Select the smaller value of *P* or (*T*–*P*). Then, carbonate alkalinity equals twice the smaller value. When the smaller value is *P*, the balance (*T*–2*P*) is bicarbonate. When the smaller value is (*T*–*P*), the balance (2*P*–*T*) is hydroxide. All results are expressed as $CaCO_3$. The mathematical conversion of the results is shown in Table 2320:2. (A modification of Table 2320:2 that is more accurate when $P \simeq ½T$ has been proposed.[4])

Alkalinity relationships also may be computed nomographically (see Carbon Dioxide, Section 4500-CO_2). Accurately measure pH, calculate OH^- concentration as milligrams $CaCO_3$ per liter, and calculate concentrations of CO_3^{2-} and HCO_3 as milligrams $CaCO_3$ per liter from the OH^- concentration, and the phenolphthalein and total alkalinities by the following equations:

$$CO_3^{2-} = 2P - 2\left[OH^-\right]$$

$$HCO_3^- = T - 2P + \left[OH^-\right]$$

Similarly, if difficulty is experienced with the phenolphthalein endpoint, or if a check on the phenolphthalein titration is desired, calculate phenolphthalein alkalinity as $CaCO_3$ from the results of the nomographic determinations of carbonate and hydroxide ion concentrations:

$$P = 1/2\left[CO_3^{2-}\right] + \left[OH^-\right]$$

6. Precision and Bias

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before the analysis.

In the range of 10 to 500 mg/L, when the alkalinity is due entirely to carbonates or bicarbonates, a standard deviation of 1 mg/L $CaCO_3$ can be achieved. Forty analysts in 17 laboratories analyzed synthetic samples containing increments of bicarbonate equivalent to 120 mg/L $CaCO_3$. The titration procedure of 2320 B.4*b* was used, with an endpoint pH of 4.5. The standard deviation was 5 mg/L and the average bias (lower than the true value) was 9 mg/L.[5]

Sodium carbonate solutions equivalent to 80 and 65 mg/L $CaCO_3$ were analyzed by 12 laboratories according to the procedure of 2320 B.4*c*.[6] The standard deviations were 8 and 5 mg/L, respectively, with negligible bias.[6] Four laboratories analyzed 6 samples having total alkalinities of about 1000 mg/L $CaCO_3$ and containing various ratios of carbonate:bicarbonate by the procedures of both 2320 B.4*a* and *c*. The pooled standard deviation was 40 mg/L, with negligible difference between the procedures.

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2330

CALCIUM CARBONATE SATURATION

Approved by Standard Methods Committee, 2016. Editorial revisions, 2021. Joint Task Group: John D. Kenny (chair), Paul J. Kemp, Devon A. Morgan, Stephen J. Randtke, William R. Ray, Ravindra M. Srivastava, Lawrence K. Wang.

2330 A. INTRODUCTION

1. General Discussion

Calcium carbonate ($CaCO_3$) saturation indices are commonly used to evaluate a water's scale-forming and scale-dissolving tendencies to help prevent $CaCO_3$ scaling in piping and equipment (e.g., industrial heat exchangers or domestic water heaters). The indices can be applicable in reducing corrosion in iron, steel, and cement piping, but not in controlling lead and copper release.

Water oversaturated with $CaCO_3$ tends to precipitate $CaCO_3$. Water undersaturated with $CaCO_3$ tends to dissolve it. Saturated water (i.e., water in equilibrium with $CaCO_3$) tends neither to precipitate nor dissolve $CaCO_3$. Saturation is the dividing line between where precipitation tends to occur (likely) or not occur (not likely). Dissolved total alkalinity (Section 2320), total calcium (Section 3500-Ca), pH (Section 4500-H$^+$), and temperature (Section 2550) must be measured to calculate the $CaCO_3$ saturation indices described here. Ionic strength also must be calculated or estimated from total dissolved solids (TDS) (Section 2540 C) or conductivity (Section 2510) measurements.

Measure pH at the system's water temperature using a temperature-compensated pH meter. If pH is measured at a different temperature in the laboratory, for example, correct the measured pH.[1–7] When measuring pH, minimize CO_2 exchange between sample and atmosphere. Ideally, seal the sample from the atmosphere during measurements.[8] At a minimum, avoid vigorously stirring unsealed samples.

