

## Standard Methods for the Examination of Water and Wastewater

samples containing sulfuric, acetic, and formic acids and aluminum chloride by the procedures of ¶s 4*b* and 4*d*. The mean acidity of one sample (to pH 3.7) was 487 mg CaCO<sub>3</sub>/L, with a standard deviation of 11 mg/L. The bromphenol blue titration of the same sample was 90 mg/L greater, with a standard deviation of 110 mg/L. The other sample had a potentiometric titration of 547 mg/L, with a standard deviation of 54 mg/L, while the corresponding indicator result was 85 mg/L greater, with a standard deviation of 56 mg/L. The major difference between the samples was the substitution of ferric ammonium citrate, in the second sample, for part of the aluminum chloride.

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## 2320 ALKALINITY\*#(29)

### 2320 A. Introduction

#### 1. Discussion

Alkalinity of a water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents. The measured values also may include contributions from borates, phosphates, silicates, or other bases if these are present. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of a water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity less than, or only slightly greater than, that of the water supply. Properly operating anaerobic digesters typically have supernatant alkalinities in the range of 2000 to 4000 mg calcium carbonate (CaCO<sub>3</sub>)/L.<sup>1</sup>

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### 2. Reference

1. POHLAND, F.G. & D.E. BLOODGOOD. 1963. Laboratory studies on mesophilic and thermophilic anaerobic sludge digestion. *J. Water Pollut. Control Fed.* 35:11.

## 2320 B. Titration Method

### 1. General Discussion

*a. Principle:* Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end-point pH used. For methods of determining inflection points from titration curves and the rationale for titrating to fixed pH end points, see Section 2310B.1*a*.

For samples of low alkalinity (less than 20 mg CaCO<sub>3</sub>/L) use an extrapolation technique based on the near proportionality of concentration of hydrogen ions to excess of titrant beyond the equivalence point. The amount of standard acid required to reduce pH exactly 0.30 pH unit is measured carefully. Because this change in pH corresponds to an exact doubling of the hydrogen ion concentration, a simple extrapolation can be made to the equivalence point.<sup>1,2</sup>

*b. End points:* When alkalinity is due entirely to carbonate or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of carbon dioxide (CO<sub>2</sub>) at that stage. CO<sub>2</sub> concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration. The pH values in Table 2320:I are suggested as the equivalence points for the corresponding alkalinity concentrations as milligrams CaCO<sub>3</sub> per liter. “Phenolphthalein alkalinity” is the term traditionally used for the quantity measured by titration to pH 8.3 irrespective of the colored indicator, if any, used in the determination. Phenolphthalein or metacresol purple may be used for alkalinity titration to pH 8.3. Bromcresol green or a mixed bromcresol green-methyl red indicator may be used for pH 4.5.

*c. Interferences:* Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally. Do not filter, dilute, concentrate, or alter sample.

*d. Selection of procedure:* Determine sample alkalinity from volume of standard acid required to titrate a portion to a designated pH taken from ¶ 1*b*. Titrate at room temperature with a properly calibrated pH meter or electrically operated titrator, or use color indicators. If using color indicators, prepare and titrate an indicator blank.

Report alkalinity less than 20 mg CaCO<sub>3</sub>/L only if it has been determined by the low-alkalinity method of ¶ 4*d*.

Construct a titration curve for standardization of reagents.

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Color indicators may be used for routine and control titrations in the absence of interfering color and turbidity and for preliminary titrations to select sample size and strength of titrant (see below).

*e. Sample size:* See Section 2310B.1*e* for selection of size sample to be titrated and normality of titrant, substituting 0.02*N* or 0.1*N* sulfuric (H<sub>2</sub>SO<sub>4</sub>) or hydrochloric (HCl) acid for the standard alkali of that method. For the low-alkalinity method, titrate a 200-mL sample with 0.02*N* H<sub>2</sub>SO<sub>4</sub> from a 10-mL buret.

*f. Sampling and storage:* See Section 2310B.1*f*.

