



# W-INDEX

Water INDEX calculations  
Version 5.0 for Excel

(c) 2006

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# W-index

## Water-INDEX calculations

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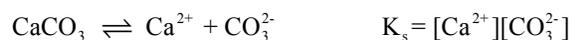
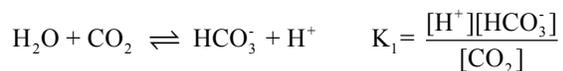
### Why do we have scaling?

Calcium and magnesium provide hardness in a solution. By itself, hardness does not present any problems. A calcium solution at a pH of 3 may have hardness, but it is not going to scale. This Section looks at the scaling or precipitation fouling that results when alkalinity is present with the hardness and how this scaling forms on heat-transfer surfaces in cooling systems.

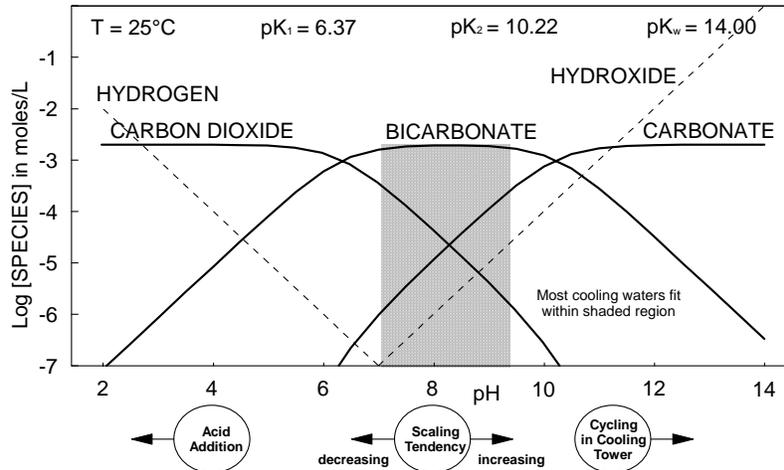
### Hardness

The presence of combinations of calcium, magnesium and alkalinity (carbon dioxide) that produce "hardness" in the water can lead to scale formation, particularly on heat-transfer surfaces. Scaling or precipitation fouling is a frequent problem in cooling systems. The evaporation and/or heating that takes place within the system converts relatively soluble alkalinity and calcium from the raw water into insoluble calcium carbonate. If flowrates are high, calcium carbonate may be carried in suspension through the system before it settles. Given the right conditions, it could settle in the cooling tower sump or be lost through the bleedoff system or by filtration. If the flowrate in the boundary layer adjacent to the tube surface is low, some settling may occur. As cooling towers are outside and to some extent act as air washers, there is the added likelihood of microbiological fouling occurring simultaneously. The slime forming bacteria provide an additional attachment mechanism that helps bond solid material to the walls. As the thickness of the solid builds up, the ability of the system to cool critical components will be lost.

When a single material such as calcium carbonate deposits on the walls of heat transfer surfaces, the resultant crystals tend to be very hard. In the equilibrium between carbon dioxide gas (from the air) and water, calcium carbonate will be the insoluble product. The equilibria in naturally occurring waters include the various carbonate species (the top pair of equations), the self dissociation of water (the middle equation) and the solubility of calcium carbonate in the form of calcite (the last equation).



The figure derived from these equations shows the relative abundance of the various species vs. pH over the range from 2-14. In the pH 7-8 range, typical of most raw waters, the main species is the bicarbonate ion. Under acid conditions it is predominantly carbon dioxide and just the opposite under caustic conditions where it is predominantly carbonate. In a cooling tower, there is a concentrating mechanism which increases the pH and converts soluble bicarbonate to insoluble carbonate ion.



