

Standard Methods for the Examination of Water and Wastewater

2330 CALCIUM CARBONATE SATURATION*#(1)

2330 A. Introduction

1. General Discussion

Calcium carbonate (CaCO_3) saturation indices commonly are used to evaluate the scale-forming and scale-dissolving tendencies of water. Assessing these tendencies is useful in corrosion control programs and in preventing CaCO_3 scaling in piping and equipment such as industrial heat exchangers or domestic water heaters.

Waters oversaturated with respect to CaCO_3 tend to precipitate CaCO_3 . Waters undersaturated with respect to CaCO_3 tend to dissolve CaCO_3 . Saturated waters, i.e., waters in equilibrium with

CaCO_3 , have neither CaCO_3 -precipitating nor CaCO_3 -dissolving tendencies. Saturation represents the dividing line between “precipitation likely” and “precipitation not likely.”

Several water quality characteristics must be measured to calculate the CaCO_3 saturation indices described here. Minimum requirements are total alkalinity (2320), total calcium (3500-Ca), pH (4500- H^+), and temperature (2550). The ionic strength also must be calculated or estimated from conductivity (2510) or total dissolved solids (2540C) measurements. Measure pH at the system’s water temperature using a temperature-compensated pH meter. If pH is measured at a different temperature, for example in the laboratory, correct the measured pH.¹⁻³ In measuring pH and alkalinity, minimize CO_2 exchange between sample and atmosphere. Ideally, seal the sample from the atmosphere during measurements⁴; at a minimum, avoid vigorous stirring of unsealed samples.

There are two general categories of CaCO_3 saturation indices: indices that determine whether a water has a *tendency* to precipitate CaCO_3 (i.e., is oversaturated) or to dissolve CaCO_3 (i.e., is undersaturated) and indices that estimate the *quantity* of CaCO_3 that can be precipitated from an oversaturated water and the amount that can be dissolved by an undersaturated water. Indices in the second category generally yield more information but are more difficult to determine.

2. Limitations

It is widely assumed that CaCO_3 will precipitate from oversaturated waters and that it cannot be deposited from undersaturated waters. Exceptions may occur. For example, CaCO_3 deposition from oversaturated waters is inhibited by the presence of phosphates (particularly polyphosphates), certain naturally occurring organics, and magnesium.⁵⁻⁷ These materials can act as sequestering agents or as crystal poisons. Conversely, CaCO_3 deposits have been found in pipes conveying undersaturated water. This apparent contradiction is caused by high

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pH (relative to the bulk water pH) in the immediate vicinity of certain areas (cathodes) of corroding metal surfaces. A locally oversaturated condition may occur even if the bulk water is undersaturated. A small, but significant, amount of CaCO_3 can be deposited.

The calculations referred to here, even the most sophisticated computerized calculations, do not adequately describe these exceptions. For this reason, do not consider saturation indices as absolutes. Rather, view them as guides to the behavior of CaCO_3 in aqueous systems and supplement them, where possible, with experimentally derived information.

Similarly, the effects predicted by the indices do not always conform to expectations. The relationship between the indices and corrosion rates is a case in point. Conceptually, piping is protected when CaCO_3 is precipitated on its surfaces. CaCO_3 is believed to inhibit corrosion by clogging reactive areas and by providing a matrix to retain corrosion products, thus further sealing the surfaces. Waters with positive indices traditionally have been assumed to be protective while waters with negative indices have been assumed to be not protective, or corrosive. The expected relationship is observed sometimes,^{8,9} but not always.^{10,11} Unexpected results may be due in part to limited capability to predict CaCO_3 behavior. Also, water characteristics not directly involved in the calculation of the indices (e.g., dissolved oxygen, buffering intensity, chloride, sulfate, and water velocity) may influence corrosion rates appreciably.^{9,12-16} Thus, do not estimate corrosion rates on the basis of CaCO_3 indices alone.

3. References

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2330 B. Indices Indicating Tendency of a Water to Precipitate CaCO₃ or Dissolve CaCO₃

1. General Discussion

Indices that indicate CaCO₃ precipitation or dissolution tendencies define whether a water is oversaturated, saturated, or undersaturated with respect to CaCO₃. The most widely used indices are the Saturation Index (SI); the Relative Saturation (RS), also known as the Driving Force Index (DFI); and the Ryznar Index (RI). The SI is by far the most commonly used and will be described here. The RS and SI are related (see Equation 6, Section 2330D). The RI¹ has been used for many years, sometimes with good results. Because it is semi-empirical it may be less reliable than the SI.

