



An Overview of Calcium Carbonate Saturation Indices as a Criterion to Protect Desalinated Water Transmission Lines From Deterioration

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ABSTRACT

A number of calcium carbonate (CaCO_3) saturation indices are being used for many years to evaluate the scale forming or scale dissolving tendencies of water. Assessment of these tendencies is useful in corrosion control program of water transmission lines and preventing CaCO_3 scaling inside plumbing and equipment, such as industrial heat exchangers or even domestic water heaters. The most commonly used indices are Langelier Saturation Index (LSI or SI), Ryznar Stability Index (RSI), Relative Saturation Index (RS) - also known as Driving Force Index (DFI), which was proposed by McCauley in 1960. However, there are some more indices which are listed and cited in the literature, viz., Aggressive Index (AI), Larson Ratio (LR), Saturation Disequilibrium Index (SDI), Riddick Index (RI), Buffer Intensity Index (β), the Momentary Excess Index (MEI), which was proposed by Dye in 1952, etc. There is one more index for CaCO_3 scale prediction in cooling tower systems, known as Practical Scale Index (PSI). Many indices reported in the literature are essentially the same but expressed differently. Some of these indices are either absolutely empirical or defined in such a way that during computation the thermodynamic properties or the parameters of water chemistry that influence the corrosion or scale formation are often neglected. Each of these indices have served some useful purposes, but many have been controversial, incompletely understood and misapplied for a number of decades, particularly when they are used without recognition of their specific applications and limitations. Many of the indices are more useful in helping to understand possible causes of the problem rather than being useful in a predictive sense. In general, indices based on CaCO_3 saturation have not been shown to have any significant predictive value for the corrosion and/or leaching of lead, zinc, and copper from brass, bronze, soldered joints, and their respective pipe materials. In this paper a subset of various indices, which have appeared in the literature and their known limitations to indicate the inhibition property of water, will be addressed. A better understanding and proper application of these indices may prove helpful in deciding or designing the post-treatment strategy of highly aggressive desalinated waters for safe transmission and inhibit corrosion of metal surfaces or dissolution of cement-mortar lining of the transport pipelines.

SOME CONVENTIONAL SATURATION INDICES

Langelier's Saturation Index (LSI)

The LSI is the most widely used, or misused, index in the water treatment and distribution field (Langelier 1936). This index is based on the effect of pH on the equilibrium solubility of CaCO_3 . The pH at which water is saturated with CaCO_3 is known as the pH of Saturation (pH_s). The LSI can be defined mathematically by the following equation:

$$\text{LSI} = \text{pH} - \text{pH}_s$$

and

$$\text{pH}_s = \text{p}K_2 - \text{p}K_s + \text{p}[\text{Ca}^{2+}] + \text{p}[\text{HCO}_3^-] + 5\text{p}f_m$$

Where, $\text{p}K_2$ is second dissociation constant for carbonic acid at water temperature, $\text{p}K_s$ is solubility product of CaCO_3 at water temperature, $[\text{Ca}^{2+}]$ is calcium ion concentration in g moles/L, f_m is activity coefficient for monovalent species at the specified temperature and 'p' preceding a variable

designates $-\log_{10}$ of that variable.

Tables 1a and 1b show the estimated equilibrium constants and activity coefficients and the pre-calculated values for $\text{p}K$ and A at selected temperatures respectively.

The tendency of water as a result of above equation can be interpreted as follows:

If LSI value > 0 , i.e., +ve, it indicates that the water is supersaturated and tends to precipitate a scale layer of CaCO_3 . If LSI value = 0, it indicates that the water is saturated (in equilibrium) with CaCO_3 . A scale layer of CaCO_3 is neither precipitated nor dissolved. If LSI value < 0 , i.e., -ve, it indicates that the water is undersaturated, and hence tends to dissolve solid CaCO_3 as it is aggressive or corrosive in nature. Hence, as per established conventions, while maintaining LSI positive for oversaturated waters, the lesser value of pHs must always be used (Rossum & Merrill 1983).

Liberman & Liberman (1999) have suggested that for a

Table 1a: Estimated equilibrium constants and activity coefficients (Source: APHA 1998).