### 2. Apparatus

See Section 2310B.2.

### 3. Reagents

*a. Sodium carbonate solution, approximately 0.05*N*:* Dry 3 to 5 g primary standard Na<sub>2</sub>CO<sub>3</sub> at 250°C for 4 h and cool in a desiccator. Weigh  $2.5 \pm 0.2$  g (to the nearest mg), transfer to a 1-L volumetric flask, fill flask to the mark with distilled water, and dissolve and mix reagent. Do not keep longer than 1 week.

*b. Standard sulfuric acid or hydrochloric acid, 0.1*N*:* Prepare acid solution of approximate normality as indicated under Preparation of Desk Reagents. Standardize against 40.00 mL 0.05*N* Na<sub>2</sub>CO<sub>3</sub> solution, with about 60 mL water, in a beaker by titrating potentiometrically to pH of about 5. Lift out electrodes, rinse into the same beaker, and boil gently for 3 to 5 min under a watch glass cover. Cool to room temperature, rinse cover glass into beaker, and finish titrating to the pH inflection point. Calculate normality:

$$\text{Normality, } N = \frac{A \times B}{53.00 \times C}$$

where:

*A* = g Na<sub>2</sub>CO<sub>3</sub> weighed into 1-L flask,

*B* = mL Na<sub>2</sub>CO<sub>3</sub> solution taken for titration, and

*C* = mL acid used.

Use measured normality in calculations or adjust to 0.1000*N*; 1 mL 0.1000*N* solution = 5.00 mg CaCO<sub>3</sub>.

*c. Standard sulfuric acid or hydrochloric acid, 0.02*N*:* Dilute 200.00 mL 0.1000*N* standard acid to 1000 mL with distilled or deionized water. Standardize by potentiometric titration of

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15.00 mL 0.05N Na<sub>2</sub>CO<sub>3</sub> according to the procedure of ¶ 3b; 1 mL = 1.00 mg CaCO<sub>3</sub>.

*d. Bromcresol green indicator solution, pH 4.5 indicator:* Dissolve 100 mg bromcresol green, sodium salt, in 100 mL distilled water.

*e. Mixed bromcresol green-methyl red indicator solution:*<sup>3</sup> Use either the aqueous or the alcoholic solution:

1) Dissolve 100 mg bromcresol green sodium salt and 20 mg methyl red sodium salt in 100 mL distilled water.

2) Dissolve 100 mg bromcresol green and 20 mg methyl red in 100 mL 95% ethyl alcohol or isopropyl alcohol.

*f. Metacresol purple indicator solution, pH 8.3 indicator:* Dissolve 100 mg metacresol purple in 100 mL water.

*g. Phenolphthalein solution, alcoholic, pH 8.3 indicator.*

*h. Sodium thiosulfate, 0.1N:* See Section 2310B.3i.

### 4. Procedure

*a. Color change:* See Section 2310B.4b.

*b. Potentiometric titration curve:* Follow the procedure for determining acidity (Section 2310B.4c), substituting the appropriate normality of standard acid solution for standard NaOH, and continue titration to pH 4.5 or lower. Do not filter, dilute, concentrate, or alter the sample.

*c. Potentiometric titration to preselected pH:* Determine the appropriate end-point pH according to ¶ 1b. Prepare sample and titration assembly (Section 2310B.4c). Titrate to the end-point pH without recording intermediate pH values and without undue delay. As the end point is approached make smaller additions of acid and be sure that pH equilibrium is reached before adding more titrant.

*d. Potentiometric titration of low alkalinity:* For alkalinities less than 20 mg/L titrate 100 to 200 mL according to the procedure of ¶ 4c, above, using a 10-mL microburet and 0.02N standard acid solution. Stop the titration at a pH in the range 4.3 to 4.7 and record volume and exact pH. Carefully add additional titrant to reduce the pH exactly 0.30 pH unit and again record volume.