2. Saturation Index by Calculation

SI is determined from Equation 1.

$$SI = pH - pH_s \quad (1)$$

where:

pH = measured pH and

pH_s = pH of the water if it were in equilibrium with CaCO₃ at the existing calcium ion [Ca²⁺] and bicarbonate ion [HCO₃⁻] concentrations.

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A positive SI connotes a water oversaturated with respect to CaCO_3 . A negative SI signifies an undersaturated water. An SI of zero represents a water in equilibrium with CaCO_3 .

a. *Analytical solution for pH_s* : Determine pH_s as follows²:

$$pH_s = pK_2 - pK_s + p[\text{Ca}^{2+}] + p[\text{HCO}_3^-] + 5 pf_m \quad (2)$$

where:

K_2 = second dissociation constant for carbonic acid, at the water temperature,

K_s = solubility product constant for CaCO_3 at the water temperature,

$[\text{Ca}^{2+}]$ = calcium ion concentration, g-moles/L,

$[\text{HCO}_3^-]$ = bicarbonate ion concentration, g-moles/L, and

f_m = activity coefficient for monovalent species at the specified temperature.

In Equation 2, p preceding a variable designates $-\log_{10}$ of that variable.

Calculate values of pK_2 , pK_s , and pf_m required to solve Equation 2 from the equations in Table 2330:I. To save computation time, values for pK_2 and pK_s have been precalculated for selected temperatures (see Table 2330:II).

Table 2330:II gives several values for pK_s . Different isomorphs of CaCO_3 can form in aqueous systems, including calcite, aragonite, and vaterite. Each has somewhat different solubility properties. These differences can be accommodated when computing pH_s simply by using the pK_s for the compound most likely to form. The form of CaCO_3 most commonly found in fresh water is calcite. Use the pK_s for calcite unless it is clear that a different form of CaCO_3 controls CaCO_3 solubility.

Estimate calcium ion concentration from total calcium measurements with Equation 3.

$$[\text{Ca}^{2+}] = Ca_t - Ca_{ip} \quad (3)$$

where:

Ca_t = total calcium, g-moles/L, and

Ca_{ip} = calcium associated with ion pairs such as CaHCO_3^+ , CaSO_4^0 , and CaOH^+ .

Calcium associated with ion pairs is not available to form CaCO_3 .

Estimate $[\text{HCO}_3^-]$, the bicarbonate ion concentration, from Equation 4.

$$[\text{HCO}_3^-] = \frac{Alk_t - Alk_o + 10^{(pf_m - pH)} - 10^{(pH + pf_m - pK_w)}}{1 + 0.5 \times 10^{(pH - pK_2)}} \quad (4)$$

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where:

Alk_t = total alkalinity, as determined by acid titration to the carbonic acid end point, g-equivalents/L,

K_w = dissociation constant for water, at the water temperature, and

Alk_o = alkalinity contributed by NH_3^0 , $H_3SiO_4^-$, HPO_4^{2-} , $B(OH)_4^-$, CH_3COO^- (acetate), HS^- , and ion pairs such as $CaHCO_3^+$ and $MgOH^+$. These contributions usually are small compared to the contributions of components normally considered (HCO_3^- , CO_3^{2-} , OH^- , and H^+).

Calculations can be simplified. For example, in Equation 4, terms containing exponents (e.g., $10^{(pH + pf_m - pk_w)}$) usually can be neglected for waters that are approximately neutral (pH 6.0 to 8.5) with alkalinity greater than about 50 mg/L as $CaCO_3$. The terms Ca_{ip} in Equation 3 and Alk_o in Equation 4 are difficult to calculate without computers. Therefore they usually are neglected for hand calculations. The simplified version of Equation 2 under such conditions is:

$$pH_s = pK_2 - pK_s + p[Ca_t] + p[Alk_t] + 5 pf_m$$

1) Sample calculation—The calculation is best illustrated by working through an example. Assume that calcite controls $CaCO_3$ solubility and determine the SI for a water of the following composition:

Constituent	Concentration		
	mg	÷ mg mole	= g-moles/L
Calcium	152	40 000	3.80×10^{-3}
Magnesium	39	24 312	1.60×10^{-3}
Sodium	50	22 989	2.18×10^{-3}
Potassium	5	39 102	1.28×10^{-4}
Chloride	53	35 453	1.49×10^{-3}
Alkalinity (as $CaCO_3$)	130	50 000	$2.60 \times 10^{-3*}$
Sulfate	430	96 060	4.48×10^{-3}
Silica (as SiO_2)	15	60 084	2.50×10^{-4}

*g-equivalents.