**Carbonate Equilibrium Diagram for Cooling Water**

In the language of the water-treatment industry, the term alkalinity refers to both the carbonate species and hydroxide. The total alkalinity will be the sum of the individual species:

$$\text{Alk} = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-]$$

Substituting the various equilibria into the above equation and multiplying by  $[\text{H}^+]_s$  (the hydrogen ion concentration at saturation) yields a standard *quadratic* equation that can be solved for  $[\text{H}^+]_s$ .

$$\frac{K_s}{[\text{Ca}^{2+}]K_2} [\text{H}^+]_s^2 + \left( \frac{2K_s}{[\text{Ca}^{2+}]} - \text{Alk} \right) [\text{H}^+]_s + K_w = 0$$

As pH is defined as the negative logarithm of  $[\text{H}^+]$  to the base 10;  $\text{pH}_s$ , the pH at saturation, then would be  $-\log [\text{H}^+]_s$ . It is this  $\text{pH}_s$  that forms the basis of the scaling index calculations.

## **Predicting Scaling**

There are three scaling indices in common usage. All three utilize this  $\text{pH}_s$ . Each index has people who prefer them and others who disagree with them. Over the years, the calculations were simplified through use of nomograms that were applicable over a rather limited range. Today, it is more common to do a rigorous calculation using computer programs. All calculations within this manual were performed using W-index which gives results within  $\pm 0.02$  of the values obtained by the AWWA. Details of the methods behind the calculations are described in *Standard Methods for the Examination of Water and Wastewater*, or as more called, *Standard Methods*. This is a joint publication of the American Public Health Association, the American Water Works Association and the Water Environment Federation.

- The **Langelier Saturation Index** or **LSI**<sup>1</sup> was the first attempt to quantify the tendency to form scale. It is defined simply as the difference between the actual system pH (the measured value) and the saturation pH<sub>s</sub>. This index provides a simple criterion by which the likelihood of scaling can be predicted.

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

A positive LSI indicates a potential for scale formation. A negative LSI indicates that scaling is unlikely and would also imply that any existing scale would be removed over time. An LSI of zero indicates the system is in equilibrium. As the LSI represents an equilibrium position, it can not state how fast nor how extensively things happen as that depends upon the nature of the driving force which pushes it. This driving force could come from an increase in temperature as the water goes through the condenser. As a general guideline, Feitler<sup>2</sup> suggested +0.6 as the threshold above which scaling is likely. Ferguson<sup>3</sup> showed the relationship between ion association and the computed value of the LSI. Many authors have published charts and tables where they have set +0.5 as moderate, +1.0 as severe and +2.0 as very severe scaling. These are readily available guidelines within the industry, which can be found within various trade journals and water-treatment handbooks. Micheletti<sup>4</sup> suggested that the effects of ion pairing should be evaluated to understand why various scaling indices work or fail with different waters.

pH<sub>s</sub> comes from the solution of a quadratic equation. The solution to this quadratic equation is rather unusual in that both solutions have some real meaning. The positive root is valid below 10.4, the bicarbonate-carbonate equivalence point at 25°C. This covers essentially all cooling waters. In this system, the negative root is valid above the bicarbonate-carbonate equivalence point (pH >10.4) and is used for high-pH applications that involve the carbonate-hydroxide equilibrium. When calculating scaling indices in this region, there is a total reversal of the LSI calculation.

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

The likelihood of scaling increases as the pH goes up to 10.4, the bicarbonate-carbonate equivalence point. As the pH goes higher, the potential for scaling starts to fall. Here, it is going away from the bicarbonate-carbonate equivalence point into the region of the carbonate-hydroxide equilibrium. Calcium hydroxide (lime) is much more soluble than calcium carbonate. The high-pH situation is very commonly encountered with mining and milling operations, hydraulic ash transport systems and scrubber systems as might be found in a basic oxygen furnace. There is no equivalent high-pH situation with the other indices. The fact that the high-pH calculations function only with the LSI is an indication that the empirical basis of the RSI and PSI calculations operate only over a very limited period.

