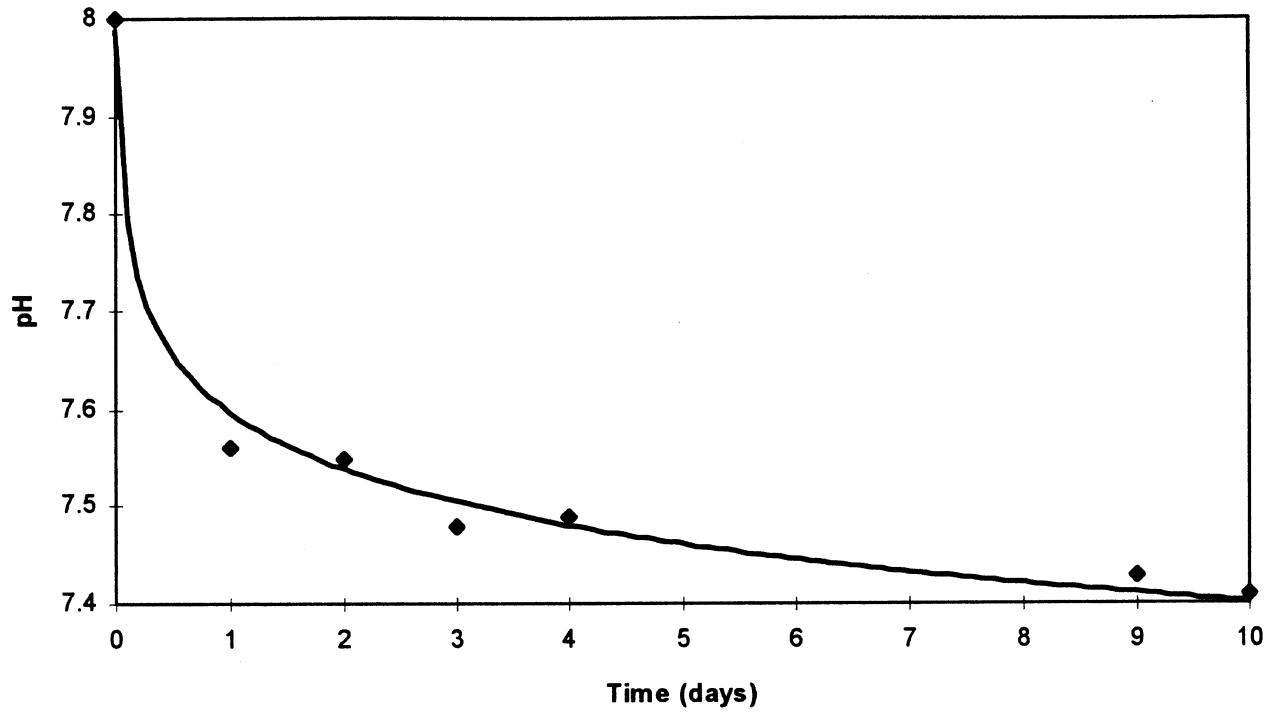


Figure 1 – pH Decrease During Precipitation of CaCO_3
 (Initial Conditions: pH 8.0, Alkalinity 98 ppm, SI 0.59)

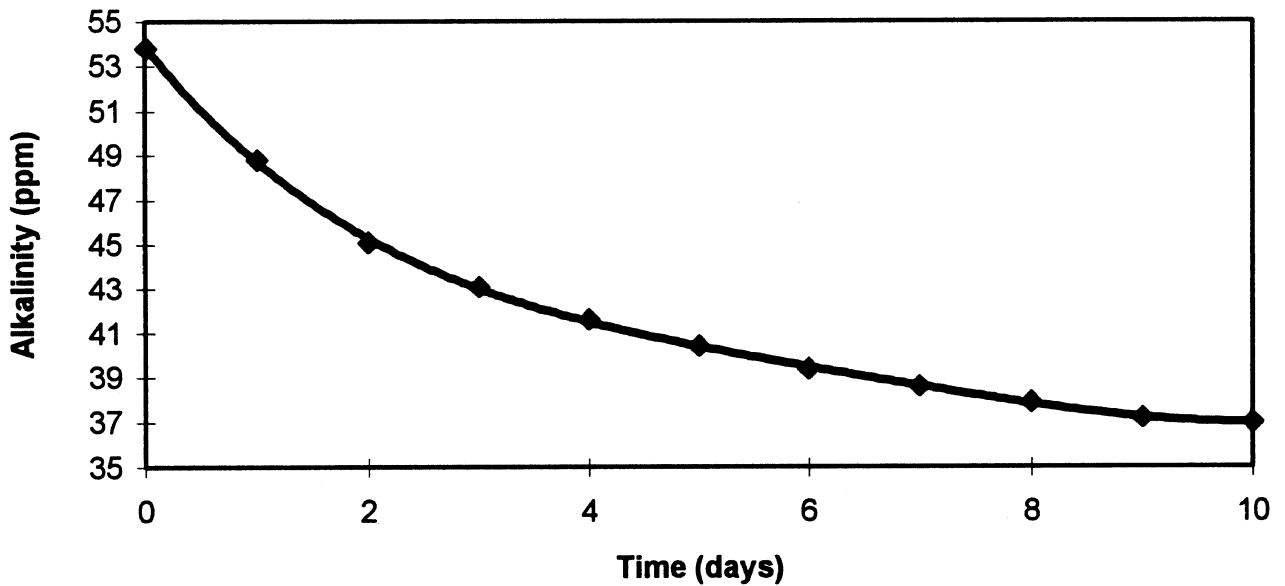


Figure 2 – Decrease in Alkalinity During Precipitation of CaCO_3
 (Initial Conditions: pH 7.4, Alkalinity 54 ppm, SI 0.63)

pH_i/pH_f	Alkalinity (ppm)	Hardness (ppm)	SI_i/SI_f	Buffer Intensity (ppm)	Loss of Carbonate Alkalinity (ppm)
7.40/6.84	54	2518	0.63/-0.09	8.6	16.8
7.40/6.98	96	1259	0.58/-0.02	15.9	31.8
7.40/6.99	138	839	0.56/-0.06	23.3	47.6
8.00/7.33	54	632	0.63/-0.13	3.3	9.4
8.00/7.40	98	316	0.59/-0.14	5.9	20.6
8.00/7.46	144	211	0.58/-0.09	8.7	27.8