Water temperature = 20°C (293.2°K); pH = 9.00.

Before evaluating pf_m in Equation 2, determine the ionic strength (I) and another

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constant (A). Estimate ionic strength from the first equation of Table 2330:I, assuming all the alkalinity is due to bicarbonate ion. Use the alkalinity concentration (2.60×10^{-3}) and the bicarbonate charge (-1) to calculate the contribution of alkalinity to ionic strength. Assume silica is mostly H_4SiO_4 . Because H_4SiO_4 has zero charge, silica does not contribute to ionic strength.

$$\begin{aligned} I &= 0.5 [4(3.80 \times 10^{-3}) + 4(1.60 \times 10^{-3}) + 2.18 \times 10^{-3} + \\ &\quad 1.28 \times 10^{-4} + 1.49 \times 10^{-3} + 2.60 \times 10^{-3} \\ &\quad + 4(4.48 \times 10^{-3})] \\ &= 2.29 \times 10^{-2} \text{ g-moles/L} \end{aligned}$$

In the absence of a complete water analysis, estimate ionic strength from conductivity or total dissolved solids measurements (see alternative equations, Table 2330:I).

Estimate A from the equation in Table 2330:I, after first determining the dielectric constant E from the formula in the same table. Alternatively, use precalculated values of A in Table 2330:II. In Table 2330:II, $A = 0.506$ at 20°C .

Next estimate pf_m from the equation in Table 2330:I

$$\begin{aligned} pf_m &= 0.506 \\ &\times \left[\frac{\sqrt{2.29 \times 10^{-2}}}{1 + \sqrt{2.29 \times 10^{-2}}} - 0.3 (2.29 \times 10^{-2}) \right] \\ &= 0.063 \end{aligned}$$

Determine $[\text{HCO}_3^-]$ from Equation 4. Neglect Alk_o , but because the pH exceeds 8.5, calculate the other terms. From Table 2330:II, $pK_2 = 10.38$ and $pK_w = 14.16$.

$$\begin{aligned} [\text{HCO}_3^-] &= \frac{2.60 \times 10^{-3} + 10^{(0.063 - 9.0)} - 10^{(9.0 + 0.063 - 14.16)}}{1 + 0.5 \times 10^{(9.0 - 10.38)}} \\ &= 2.54 \times 10^{-3} \text{ g-moles/L} \end{aligned}$$

Therefore $p[\text{HCO}_3^-] = 2.60$.

Determine $[\text{Ca}^{2+}]$ from Equation 3. Neglect Ca_{ip} .

$$[\text{Ca}^{2+}] = Ca_t = 3.80 \times 10^{-3} \text{ g-moles/L}$$

Therefore $p[\text{Ca}^{2+}] = 2.42$.

From Table 2330:II, pK_s for calcite is 8.45.

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Determine pH_s from Equation 2:

$$pH_s = 10.38 - 8.45 + 2.42 + 2.60 + 5(0.063) = 7.27$$

And finally, determine SI from Equation 1:

$$SI = 9.00 - 7.27 = 1.73$$

The positive SI indicates the water is oversaturated with respect to calcite.

2) Effect of neglecting Ca_{ip} and Alk_o —If Ca_{ip} is neglected, pH_s is underestimated and SI is overestimated by an amount equal to $p(1 - Y_{Ca_{ip}})$, where $Y_{Ca_{ip}}$ is the fraction of total calcium in ion pairs. For example, if $Y_{Ca_{ip}} = 0.30$ then the estimate for SI is 0.15 units too high. Similarly, if Alk_o is neglected, SI is overestimated by an amount equal to $p(1 - Y_{Alk_o})$, where Y_{Alk_o} is the fraction of total alkalinity contributed by species other than HCO_3^- , CO_3^{2-} , OH^- , and H^+ . The effects of neglecting Ca_{ip} and Alk_o are additive.

Ca_{ip} and Alk_o may be neglected if the factors $Y_{Ca_{ip}}$ and Y_{Alk_o} are small and do not interfere with interpretation of the SI . The factors are small for waters of low and neutral pH, but they increase as pH values approach and exceed 9. At high pH values, however, the SI is typically much larger than its overestimate, so neglecting Ca_{ip} and Alk_o causes no problem. To return to the example above, when calculations were done with a computerized water chemistry code (SEQUIL) (see Table 2330:III) that considers Ca_{ip} and Alk_o , the SI was 1.48, i.e., 0.25 units lower than the result obtained by hand calculations. In this instance, neglecting Ca_{ip} and Alk_o did not interfere with interpreting the result. Both calculations showed the water to be strongly oversaturated.

