# Corrections, Potential Errors, and Significance of the Saturation Index

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*Calculation of the saturation index requires a knowledge of the water temperature and the concentrations of total alkalinity, calcium hardness, and cyanuric acid. Total alkalinity must be corrected for cyanuric acid present as cyanurate ion as well as the concentrations of other significant alkaline species. In addition, the concentrations of complex forming ions other than bicarbonate such as sulfate and magnesium are required. Although these ions decrease the saturation index by reducing the concentrations of calcium hardness and carbonate alkalinity through ion pair formation, the effect is small except at very high levels of these ions.*

*Cumulative errors in typical swimming pool test kit analysis can result in a potential deviation in the calculated saturation index of ±0.14 for water with 120 ppm total alkalinity, 300 ppm calcium hardness, and 100 ppm cyanuric acid.*

*The saturation index is not a corrosion index but rather a scaling index, i.e., it is an indicator of the calcium carbonate scaling or scale dissolving tendency of water and not of corrosion.*

## Effect of Complex Formation

The typical saturation index calculation does not take into account the effect of ion pair formation. Ion pairs are partially ionized complexes. Ion pair formation reduces the concentration of alkalinity and hardness and therefore will affect the saturation index. Table 2 shows computer calculated values of the percent complexation of metal ions by bicarbonate, carbonate, and sulfate ions for water with the composition in Table 1.

The calculated data in Table 2 show that $CaHCO_3^+$

| Temperature | 85 °F | $Mg^{2+}$ | 20 ppm |
|---|---|---|---|
| pH | 7.5 | $Na^+$ | 220 ppm |
| Total alkalinity | 120 ppm | $SO_4^{2-}$ | 50 ppm |
| Hardness | 300 ppm | TDS | 1000 ppm |
| Cyanuric acid | 50 ppm | | |

## Table 1 – Example Water for Ion Pair Formation Calculation

| Ion Pair Formation Reaction | Log Equilibrium Constant* | % Complexation of Metal Ion |
|---|---|---|
| $Ca^{2+} + HCO_3^- \rightleftharpoons CaHCO_3^+$ | 1.106 | 1.32 |
| $Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3^\circ$ | 3.224 | 0.02 |
| $Ca^{2+} + SO_4^{2-} \rightleftharpoons CaSO_4^\circ$ | 2.30 | 2.07 |
| $Mg^{2+} + HCO_3^- \rightleftharpoons MgHCO_3^+$ | 1.07 | 1.23 |
| $Mg^{2+} + CO_3^{2-} \rightleftharpoons MgCO_3^\circ$ | 2.98 | 0.02 |
| $Mg^{2+} + SO_4^{2-} \rightleftharpoons MgSO_4^\circ$ | 2.37 | 2.67 |
| $Na^+ + HCO_3^- \rightleftharpoons NaHCO_3^\circ$ | −0.25 | 0.08 |
| $Na^+ + CO_3^{2-} \rightleftharpoons NaCO_3^-$ | 1.27 | 0.001 |
| $Na^+ + SO_4^{2-} \rightleftharpoons NaSO_4^-$ | 0.70 | 0.11 |

*Stumm and Morgan 1996

## Table 2 – Complexation of Metal Ions By Various Anions

and $CaSO_4^\circ$ are the major calcium complexes formed in swimming pool water. Sulfate ion is a stronger complex former than bicarbonate ion. Although carbonate ion is the strongest ion pair former (based on its equilibrium constant) of the three anions considered, its concentration at normal pool pH is very low and thus its effect on the saturation index is negli-

gible. At the low magnesium ion concentrations found in most source waters, the effect of $MgHCO_3^+$ formation can be neglected. Although the sulfate ion concentration in source waters is generally low, the sulfate ion concentration increases with time in pools using sodium bisulfate for pH adjustment.

The effect of complex formation on the saturation index, based on the above example, is shown in Table 3. The effective concentrations of alkalinity and hardness are decreased resulting in a lower saturation index. Whereas, calcium and magnesium ions reduce the effective alkalinity, sulfate ions reduce the effective calcium hardness. Sulfate ions have a greater effect on the saturation index than magnesium ions as shown by the plot in Figure 1. Sulfate ion itself has a small effect on the increase in the saturation index which varies as follows: $\Delta SI$ is $-0.02$ and $-0.04$ at 100 and 200 ppm sulfate ion, respectively. The effect of sulfate ion is similar to that of bicarbonate ion on a parts per million basis. Except for precise work, the correction to the saturation index due to complex formation can be neglected at normal levels of alkalinity and moderate concentrations of magnesium and sulfate ions. However, at higher concentrations of magnesium and sulfate ions, a correction may be necessary.