Equation	Temperature Range
When complete mineral analysis is available:	—
$I = 1/2 \sum_{i=1}^i [X_i] Z_i^2$	—
when only conductivity is available:	—
$I = 1.6 \times 10^{-5} C$	—
When only TDS is available:	—
$I = \text{TDS}/40\,000$	—
$pf_m = A \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.31 \right] \quad (\text{valid to } I < 0.5)$	—
$A + 1.82 \times 10^6 (ET)^{-1.5}$	—
$E = \frac{60\,954}{T + 116} - 68.937$	—
$pK_2 = 107.8871 + 0.032\,528\,49T - 5151.79/T - 38.925\,61 \log_{10} T + 563\,713.9/T^2$	273 – 373
$pK_w = 4471/T + 0.017\,06T - 6.0875$	280 – 338
$pK_{sc} = 171.9065 + 0.077\,993T - 2839.319/T - 71.595 \log_{10} T$	273 – 363
$pK_{sa} = 171.9773 + 0.077\,993T - 2903.293/T - 71.595 \log_{10} T$	273 – 363
$pK_{sv} = 172.1295 + 0.077\,993T - 3074.688/T - 71.595 \log_{10} T$	273 – 363

*I = ionic strength

[X_i] = concentration of component i, g-moles/LZ_i = charge of species i

C = conductivity, μmhos/cm

TDS = total dissolved solids, mg/L

pY = -log₁₀ of the value of any function Yf_m = activity coefficient for monovalent species

E = dielectric constant

T = temperature, °K (°C + 273.2)

K₂ = second dissociation constant for carbonic acidK_w = dissociation constant for waterK_{sc} = solubility product constant for calciteK_{sa} = solubility product constant for aragoniteK_{sv} = solubility product constant for vaterite

Table 1b: Precalculated values for pK and A at selected temperatures.

Temperature °C	pK ₂	pK _s			pK _w	A
		Calcite	Aragonite	Vaterite		
5	10.55	8.39	8.24	7.77	14.73	0.494
10	10.49	8.41	8.26	7.80	14.53	0.498
15	10.43	8.43	8.28	7.84	14.34	0.502
20	10.38	8.45	8.31	7.87	14.16	0.506
25*	10.33	8.48	8.34	7.91	13.99	0.511
30	10.29	8.51	8.37	7.96	13.83	0.515
35	10.25	8.54	8.41	8.00	13.68	0.520
40	10.22	8.58	8.45	8.05	13.53	0.526
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	-	0.562
80	10.13	8.99	8.88	8.55	-	0.576
90	10.14	9.12	9.02	8.70	-	0.591

Note: All values determined from the equations of Table 1-a, A is also used to calculate pf_m (see the above Table 1-a).*pf_m estimated from TDS values at 25°C are as follows:

TDS	pf _m	TDS	pf _m
100	0.024	800	0.060
200	0.033	1000	0.066
400	0.044		

water with pH = 8, calcium @ 40 ppm and bicarbonate @ 122 ppm must be present to attain a non-corrosive state. The equality can take place for different pH values. For a water with pH = 8.2, calcium @ 30 ppm and bicarbonate ions @ 91.5 ppm must be present for a non-corrosive state. This means that a higher pH of potable water is acceptable rather than a lower quantity of calcium and bicarbonate ions required for achieving a non-corrosive state (Lieberman & Liberman 1999).

The parameters necessary to calculate the LSI are: total alkalinity, calcium hardness, ionic strength or total dissolved solids (TDS) and a conversion factor to ionic strength (implied in many tables), pH (actual), temperature (T) and pH_s (APHA 1998)

Fig. 1 shows an example of LSI calculation of a given water sample. But, following problems have been encountered and reported with the LSI when used as a saturation index (Internal Corrosion of Water Distribution Systems, 1986, Schock 1984, 1985).

1. Complexation of Ca^{2+} and HCO_3^- is not accounted for, although this is possible if the needed analytical data are available. In the presence of polyphosphates, the equations defining pH_s will overestimate CaCO_3 saturation unless correction factors are added to account for the complexation.
2. The crystalline form of $\text{CaCO}_3(\text{s})$ has been usually assumed to be calcite. The presence of another form of $\text{CaCO}_3(\text{s})$, aragonite, which has a higher solubility, has, however, been observed in several systems. The formation of other forms of $\text{CaCO}_3(\text{s})$ may account for some of the observations of substantial supersaturation with respect to calcite.
3. A deposit of $\text{CaCO}_3(\text{s})$, does not necessarily aid in preventing corrosion.
4. CaCO_3 , if present in high enough concentrations, can also be deposited from waters with a negative LSI because of the localized high pH next to the surface of pipe, which is generally generated by the cathodic reactions.
5. The preoccupation of many with maintaining a positive LSI has led to excessive deposition of $\text{CaCO}_3(\text{s})$ and significant decreases in the capacity of distribution systems to carry water (Frederick 1990)

It is worth to mention that the presence of dissolved oxygen (DO) in the water may cause water with a “zero” LSI to be corrosive rather than “neutral” (Drew Principles of Industrial Water Treatment 1988). Hence, caution must be observed in employing LSI for controlling corrosion or deposit formation, since there are other factors also that may turn its application to be inappropriate. These factors include temperature differences within a system, change of operating

conditions and the difference in chemical treatments in the water transport system (Drew Principles of Industrial Water Treatment 1988).

