Scaling Potential Index (SPI) for $CaCO_3$ Based on Gibbs Free Energies

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A new index (SPI) incorporating the theoretical thermodynamic relationships relating the equilibrium and solubility constants to the Gibbs free energy of reactions is obtained for assessing the scaling potential of carbonate system. Also inclusion of activity and specific ion interactive forces extends the applicability of the SPI over a wide salinity ranges and in presence of other cations and anions that is usually encountered in brackish water and sea water reverse osmosis desalination units, in concentrate management, and in differentiating between reverse osmosis and nanofiltration modules that have different passages for mono-valent and di-valent ions. Some of the industrially used empirical indices for prediction $CaCO_3$ scaling potential are reviewed and their shortcomings are discussed. The theoretically calculated results for SPI have been compared and validated with experimental values and with other commonly and industrially used indices. The results show that SPI is a better predictive approach. This method could be easily extended to take into account the pressure effects in membrane units. Furthermore, the same principle could be applied and the procedure could easily be extended to other salts. This index is a measure of the scaling potential and provides a conservative measure. Use of Gibbs free energy not only provides a theoretical means for assessing the scaling potential but also will enable future incorporation of the interactive and solvent effects in determining the solubility constants which could become readily possible with the advances in computational chemistry and incorporation of the kinetic and hydrodynamic effects in the future studies from the first principles. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 1782–1789, 2005
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Introduction

Desalination continues to be plagued by the persistent problem of fouling which limits the operation of these units. Fouling which refers to the attachment or adsorption and accumulation of undesired substances (foulants) onto the surface results in a continuous decline in water production and in the overall efficiency of the system; as such fouling increases the operation and maintenance costs. The properties of the process feed and the operating conditions determine the extent of fouling. In desalination and water-reuse foulants can be commonly classified into sparingly soluble inorganic salts, colloids, particulate matters, dissolved organic compounds and biological matters. Fouling by inorganic solutes is referred to as crystallization fouling and commonly referred to as scaling; however, there is recent evidence [1–4] that particulate fouling is another mode of deposition by inorganic solutes. The extent of fouling in desalination is usually associated with the properties of the process feed and the operating conditions. Various indices have been proposed to assess the fouling propensity of water. Supersaturation or a function of that is usually used to predict the scaling potential from inorganic solutes. Some of the author's recent articles[5–8] address the complexities that exist in feed water characterization and identify the challenges and future strategies in general.

Calcium carbonate is a sparingly soluble salt and it is a major

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cause of concern in scaling and operation of the desalination units. Various indices have been proposed and they are being used in practice to predict the scaling propensity of given water. These indices are developed based on the empirical relationships for solubility and dissociation constants and with simplifications to make their use readily practical. Langelier Saturation Index (LSI) and Stiff and Davis Stability Index (S&DSI) are the indices normally used to predict the scaling propensity of water with respect to calcium carbonate. Some other saturation indices that have found wide acceptance are Rysner Stability Index (RSI), Puckorius Scaling Index (PSI), Larson-Skold Index (L&SI), and Oddo-Tomson Index (O&TI). This article briefly discusses the chemistry of carbonic species and calcium carbonate, various indices commonly used and the simplifications that are employed within them, and then follows by suggesting a more fundamental approach based on the Gibbs free energies of reactions and use of activity instead of concentration to cover the wide salinity ranges encountered in today's desalination units. The prediction of SPI have been compared with experimental data and are in good agreements and in fact better agreement than commonly used empirical indices. Furthermore, the SPI approach provides the opportunity for theoretically including the interactive and hydrodynamic effects in future work.

Chemistry and Indices Currently Used for Calcium Carbonate

Calcium carbonate is an inverse solubility salt meaning that its solubility decreases with increasing temperature. It occurs naturally in three crystal structures: calcite, aragonite and vaterite. Calcite has a hexagonal crystal system and is thermodynamically stable polymorph. There are more than 600 reported crystal habits for calcite in contrast to 10–15 for other isostructural carbonates. Aragonite has an orthorhombic system with circular or elongated crystal habits, and is metastable and irreversibly changes to calcite when heated to about 400 °C in dry air; the rate of change increases with increasing temperature. The transformation is much more rapid when in contact with water or solutions containing calcium carbonate and may take place at room temperatures. In the commercial forms of precipitated calcium carbonate where aragonite predominates, crystals have parallel sides and large length-to-width ratios - rapid precipitation, high concentration of reactants, high temperatures, and the presence of divalent cations increase the tendency to produce aragonite. Also, the presence of sodium chloride tends to favor formation of aragonite.[9] As such calcite tends to be more predominant in thermal desalination units. In membrane desalination units that are subject to higher salinity and also more concentrated solutions, aragonite is likely to be more predominant. Vaterite is metastable and changes to calcite and aragonite under geological conditions; it is also found during the high-temperature precipitation of calcium carbonate.