### 5. Calculations

*a. Potentiometric titration to end-point pH:*

$$\text{Alkalinity, mg CaCO}_3/\text{L} = \frac{A \times N \times 50\,000}{\text{mL sample}}$$

where:

A = mL standard acid used and

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$N$  = normality of standard acid

or

$$\text{Alkalinity, mg CaCO}_3/\text{L} = \frac{A \times t \times 1000}{\text{mL sample}}$$

where:

$t$  = titer of standard acid, mg CaCO<sub>3</sub>/mL.

Report pH of end point used as follows: “The alkalinity to pH \_\_\_\_\_ = \_\_\_\_\_ mg CaCO<sub>3</sub>/L” and indicate clearly if this pH corresponds to an inflection point of the titration curve.

*b. Potentiometric titration of low alkalinity:*

Total alkalinity, mg CaCO<sub>3</sub>/L

$$= \frac{(2B - C) \times N \times 50\,000}{\text{mL sample}}$$

where:

$B$  = mL titrant to first recorded pH,

$C$  = total mL titrant to reach pH 0.3 unit lower, and

$N$  = normality of acid.

*c. Calculation of alkalinity relationships:* The results obtained from the phenolphthalein and total alkalinity determinations offer a means for stoichiometric classification of the three principal forms of alkalinity present in many waters. The classification ascribes the entire alkalinity to bicarbonate, carbonate, and hydroxide, and assumes the absence of other (weak) inorganic or organic acids, such as silicic, phosphoric, and boric acids. It further presupposes the incompatibility of hydroxide and bicarbonate alkalinities. Because the calculations are made on a stoichiometric basis, ion concentrations in the strictest sense are not represented in the results, which may differ significantly from actual concentrations especially at pH > 10. According to this scheme:

1) Carbonate (CO<sub>3</sub><sup>2-</sup>) alkalinity is present when phenolphthalein alkalinity is not zero but is less than total alkalinity.

2) Hydroxide (OH<sup>-</sup>) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.

3) Bicarbonate (HCO<sub>3</sub><sup>-</sup>) alkalinity is present if phenolphthalein alkalinity is less than half the

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total alkalinity. These relationships may be calculated by the following scheme, where  $P$  is phenolphthalein alkalinity and  $T$  is total alkalinity (§ 1b):

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  $(T - 2P)$  is bicarbonate. When the smaller value is  $(T - P)$ , the balance  $(2P - T)$  is hydroxide. All results are expressed as  $\text{CaCO}_3$ . The mathematical conversion of the results is shown in Table 2320:II. (A modification of Table 2320:II that is more accurate when  $P \approx \frac{1}{2}T$  has been proposed.<sup>4</sup>)

Alkalinity relationships also may be computed nomographically (see Carbon Dioxide, Section 4500- $\text{CO}_2$ ). Accurately measure pH, calculate  $\text{OH}^-$  concentration as milligrams  $\text{CaCO}_3$  per liter, and calculate concentrations of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  as milligrams  $\text{CaCO}_3$  per liter from the  $\text{OH}^-$  concentration, and the phenolphthalein and total alkalinities by the following equations:

$$\text{CO}_3^{2-} = 2P - 2[\text{OH}^-]$$

$$\text{HCO}_3^- = T - 2P + [\text{OH}^-]$$

Similarly, if difficulty is experienced with the phenolphthalein end point, or if a check on the phenolphthalein titration is desired, calculate phenolphthalein alkalinity as  $\text{CaCO}_3$  from the results of the nomographic determinations of carbonate and hydroxide ion concentrations:

$$P = \frac{1}{2} [\text{CO}_3^{2-}] + [\text{OH}^-]$$

### 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  $\text{CaCO}_3$ /L can be achieved. Forty analysts in 17 laboratories analyzed synthetic samples containing increments of bicarbonate equivalent to 120 mg  $\text{CaCO}_3$ /L. The titration procedure of § 4b was used, with an end point pH of 4.5. The standard deviation was 5 mg/L and the average bias (lower than the true value) was 9 mg/L.<sup>5</sup>

Sodium carbonate solutions equivalent to 80 and 65 mg  $\text{CaCO}_3$ /L were analyzed by 12 laboratories according to the procedure of § 4c.<sup>6</sup> The standard deviations were 8 and 5 mg/L, respectively, with negligible bias.<sup>6</sup> Four laboratories analyzed six samples having total alkalinities of about 1000 mg  $\text{CaCO}_3$ /L and containing various ratios of carbonate/bicarbonate by the procedures of both § 4a and § 4c. The pooled standard deviation was 40 mg/L, with negligible difference between the procedures.