Analyses of many protective scales have shown that many types of solids other than $\text{CaCO}_3(\text{s})$ are present which provide resistance to corrosion. Sontheimer et al. (1981) reviewed it for iron and steel and many other types of pipe materials. Furthermore, many examples of the failure of the LSI to predict corrosivity do exist. Water with a negative value of LSI can be noncorrosive, although some Ca^{2+} ions appear to be necessary for the deposit to be protective on iron and steel material (Lee et al. 1980).

Thus, we can say that LSI should be used only as one of several pieces of data to indicate corrosivity or deposition of CaCO_3 in any water transport system. It should be supplemented with observations of pipe that has been in use, analytical data of dissolved and/or particulate corrosion products, consideration of specific chemical factors of the material, and pipe loop studies, if possible.

Kutty et al. (1992) after reviewing a number of approaches have concluded that it should be clear that none of the indices studied (i.e., LSI, RSI, AI and indices based on water quality parameters) can correctly predict the corrosive and scale forming nature of water. Apart from this, lack of proper understanding of the indices by individual users may also contribute to considerable confusions.

Ryzner Stability/Saturation Index (RSI)

Ryzner defined a “Stability Index” in 1944 which is known as Ryzner Index (Ryzner 1944, Montgomery 1985). Some people also term it as “Ryzner Saturation Index” (RSI) (AWWA 1986, Loewenthal & Marais 1976, Merrill & Sanks 1977, 1978). It is mathematically defined as follows:

$$\text{RSI} = 2 \text{pH}_s - \text{pH}$$

Where, pH_s is Langelier’s saturation pH.

It was developed from empirical observations or corrosion rates and film formation in steel mains and heated water in glass coils. Ryzner generated a curve based on field results showing incrustation or corrosion as a function of RSI. It is an empirical method for predicting scaling tendencies of waters.

While discussing its limitations, Kutty et al. (1992) have clearly stated that since pH_s is calculated using above equation, all limitations discussed under LSI are applicable here as well hence, this index is often used in combination with the LSI to improve the accuracy in predicting the scaling or corrosion tendencies of water. Table 2 illustrates the usage of RSI or the tendencies of waters at various RSI values (Drew Principles of Industrial Water Treatment 1988).