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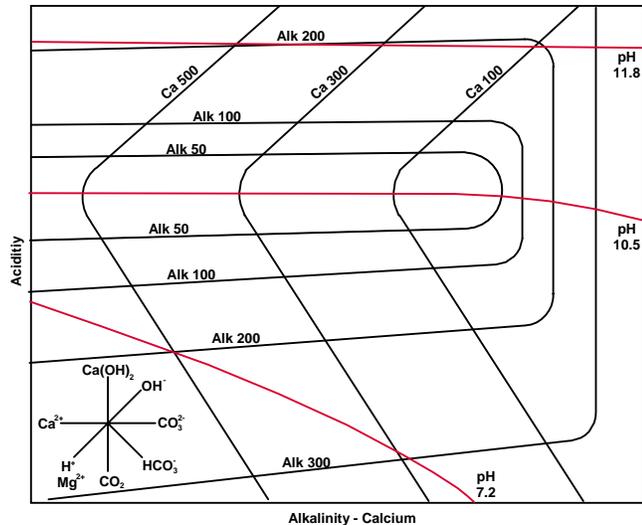
<sup>1</sup> W. F. Langelier, *The analytical control of anti-corrosion water treatment*, Journal of the American Water Works Association, V28 #10, pp 1500-1521, 1936. W. F. Langelier, *Chemical equilibria in water treatment*, Journal of the American Water Works Association, V38 #2, pp 169-178, 1946.

<sup>2</sup> H. Feitler, *Critical pH scaling indexes*, Paper #144, Corrosion 75, Toronto, ON, April 14-18, 1975.

<sup>3</sup> R. L. Ferguson, *Computerized ion association model profiles complete range of cooling system parameters*, Paper IWC-147, International Water Conference, Pittsburgh, PA, 1991.

<sup>4</sup> W. C. Micheletti, Prepared discussion of: *Cooling water scale and scaling indices: what they mean - how to use them effectively - how they can cut treatment costs*, Paper IWC-47, International Water Conference, Pittsburgh, PA, 1999.

In 1952, Caldwell and Lawrence<sup>5</sup> develop what is now known as a Caldwell-Lawrence diagram. The intent was to come up with a simplified approach to implementing water-conditioning chemistry. This diagram consists of a family of curves for different alkalinity, calcium and pH values. The value for  $pH_s$  can be obtained by finding the junction of the calcium and alkalinity lines for the particular water. The  $pH_s$  value corresponded to the pH value that crossed this junction. While both a low and a high pH value could be obtained, only one was really possible and the choice would be obvious from the situation. In 1976, Loewenthal<sup>6</sup> and Marais developed a modified Caldwell-Lawrence Diagram that incorporated ionic activity corrections. The sketch shows a simplified layout.



**Modified Caldwell-Lawrence Diagram**

- The **Ryznar Stability Index** or **RSI**<sup>7</sup> is defined by a simple empirical relationship that was found by trial and error and seems to be representative of a large number of waters from a limited number of geographical regions.

$$RSI = 2pH_s - pH$$

Unlike the LSI, there is no theoretical basis for its operation. It was based solely upon scaling performance observed in a large number of water samples. For those waters, it was seen that scaling was unlikely to occur if the value is  $<6$  with an increasing likelihood as it goes lower. It is considered as likely to go the other way and dissolve scale if  $>7$ . It should be noted that when an empirical relationship is introduced that applies to a large number of water samples, there may also be many water samples for which it does not apply.

- The **Practical or Puckorius Scaling Index**<sup>8</sup> is a variation of the RSI. As with the RSI, it is also an empirical relationship, but differs from the RSI by using a calculated pH, referred to as the equilibrium pH, instead of the measured pH. This  $pH_{eq}$  is also an empirical relationship based upon measurements in a large number of water samples.

<sup>5</sup> D. Caldwell and W.B. Lawrence, *Water softening and conditioning problems*, Industrial and Engineering Chemistry, Vol 45 #3, pp 535-548, 1953.