To assess the scaling propensity of calcium carbonate, its chemistry and the speciation of carbonic series need to be first understood. Since it is difficult to distinguish between the dissolved carbon dioxide ($CO_{2(aq)}$) and carbonic acid (H_2CO_3), a hypothetical term ($H_2CO_3^*$) is used to represent the sum of both constituents. The equations describing the carbonate speciation are listed in Table 1. as functions of equilibrium constants (K's), total alkalinity (TA), total carbon species (C_T), and activity coefficients (γ's). For open systems Henry's law is used to relate the P_{CO_2}, the partial pressure (atm) of $CO_{(g)}$ in the gas, in equilibrium to that with the liquid. All bracketed values in Table 1 are in mol/lit.

Table 1. Equations Describing Speciation and Constants for Calcium Carbonate

$$Ca^{2+} + CO_3^{2-} \underset{K_{SP}}{\rightleftarrows} CaCO_{3\downarrow(s)} \tag{8}$$

$$CO_{2(g)} \overset{K_H}{\rightleftarrows} CO_{2(aq)} \tag{9}$$

$$CO_{2(aq)} + H_2O \overset{K_m}{\rightleftarrows} H_2CO_3 \tag{10}$$

$$CO_{2(aq)} + H_2CO_3 = H_2CO_3^* \tag{11}$$

$$H_2CO_3 \overset{K_1'}{\rightleftarrows} H^+ + HCO_3^- \tag{12}$$

$$H_2CO_3^* \overset{K_1}{\rightleftarrows} H^+ + HCO_3^- \tag{13}$$

$$HCO_3^- \overset{K_2}{\rightleftarrows} H^+ + CO_3^{2-} \tag{14}$$

$$C_T = [HCO_3^-] + [H_2CO_3^*] + [CO_3^{2-}] \tag{15}$$

$$[T.A.] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \tag{16}$$

$$[CO_3^{2-}] = \frac{[T.A.] + [H^+] - [OH^-]}{2(1 + [H^+]\gamma_{H^+}\gamma_{CO_3^{2-}}/(2\gamma_{HCO_3^-}K_2))} \tag{17}$$

$$[HCO_3^-] = \frac{[T.A.] + [H^+] - [OH^-]}{(1 + 2\gamma_{HCO_3^-}K_2/(\gamma_{H^+}\gamma_{CO_3^{2-}}[H^+]))} \tag{18}$$

$$[H_2CO_3^*] = \frac{[T.A.] + [H^+] - [OH^-]}{\gamma_{H_2CO_3^*}\ K_1(1 + 2\gamma_{HCO_3^-}K_2/(\gamma_{H^+}\gamma_{CO_3^{2-}}[H^+]))/(\gamma_{H^+}\gamma_{HCO_3^-}[H^+])} \tag{19}$$

$$K_{sp} = \gamma_{CO_3^{2-}}[CO_3^{2-}] \cdot \gamma_{Ca^{2+}}[Ca^{2+}] \tag{20}$$

$$K_1 = \gamma_{H^+}[H^+] \cdot \gamma_{HCO_3^-}[HCO_3^-]/\gamma_{H_2CO_3^*} \cdot [H_2CO_3^*] \tag{21}$$

$$K_2 = \gamma_{H^+}[H^+] \cdot \gamma_{CO_3^{2-}}[CO_3^{2-}]/\gamma_{HCO_3^{2-}}[HCO_3^-] \tag{22}$$

$$K_1' = \gamma_{H^+}[H^+] \cdot \gamma_{HCO_3^-}[HCO_3^-]/\gamma_{H_2CO_3}[H_2CO_3] \tag{23}$$

$$K_m = \gamma_{H_2CO_3} \cdot [H_2CO_3]/\gamma_{CO_2} \cdot [CO_{2(aq)}] \tag{24}$$