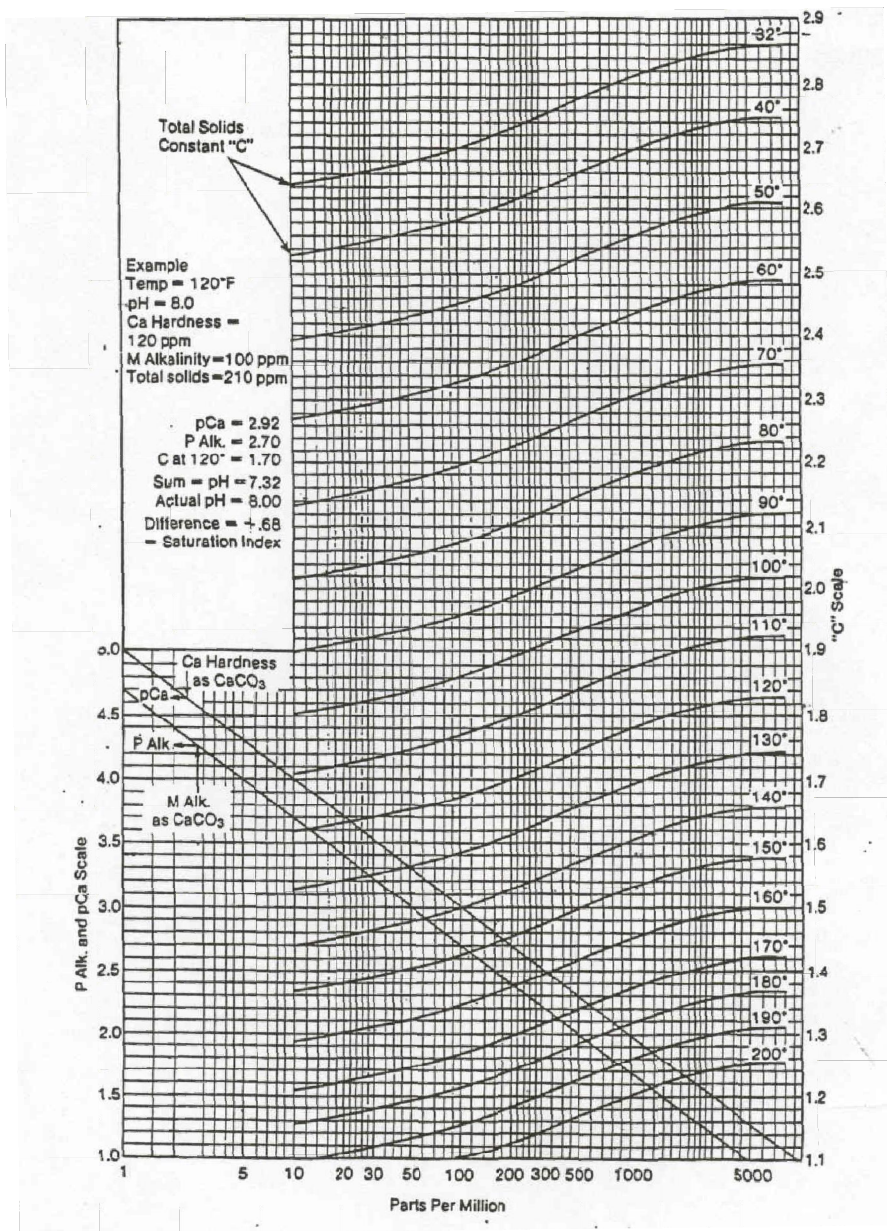


Fig. 1: Langelier saturation index.

Table 2: The usage of Ryzner stability index.

Ryzner Stability Index	Tendency of Water
4.0-5.0	Heavy scale
5.0-6.0	Light scale
6.0-7.0	Little scale or corrosion
7.0-7.5	Corrosion significant
7.5-9.0	Heavy corrosion
9.0 and higher	Corrosion intolerable

RSI values between 6.5 and 7.0 are considered to be approximately at saturation equilibrium with CaCO_3 . RSI values > 7.0 are interpreted as undersaturated and, therefore, would tend to dissolve any existing solid CaCO_3 . Waters with RSI values < 6.5 are saturated and, hence, would tend to be scale forming (Frederick 1990)

Ludwig & Hetschel (1989) have compared LSI and RSI and found that water becomes increasingly corrosive as the alkalinity decreases despite a saturation index $\text{LSI} = 0$.

RSI does not have any particular theoretical justification other than that from mathematical and chemical considerations. It tends to favour waters of higher hardness and alkalinity which would naturally have a greater potential to deposit CaCO_3 if their pH exceeded their pH_s . Thus, in that respect it is somewhat consistent with the observations of CaCO_3 deposition potential described by Loewenthal & Marais (1976) and Merrill & Sanks (1977, 1978). A notable internal inconsistency of RSI is that the value for saturation equilibrium varies with pH_s of the water; for example, if $\text{pH}_s = 7.0$, the RSI for saturation equilibrium is 7, but if $\text{pH}_s = 9$, the RSI for saturation equilibrium is 9. Therefore, the interpretation of the index must be adjusted with the pH_s .

In short RSI, although commonly used, does not offer any tangible advantages to a variety of other methods for computing the CaCO_3 saturation state and deposition potential.

It is worth to note that the word "corrosive" points out one of the major errors in the use of any of the modifications of the solubility equations for CaCO_3 . The undersaturation of water with respect to CaCO_3 does not make it corrosive, but only defines its state with respect to solid CaCO_3 . If a protective coating of CaCO_3 is not present, none of the indices relate to corrosion.

The Aggressive Index (AI)

It relates to the effect of water on an in-place calcium containing material. It is used for estimating the leaching of the cement matrix from asbestos-cement (A-C) pipes. The aggressive index (AI) for such cases is defined as follows:

$$\text{AI} = \text{pH} + \log AH$$

Where, A is the alkalinity and H is the calcium hardness, both expressed in mg/L as CaCO_3 .

The above equation shows a preliminary approximation of the attack on cement matrix and subsequent release of asbestos fibres in some cases. It may also be applicable to the cement lining in steel pipes (Edward 2004).

Waters with an AI value less than 10 are considered highly aggressive, while waters with AI values between 10-12 indicate moderate corrosion and AI values above 12 in-

dicating scaling (Muhammad & Shaukat 1989).

The AI has been critically evaluated by several researchers (Rossum & Merrill 1983, Internal Corrosion of Water Distribution Systems 1986, Schock & Buelow 1981, Schock & Neff 1982) and several serious shortcomings have been noted as a deposition tendency indicator and the index which may be used for the protection of A-C pipes. Therefore, because the AI is only a simplistic approximation of LSI (Frederick 1990), Kutty et al. 1992 have concluded that like RSI, AI is also a semi-empirical quantity and has many more limitations than LSI. For detail, please also refer to AWWA (1977).