The potential for misinterpretation is most acute in nearly-saturated waters of high sulfate concentration. Recirculating cooling water is an example. Calcium is sequestered by the robust $CaSO_4^0$ ion pair and the SI can be overestimated by as much as 0.3 to 0.5 units, even at neutral pH. Under these conditions, the SI may be thought to be zero (neither scale-forming or corrosive) when in fact it is negative.

Resolve this problem by determining pH_s using computerized water chemistry codes that consider ion pairs and the other forms of alkalinity. Section 2330D provides information about water chemistry codes. The most accurate calculations are obtained when a complete mineral analysis is provided.

An alternative but somewhat less rigorous procedure involves direct measurement of (Ca^{2+}) , the calcium ion activity, with a calcium specific-ion electrode.⁹ Use Equation 5 to determine $p[Ca^{2+}]$; then use $p[Ca^{2+}]$ in Equation 2.

$$p[Ca^{2+}] = p(Ca^{2+}) - 4pf_m \quad (5)$$

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This approach eliminates the need to determine Ca_{ip} . However, no equivalent procedure is available to bypass the determination of Alk_o .

b. Graphical solutions for pH_s : Caldwell-Lawrence diagrams can be used to determine pH_s .¹⁰⁻¹² The diagrams are particularly useful for estimating chemical dosages needed to achieve desired water conditions. Consult the references for descriptions of how to use the diagrams; see Section 2330D for additional information about the diagrams.

3. Saturation Index by Experimental Determination

a. Saturometry: Saturometers were developed to measure the relative saturation of seawater with respect to $CaCO_3$. A water of known calcium and pH is equilibrated with $CaCO_3$ in a sealed flask containing a pH electrode. The water temperature is controlled with a constant-temperature bath. During equilibration the pH decreases if $CaCO_3$ precipitates and increases if $CaCO_3$ dissolves. When the pH stops changing, equilibrium is said to have been achieved. The initial pH and calcium values and the final pH value are used to calculate the relative saturation (RS).¹³ Equation 6, Section 2330D, may then be used to determine SI.

A major advantage of this method is that the approach to equilibrium can be tracked by measuring pH, thus minimizing uncertainty about the achievement of equilibrium. The method is most sensitive in the range of minimum buffering intensity (pH 7.5 to 8.5). The calculations do not consider ion pairs or noncarbonate alkalinity, except borate. The technique has been used for *in situ* oceanographic measurements¹⁴ as well as in the laboratory.

The saturometry calculations discussed above use K_s of the $CaCO_3$ phase assumed to control solubility. Uncertainties occur if the identity of the controlling solid is unknown. Resolve these uncertainties by measuring K_s of the controlling solid. It is equal to the $CaCO_3$ activity product, $[Ca^{2+}] \times [CO_3^{2-}]$, at equilibrium. Calculate the latter from the equilibrium pH and initial calcium, alkalinity, and pH measurements.¹⁵

*b. Alkalinity difference technique:*¹⁶ SI also can be determined by equilibrating water of known pH, calcium, and alkalinity with $CaCO_3$ in a sealed, constant-temperature system. The $CaCO_3$ activity product before equilibration is determined from initial calcium, pH, and alkalinity (or total carbonate) values. The $CaCO_3$ solubility product constant (K_s) equals the $CaCO_3$ activity product after equilibration, which is determined by using the alkalinity change that occurred during equilibration. RS is found by dividing the initial activity product by K_s . Calculate SI by using Equation 6 (see Section 2330D.1). The advantage of this method is that it makes no assumptions about the identity of the $CaCO_3$ phase. However it is more difficult to determine when equilibrium is achieved with this method than with the saturometry method.

Whatever the method used, use the temperatures that are the same as the temperature of the water source. Alternatively, correct test results to the temperature of the water source.¹⁶

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2330 C. Indices Predicting the Quantity of CaCO_3 That Can Be Precipitated or Dissolved

The Calcium Carbonate Precipitation Potential (CCPP) predicts both tendency to precipitate or to dissolve CaCO_3 and quantity that may be precipitated or dissolved. The CCPP also is known by other names, e.g., Calcium Carbonate Precipitation Capacity (CCPC).

The CCPP is defined as the quantity of CaCO_3 that theoretically can be precipitated from oversaturated waters or dissolved by undersaturated waters during equilibration.¹ The amount that actually precipitates or dissolves may be less, because equilibrium may not be achieved. The CCPP is negative for undersaturated waters, zero for saturated waters, and positive for oversaturated waters.