There are two general categories of $CaCO_3$ saturation indices:

- indices that determine whether a water has a *tendency* to precipitate or to dissolve $CaCO_3$, and
- indices that estimate the *quantity* of $CaCO_3$ that can be precipitated or dissolved.

2. Limitations

It is widely assumed that $CaCO_3$ precipitates from oversaturated waters and cannot be deposited by undersaturated waters, but there are exceptions. For example, phosphates (particularly polyphosphates), certain naturally occurring organics, sulfate, magnesium, and some trace metals (e.g., zinc) can act as sequestering agents or crystal poisons, inhibiting oversaturated waters from depositing $CaCO_3$.[9–12] Conversely, $CaCO_3$ deposits have been found in pipes conveying undersaturated water due to high pH (relative to bulk water pH) next to certain areas (cathodes) of corroding metal surfaces. Even if the bulk water is undersaturated, a locally oversaturated condition can cause a small, but significant, amount of $CaCO_3$ to be deposited.

The calculations referred to here—even the most sophisticated computerized calculations—do not adequately describe these exceptions, so 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.

Waters with positive indices are sometimes assumed to be protective, while waters with negative indices are sometimes assumed to be corrosive. In actuality, this relationship is observed with some materials,[13,14] but not with others.[15,16] The indices can relate to corrosion rates through the clogging of reactive areas by $CaCO_3$ precipitation, which can provide a matrix to retain corrosion products, further sealing surfaces. Calcium carbonate scales can reduce corrosion of unlined iron pipe; however, water characteristics not directly involved in calculating the indices [e.g., dissolved oxygen (DO), buffering intensity, chloride, sulfate, and water velocity] can influence corrosion rates appreciably.[12,14,17–22] Calcium carbonate scales can also reduce the release of free lime in cement-mortar-lined and asbestos-cement pipes. Significant $CaCO_3$ films rarely deposit on lead, galvanized, and copper cold-water pipes.[12,22] Calcium carbonate saturation indices are not predictive of corrosion for lead, copper, or leaded brass pipes.[23–25] While the U.S. Environmental Protection Agency required community water-supply systems to determine $CaCO_3$ saturation indices from 1980 to 1994, the requirement was appealed in 1994 due to misuse as corrosion indices.[25]

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2330 B. INDICES INDICATING A WATER'S TENDENCY TO PRECIPITATE OR DISSOLVE $CaCO_3$

1. General Discussion

Indices that indicate $CaCO_3$ precipitation or dissolution tendencies define whether a water is oversaturated, saturated, or undersaturated with $CaCO_3$. The most widely used indices are the Saturation Index (SI), Relative Saturation (RS) [also known as the *Driving Force Index* (DFI) and the *Saturation Ratio* (SR)], and the Ryznar Index (RI). The SI is by far the most commonly used and is described here.

The RS and SI are related (2330 D.1, Equation 7). The RI[1] has been used for many years, sometimes with good results. Because it is semi-empirical, however, it may be less reliable than the SI.

2. Saturation Index by Calculation

SI is determined from Equation 1:

$$SI = pH - pH_s \tag{1}$$

where:

pH = measured pH, and
pH_s = pH of the water if it were in equilibrium with $CaCO_3$ at the existing calcium ion $[Ca^{2+}]$ and bicarbonate ion $[HCO_3^-]$ concentrations.

Table 2330:1. Estimating Equilibrium Constants and Activity Coefficients

Equation	Temperature Range (K)	References
When complete mineral analysis is available:		
$I = 1/2\sum_{i=1}^{i}[X_i]Z_i^2$	–	1
When a complete mineral analysis is not available: $I = TDS/40{,}000$	–	2
When only conductivity is available: $I = 1.6 \times 10^{-5}\, C$	–	3
$pf_m = A\left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right]$ (valid to $I < 0.5$)	–	1
$A = 1.82 \times 10^6\,(ET)^{-1.5}$	–	1
$E = 308.67e^{-0.0045976(T)}$	273–373	4
$pK_1 = 356.3094 + 0.06091964\,T - 21\,834.37/T - 126.8339\,\log_{10}T + 1\,684\,915/T^2$	273–373	5
$pK_2 = 107.8871 + 0.03252849\,T - 5\,151.79/T - 38.92561\,\log_{10}T + 563\,713.9/T^2$	273–373	5
$pK_w = 4470.99/T + 0.017060\,T - 6.0875$	273–333	6
$pK_{sc} = 171.9065 + 0.077993\,T - 2\,839.319/T - 71.595\,\log_{10}T$	273–363	5
$pK_{sa} = 171.9773 + 0.077993\,T - 2\,903.293/T - 71.595\,\log_{10}T$	273–363	5
$pK_{sv} = 172.1295 + 0.077993\,T - 3\,074.688/T - 71.595\,\log_{10}T$	273–363	5