Larson Ratio (LR)

It is well understood that chloride (Cl^-) and sulphate (SO_4^{2-}) can drastically affect the behaviour of ferrous materials. Both corrosion rates and iron uptake into the water from the pipe have been determined to be increased sharply as the concentration of sodium chloride or sodium sulphate is increased in the solution (Internal Corrosion of Water Distribution System 1986). The effects of Cl^- and SO_4^{2-} on iron and mild steel corrosion were found primarily related to their concentrations relative to HCO_3^- . The work of Larson & Skold (1957) have suggested that the ratio, sometimes called the Larson ratio (LR) should be less than 5. This ratio can be defined as below:

$$\text{LR}_1 = \frac{[\text{Cl}^-] + 2[\text{SO}_4^{2-}]}{[\text{HCO}_3^-]}$$

Or,

$$\text{LR}_2 = \frac{[\text{Cl}^-]}{[\text{HCO}_3^-]}$$

Here, the square braces indicate the concentrations of respective ions in mol/L .

Chloride ion has been noted for its role in breaking down passivating films developed on many ferrous metals and alloys. It is considered as one of the main causes of pitting of stainless steels (Internal Corrosion of Water Distribution System 1986).

If water contains an appreciable amount of calcium, it may act in conjunction with the pH and bicarbonate concentration to buffer the pH rise from corrosion reactions or to form a carbonate-containing passivating film on the surface of the pipe. Therefore, the bicarbonate concentration is also an important variable in iron and steel corrosion (Frederick 1990).

Larson (1975) had showed that an LSI value of 0.9 is necessary to precipitate $10 \text{ mg CaCO}_3/\text{L}$ at an alkalinity of $50 \text{ mg CaCO}_3/\text{L}$, but an LSI value of only 0.2 is necessary for the same amount of CaCO_3 precipitation if the alkalinity

is 200 mg/L. This might indicate that maintaining an LSI between 0 to 0.2 is not sufficient to guarantee the non corrosivity of water at low alkalinity, as has been addressed by Kutty et al. (1992).

Observations of corrosion in water of different quality (Bard 1966) showed the rate of corrosion of mild steel to increase significantly if LR_2 was greater than 0.1 to 0.2. Further research work is needed to fully establish the effect of Cl^- and SO_4^{2-} ions on iron and even other materials (Frederick 1990).

SOME OTHER SATURATION INDICES

Considering the inadequacy of predicting corrosion behaviour of water from the magnitude of $CaCO_3$ saturation-based indices, few other indices have also been suggested which are discussed here as under:

Practical Scale Index (PSI)

Some $CaCO_3$ scaling indices were found to be ineffective and inaccurate in scale prediction in concentrated cooling tower at pH levels above 7.5 which led many water treatment vendors to a misunderstanding on the use of these indices because most of the indices were developed and generally used for drinking water. But while using LSI and RSI for cooling tower systems, several problems were encountered, such as the results obtained by each index do not agree with the other. Often it was noticed that application of LSI and RSI to define the condition of the same sample of water gave contradictory results (Kutty et al. 1992), LSI indicating scale deposition whereas RSI showing no scale. Another worth noting problem was that both LSI and RSI predicted scale deposition but in actual practice nothing occurred. Puckorius & Brooke (1991) have claimed that RSI was found more accurate and meaningful than LSI in case of cooling water systems. Hence, they after an extensive study of over a decade have developed a new index, known as Practical Scale Index (PSI), for $CaCO_3$ scale prediction in cooling tower systems. It takes into account some of short falls of LSI and RSI, hence, seems to be more reliable and provides a more accurate and practical indication of $CaCO_3$ scaling tendencies of water.

The basis of PSI is the pH_s of $CaCO_3$ which had also been the basis of both LSI and RSI. PSI in terms of mathematical equation can be defined as below:

$$PSI = 2pH_s - pH_e$$

Where, pH_e is the equilibrium pH based on the value of total alkalinity.

The measured or actual pH value is not used in the

calculation of PSI as in other indices. The basic difference here is that PSI converts the total alkalinity value to pH_e which is mathematically represented as :

$$pH_e = 1.485 \log TA + 4.54$$

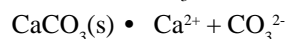
Where, TA is total alkalinity. The control range of PSI in brief is described as: If a PSI value > 6 , it indicates no scale deposition, but if a PSI value < 6 , it indicates scaling. Table 3 shows a comparative scaling severity of RSI and LSI/PSI. For further detail also refer to Puckorius & Brooke (1991).