**Figure 1 – Saturation Index Correction vs. ppm $Mg^{2+}$ and $SO_4^{2-}$**

|  | Original Value | Corrected Value |
|---|---|---|
| Carb. Alkalinity, ppm | 103.7 | 100.7 |
| Ca Hardness, ppm | 300 | 289.8 |
| Saturation Index | 0.17 | 0.14 |

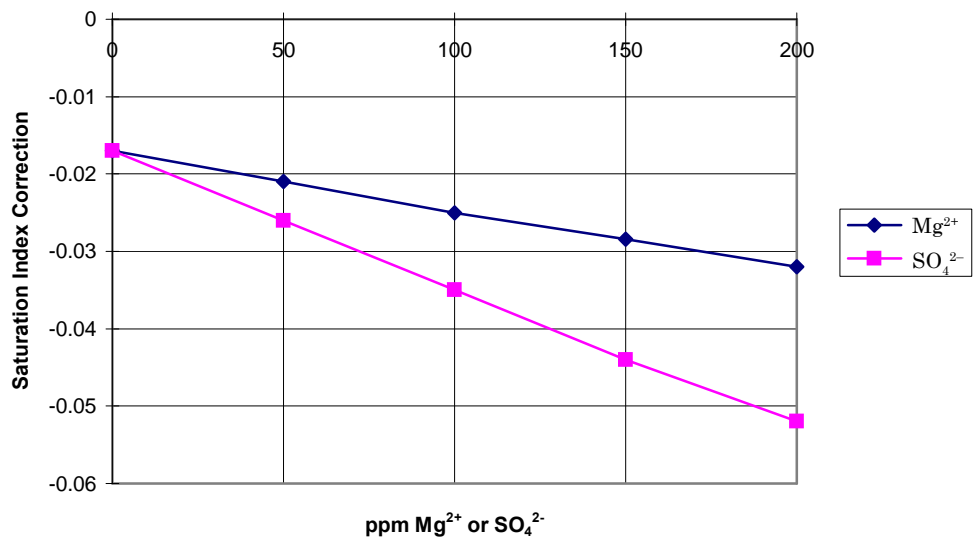## Table 3 – Effect of Complex Formation on Alkalinity, Hardness, and Saturation Index

## Calculation of the Saturation Index

Calculation of the saturation index requires the following measurements and analytical data:

a) water temperature

b) pH measured at the temperature of the pool or spa water

c) total alkalinity

d) calcium hardness

e) concentration of cyanuric acid and other alkaline substances present in significant amounts, e.g., borate

f) total dissolved solids or conductivity

In addition to the pH, total alkalinity, Ca hardness, cyanuric acid, and TDS measurements, the following corrections are necessary:

a) correct total alkalinity for cyanurate ion and other alkaline substances (Wojtowicz 1995):

$$Alk_{corr} = Alk_{tot} - 1/3 \cdot ppm\ CA$$

b) select temperature correction term TC from Table or plot or calculate using the equation (Wojtowicz 1997):

$$TC = -0.276 + 0.00861 \cdot {}^{\circ}F$$

c) ionic strength correction: select value of C from Table (Wojtowicz 1997) or calculate by the equation:

$$C = -11.30 - 0.333 \cdot Log\ TDS$$

d) ion pair formation: corrections for $Mg^{2+}$ and for $SO_4^{2-}$ in water with approximately 100 ppm carbonate alkalinity can be obtained from Figure

1 or calculated by the equation:

$$\Delta SI = -0.017 - 7.5 \cdot 10^{-5} \cdot Mg^{2+} - 1.8 \cdot 10^{-4} \cdot SO_4^{2-}$$

## Potential Effect Of Test Kit Analysis Errors On The Saturation Index

Table 4 shows the effect of potential errors in typical swimming pool test kit analysis on the calculated value of the saturation index. If all of the errors are in the same direction, the cumulative deviation in the saturation index can amount to ±0.14. Use of pH meters for pH measurement, digital titrators for alkalinity and hardness, and photometers for CA determination can reduce analytical errors to a minimum.

| Parameter | Level | Potential Error | Effect On SI |
|---|---|---|---|
| pH | | ±0.1 | ±0.1 |
| T. Alkalinity | 120 ppm | ±10 ppm | ±0.05[a] |
| Ca Hardness | 300 ppm | ±10 ppm | ±0.0145[a] |
| Cyanuric Acid | 100 ppm | ±15 ppm[b] | ±0.025[a,d] |
| Borate | 100 ppm | [c] | |

a) Calculated assuming other variables are constant.

b) The error in cyanuric acid measurement is ±15%.

c) Since boric acid is only slightly ionized at pool pH, the contribution of analytical errors is negligible.

d) The effect of the error in cyanuric acid measurement is opposite in sign to that caused by errors in alkalinity or hardness.

## Table 4 – Effect Of Test Kit Analysis Errors On The Saturation Index

### Significance of the Saturation Index

According to Langelier (1936), "The saturation index is an indication of directional tendency and of driving force but not of capacity". That is, the saturation index does not predict the quantity of calcium carbonate that can precipitate or dissolve under given conditions (Wojtowicz 1996). The saturation index is not a corrosion index but rather a scaling index, i.e., it is an indicator of the carbonate scaling or carbonate scale dissolving tendency of water and not of corrosion.

Corrosion of metallic surfaces is influenced by many factors such as dissolved oxygen, chloride and sulfate ions, as well as alkalinity, hardness, buffer intensity, and the saturation index (Pisigan 1981).

Although calcium carbonate coatings can provide protection against corrosive water, formation of effective coatings may require special techniques (McCauley 1960).

Although Van Waters and Rogers (1964) state that SI values in the –0.5 to +0.5 range are acceptable in swimming pools, a negative SI should be avoided due to the possibility of etching of concrete, plaster, or grout surfaces.

## References

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