I = ionic strength; $[X_i]$ = concentration of component i (moles/L); Z_i = charge of species i; TDS = total dissolved solids (mg/L); C = conductivity (µmhos/cm); $pY = -\log_{10}$ of the value of any factor Y; f_m = activity coefficient for monovalent species; E = dielectric constant; T = temperature, K (°C + 273.15); K_1 = first dissociation constant for carbonic acid, including $CO_{2(aq)}$; K_2 = second dissociation constant for carbonic acid; K_w = dissociation constant for water; K_{sc} = solubility product constant for calcite; K_{sa} = solubility product constant for aragonite; K_{sv} = solubility product constant for vaterite.

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If SI is positive, the water is oversaturated with $CaCO_3$; if negative, the water is undersaturated. If SI is zero, the water is in equilibrium with $CaCO_3$.

a. Analytical solution for pH_s: Determine pH_s as follows:[2]

$$pH_s = pK_2 - pK_s + p\left[\mathrm{Ca}^{2+}\right] + p\left[\mathrm{HCO_3}^-\right] + 5\,pf_m \tag{2}$$

where:

p = when preceding a variable, designates $-\log_{10}$ of that variable,
K_2 = second dissociation constant for carbonic acid at water temperature,
K_s = solubility product constant for $CaCO_3$ at water temperature,
$[Ca^2+]$ = calcium ion concentration (moles/L),
$[HCO_3^-]$ = bicarbonate ion concentration (moles/L), and
f_m = activity coefficient for monovalent species at the specified temperature.

Using the equations in Table 2330:1, calculate the values of pK_2, pK_s, and pf_m required to solve Equation 2. To save computation time, values for pK_2 and pK_s have been precalculated for selected temperatures (Table 2330:2). Table 2330:2 gives several values for pK_s because different isomorphs of $CaCO_3$ (e.g., calcite, aragonite, and vaterite) can form in aqueous systems, and each has somewhat different solubility properties. To accommodate for such differences when computing pH_s, use the pK_s for the compound most likely to form. For example, calcite is the form of $CaCO_3$ most commonly found in fresh water.

Estimate the calcium ion concentration from total calcium measurements as follows:

$$\left[Ca^{2+}\right] = Ca_t - Ca_{ip} \tag{3}$$

where:

Ca_t = total calcium (moles/L) and
Ca_{ip} = calcium associated with ion pairs (e.g., $CaHCO_3^+$, $CaSO_4^0$, and $CaOH^+$).

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

Estimate $[HCO_3^-]$, the bicarbonate ion concentration, as follows:[3]

$$\left[\mathrm{HCO_3}^-\right] = \frac{Alk_t - Alk_0 + 10^{(pf_m - pH)} - 10^{(pH + pf_m - pK_w)}}{1 + 2\times 10^{(pH + 3pf_m - pK_2)}} \tag{4}$$

where:

Alk_t = total alkalinity, as determined by acid titration to the carbonic acid endpoint, equivalents/L;
Alk_o = alkalinity contributed or consumed by NH_3^0, $H_3SiO_4^-$, $H_2SiO_4^{2-}$, HPO_4^{2-}, PO_4^{3-}, H_3PO_4, $B(OH)_4^-$, CH_3COO^- (acetate), HS^-, S^{2-}, ion pairs (e.g., $CaHCO_3^+$ and $MgOH^+$), and other species that neutralize strong acid when titrating to the carbonic acid endpoint, which can include organic acids (e.g., fulvic and humic acids) with equivalents/L contributions that are usually small compared to those of (HCO_3^-, CO_3^{2-}, OH^-, and H^+); and
K_w = dissociation constant for water, at water temperature.