Saturation or Disequilibrium Index (SDI)

For any solid solubility reactions SDI can be defined as follows:

$$SI_x = \log_{10} \left[\frac{IAP_x}{K_x} \right]$$

Where, IAP_x and K_x are the ion activity product and solubility product constant, respectively, for mineral x . For example, since $CaCO_3$ (calcite) on dissolving gives:



Hence, the expression for $SI_{calcite}$ would be:

$$SI_{calcite} = \log_{10} \left[\frac{\{Ca^{2+}\} \{CO_3^{2-}\}}{K_s} \right]$$

Here, the braces represent activities rather than the respective concentrations. For detail also refer to (Frederick 1990).

Riddick Index (RI)

Attempts have been made to develop corrosion indices by correlating corrosivity to all water quality parameters that might affect corrosion. In 1944 one such effort by Riddick (Singley 1981) yielded following index:

$$RI = \frac{75}{ALK} \left[CO_2 + 0.5(\text{hardness} - ALK) + Cl^- + 2NO_3^- \left(\frac{10}{SiO_2} \right) - \frac{(DO+2)}{DO_m} \right]$$

Where, hardness and alkalinity (ALK) are expressed in mg/L as $CaCO_3$, NO_3^- in mg/L as nitrogen, and the remaining parameters in mg/L as such.

This index was developed using data for the soft waters of the northeastern United States and successfully applied there. But RI is not applicable to higher hardness waters (Singley 1981, Frederick 1990).

RI values of less than 25 indicate noncorrosive water, RI values between 26 and 50 indicate moderately corrosive water, and RI values from 51 to 75 indicate corrosive water, and RI values greater than 75 indicate very corrosive water.

Table 3: A comparative scaling severity of RSI and LSI/PSI.

LSI	PSI/RSI	Condition
3.0	3.0	Extremely severe
2.0	4.0	Very severe
1.0	5.0	Severe
0.5	5.5	Moderate
0.2	5.8	Slight
0.0	6.0	Stable water (No scaling, no tendency to dissolve scale)
0.2	6.5	No scaling, very slight tendency to dissolve scale
0.5	7.0	No scaling, slight tendency to dissolve scale
1.0	8.0	No scaling, moderate tendency to dissolve scale
2.0	9.0	No scaling, strong tendency to dissolve scale
3.0	10.0	No scaling, very strong tendency to dissolve scale

$$\beta_{\text{alk}}^s = \left[\frac{K_1'}{\text{DIC}[\text{Ca}^{2+}]K_1'K_2'} \right] \left[\frac{F}{2[\text{H}^+] + K_1'} \right] \times \left[\frac{\text{DIC}K_1'([\text{H}^+]^2 + 4K_2[\text{H}^+] + K_1'K_2')}{F^2} \right] + \left[\frac{K_w'}{[\text{H}^+]^2} \right] + 1$$

Fig. 2: Equation for calculating Buffer Intensity Index (β)

Buffer Intensity Index (b)

The buffer intensity or capacity (β) has also been suggested as a useful corrosion indicator. The effect of β seems to be closely linked with CaCO_3 precipitation. High values of β do not necessarily inhibit corrosion (Singley 1981) because for any given pH the highest alkalinity has the highest buffer capacity, but it shows the least favourable value of CaCO_3 precipitation potential (CCPP-OH). The CaCO_3 precipitation capacity (CCPC) can be defined as the quantity of CaCO_3 that can be theoretically precipitated from oversaturated waters or dissolved by undersaturated waters during equilibration. The amount that actually precipitates or dissolves may be less, otherwise equilibrium may not be achieved. The CCPP value is -ve for undersaturated waters, zero for saturated waters and +ve for oversaturated waters (APHA 1998).

The CaCO_3 buffer intensity (β^s_{alk}) has been discussed as another potentially useful measure. Stumm (1960) realized the need to develop an index to take care of the drastic pH changes that occur in solutions in the immediate vicinity of the corroding elements. Stumm, therefore, proposed a quality of water called the buffer intensity. This index gives an estimate of the sensitivity of the CaCO_3 saturation of the solution to changes in alkalinity. This index is defined as the equation given in Fig. 2. (Frederick 1990).

Where, DIC is dissolved inorganic carbonate in mol/L and F is the free energy which can be further defined as follows:

$$F = [\text{H}^+]^2 + [\text{H}^+] K_1' + K_1' K_2'$$

In general, scale formation would be enhanced by regions in which β^s_{alk} is small, which would be where DIC is larger or $[\text{Ca}^{2+}]$ is larger (Montgomery 1985). In other words, corrosion rates are expected to decrease as β increases, since heterogeneity in pH will be minimized adjacent to the corroding electrodes. Stumm (1960) demonstrated that the rate of corrosion decreases in a uniform manner as β increases, except in water samples low in calcium and with an LSI value < -1.5 . This approach parallels the advice given by Merrill and Sanks in defining a water with good scale formation characteristics (Merrill & Sanks 1977, 1978).