<sup>6</sup> R.E. Loewenthal and G.v.R Marais, *Carbonate Chemistry of Aquatic Systems: Theory & Application*, Ann Arbor Science Publishers, Ann Arbor, MI, 1976, ISBN 0-250-40141-X.

<sup>7</sup> J. W. Ryznar, *A new index for determining amount of scale formed in water*, Journal of the American Water Works Association, V36 #2, pp 472-486, 1949.

<sup>8</sup> P. Puckorius, *Get a better reading on scaling tendency of cooling water*, Power, pp 79-81, Sep. 1983, P. R. Puckorius and J. M. Brooke, *A new practical index for calcium carbonate scale prediction in cooling systems*, Corrosion, pp 280-284, April 1991, P. R. Puckorius and G. R. Loretitsch, *Cooling water scale and scaling indices: what they mean - how to use them effectively - how they can cut treatment costs*, Paper IWC-47, International Water Conference, Pittsburgh, PA, 1999.

$$\text{PSI} = 2\text{pH}_s - \text{pH}_{\text{eq}} \quad \text{where } \text{pH}_{\text{eq}} = 1.465 \log(\text{M Alkalinity}) + 4.54$$

As with the RSI, the PSI considers scaling as unlikely to occur if the value is  $<6$  with an increasing likelihood as it goes lower. It is considered as likely to dissolve scale if  $>7$ . It is of interest to note that the calculation does not use the actual measured system pH. One of the methods to reduce scaling is to lower the pH, which also lowers the alkalinity. A scaling index would be expected to respond to this change. When used in an application where acid was added, the LSI and RSI did show a reduced scaling potential; the PSI did not.

**Which index should be used?** The LSI has a logical theoretical basis; while, the RSI and PSI are empirical relationships that utilize the  $\text{pH}_s$  from Langelier and try to come up with an improved prediction based upon empirical from a limited number of water samples. As the choice of index can give quite a different picture, one of the most difficult tasks in making predictions is to choose the most appropriate index and know why. How does one get biases? In one project, the author compared the scaling potential for several Western Canadian waters using all three. The LSI agreed with experience much more often than did the other two.

Water A: reported as highly scaling, average of 8 values:

- LSI = 1.41 - high potential for scaling
- RSI = 5.81 - moderate potential for scaling
- PSI = 6.16 - scaling not likely to occur

Water A after pH control with  $\text{CO}_2$  addition, average of 7 values:

- LSI = 0.90 - moderate potential for scaling
- RSI = 6.31 - scaling not likely to occur
- PSI = 6.18 - scaling not likely to occur - (the same value as without  $\text{CO}_2$  addition)

Water B: reported scaling problem in condenser

- LSI = 0.66 - moderate potential for scaling
- RSI = 7.20 - scaling unlikely, may dissolve existing scale
- PSI = 7.37 - scaling unlikely, may dissolve existing scale

Water C: reported severe scaling in condenser and need to acid clean twice a year.

- LSI = 1.59 - high potential for scaling
- RSI = 6.38 - scaling unlikely
- PSI = 7.93 - scaling unlikely, may dissolve existing scale

Water D: reported moderate scaling in condenser and need to acid clean every second year

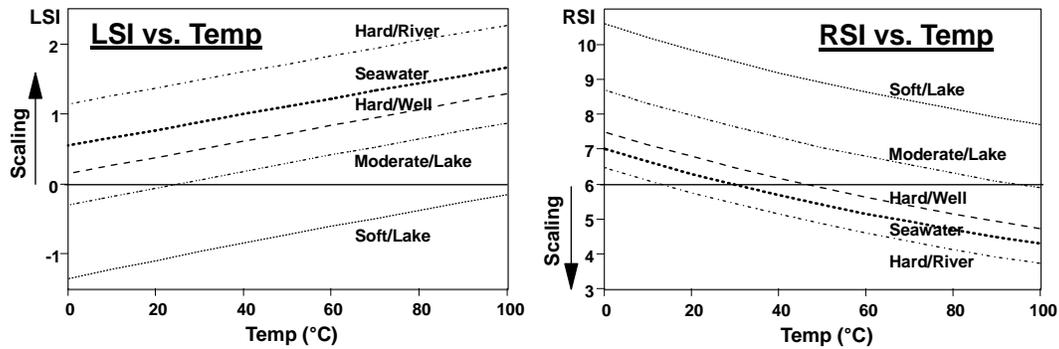
- LSI = 1.36 - high potential for scaling
- RSI = 5.97 - scaling unlikely
- PSI = 6.95 - scaling not likely to occur