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## 2330 CALCIUM CARBONATE SATURATION\*<sup>#</sup>(30)

### 2330 A. Introduction

#### 1. General Discussion

Calcium carbonate ( $\text{CaCO}_3$ ) 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  $\text{CaCO}_3$  scaling in piping and equipment such as industrial heat exchangers or domestic water heaters.

Waters oversaturated with respect to  $\text{CaCO}_3$  tend to precipitate  $\text{CaCO}_3$ . Waters undersaturated with respect to  $\text{CaCO}_3$  tend to dissolve  $\text{CaCO}_3$ . Saturated waters, i.e., waters in equilibrium with

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$\text{CaCO}_3$ , have neither  $\text{CaCO}_3$ -precipitating nor  $\text{CaCO}_3$ -dissolving tendencies. Saturation represents the dividing line between “precipitation likely” and “precipitation not likely.”

Several water quality characteristics must be measured to calculate the  $\text{CaCO}_3$  saturation indices described here. Minimum requirements are total alkalinity (2320), total calcium (3500-Ca), pH (4500- $\text{H}^+$ ), 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.<sup>1-3</sup> In measuring pH and alkalinity, minimize  $\text{CO}_2$  exchange between sample and atmosphere. Ideally, seal the sample from the atmosphere during measurements<sup>4</sup>; at a minimum, avoid vigorous stirring of unsealed samples.

There are two general categories of  $\text{CaCO}_3$  saturation indices: indices that determine whether a water has a *tendency* to precipitate  $\text{CaCO}_3$  (i.e., is oversaturated) or to dissolve  $\text{CaCO}_3$  (i.e., is undersaturated) and indices that estimate the *quantity* of  $\text{CaCO}_3$  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  $\text{CaCO}_3$  will precipitate from oversaturated waters and that it cannot be deposited from undersaturated waters. Exceptions may occur. For example,  $\text{CaCO}_3$  deposition from oversaturated waters is inhibited by the presence of phosphates (particularly polyphosphates), certain naturally occurring organics, and magnesium.<sup>5-7</sup> These materials can act as sequestering agents or as crystal poisons. Conversely,  $\text{CaCO}_3$  deposits have been found in pipes conveying undersaturated water. This apparent contradiction is caused by high 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  $\text{CaCO}_3$  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  $\text{CaCO}_3$  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  $\text{CaCO}_3$  is precipitated on its surfaces.  $\text{CaCO}_3$  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



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corrosive. The expected relationship is observed sometimes,<sup>8,9</sup> but not always.<sup>10,11</sup> Unexpected results may be due in part to limited capability to predict  $\text{CaCO}_3$  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.<sup>9,12-16</sup> Thus, do not estimate corrosion rates on the basis of  $\text{CaCO}_3$  indices alone.

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### 2330 B. Indices Indicating Tendency of a Water to Precipitate $\text{CaCO}_3$ or Dissolve $\text{CaCO}_3$

#### 1. General Discussion

Indices that indicate  $\text{CaCO}_3$  precipitation or dissolution tendencies define whether a water is oversaturated, saturated, or undersaturated with respect to  $\text{CaCO}_3$ . 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 RI<sup>1</sup> 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  $\text{CaCO}_3$  at the existing calcium ion  $[\text{Ca}^{2+}]$  and bicarbonate ion  $[\text{HCO}_3^-]$  concentrations.