Some Other Empirical Indices

Pathak in 1971 devised a nomograph to evaluate a rating system for copper pipes developed by Lucey in 1967. This index included the consideration of Na^+ , Cl^- , SO_4^{2-} ions, pH and DO. But this method has not been widely evaluated (Montgomery 1985).

Similarly, some Israeli researchers have also developed an index to characterize the corrosiveness of the hard waters found in different regions of the world. Hardness, Cl^- , alkalinity and SO_4^{2-} are mainly considered in this index. It was formulated as:

$$I = \text{AH} + \text{B}[(\text{Cl}^-) + (\text{SO}_4^{2-})]e^{-1/\text{AH}} + \text{C}$$

Where, A = 0.00035, B = 0.34, C = 19.0 and H = hardness

Waters having an index (I) value less than 200 were considered corrosive, waters having index values between 200 and 500 were found moderately corrosive, and waters

Table 4: Graphs and computer softwares that can be used to calculate CaCO₃ saturation indices (Source: APHA 1998)

Item†	CaCO ₃ Indices Basis for calculation of SI	CCPP	Approximate Temperature Range °C	Approximate Limit of Ionic Strength	Ion Pairs Considered	Alk ₀ Considered ††	Minimum Equipment Required
1. Caldwell Lawrence Diagrams	pH _{sa}	P, D	2-25	0.030	No	No	Diagrams
2. ACAPP	RS	P, D	-10 –110	6+	Yes	Yes	IBM-compatible PC, 512K bytes of RAM, MS DOS or PC DOS v.2.1 or higher
3. DRIVER	RS	P	7-65	2.5	Yes	Yes	Mainframe computer
4. INDEX C	pH _{sa} , pH _{sb}	P, D	0-50	0.5	No	No	Hewlett-Packard 41C calculator, with three memory modules
5. LEQUIL	RS	No	5-90	0.5	Yes	Yes	IBM-compatible PC, 256K RAM, Lotus 1-2-3 or work-alike, PC DOS or MS DOS v2.0 or higher
6. MINTEQA1	RS	P, D	0-100	0.5	Yes	Yes	IBM-compatible PC, 512K bytes of RAM, PC DOS v.3.0 or higher, 10 megabyte hard disk drive, math coprocessor useful but not required
7. PHREEQE Standard	RS	P, D	0-100	0.5	Yes	Yes	IBM-compatible PC, known to work with 512K RAM, PC DOS or MS DOS v.2.11 or higher. Also available for mainframe computers.
For high Salinity Waters	RS	P, D	0-80	7-8	Yes	Yes	IBM-compatible PC, 640K RAM recommended, with math coprocessor, MS DOS v.3.2 or higher
8. SEQUIL	RS	P, D	7-65	2.5	Yes	Yes	IBM-compatible PC, 512K bytes of RAM, MS DOS or PC DOS v.2.1 or higher
9. SOLMINEQ.88	RS	P, D	0-350	6	Yes	Yes	IBM-compatible PC, 640K RAM, math coprocessor, PC DOS or MS DOS v.3.0 or higher. Also available for mainframe computer
10. WTRCHEM	pH _{sa}	P, D	0-100	0.5	No	No	Any PC equipped with a BASIC interpreter, 5K RAM
11. WATEQ4F	RS	No	0-100	0.5	Yes	Yes	IBM-compatible PC, known to work with 512K RAM, PC DOS or MS DOS v.2.11 or higher

*SI = saturation index

CCPP = CaCO₃ precipitation potentialpH_{sa} = alkalinity-based pH_spH_{sb} = bicarbonate-based pH_sP = calculates amount of CaCO₃ theoretically precipitatedD = calculate amount of CaCO₃ theoretically dissolved