Water E: reported severe scaling in condenser and need to acid clean every year

- LSI = 1.97 - high potential for scaling
- RSI = 5.03 - scaling not likely to occur
- PSI = 6.06 - scaling unlikely

Water F: scaling a problem, town installed cold-lime softener

- LSI = 1.45 - high potential for scaling
- RSI = 5.69 - scaling not likely to occur
- PSI = 6.21 - scaling not likely to occur



Why do these differences exist? The Langelier Index indicates an equilibrium position. This is established by thermodynamic reasoning. There is no guarantee that scaling will or will not occur, even if the index so indicates. The Ryznar and Puckorius indices were developed as a means to improve the ability to make a prediction. The ability to improve that prediction is more than a matter of shopping for the index that most meets the desired result. It is really a need to recognize that the decision *to scale or not to scale* rests with another branch of chemistry called kinetics. Kinetics looks at how fast the scaling will occur or whether there is enough energy available to push the process over the potential energy barrier. The factors that come into play include the actual temperature changes at the heated surface and how fast they occur, turbulence, changes in concentration, and residence time near the heated surface.

It is the composition of the water that dictates whether or not it is likely to scale. One of the biggest sources of freshwater in the world is the Great Lakes system shared by Canada and the USA. The softest water in the chain is Lake Superior, which is on a base of igneous rock. At the other end of the chain is Lake Ontario, which is a moderately hard water over a limestone base. In the two charts below, Lakes Superior and Ontario are listed as Soft Lake and Moderate Lake respectively. The lakes are huge bodies of water and the conditions within them tend to be very stable. They are sitting at or close to equilibrium. At ambient temperature, the LSI<sup>9</sup> value of Lake Superior is negative as there isn't enough carbonate on an igneous rock base and it is trying to dissolve carbonates where Lake Ontario is close to zero. Other sources of water for cooling purposes can come from rivers, wells and lakes of varying composition and from seawater. The chart below takes five of these sources and compares the changes in the LSI and RSI as the water goes from freezing to boiling.

With the heating or concentrating that occurs in a cooling system, the soft water from Lake Superior can never get enough carbonate into it, while the moderate water from Lake Ontario moves quickly into the scaling region as it goes warmer. On the other hand, the more concentrated waters will start to form scales at relatively low temperatures. It follows that combining the temperature with concentrating would further aggravate the situation. This is what happens in a cooling tower. Looking again at the two charts, it can be seen that the hard waters are more scaling. Some very-hard well waters tend to be scaling under any conditions where they warm up only slightly.

In all natural waters, there is a balance among dissolved carbon dioxide (often incorrectly called carbonic acid), bicarbonate ion and carbonate ion. Many inland waters are considered as hard because they contain high concentrations of both the carbonate species and calcium. They will precipitate a calcium carbonate scale if they are heated and that is just what happens as they pass

<sup>9</sup> The LSI values in these graphs were calculated using the computer program W-index.

through the condenser or other heat exchanger. The likelihood that scaling will occur can be estimated from the Langelier Saturation Index or LSI. A zero value indicates equilibrium. A positive value indicates that scaling is likely and a negative value indicates that it is unlikely. Often it doesn't start to form until the LSI exceeds somewhere in the 0.6 region. This may be a result of a need to get that extra kick to push the scaling reaction to overcome the potential energy barrier that stands in the way of getting the scaling reaction to occur. It may also be a result of a need for more rigorous calculations that go beyond the carbonate itself and look at the interactions of all the ions in the solution.