Calculations can be simplified. In Equation 4 for example, terms containing exponents [e.g., $10^{(pH + pfm - pkw)}$] usually can be neglected for waters whose pH is 6.0 to 8.5 and alkalinity is more 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, so they usually are neglected in hand calculations. The simplified version of Equation 2 under such conditions is:

$$pH_s = pK_2 - pK_s + p[Ca_t] + p[Alk_t] + 5pf_m \tag{5}$$

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 with the following composition:

Constituent	Calculate Molar Concentration (mg/L ÷ mg/mole = moles/L)		
Calcium	152	40 078	3.79×10^3
Magnesium	39	24 305	1.60×10^3
Sodium	50	22 990	2.17×10^3
Potassium	5	39 098	1.28×10^4
Chloride	53	35 450[a]	1.50×10^3
Alkalinity (as $CaCO_3$)	130	50 000[b]	2.60×10^3[c]
Sulfate	430	96 060[a]	4.48×10^{-3}
Silica (as SiO_2)	15	60 083[a]	2.50×10^{-3}

[a] Based on conventional atomic weights. See Haynes WM, ed. CRC handbook of chemistry and physics, 96th ed. Boca Raton (FL): CRC Press; 2015.

[b] Although a more accurate value of the equivalent weight of $CaCO_3$ can be calculated from standard atomic weights, a value of 50 000 should be used because that is the value used to convert the results of an alkalinity titration into an alkalinity concentration in units of mg/L as $CaCO_3$ (Section 2320 B).

[c] Equivalents/L.

Note: Water temperature = 20 °C (293.15K); pH = 9.00.

Before evaluating pf_m in Equation 2, determine the ionic strength (I) and another constant (A). Using the first equation in Table 2330:1, estimate the ionic strength assuming all the alkalinity is due to bicarbonate ion (an assumption that introduces only a small error at pH 9.00). Use the alkalinity concentration (2.60×10^{-3}) and the bicarbonate charge (−1) to calculate alkalinity's contribution to ionic strength. Likewise, assume silica is mostly H_4SiO_4 at pH 9.00, as the other species typically can be neglected when pH is ≤9. Because H_4SiO_4 has zero charge, it does not contribute to ionic strength.

$$\begin{aligned} I = \tfrac{1}{2}\sum_{i=1}^{i}[X_i]Z_i^2 &= 0.5\times\Big[\left(3.79\times10^{-3}\right)\times2^2 + \left(1.60\times10^{-3}\right)\times2^2 \\ &+ \left(2.17\times10^{-3}\right)\times1^2 + \left(1.28\times10^{-4}\right)\times1^2 + \left(1.50\times10^{-3}\right)\times1^2 \\ &+ \left(2.60\times10^{-3}\right)\times1^2 + \left(4.48\times10^{-3}\right)\times2^2\Big] = 2.29\times10^{-2}\ \text{moles/L} \end{aligned}$$

In the absence of a complete water analysis, estimate ionic strength from TDS measurements or, as a last resort, from conductivity (see alternative equations in Table 2330:1).

Determine the dielectric constant E and then estimate A (see equations in Table 2330:1). Alternatively, use precalculated values of A in Table 2330:2 (e.g., $A = 0.505$ at 20 °C).

Next, estimate pf_m using the equation in Table 2330:1:

$$pf_m = 0.505\times\left[\frac{\sqrt{2.29\times10^{-2}}}{1+\sqrt{2.29\times10^{-2}}}-0.3\left(2.29\times10^{-2}\right)\right]=0.063$$

Determine $[HCO_3^-]$ from Equation 4. Neglect Alk_o, but because the pH is >8.5, calculate the other terms. Table 2330:2 indicates that $pK_2 = 10.38$ and $pK_w = 14.16$.

$$\left[HCO_3^-\right]=\frac{2.60\times10^{-3}+10^{(0.063-9.00)}-10^{(9.00+0.063-14.16)}}{1+2\times10^{[9.00+3(0.063)+10.38]}}$$
$$=2.30\times10^{-3}\ \text{moles / L}$$

Therefore, $p[HCO_3^-] = 2.64$.

Determine $[Ca^{2+}]$ from Equation 3; neglect Ca_{ip}:

$$\left[Ca^{2+}\right]=Ca_t=3.80\times10^{-3}\ \text{moles/L}$$

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

Table 2330:2 indicates that the pK_s for calcite is 8.45. Determine pH_s using Equation 2:

$$pH_s = 10.38 - 8.45 + 2.42 + 2.64 + 5\ (0.063) = 7.31$$

And finally, determine SI using Equation 1:

$$SI = 9.00 - 7.31 = 1.69$$

The positive SI indicates that the water is oversaturated with calcite.