$$K_H = \gamma_{CO_{2(aq)}} \cdot [CO_{2(aq)}]/P_{CO_{2(g)}} \tag{25}$$

Table 2. Commonly Used Indices for $CaCO_3$

Name and Criteria	Formula
Langelier Saturation index (LSI) LSI < 0 corrosive LSI > 0 scale forming "C" obtained empirically	$LSI = pH - pH_s$ (26) $pH_s = p[\mathrm{Ca}] + p[\mathrm{HCO_3^-}] + \text{“}C\text{”}$ (27) $C = 9.3 + 0.1(\mathrm{Log}[TDS] - 1) - 13.12\ \mathrm{Log}(T) + 34.95$ (28)
Stiff-Davis Stability Index (S&DSI) S&DSI < 0 corrosive S&DSI > 0 scale forming "K" is a function of ionic strength	$S\ \&\ DSI = pH - pH_s$ (29) $pH_s = p[\mathrm{Ca}] + p[\mathrm{HCO_3^-}] + \text{“}K\text{”}$ (30)
Ryznar stability index (RSI) RSI $\leqslant 6$ scale forming RSI $\geqslant 7$ corrosive	$RSI = 2pH_s - pH$ (31)
Puckorius Scaling Index (PSI) PSI $\leqslant 6$ scale forming PSI $\geqslant 7$ corrosive	$PSI = 2(pH_s) - pH_{eq}$ (32) $pH_{eq} = 1.465\ \log[Alkalinity] + 4.54$ (33) $[Alkalinity] = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{OH^-}]$ (34)
Larson-Skold Index (L&SI) Corrosive measure in presence of Cl^- & SO_4^{2-}	$L\ \&\ SI = (\mathrm{Cl^-} + \mathrm{SO_4^{2-}})/(\mathrm{HCO_3^-} + \mathrm{CO_3^{2-}})$ (35)

The indices commonly used in practice for calcium carbonate scaling are empirically formulated as listed in Table 2 with bracketed terms being concentrations in mg/L. These indices are briefly discussed later; original publications are cited for detailed discussion.

Langelier Saturation Index (LSI)[10]

The LSI (Eq. 26 in Table 2) is an equilibrium model derived from the theoretical concept of saturation and with some added simplifications and uses pH of the solution and compares it with the pHs at which the respective solution is saturated with respect to calcium carbonate and is a measure of the difference between these two pH values. The LSI is probably the most widely used indicator of scale potential of water, and is purely an equilibrium index and deals only with the thermodynamic driving force for calcium carbonate scale formation and growth, and is only applicable to low total dissolved solid (TDS) values because in its derivation the activity coefficients are assumed to be unity.

Stiff-Davis Stability Index (S&DSI)[11]

The S&DSI (Eq. 29 in Table 2) attempts to overcome the shortcomings of the LSI with respect to high TDS waters and the impact of "common ion" effects. In the S&DSI, the solubility product used to predict the pH of saturation (pHs) for a water is empirically modified (Eq. 30) where "K" is related to the solution's ionic strength (I) and temperature (T). Stiff-Davis Index will predict a given water to be less scale forming than the LSI calculated for the same water chemistry and conditions. The deviation between the indices increases with increases in ionic strength of the solution.

Ryznar Stability Index (RSI)[12]

The RSI correlates an empirical database of scale thickness observed in municipal water systems to the water chemistry and like the LSI, the RSI has its basis in the concept of saturation level. Ryznar attempted to quantify the relationship between calcium carbonate saturation state and scale formation by Eq. 31 where pH is the solution pH and pHs is that at saturation. The scaling tendency increases as the index decreases; as a rough rule, water is considered scale forming for RSI $\leqslant 6$ and corrosive for RSI, $\geqslant 7$.

Puckorius Scaling Index (PSI)[13]

The PSI takes into account two other critical parameters: the buffering capacity of the water, and the maximum quantity of precipitate that can form in bringing water to equilibrium. When the carbonate ions are consumed to form $CaCO_{3(s)}$, the solution pH decreases according to Eq. 14. If the pH decrease is very rapid, such water is called to have low buffering capacity and it usually happens for waters that have high calcium concentrations and relatively lower carbonate. Such waters have the driving force for formation of the precipitate if the ion activity product of the solution is higher than the thermodynamic solubility product, but do not have the capacity to hold the precipitate because of low buffering capacity and pH drop which ultimately dissolves the formed precipitate. The PSI is calculated in the same manner similar to the RSI with one difference: PSI uses (Eq. 33) the equilibrium pH to consider the buffering effect while RSI uses the system pH.