Major electrical generating stations or industrial facilities using once-through cooling transport very large volumes of water. The temperature of the discharge can have a very significant impact upon the aquatic life in the region where it returns to the lake or river. To limit this impact, most operating licenses limit the temperature rise ( $\Delta T$ ) for the discharged water. Typically, that limit is a 11 C° or 20 F° rise above that of the incoming water. As can be seen from the plot of LSI vs. temperature, that represents an LSI change in the range of 0.1 - 0.2. That's a very small change and isn't really going to make all that much difference. A frequently-made assumption is that the onset of scaling is based upon the difference between the inlet and outlet temperature. It must be remembered that the measured  $\Delta T$  between inlet and outlet is an averaged value. The surface temperature in the tubes of a large surface condenser may be 20-30°C or 70-90°F while that on a mould surface in steelmaking continuous casting machine can be as high as 140°C or 280°F. The water near the heat-exchange surface may approach those temperatures and be subjected to the type of scaling that might be expected. When this hot water mixes with the bulk fluid, the bulk temperature will warm it up a bit, but not enough to account for massive scaling. It is these local temperatures that play the bigger role.

### **Additional Useful Indices**

There are many useful indicators that scaling or other problems may or may not occur with different species. The ones listed below are the simple ones. If one wants to get into detail with other species and the related ion-pairing calculations, the computer program WaterCycle<sup>10</sup> is recommended. It does the rigorous calculation that is needed for a wide variety of scaling species and calculates dosages for a large number of commercially available scale modifiers.

#### **Carbonate Saturation Level**

A very useful indicator comes from the relationship between the Ion Activity Product (IAP) and the equilibrium constant ( $k_{sp}$ ). A simple ratio, IAP/ $k_s$ , relates the ion activity product to the solubility product constant to give a rough indication of the degree of supersaturation. The relationship is given by:

$$\frac{IAP}{k_s} = \frac{[Ca^{2+}] \times \alpha_{Ca^{2+}} \times [CO_3^{2-}] \times \alpha_{CO_3^{2-}}}{k_{sp} \text{ for } CaCO_3}$$

where a value of:  
 < 1 indicates undersaturation  
 = 1 indicates equilibrium and  
 > 1 indicates supersaturation.

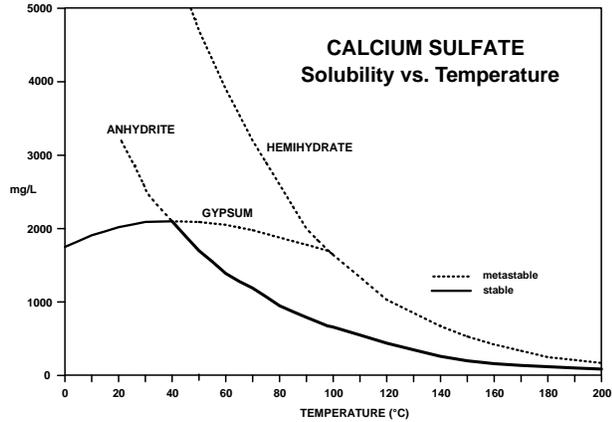
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<sup>10</sup> R. L. Ferguson, *Computerized ion association model profiles complete range of cooling system parameters*, Paper IWC-147, International Water Conference, Pittsburgh, PA, 1991.

In a typical system, a value of 1.2 to 1.5 can often be achieved before scaling occurs. If it goes higher, scaling is likely. If it is less than 1, scaling is unlikely and any existing scale is likely to dissolve.