2) *Effects of neglecting Ca_{ip} and Alk_o*—If Ca_{ip} is neglected, then pH_s is underestimated and SI is overestimated by $p(1-Y_{Ca_{ip}})$, 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. If Alk_o is neglected, then SI is overestimated by $p(1-Y_{Alk_o})$, 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.

Nevertheless, Ca_{ip} and Alk_o may be neglected if $Y_{Ca_{ip}}$ and Y_{Alk_o} are small and do not interfere with the interpretation of SI. These factors are usually small for natural waters with low TDS concentrations and neutral pH values, but may increase in some waters as pH values approach and exceed 9. At high pH values, however, SI is typically much larger than its overestimated index value, in which case neglecting Ca_{ip} and Alk_o is no problem. For instance, if the sample calculation in the example above was done using water-chemistry software (MINTEQA2) that considers Ca_{ip} and Alk_o (see Table 2330:3), SI would be 1.51 (0.18 units lower than the result obtained by hand calculations). In other words, 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 with high sulfate concentration (e.g., recirculating cooling water). The robust $CaSO_4^0$ ion pair sequesters calcium, which can result in an SI overestimated by as much as 0.3 to 0.5 units, even at neutral pH. So SI may be thought to be zero (neither scale-forming nor corrosive) when in fact it is negative. To resolve this problem, determine pH_s using water-chemistry software that considers ion pairs and other forms of alkalinity (2330 D). Such calculations are most accurate when a complete mineral analysis is used.

Table 2330:2. Precalculated Values For pK and A at Selected Temperatures

Temperature °C	pK_2	pK_S Calcite	Aragonite	Vaterite	pK_w	A
0	10.63	8.38	8.22	7.74	14.94	0.489
5	10.55	8.39	8.24	7.77	14.73	0.493
10	10.49	8.41	8.26	7.80	14.53	0.496
15	10.43	8.43	8.28	7.84	14.34	0.501
20	10.38	8.45	8.31	7.87	14.17	0.505
25[a]	10.33	8.48	8.34	7.91	13.99	0.510
30	10.29	8.51	8.37	7.96	13.83	0.514
35	10.25	8.54	8.41	8.00	13.68	0.520
40	10.22	8.58	8.45	8.05	13.53	0.525
45	10.20	8.62	8.49	8.10	13.39	0.531
50	10.17	8.66	8.54	8.16	13.26	0.537
60	10.14	8.76	8.64	8.28	13.02	0.549
70	10.13	8.87	8.75	8.40	–	0.563
80	10.13	8.99	8.88	8.55	–	0.578
90	10.14	9.12	9.02	8.70	–	0.593

Note: All values determined from the equations of Table 2330:1.
A is used to calculate pf_m (see Table 2330:1).
[a] pf_m estimated from TDS values at 25 °C as follows:

TDS	pf_m
100	0.024
200	0.033
400	0.045
800	0.060
1000	0.066

Calcium complexed by organic matter and organic acid contributions to Alk_o can be difficult to characterize and integrate into water chemistry software. The fraction of calcium complexed by organic matter typically is expected to be small in distribution systems.[4] The contribution of organic acids to Alk_o can be significant in some waters[5] but will be small in natural waters with low concentrations of natural organic matter (NOM).

Another somewhat less rigorous procedure involves direct measurement of calcium ion activity $\{Ca^{2+}\}$ with a calcium-specific ion electrode.[6] Use Equation 6 to determine $p[Ca^{2+}]$; then use $p[Ca^{2+}]$ in Equation 2.

$$p\left[\mathrm{Ca}^{2+}\right]=p\left\{\mathrm{Ca}^{2+}\right\}-4pf_m \tag{6}$$

This approach eliminates the need to determine Ca_{ip}.

Alk_o can be determined in organic-free waters if a complete mineral analysis is used with suitable chemical-equilibrium software. Alternatively, Alk_o can be determined either in organic-laden or organic-free waters as described below if carbonate alkalinity (Alk_c) can be obtained, where Alk_c is the alkalinity contributed by carbonate species (HCO_3^- and CO_3^{2-}). Alk_c can

Table 2330:3. Graphical and Computer Methods That Can Be Used to Calculate $CaCO_3$ Saturation Indices