Larson-Skold Index (L&SI)[14]

The L&SI has been correlated to the ratios of chloride and sulfate ions to that of carbonate and bicarbonate, all in equivalent per million (epm) units, according to Eq. 35 and is used to describe corrosivity of water toward mild steel. This guideline states that for L&SI $\leqslant 0.8$, chlorides and sulfates would not interfere with natural film formation; for $0.8 \leqslant$ L&SI $\leqslant 1.2$ chlorides and sulfates might interfere with natural film formation; and for L&SI $\geqslant 1.2$ there is a tendency for corrosion as the chlorides and sulfates would interfere with natural film formation. The L&SI is empirically correlated for Great Lake waters and its extrapolations to other waters, such as those with low or extreme alkalinity that are out of the original experimental range would be questionable.

Table 3. The Associated Gibbs Free Energies of Reactions for Calcium Carbonate System

Reaction	$\Delta_r G_K^\phi$ @ $\varphi = 25°C$ (kcal/mol)	$\Delta_r H_K^\phi$ @ $\varphi = 25°C$ (kcal/mol)	pK @ 25°C
First dissociation, K_1, Equation (13)	8.69	1.82	6.3
Second dissociation, K_2, Equation (14)	14.09	3.55	10.3
K'_1, Equation (12)	4.82		3.5
K_m, Equation (10)	3.87		2.8
K_H (mol/l/atm), Equation (9)	2.05	−4.64	1.5
Precipitation, K_{SP}, Equation (8)	11.4	−2.95	8.36

Oddo-Tomson Index (O&TI)[15]

The impact of pressure on partial pressure of carbon dioxide and pH is taken into account in this index. The O&TI is empirical and incorporates corrections for the presence of two or three phases (water, gas, and oil). The interpretation of the index is the same as those for Langelier and Stiff-Davis indices.

A Thermodynamic Approach Based on Gibbs Free Energy

The discussed earlier indices are mostly empirically based; even the LSI and S & DSI, which are based on the theoretical concept of saturation, include simplifications and empirical relationships in their derivation. As can be noted, these indices were developed mostly at times that access to computational facilities was limited if possible at all. As such, there was a need for simplifications and empirical modifications. However, with the advances in computational capabilities and access to them in today's date, one can easily resort to a completely theoretical approach for assessing the scaling propensity with respect to all salts. In addition, most these indices are for low salinities and the effect of ionic strength is taken into account empirically. Today's application of reverse osmosis to seawater desalination mandates assessing the scaling potential at very high salinities and in the presence of myriad of cations and anions that could entail various ion-interactive forces. As such, it is preferable to use a completely theoretical procedure for the calcium carbonate as is discussed later.

On the basis of thermodynamic principles, water having an ionic activity product for calcium and carbonate ions greater than the thermodynamic solubility constant (Eq. 1) would have a potential to form calcium carbonate scale

$$\{CO_3^{2-}\}\{Ca^{2+}\} > K_{sp} \tag{1}$$

The thermodynamic solubility product K_{sp}, is a function of the standard molar Gibbs free energy of reaction ($\Delta_r G^\phi$) according to Eq. 2, and is related to the standard Gibbs free energy of formation by Eq. 3

$$-RT\ln(K_{sp}) = \Delta_r G^\phi \tag{2}$$

$$\Delta_r G^\phi = (\Delta_f G^\phi)_{products} - (\Delta_f G^\phi)_{reactants} \tag{3}$$

R is the gas constant (1.987×10^{-3}kcal/mol.K), and T is the temperature (K). Values of $\Delta_f G^\phi$ for many pure compounds are known in the literature, and as such, the K_{sp} for pure compounds can be calculated. The challenge arises when mixed precipitates are formed and for which the Gibbs free energy is different from that of a pure compound,[5,6,8] and as such, the thermodynamic solubility product of the pure precipitate is different from that in the presence of impurities and also in coprecipitating systems. However, if one uses the basic theoretical approach, the modification due to presence of salt mixtures and other impurities would become possible as the knowledge in this area progresses. The additional information will become available by experimental procedure and most importantly by advances in computational chemistry and applications of molecular modeling.