### Sulfate Scaling

Calcium sulfate (gypsum) is two orders of magnitude more soluble than calcium carbonate. This means that the sulfate is much less likely to drop out of solution when both are present. The solubility of calcium sulfate can be a significant concern in water systems that contain large concentrations of both calcium and sulfate. This type of water might be present with oil-field brines.



Skillman<sup>11</sup> developed a simple sulfate solubility index for estimating the likelihood of calcium sulfate scaling in this type of application. It is of the form:

$$\text{Skillman Index} = \frac{S_{\text{actual}}}{S_{\text{theoretical}}} \quad \text{where } S_{\text{theoretical}} = 1000 \times \left( \sqrt{(X^2 + 4k_{\text{sp}})} - x \right)$$

where the ratio will be for either the calcium or sulfate, whichever is the limiting species. The concentration will be in meq/L. In Skillman's paper, he used an oil-field brine with the following composition: 1,257 mg/L Na<sup>+</sup>, 808 mg/L Ca<sup>2+</sup>, 242 mg/L Mg<sup>2+</sup>, 2,025 mg/L Cl<sup>-</sup>, 2,428 mg/L SO<sub>4</sub><sup>2-</sup> and 443 mg/L HCO<sub>3</sub><sup>-</sup>.

The  $x$  in the equation is the excess common-ion concentration of the calcium and sulfate ions and can be calculated by:

$$\begin{aligned} x &= \{2.5 \times [\text{Ca}^{2+}] - 1.04 \times [\text{SO}_4^{2-}]\} \times 10^{-5} \text{ M/L} \\ &= \{2.5 \times 808 - 1.04 \times 2428\} \times 10^{-5} = 0.5 \times 10^{-2} \text{ M/L} \end{aligned}$$

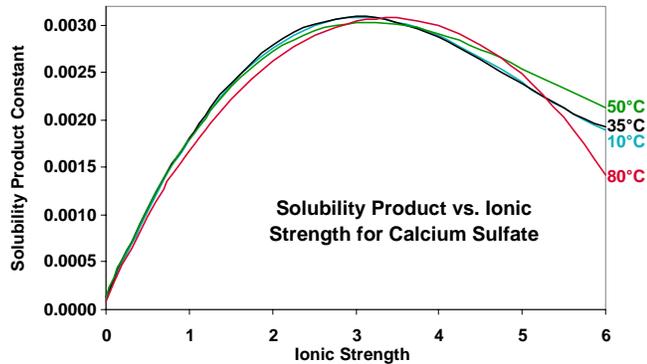
where the square brackets represent the concentrations of the species in mg/L. The ionic strength of the solution is needed for the calculations. It can be calculated from the measured TDS or as Skillman did, estimated its value from the concentrations of some of the main species in water by multiplying each by their respective conversion factors.

$$\begin{aligned} U &= 2.2 \times [\text{Na}^+] + 5.0 \times [\text{Ca}^{2+}] + 8.2 \times [\text{Mg}^{2+}] + 1.4 \times [\text{Cl}^-] + 2.1 \times [\text{SO}_4^{2-}] + 0.8 \times [\text{HCO}_3^-] \times 10^{-5} \\ &= 2.2 \times 1257 + 5.0 \times 808 + 8.2 \times 242 + 1.4 \times 2025 + 2.1 \times 2428 + 0.8 \times 443 \times 10^{-5} = 0.17 \end{aligned}$$

<sup>11</sup> H.L. Skillman J.P. McDonald, Jr. and H.A. Stiff, Jr., *A simple, accurate, fast method for calculating calcium sulfate solubility in oil field brine*, Paper No. 906-14-I, Spring Meeting of the Southwestern District, Division of Production, American Petroleum Institute, Lubbock, Texas, 1969.

This value corresponds to  $k_{sp} = 4.65 \times 10^{-4}$

To obtain that  $k_{sp}$  value, Skillman developed a family of curves relating the calcium sulfate solubility product constant,  $k_{sp}$  with the ionic strength. The  $k_{sp}$  was obtained by the value corresponding to the ionic strength on the curve for the appropriate temperature. Later computerized versions did least-squares fits to the curves to approximate them with a polynomial. In Skillman's example, he determined the value of  $k_{sp}$  from his curve for 95°F/35°C.