	$CaCO_3$ Indices						
Item[a]	Basis for Calculation of SI	CCPP	Approximate Temperature Range °C	Approximate Limit of Ionic Strength	Ion Pairs Considered?	Alk_o Considered?	Operating System
Caldwell-Lawrence Diagrams[1-6]	pH_{sb}	P, D	2–25	0.030	No	No	Graphical Diagrams
MINTEQA2[7,8]	RS	P, D	0–100	0.5	Yes	Yes	Windows 98, NT, 2000, XP
PHREEQC[9]	RS	P, D	0–100	0.5	Yes	Yes	Windows 95, 98, NT 4.0, ME 2000, XP, Mac OS 9 and X, and Linux
PHREEQC Standard for high salinity waters[9]	RS	P, D	0–80	7–8	Yes	Yes	Windows 95, 98, NT 4.0, ME 2000, XP, Mac OS 9 and X, and Linux
WATEQ4F[10]	RS	D	0–100	0.5	Yes	Yes	Any PC capable of running DOS or MS DOS
MINEQL+[11]	RS	P, D	0–100	0.5	Yes	Yes	Windows 7, 8 and 10
Visual MINTEQ[12]	RS	P, D	0–100	0.5	Yes	Yes	Windows 7, 8 and 10

SI = saturation index; CCPP = $CaCO_3$ precipitation potential; $pH_{sb} = pH_s$ based on a hypothetical bicarbonate concentration calculated using the saturation pH;
P = calculates amount of $CaCO_3$ theoretically precipitated; D = calculates amount of $CaCO_3$ theoretically dissolved; RS = relative saturation (recommended); PC = personal computer.

References

1. *Loewenthal RE, Marais GVR. Carbonate chemistry of aquatic systems: theory and applications. Ann Arbor (MI): Ann Arbor Science Publishers, 1976.* Note: Supplies 10.2- x 11.4-cm diagrams, with documentation.
2. *Merrill DT, Sanks RL. Corrosion control by deposition of CaCO3 films. Part I: a practical approach for plant operators. 1977;69(11):592–599.* Note: Provides 10.2- by 16.5-cm diagrams, with documentation.
3. *Merrill DT, Sanks RL. Corrosion control by deposition of CaCO3 films. Part II: a practical approach for plant operators. 1977;69(12):634–640.* Note: Provides 10.2- by 16.5-cm diagrams, with documentation.
4. *Merrill DT, Sanks RL. Corrosion control by deposition of CaCO3 films. Part III: a practical approach for plant operators. 1978:70(1):12–18.* Note: Provides 10.2- by 16.5-cm diagrams, with documentation.
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12. *John Peter Gustafsson at KTH Royal Institute of Technology. http://vminteq.lwr.kth.se/ [accessed February 2021].* Note: Links to software and documentation.

be calculated if the total inorganic carbon (C_t) concentration is known, where C_t is the sum of the carbonate species [$CO_{2(aq)}$, H_2CO_3, HCO_3^-, and CO_3^{2-}]. C_t is also known as *dissolved inorganic carbon* (DIC). Some total organic carbon (TOC) analyzers can measure C_t via acidification, purging, and $CO_{2(g)}$ detection.

$CO_{2(g)}$ detection with nondispersive infrared (NDIR) sensors virtually eliminates interference from other volatile compounds at low pH (e.g., purgeable organic carbon, hydrogen sulfide) because the sensors use wavelengths that select for $CO_{2(g)}$ absorbance. Conductivity-based $CO_{2(g)}$ detection with a gas-permeable membrane will register interference from volatile weak acids (e.g., hydrogen sulfide), but this interference is negligible for typical waters. If C_t is obtained, calculate Alk_c as follows:

$$Alk_c = C_t\left(\frac{10^{(pf_m-pH-pK_1)}+2\times10^{(4pf_m-pK_1-pK_2)}}{10^{-2pH}+10^{(pf_m-pH-pK_1)}+10^{(4pf_m-pK_1-pK_2)}}\right)$$

where:

K_1 = first dissociation constant for carbonic acid, including $CO_{2(aq)}$, at water temperature.

Estimate Alk_o by subtracting Alk_c from Alk_t (i.e., $Alk_o = Alk_t - Alk_c$).