The dissociation constants of the carbonic species are also an exponential function of the Gibbs free energy of reactions and for which the values are calculated from the Gibbs energies of formation of reactants and products provided in the literature. The constants for carbonic species at 25°C are listed in Table 3. The literature values for Gibbs free energy, and solubility and equilibrium constants are available for standard conditions of 25°C. Values at other temperatures are obtained from Eq. 4 as the change in the enthalpy of reaction can be considered constant within limited temperature ranges while the change in the Gibbs free energy significantly depends on the temperature

$$-RT\ln(K) = \Delta_r G^T = \frac{T}{298.15}\Delta_r G^{298} + \Delta_r H^{298}\left(1 - \frac{T}{298.15}\right) \tag{4}$$

As mentioned previously, water having a calcium and carbonate ionic activity product higher than K_{sp} for $CaCO_3$ has the potential to precipitate calcium carbonate, but not necessarily have the capacity to do so; neither the kinetics of precipitation might allow the formation of the precipitate within the unit. As such, this potential for scale formation indicates a conservative measure for predication of scaling propensity. One could translate this in terms of the solution *pH* by some restructuring of the relevant equations (Eqs. 9 to 22) describing the speciation of carbonic series and obtain that any water having *pH* greater than pH_{sat} (Eq.5) would have a potential to precipitate calcium carbonate

$$\begin{aligned} pH_{sat} = {} & p[Ca] + p[HCO_3^-] \\ & + p[(Exp((\Delta_r G_{Ksp}^T - \Delta_r G_{K2}^T)/RT)) \cdot \gamma_{Ca^{2+}} \cdot \gamma_{HCO_3^-}] \end{aligned} \tag{5}$$

Temperature T is in degrees Kelvin, the first two bracketed terms represent the concentration of calcium and bicarbonate ions (mol/L), and the activity coefficients, γ, for calcium, bicarbonate and hydrogen ions are determined from the Pitzer Eq. 16, which takes into account both ionic strength and electrostatic effects. Therefore, a scaling potential index (SPI)

Table 4. Equations for Calculations of Activity Coefficients

$$\ln \gamma_X = (|z_+|)^2 \left\{ -A_\phi \left[\frac{\sqrt{I_s}}{1 + 1.2\sqrt{I_s}} + \frac{2}{1.2} \ln(1 + 1.2\sqrt{I_s}) \right] + \sum_c \sum_a m_c m_a \beta''_{ca} + \sum_c \sum_{c''} m_c m_{c''} \phi''_{cc''} + \sum_a \sum_{a''} m_a m_{a''} \phi''_{aa''} \right\}$$

$$+ \sum_a m_a \left\{ 2\beta_{Xa} + \frac{1}{2} \left(\sum_c m_c |z_c| + \sum_a m_a |z_a| \right) \ell_{Xa} \right\} + \sum_c m_c \left(2\phi_{Xc} + \sum_a m_a \psi_{Xca} \right) + \sum_a \sum_{a''} m_a m_{a''} \psi_{aa''X} + |z_+| \sum_c \sum_a m_c m_a \ell_{ca} \quad (36)$$

$$\ln \gamma_Y = (|z_-|)^2 \left\{ -A_\phi \left[\frac{\sqrt{I_s}}{1 + 1.2\sqrt{I_s}} + \frac{2}{1.2} \ln(1 + 1.2\sqrt{I_s}) \right] + \sum_c \sum_a m_c m_a \beta''_{ca} + \sum_c \sum_{c''} m_c m_{c''} \phi''_{cc''} + \sum_a \sum_{a''} m_a m_{a''} \phi''_{aa''} \right\}$$

$$+ \sum_c m_c \left\{ 2\beta_{cY} + \frac{1}{2} \left(\sum_c m_c |z_c| + \sum_a m_a |z_a| \right) \ell_{cY} \right\} + \sum_a m_a \left(2\phi_{Ya} + \sum_c m_c \psi_{Yac} \right) + \sum_c \sum_{c''} m_c m_{c''} \psi_{cc''Y} + |z_-| \sum_c \sum_a m_c m_a \ell_{ca} \quad (37)$$

$$\ln \gamma_\pm = \nu^{-1} (\nu_X \ln \gamma_X + \nu_Y \ln \gamma_Y) \quad (38)$$

for calcium carbonate can be obtained by subtracting the solution pH from that at saturation as shown in Eq. 6, which indicates water having a scaling potential for positive values of SPI

$$SPI = pH - pH_{sat} \quad (6)$$

Equation 5 will be reduced to Eq. 7 for 25°C by replacing the values of Gibbs free energy from Table 1. At other temperatures within the range experienced in membrane processes, the Gibbs free energy can be obtained from Eq. 4 and should be used in conjunction with Equation 5

$$pH_{sat} = p[\mathrm{Ca}] + p[\mathrm{HCO_3^-}] + p[(\mathrm{Exp}(-4.557) \cdot \gamma_{\mathrm{Ca}^{2+}} \cdot \gamma_{\mathrm{HCO_3^-}}] \quad (7)$$