1. Calculating CCPP

The CCPP does not lend itself to hand calculations. Preferably calculate CCPP with computerized water chemistry models and Caldwell-Lawrence diagrams (see Section 2330D).

The most reliable calculations consider ion pairs and the contribution to alkalinity of other species besides HCO_3^- , CO_3^{2-} , OH^- , and H^+ . Models that do not consider these factors overestimate the amount of CaCO_3 that can be precipitated and underestimate the amount of CaCO_3 that can be dissolved.

2. Experimental Determination of CCPP

Estimate CCPP by one of several experimental techniques.

a. Saturometry: See Section 2330B. The CCPP is determined as part of the RS calculation.

b. Alkalinity difference technique: See Section 2330B. The CCPP equals the difference between alkalinity (or calcium) values of the initial and equilibrated water, when they are expressed as CaCO_3 .

c. Marble test: The marble test¹⁻⁵ is similar to the alkalinity difference technique. The CCPP equals the change in alkalinity (or calcium) values during equilibration, when they are expressed as CaCO_3 .

d. Enslow test: The Enslow test⁵ is a continuous version of the alkalinity difference or marble tests. Water is fed continuously to a leveling bulb or separatory funnel partly filled with CaCO_3 . The effluent from this device is filtered through crushed marble so that the filtrate is assumed to be in equilibrium with CaCO_3 . The CCPP equals the change in alkalinity (or calcium) values that occurs during passage through the apparatus.

*e. Calcium carbonate deposition test:*⁶ The calcium carbonate deposition test (CCDT) is

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an electrochemical method that measures the electric current produced when dissolved oxygen is reduced on a rotating electrode. When an oversaturated water is placed in the apparatus, CaCO_3 deposits on the electrode. The deposits interfere with oxygen transfer and the current diminishes. The rate of CaCO_3 deposition is directly proportional to the rate at which the current declines. The CCDT and the CCPP are related, but they are not the same. The CCDT is a rate, and the CCPP is a quantity.

For realistic assessments of the CCPP (or CCDT) keep test temperature the same as the temperature of the water source. Alternatively, correct test results to the temperature of the water source.

3. References

1. MERRILL, D.T. & R.L. SANKS. 1978, 1979. Corrosion control by deposition of CaCO_3 films: A practical approach for plant operators. *J. Amer. Water Works Assoc.* 70:592; 70:634 & 71:12.
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2330 D. Diagrams and Computer Codes for CaCO_3 Indices

1. Description

Table 2330:III lists diagrams and computer codes that can be used to determine the SI and CCPP. It also provides a brief description of their characteristics.

Many computer codes do not calculate *SI* directly, but instead calculate the relative saturation (*RS*). When *RS* data are presented, calculate the *SI* from:¹

$$SI = \log_{10}RS \quad (6)$$

where:

RS = ratio of CaCO_3 activity product to CaCO_3 solubility product constant.

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The diagrams and a few of the codes define pH_s as the pH the water would exhibit if it were in equilibrium with CaCO_3 at the existing calcium and total alkalinity concentrations.² This definition of pH_s differs from the definition following Equation 1 because alkalinity is used instead of bicarbonate. Within the pH range 6 to 9, alkalinity-based pH_s and bicarbonate-based pH_s are virtually equal, because total alkalinity is due almost entirely to bicarbonate ion. Above pH 9 they differ and Equation 6 no longer applies if SI is calculated with alkalinity-based pH_s . However, if SI is determined from bicarbonate-based pH, Equation 6 continues to apply.

Furthermore, calculating SI with alkalinity-based pH_s reverses the sign of the SI above pH values of approximately pK_2 , i.e., a positive, not the usual negative, SI connotes an undersaturated water.³ With bicarbonate-based pH_s or RS , sign reversal does not occur, thereby eliminating the confusing sign change. For these reasons, bicarbonate-based pH_s or RS is preferred. Table 2330:III lists the definition of pH_s used for each code.

Some models calculate only the amount of CaCO_3 that can be precipitated but not the amount of CaCO_3 that can be dissolved. Others calculate both.

The diagrams and codes can be used to determine many more parameters than the CaCO_3 saturation indices. A fee may be charged for computer software or graphs. The information in Table 2330:III describes parameters each code uses to calculate SI . Contact the sources listed below the table for current information.

2. References

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Endnotes

1 (Popup - Footnote)

* APPROVED BY STANDARD METHODS COMMITTEE, 1993.