A positive SI connotes a water oversaturated with respect to  $\text{CaCO}_3$ . A negative SI signifies an undersaturated water. An SI of zero represents a water in equilibrium with  $\text{CaCO}_3$ .

a. *Analytical solution for  $pH_s$* : Determine  $pH_s$  as follows<sup>2</sup>:

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

where:

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

$K_s$  = solubility product constant for  $\text{CaCO}_3$  at the water temperature,

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- $[Ca^{2+}]$  = calcium ion concentration, g-moles/L,  
 $[HCO_3^-]$  = 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.

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

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  $[HCO_3^-]$ , the bicarbonate ion concentration, from Equation 4.

$$[HCO_3^-] = \frac{Alk_t - Alk_o + 10^{(pf_m - pH)} - 10^{(pH + pf_m - pK_w)}}{1 + 0.5 \times 10^{(pH - pK_2)}} \quad (4)$$

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 ( $HCO_3^-$ ,  $CO_3^{2-}$ ,  $OH^-$ ,

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and  $H^+$ ).

Calculations can be simplified. For example, in Equation 4, terms containing exponents (e.g.,  $10^{(pH + pf_m - p_{kw})}$ ) 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	$3.80 \times 10^{-3}$
Magnesium	39		24 312	$1.60 \times 10^{-3}$
Sodium	50		22 989	$2.18 \times 10^{-3}$
Potassium	5		39 102	$1.28 \times 10^{-4}$
Chloride	53		35 453	$1.49 \times 10^{-3}$
Alkalinity (as $CaCO_3$ )	130		50 000	$2.60 \times 10^{-3*}$
Sulfate	430		96 060	$4.48 \times 10^{-3}$
Silica (as $SiO_2$ )	15		60 084	$2.50 \times 10^{-4}$

\*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 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 ( $2.60 \times 10^{-3}$ ) 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.

$$I = 0.5 [4(3.80 \times 10^{-3}) + 4(1.60 \times 10^{-3}) + 2.18 \times 10^{-3} +$$

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$$\begin{aligned}
 &1.28 \times 10^{-4} + 1.49 \times 10^{-3} + 2.60 \times 10^{-3} \\
 &+ 4(4.48 \times 10^{-3}) \\
 &= 2.29 \times 10^{-2} \text{ g-moles/L}
 \end{aligned}$$

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  $20^\circ\text{C}$ .

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.

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:

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$$SI = 9.00 - 7.27 = 1.73$$

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.<sup>9</sup> Use Equation 5 to determine  $p[Ca^{2+}]$ ; then use  $p[Ca^{2+}]$  in Equation 2.

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

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

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*b. Graphical solutions for  $pH_s$ :* Caldwell-Lawrence diagrams can be used to determine  $pH_s$ .<sup>10-12</sup> 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  $\text{CaCO}_3$ . A water of known calcium and pH is equilibrated with  $\text{CaCO}_3$  in a sealed flask containing a pH electrode. The water temperature is controlled with a constant-temperature bath. During equilibration the pH decreases if  $\text{CaCO}_3$  precipitates and increases if  $\text{CaCO}_3$  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).<sup>13</sup> 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 measurements<sup>14</sup> as well as in the laboratory.

The saturometry calculations discussed above use  $K_s$  of the  $\text{CaCO}_3$  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  $\text{CaCO}_3$  activity product,  $[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]$ , at equilibrium. Calculate the latter from the equilibrium pH and initial calcium, alkalinity, and pH measurements.<sup>15</sup>

*b. Alkalinity difference technique:*<sup>16</sup> SI also can be determined by equilibrating water of known pH, calcium, and alkalinity with  $\text{CaCO}_3$  in a sealed, constant-temperature system. The  $\text{CaCO}_3$  activity product before equilibration is determined from initial calcium, pH, and alkalinity (or total carbonate) values. The  $\text{CaCO}_3$  solubility product constant ( $K_s$ ) equals the  $\text{CaCO}_3$  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  $\text{CaCO}_3$  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.<sup>16</sup>

### 4. References

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### 2330 C. Indices Predicting the Quantity of $\text{CaCO}_3$ That Can Be Precipitated or Dissolved

The Calcium Carbonate Precipitation Potential (CCPP) predicts both tendency to precipitate or to dissolve  $\text{CaCO}_3$  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  $\text{CaCO}_3$  that theoretically can be precipitated from oversaturated waters or dissolved by undersaturated waters during equilibration.<sup>1</sup> 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  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ , and  $\text{H}^+$ . Models that do not consider these factors overestimate the amount of  $\text{CaCO}_3$  that can be precipitated and underestimate the amount of  $\text{CaCO}_3$  that can be dissolved.