The SPI obtained from Equation 6 only indicates the potential for scale formation and provides a conservative estimate for assessment of water quality. However, for a given water quality the SPI might be positive but the scale might not form as a result of the following

1. The kinetics of the reaction might be too slow.
2. The induction period for formation of the precipitate might be very long.
3. Due to low buffering capacity, the water might not have the capacity to hold the precipitate.

Thus, the SPI is a conservative estimate for determining the recovery limits in desalination units. The SPI is an index completely based on the principles of thermodynamics and without considerations for kinetics of the process and system hydrodynamics. Both kinetics and hydrodynamics of the system affect the capacity of a specific system for scale formation and need to be taken into consideration. As well, the effect of impurities on kinetics and thermodynamics of precipitation should be taken into account while assessing the scaling potential of a system. Presence of impurities usually reduces the induction times and accelerates kinetics of precipitation. The effects of impurities can be included through incorporation of computational chemistry which is another aspect of the author's work and its fundamentals are discussed elsewhere. Hydrodynamic effects should be considered from the microscopic points of view. The recent works by author's research group have shown[1,5,7,8,17-27] that the effects of impurities, mixed salts, and residence time distribution within the system cannot and should not be ignored as they may have significant implications on the scale formation. A theoretical approach as proposed here would enable inclusion of these factors from first principles and incorporation with molecular modeling, as well as computational fluid dynamics.

Validation with Experiments and Comparative Assessments

The earlier proposed theoretical approach has been assessed by comparing the calculated values with experimental data of K_{sp} and pH_s, as well as by comparing SPI with predictions of the two most commonly used indices (LSI and S&DSI).

First, the calculated value of K_{sp} is compared with that obtained empirically.[9] The Gibbs free energies of formation for calcite and for aragonite are obtained from the literature and are, respectively −269.8 and −269.2 (kcal/mol). The literature[29] also lists the Gibbs free energies of formation for aqueous calcium and carbonate ions to be −132.18 and −126.22 kcal/mol, respectively. Thus, for calcium carbonate in calcite form, the $\Delta_r G^\phi$ can be calculated from the earlier values, and Eq. 3 to be 11.4 kcal/mol. Using Equations 2 and4, this would result in a K_{sp} value of 4.39×10^{-9} at 25°C and 4.04×10^{-9} at 30°C. The calculated value of 4.04×10^{-9} at 30°C is in very good agreement with the experimental value 9 of $3.7 \pm 0.4 \times 10^{-9}$ at 30°C.

The activity coefficients are required to calculate the saturation pH in Eqs. 5 and 7, and, hence, the SPI. Several equations and relationships were proposed and are available for calculation of activity coefficients of ionic species in the solution. Debye-Huckel limiting law[30], which is usually used for calculation of the mean activity coefficient $\gamma_\pm$, is only suitable for dilute electrolyte solutions where the main deviation from ideality is assumed to be due to long-range coulomb interactions between ions and is generally accurate for solutions with an ionic strength ≤ 0.01 M.[31] As such,

Table 5. Equations for Calculation of Parameters in Pitzer Equation

$$A_\phi = 0.3770 + 4.684 \times 10^{-4}(T - 27.15) + 3.74 \times 10^{-6}(T - 273.15)^2$$

For 1,1 (e.g. NaCl), 1-2 (e.g. Na_2SO_4) or 2-1 (e.g. $CaCl_2$) electrolytes

$$\beta_{ij} = \beta_{ij}^{(0)} + \beta_{ij}^{(1)}\left\{\frac{2}{(2\sqrt{I_s})^2}\left[1 - (1 + 2\sqrt{I_s})\exp(-2\sqrt{I_s})\right]\right\}$$

$$\beta''_{ij} = \frac{\beta_{ij}^{(1)}}{I_s}\left\{\frac{-2}{(2\sqrt{I_s})^2}\left[1 - \left(1 + 2\sqrt{I_s} + \frac{(2\sqrt{I_s})^2}{2}\right)\exp(-2\sqrt{I_s})\right]\right\}$$