RS = relative saturation

PC = personal computer

RAM = random access memory

- † 1. Loewenthal and Marais provide 10.2- by 11.4-cm diagrams, with documentation; Merrill provides 10.2- by 16.5-cm diagrams, with documentation.
 2. Radian Corp., 8501 MoPac Blvd., P.O.Box 201088, Austin, TX 78720-1088 Attn: J.G. Noblett (software and documentation)
 3. Power Computing Co., 1930 Hi Line Dr., Dallas, TX 74207 (software and documentation)
 4. Brown and Caldwell, P.O.Box 8045, Walnut Creek, CA 94596-1220 Attn: D.T.Merrill (software and documentation)
 5. Illinois State Water Survey, Aquatic Chemistry Section, 2204 Griffith Dr., Champaign, IL 61820-7495 Attn: T.R.Holm (software and documentation)
 6. Center for Exposure Assessment Modeling, Environmental Research Laboratory, Office of Research & Development, U.S. Environmental Protection Agency, Athens, GA 30613 (software and documentation).
 7. U.S. Geological Survey, National Center, MS 437, Reston, VA 22902, Chief of WATSTORE Program (provides software for mainframe version of standard code); U.S. Geological Survey, Water Resources Division, MS 420, 345 Middlefield Rd., Menlo Park, CA 94025 Attn: K. Nordstrom (provides software for personal computer version of standard code); National Water Research Institute, Canada Center for Inland Waters, 867 Lakeshore Rd., Burlington, Ont, Canada L7R 4A6 Attn: A.S. Crowe (provides software and documentation for personal computer versions of both standard and high-salinity codes); U.S. Geological Survey, Books and Open File Report Section, Box 25425, Federal Center, Denver, CO 80225 (provides documentation for mainframe and personal computer versions of standard code).
 8. Power Computing Company, 1930 Hi Line Dr., Dallas, TX 74207 (software and documentation).
 9. U.S. Geological Survey, Water Resources Division, MS 427, 345 Middlefield Rd., Menlo Park, CA 94025 Attn: Y.K.Kharaka (software and documentation)
 10. D.T. Merrill, Brown and Caldwell, P.O.Box 8045, Walnut Creek, CA 94596-1220 (code listing and documentation)
 11. U.S. Geological Survey, Water Resources Division, MS 420, 345 Middlefield Rd., Menlo Park, CA 94025 Attn:K. Nordstrom (software), Books and Open File Report Section, Box 25425, Federal Center, Denver, CO 80225 (documentation).

†† Codes differ in the species included in Alk₀.

having index values greater than 500 were observed not very corrosive. But either this method has not been widely used (Montgomery 1985).

Some others have also attempted to develop similar correlations, like Singley (1981) etc., but none of any universal effectiveness has yet been developed.

FEW KNOWN LIMITATIONS OF CONVENTIONAL SATURATION INDICES

During the last decade, a joint task group under American Water Works Association (AWWA) working on CaCO_3 saturation has reviewed different saturation indices, highlighted several possible sources of errors in computing various indices and suggested improved methods of determination (Douglas et al. 1990). They have also highlighted following limitations of these saturation indices:

1. Oversaturation does not guarantee CaCO_3 precipitation. A certain degree of oversaturation must be present before crystal nucleation can occur. The water may be oversaturated but not sufficiently so to initiate nucleation.
2. CaCO_3 deposition from oversaturated waters is inhibited by the presence of phosphates (particularly polyphosphates), certain naturally occurring organics, and magnesium. These inhibitors can act as sequestering agents or as crystal poisons.
3. Conversely, CaCO_3 deposits have been found in pipes conveying unsaturated water. This apparent contradiction is caused by high pH (relative to the bulk water pH) in the immediate vicinity of certain areas (the cathodes) of corroding metal surfaces. A locally oversaturated condition may occur even if the bulk water is undersaturated. Small but significant amounts of CaCO_3 can be deposited.
4. Also, water characteristics not directly involved in the calculation of indices (e.g., DO, β , Cl⁻, SO_4^{2-} , water velocity) may appreciably influence corrosion rates. Thus, estimates of corrosion rates should not be based on CaCO_3 indices alone (Douglas et al. 1990). They have advocated for using different computer programs and graphics to calculate saturation index. Various experimental determinations of saturation indices have also to be listed. A list of various computer software, which can be used to calculate CaCO_3 saturation indices, is given in Table 4.

SUMMARY

A comparison of the different scale formation tendencies that can be obtained by using different approaches illustrates the relative utility of some out of these different indices. Hence, indices such as these must not be interpreted too literally

because other factors which influence corrosion rates appreciably, such as DO, presence of naturally occurring organics and magnesium, etc., have not been taken into consideration. Hence, all these indices do not have quantitative significance to any great degree of precision. This is why the joint task group of AWWA had suggested that for reasons, saturation indices should not be considered as absolute. Rather, they should be viewed as guides to the behaviour of CaCO_3 in aqueous systems and should be supplemented, whenever possible, with experimentally derived information (Douglas et al. 1990).

CONCLUSION AND RECOMMENDATION

It is recommended to obtain various saturation indices, such as LSI, RSI, PSI and others, by computer programs for the same sample of water, as has been suggested by the joint task group of AWWA, to conclude about the scaling tendency or corrosivity of the water.

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