Alternatively, bypass the determination of Alk_o and substitute Alk_c for the quantity "$Alk_t - Alk_o$" in Equation 4 when estimating [HCO_3^-].

b. Graphical solutions for saturation pH: Caldwell–Lawrence diagrams can be used to determine a saturation pH[7-11]; however, graphical methods do not follow the definition of pH_s provided in Equation 2. In graphical methods, the bicarbonate term is a hypothetical quantity calculated as a function of saturation pH; in Equation 2, the calculated bicarbonate concentration is a function of measured pH (see 2330 D). The diagrams can be particularly useful for estimating the chemical dosages needed to achieve desired water conditions. See 2330 D for more information about

Table 2330:4. Quality Assurance/Quality Control Examples for Saturation Index by Calculation

Parameter (units)	Values				
Example	A[a]	B	C	D	E
			Input		
Calcium (mg/L)	152	10	90	90	152
Magnesium (mg/L)	39	2	–	–	39
Sodium (mg/L)	50	10	–	–	50
Potassium (mg/L)	5	1	–	–	5
Chloride (mg/L)	53	5	–	–	53
Alkalinity (mg/L as $CaCO_3$)	130	30	200	200	130
Sulfate (mg/L)	430	10	–	–	430
Silica (mg/L as SiO_2)	15	0	–	–	15
pH	9.00	9.20	7.20	7.20	9.00
Temperature (°C)	20	15	25	25	20
Alk_0 (mg/L as $CaCO_3$)	Neglected	Neglected	Neglected	Neglected	6
Ca_{ip} (mg/L as Ca)	Neglected	Neglected	Neglected	Neglected	49
TDS (mg/L)	–	–	750	–	–
EC (μS/cm)	–	–	–	1230	–
			Output		
I (M)[b]	2.30×10^{-2}	1.47×10^{-3}	1.88×10^{-2}	3.08×10^{-2}	2.30×10^{-2}
$[HCO_3^-]$ (M)	2.29×10^{-3}	5.22×10^{-4}	3.99×10^{-3}	3.99×10^{-3}	2.19×10^{-3}
$[Ca^{2+}]$ (M)	3.79×10^{-3}	2.50×10^{-4}	2.25×10^{-3}	2.25×10^{-3}	2.57×10^{-3}
pH_s	7.30	8.79	7.19	7.25	7.49
SI	1.70	0.23	0.01	0.05	1.51

[a] The result differs from the example presented earlier due to rounding in the hand calculations.

[b] Assuming all the alkalinity is due to bicarbonate ion, a charge of 2 for Ca_{ip}, and a charge of 1 for Alk_o.

the diagrams; consult the references for descriptions of how to use them.

3. Saturation Index by Experimental Determination

a. Saturometry: Saturometers were developed to measure the degree of $CaCO_3$ saturation in seawater. Analysts equilibrate $CaCO_3$ with a water of known calcium concentration and pH in a sealed flask containing a pH electrode. The water temperature is controlled by a constant-temperature bath. During equilibration, pH decreases if $CaCO_3$ precipitates and increases if it dissolves. Equilibrium is said to have been achieved when the pH stops changing. The initial pH and calcium concentration values and the final pH value are used to estimate the carbonate concentration, which can be used to estimate RS.[12] Equation 7 (2330 D.1) 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 achieving equilibrium. The method is most sensitive in the range of minimum buffering intensity (pH 7.5 to 8.5). Although the calculations do not consider ion pairs or Alk_o, these can be included so long as their pH dependence is known. The technique has been used for *in situ* oceanographic measurements,[13] as well as in the laboratory.

The saturometry calculations discussed above use the K_s of the $CaCO_3$ phase assumed to control solubility. Uncertainties occur if the controlling solid is unknown. To resolve such uncertainties, measure 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 concentration, alkalinity, and pH measurements.[14]

b. Alkalinity difference technique:[15] *SI* also can be determined by equilibrating water of known pH, calcium concentration, 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* using Equation 7 (2330 D.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 temperatures that are the same as that of the water of interest. Alternatively, correct test results to the temperature of the water of interest.[15]

4. Quality Assurance/Quality Control

If the calculations in the "Saturation Index by Calculation" section are automated (e.g., in a spreadsheet), check that the equations were properly programmed with the data in Table 2330:4.

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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 the water's tendency to precipitate or dissolve $CaCO_3$ and the amount that may be precipitated or dissolved. The CCPP also is called *calcium carbonate precipitation capacity* (CCPC).