For 2-2 (e.g. $CaSO_4$) electrolytes:

$$\beta_{ij} = \beta_{ij}^{(0)} + \beta_{ij}^{(1)}\left\{\frac{2}{(1.4\sqrt{I_s})^2}\left[1 - (1 + 1.4\sqrt{I_s})\exp(-1.4\sqrt{I_s})\right]\right\} + \beta_{ij}^{(2)}\left\{\frac{2}{(12\sqrt{I_s})^2}\left[1 - (1 + 12\sqrt{I_s})\exp(-12\sqrt{I_s})\right]\right\}$$

$$\beta''_{ij} = \frac{\beta_{ij}^{(1)}}{I_s}\left\{\frac{-2}{(1.4\sqrt{I_s})^2}\left[1 - \left(1 + 1.4\sqrt{I_s} + \frac{(1.4\sqrt{I_s})^2}{2}\right)\exp(-1.4\sqrt{I_s})\right]\right\} + \frac{\beta_{ij}^{(2)}}{I_s}\left\{\frac{-2}{(12\sqrt{I_s})^2}\left[1 - \left(1 + 12\sqrt{I_s} + \frac{(12\sqrt{I_s})^2}{2}\right)\exp(-12\sqrt{I_s})\right]\right\}$$

$$\ell_{ij} = \frac{\ell_{ij}^{\phi}}{2(|Z_iZ_j|)^{0.5}}$$

ϕ and ψ account for interactions between ions of like sign. The 2nd virial coefficients ϕ_{ij} are

$$\phi_{ij} = \theta_{ij} + {}^E\theta_{ij} \qquad \phi''_{ij} = {}^E\theta''_{ij}$$

θ_{ij} is a single parameter for each pair of anions or cations. The terms ${}^E\theta_{ij}$ and ${}^E\theta''_{ij}$ are zero when the ions i and j are of the same charge and account for electrostatic un-symmetric mixing effects:

$${}^E\theta_{ij} = \left(\frac{|Z_iZ_j|}{4I_s}\right)\left[J(x_{ij}) - 0.5J(x_{ii}) - 0.5J(x_{jj})\right]$$

$${}^E\theta''_{ij} = \left(\frac{-{}^E\theta_{ij}}{I_s}\right) + \left(\frac{|z_iz_j|}{8I_s^2}\right)\left[x_{ij}J''(x_{ij}) - 0.5x_{ii}J''(x_{ii}) - 0.5x_{jj}J''(x_{jj})\right]$$

$$x_{ij} = 6|z_iz_j|A_\phi\sqrt{I_s}$$

$$J(x) = x\left[4 + 4.581x^{-0.7237}\exp(-0.0120x^{0.528})\right]^{-1}$$

$$J''(x) = \frac{4 + [4.581x^{-0.7237}\exp(-0.0120x^{0.528})][0.006336x^{0.528} + 1.7237]}{[4 + 4.581x^{-0.7237}\exp(-0.0120x^{0.528})]^2}$$

The 3rd virial coefficient mixing parameters ψ_{ijk} (i and j are different anions (or cations), and k is a cation (or anion)) are assumed to be independent of the concentration.

in this work which is intended to be fundamental and applicable to wide salinity ranges, Pitzer model [16] which is an expansion of Debye-Huckle and was developed for complex systems is used. Pitzer model is valid up to 6 M;[16] the activity coefficients by Pitzer[32] consider the ion interaction due to electrostatic forces, and long and short-range interactions between ions and are given in Table 4. The Debye-Huckel parameter A_ϕ, and other parameters required for calculation of activity coefficients are obtained as