#### 2. Experimental Determination of CCPP

Estimate CCPP by one of several experimental techniques.

- a. *Saturation*: 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  $\text{CaCO}_3$ .
- c. *Marble test*: The marble test<sup>1-5</sup> is similar to the alkalinity difference technique. The CCPP equals the change in alkalinity (or calcium) values during equilibration, when they are expressed as  $\text{CaCO}_3$ .
- d. *Enslow test*: The Enslow test<sup>5</sup> 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  $\text{CaCO}_3$ . The effluent from this device is filtered through crushed marble so that the filtrate is assumed to be in equilibrium with  $\text{CaCO}_3$ . The CCPP equals the change in alkalinity (or calcium) values that occurs during passage through the apparatus.
- e. *Calcium carbonate deposition test*:<sup>6</sup> The calcium carbonate deposition test (CCDT) is an electrochemical method that measures the electric current produced when dissolved oxygen is

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reduced on a rotating electrode. When an oversaturated water is placed in the apparatus,  $\text{CaCO}_3$  deposits on the electrode. The deposits interfere with oxygen transfer and the current diminishes. The rate of  $\text{CaCO}_3$  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  $\text{CaCO}_3$  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 $\text{CaCO}_3$ 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:<sup>1</sup>

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

where:

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$RS$  = ratio of  $\text{CaCO}_3$  activity product to  $\text{CaCO}_3$  solubility product constant.

The diagrams and a few of the codes define  $\text{pH}_s$  as the pH the water would exhibit if it were in equilibrium with  $\text{CaCO}_3$  at the existing calcium and total alkalinity concentrations.<sup>2</sup> This definition of  $\text{pH}_s$  differs from the definition following Equation 1 because alkalinity is used instead of bicarbonate. Within the pH range 6 to 9, alkalinity-based  $\text{pH}_s$  and bicarbonate-based  $\text{pH}_s$  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  $\text{pH}_s$ . However, if  $SI$  is determined from bicarbonate-based pH, Equation 6 continues to apply.

Furthermore, calculating  $SI$  with alkalinity-based  $\text{pH}_s$  reverses the sign of the  $SI$  above pH values of approximately  $\text{pK}_2$ , i.e., a positive, not the usual negative,  $SI$  connotes an undersaturated water.<sup>3</sup> With bicarbonate-based  $\text{pH}_s$  or  $RS$ , sign reversal does not occur, thereby eliminating the confusing sign change. For these reasons, bicarbonate-based  $\text{pH}_s$  or  $RS$  is preferred. Table 2330:III lists the definition of  $\text{pH}_s$  used for each code.

Some models calculate only the amount of  $\text{CaCO}_3$  that can be precipitated but not the amount of  $\text{CaCO}_3$  that can be dissolved. Others calculate both.

The diagrams and codes can be used to determine many more parameters than the  $\text{CaCO}_3$  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.

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### 2340      **HARDNESS\*#(31)**

#### **2340 A.      Introduction**

##### **1. Definition**

Originally, water hardness was understood to be a measure of the capacity of water to precipitate soap. Soap is precipitated chiefly by the calcium and magnesium ions present. Other polyvalent cations also may precipitate soap, but they often are in complex forms, frequently with organic constituents, and their role in water hardness may be minimal and difficult to define. In conformity with current practice, total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per liter.

When hardness numerically is greater than the sum of carbonate and bicarbonate alkalinity, that amount of hardness equivalent to the total alkalinity is called “carbonate hardness”; the