CCPP is the quantity of $CaCO_3$ that theoretically can be precipitated from oversaturated waters or dissolved by undersaturated waters during equilibration.[1-3] The amount that actually precipitates or dissolves may be more or less for several possible reasons, including

- equilibrium may not be achieved;
- temperature and ionic strength approximations;
- failure to accurately account for complexation of species involved in the reaction;
- the presence of threshold inhibitors;
- inaccurate assumptions about the solid phase that forms;
- inaccurate solubility constants, dissociation constants, or measurements; and
- differences in concentrations between the bulk phase and local environments.[4]

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 using computerized water chemistry models, spreadsheets,[5,6] or Caldwell–Lawrence diagrams (see 2330 D). The most reliable calculations consider ion pairs and the alkalinity contributions of other species besides HCO_3^-, CO_3^{2-}, OH^-, and H^+. Models that do not consider these factors overestimate how much $CaCO_3$ can be precipitated and underestimate how much can be dissolved.

2. Experimental Determination of CCPP

Estimate CCPP by one of several experimental techniques.

a. Saturometry: See 2330 B.3*a*. The CCPP is determined as part of the *RS* calculation.

b. Alkalinity-difference technique: See 2330 B.3*b*. The CCPP equals the difference between the initial and equilibrated water's alkalinity (or calcium) values, when expressed as $CaCO_3$.

c. Marble test: The marble test[1-3,7-10] is similar to the alkalinity-difference technique. The CCPP equals the change in alkalinity (or calcium) values during equilibration, when expressed as $CaCO_3$.

d. Enslow test: The Enslow test[10] 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 $CaCO_3$. Bulb or funnel effluent is then is filtered through the crushed marble so that the filtrate is assumed to be in equilibrium with $CaCO_3$. The CCPP equals the change in alkalinity (or calcium) that occurs when water passes through the apparatus.

e. Calcium carbonate deposition test:[11] The calcium carbonate deposition test (CCDT) is an electrochemical method that measures the electric current produced when DO is reduced on a rotating electrode. When an oversaturated water is placed in the apparatus, it deposits $CaCO_3$ on the electrode, interfering with oxygen transfer and diminishing the current. The $CaCO_3$ deposition rate is directly proportional to the rate at which current declines. The CCDT and the CCPP are related but not identical: CCDT is a rate and CCPP is a quantity.

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

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2330 D. GRAPHICAL AND COMPUTER METHODS FOR $CaCO_3$ INDICES

1. Description

Table 2330:3 lists some of the graphical and computer methods that can be used to determine SI and CCPP. It also provides a brief description of their characteristics.

Many computer methods calculate *RS* instead of calculating *SI* directly. When *RS* data are presented, calculate *SI* from:[1]

$$SI = log_{10}RS \qquad (7)$$

where:

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

The graphical methods use a hypothetical bicarbonate concentration calculated at the *saturation pH* (i.e., they implicitly define *saturation pH* as the pH the water would exhibit if it were in equilibrium with $CaCO_3$ at existing calcium, total alkalinity, and C_t concentrations), while the bicarbonate concentration in Equation 2 is calculated at the measured value of pH.[1,2] Basing the saturation index on a hypothetical bicarbonate concentration calculated at the saturation pH not only yields different values but also causes the sign of the index to reverse when the pH is greater than the $CaCO_3$ system's second saturation point, which can occur at a pH of approximately pK_2. When sign reversal occurs, a positive value of *SI* (not the usual negative value) connotes an undersaturated water.[3] When *SI*, pH_s, or *RS* is calculated according to the equations in 2330 B, sign reversal does not occur, thereby eliminating the confusing sign change. Furthermore, the *SI* and *RS* values thereby obtained are directly related to the Gibbs free energy (driving force) of the reaction[4–6] and fundamentally consistent with the saturation indices used in numerous other applications.[7]

Some computer methods not listed in Table 2330:3 use Equation 5 (the simplified version of Equation 2), in which bicarbonate is assumed to equal alkalinity. As discussed in 2330 B.2*a*, when pH is approximately neutral (6.0 to 8.5) and alkalinity is more than about 50 mg/L as $CaCO_3$, Equations 2 and 5 yield virtually equal values of pH_s because total alkalinity is due almost entirely to the bicarbonate ion. When pH is more than about 8.5, avoid using Equation 5 and only use Equation 7 with *SI* values determined using Equation 2.

Using a graphical or computer method that calculates pH_s from Equation 2, or *RS*, is strongly recommended. Table 2330:3 identifies the saturation pH basis used for each graphical and computer method listed.

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

Graphical and computer methods can be used to determine many more parameters than $CaCO_3$ saturation indices. A fee may be charged for computer software or graphs. Table 2330:3 describes parameters each code uses to calculate SI. Refer to the sources in the table footnotes for current information.

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