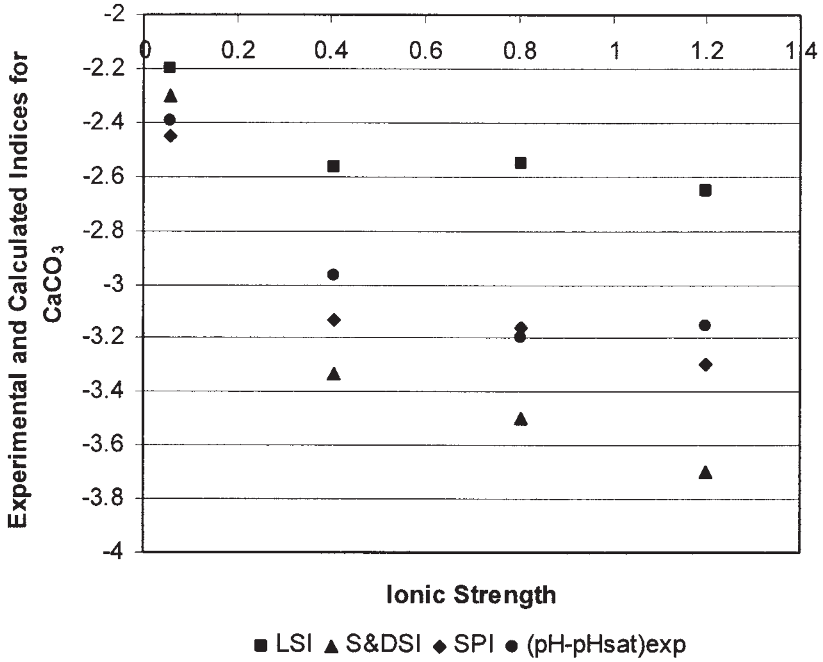

Figure 1. SPI with experimental results, LSI and S&DSI.

summarized in Table 5. The ion interaction parameters are available in the literature.[33] The ionic activity coefficients obtained from Pitzer model is then used to calculate the mean ionic activity coefficient (γ) for an electrolyte as a function of the single ionic activity coefficients.[34] The activity coefficient determined in this manner takes into account the effect of all the ionic interactions and distinguishes between the type, and the charge of ions present as opposed to the commonly used total dissolved solids incorporated into empirical correlations. As such, it could take into account the differences in scaling potential between the reverse osmosis unit and a nanofiltration unit, as the later has different passages for monovalent and divalent ions. Current scale assessment indices do not differentiate this fact.

Experiments were carried out with several feeds to compare the calculated value of SPI based on the approach discussed earlier. The saturation pH was measured experimentally, as well as that according to the SPI. The results are shown in Figure 1 for various solutions. It is clear that SPI is a better measure of assessing the scaling potential of water; it predicts values much closer than either of the two commonly used LSI and S & DSI indices. In addition as discussed earlier, it enables us to consider the ion specific interactions and passages that are important in membrane desalination that are being used increasingly in practice. The incorporation of other interactive and also hydrodynamic effects could also be addressed in the future from first principles.

Conclusions

The indices so far employed for assessing the scaling potential of calcium carbonate are based at least partially on empirical relationships. They use an empirically obtained solubility relationship and they do not take to account the effect of electrostatic forces and short and long range ionic interactions. Various indices used have been discussed in this article. Advances in computation and software development provide easy means of using theoretical relationships that provide more accurate and reliable results. A new index called the scaling potential index (SPI), based on the theoretical relationships have been obtained by incorporating the Gibbs free energy of reaction for determination of the speciation constants of the calcium carbonate system. Pitzer equation which is valid for solutions up to 6M is used for determination of the activity coefficient. Various constants required for calculation of the activity coefficients are included for waters considering Na, Cl, Ca, sulfate, carbonic species to be the dominant ionic species in the water which is the case in both seawater and brackish water systems. This index also incorporates the effect of pressure on solubility of carbon dioxide which is important in the reverse osmosis by incorporation of the Henry's law. The index can be calculated by incorporation of the system temperature, pressure, solution pH, calcium concentration and the activity coefficients for calcium and hydrogen; the relationships for calculation of activity coefficients are provided. This index can be easily modified to assess the scaling potential of other salts.

When the SPI is positive, water has the potential to form scale, when it is negative has the potential to dissolve calcium carbonate; when zero the system is at equilibrium. It should be noted that any water having a positive SPI would not have the capacity to form the scale or the kinetics might be too slow. The SPI is a conservative estimate for assessing scaling potential. The effect of system kinetics and hydrodynamics on the formation of the scale cannot be ignored. Also, when assessing the kinetic effects and the time factor, the residence time distribution within the system should be considered as opposed to the commonly used approach of basing decisions on the mean residence time within the system. Using a theoretically obtained index would enable incorporation of hydrodynamic and interactive effects from the fundamental principles in future studies.

The calculated values of SPI have been compared with experimental ones and have been in good agreement. Also, comparisons have been made between the theoretically calculated SPI in this study and the two most commonly indices (LSI and S&DSI) for calcium carbonate - SPI is a better measure predicting the scaling potential.

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