Table 5 – Precipitation of $CaCO_3$ in Presence of Seed Crystals
(Temperature 75°F, SI_i = initial SI, SI_f = final SI)

The average SI after 10 days was close to 0 (actually -0.09). The extent of precipitation was proportional to the buffer intensity and consequently increased with initial alkalinity and decreased with initial pH in agreement with expectations based on calcium carbonate precipitation potential (CCPP) discussed in a previous article (Wojtowicz 1996). However, the quantity of precipitation was greater than predicted due to loss of carbon dioxide from solution. Since loss of carbon dioxide increases pH, it also raises the saturation index, increasing the CCPP. The fact that the pH was observed to decrease with time is due to the fact that CO_2 generated by precipitation more than offset that lost by volatilization.

Effect of Seed Crystal Concentration – The rate of precipitation of calcium carbonate increases with increasing concentration of seed crystals (in agreement with theory) as shown by the data in Table 6. Without seed crystals evidence of heterogenous precipitation was observed on the surfaces of the polycarbonate containers. This contrasts with the data in glass containers, which showed no heterogeneous precipitation (see Table 2).

Seed Crystals (ppm)	Loss of Alkalinity (ppm)	
	After 1 day	After 4 days
0	0	6.7 ^a
0.1	0	10.5
0.15	0	13.5
0.30	8.5	20.5

a) Heterogeneous precipitation on the wall and bottom of the container.

Table 6 – Effect of Seed Crystal Concentration on Precipitation of $CaCO_3$
(Temperature 75°F, pH 7.6, SI 0.7, Alkalinity 80 ppm, Hardness 1250 ppm)

Effect of Cyanuric Acid – Data on the effect of cyanuric acid are shown in Table 7. The greater precipitation in the presence of cyanuric acid is due to the higher buffer intensity (Wojtowicz 1996).

Time (days)	Loss of Total Alkalinity (ppm)	
	CA = 0	CA = 100 ppm
1	11.4	22.6
2	17.0	26.9
4	21.2	30.0

Table 7 – Effect of Cyanuric Acid on Precipitation of $CaCO_3$
(Temperature 75°F, pH 7.6, SI 0.7, Carbonate Alkalinity 80 ppm, Seed crystals 0.3 ppm)

Precipitation of Calcium Carbonate in Swimming Pools

Although particulate matter (a potential source of seed crystals) is introduced into swimming pools by bathers, wind blown dust, some sanitizers, etc., homogeneous precipitation of calcium carbonate (i.e., cloudy water formation) is not a problem in well maintained pools. The combination of efficient filtration (at least one pool turnover per day) and periodic vacuuming of the pool reduces suspended and settled particulate matter to very low levels, resulting in low turbidity and sparkling water. However, heterogeneous precipitation of calcium carbonate (i.e., scale formation) can occur on plaster surfaces. Scaling is more prevalent in hard water areas such as the southwest. The higher the carbonate alkalinity and the higher the saturation index, the higher the extent of scaling.

Calcium hypochlorite contains small amounts of CaCO_3 (1–2%) and is a potential source of seed crystals. However, laboratory tests have shown that CaCO_3 largely dissolves when calcium hypochlorite is added to simulated pool water over the recommended saturation index range (i.e., 0–0.5) even at shock treatment dosage (equivalent to only 0.15–0.30 ppm CaCO_3). This is similar to the observation discussed earlier where freshly precipitated CaCO_3 dissolved completely even at an SI of 0.5. This indicates that the particle size of the CaCO_3 impurity in calcium hypochlorite is very small. It is recommended that the pH of swimming pool water be lowered to 7.2 to 7.4 prior to shock treatment and to continue recirculating the pool water through the filter for one pool turnover (6–8 hours) afterwards to ensure uniform dispersal of the sanitizer and removal of any residual suspended particulate matter.

Even if the swimming pool water balance and suspended solids concentration are favorable for

precipitation of calcium carbonate, water impurities such as magnesium ions, polyphosphates, chelating agents (such as citrate, phosphonate, etc.), and other organic matter can inhibit precipitation.

References

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About the Author

Now retired, **Mr. Wojtowicz** was a senior consulting scientist for Olin Corp. Seventeen of his 47 years of industrial experience was spent in the swimming pool chemical area and primarily involved swimming pool chemistry and process and product research on calcium hypochlorite, trichloroisocyanuric acid, and sodium dichloroisocyanurate. He holds over 55 U.S. patents and has published over 40 technical papers. He is currently a chemical consultant (Chemcon) residing at 60 Philson Court, Cheshire, CT 06410, phone #203–272–1479. His areas of expertise include swimming pool chemistry, manufacture and product and process development in hypochlorites and chloroisocyanurates, alternate sanitizers and sanitation systems (ozone, hydrogen peroxide–UV, bromine, etc.), chloramines and bromamines, computer programming, and expert witnessing.