The measured concentrations of calcium and sulfate were 808 and 2,428 mg/L respectively. Converted to meq/L they would be 40.4 and 50.5 respectively. As the value for calcium is the lower of the two, it is the one that limits the solubility as calcium sulfate. Going back to the equation earlier in this section, the numbers can now be inserted to get a value for the index.

$$\text{Skillman Index} = \frac{S_{\text{actual}}}{S_{\text{theoretical}}} = \frac{40.4}{38.4} = 1.05$$

$$\text{where } S_{\text{theoretical}} = 1000 \times \left( \sqrt{(0.25 \times 10^{-2} + 4 \times 4.65 \times 10^{-4})} - 0.5 \times 10^{-2} \right)$$

As the value of the Skillman Index is greater than 1.0, it shows the water to be slightly on the scaling side with respect to calcium sulfate.

### Larson-Skold Index

In a study to quantify the aggressiveness of a water toward pitting, Larson and Skold<sup>12</sup> developed a simple index. It was based upon chloride and sulfate being the major contributors to the aggressiveness toward corrosion and alkalinity as working to minimize their aggressiveness. The study was conducted on Great Lakes waters and tends to have some ability to predict the likelihood of pitting on waters of similar composition.

$$\text{Larson-Skold Index} = \frac{[\text{Cl}^-] + [\text{SO}_4^{2-}]}{[\text{HCO}_3^-]}$$

Where the square brackets denote concentrations of the three species in meq/L (milliequivalents per litre). This unit is chosen rather than the more common ppm as  $\text{CaCO}_3$  as the effect is based upon chemical activity. As this relationship was derived from an empirical study based upon Great Lakes waters, it's effectiveness tends to be limited to waters within a pH range between 6.6 and 8.5. Using this as a guideline, if the index is:

<sup>12</sup> T.E. Larson and R.V. Skold, *Laboratory Studies Relating Mineral Quality of Water to Corrosion of Steel and Cast Iron*, 1958 Illinois State Water Survey, Champaign, IL pp. 43 - 46: ill. ISWS C-71 also in *Corrosion* 14 pp 285-288, 1958.

- <0.8 Chloride and sulfate are unlikely to interfere with the formation of a natural film to protect the carbon steel.
- >0.8 & <1.2 Chlorides and sulfates may interfere with the formation of any natural film and the corrosion rates may be higher than expected.
- >1.2 High rates of localized corrosion may be expected.

The Larson-Skold index will be applicable in predicting the likelihood of corrosion in once-through cooling systems.

## Notes on the operation of W-index

W-index is an Excel spreadsheet. It can be loaded as any other spreadsheet. There are no macros. It's operation is almost self-explanatory. Inputs can only be entered in the Setup and Input worksheets and only into the unprotected cells that are indicated by their blue colour.

Worksheet	Notes
W-index	Introduction to W-index with some notes
Setup	<ol style="list-style-type: none"> <li data-bbox="467 590 1372 709">1 Scaling Criteria: The graphs for the scaling indices are colour coded to indicate, safe, caution and danger states. When shipped, the criteria used for the Langelier and the Puckorius-Ryznar criteria are preset at 0.0/6.0 for possible scaling and 0.6/5.0 for likely scaling. These can be altered to meet the users experience.</li> <li data-bbox="467 741 1372 856">2 Source of the Constants: The curves used to fit the equilibrium constants used for <math>pK_s</math>, <math>pK_1</math>, <math>pK_2</math> and <math>pK_w</math> come from Standard Methods. The values for <math>pK_s</math> and <math>pK_2</math> can also be set on the Setup worksheet to use values published by the AWWA.</li> </ol>
Input	<ol style="list-style-type: none"> <li data-bbox="467 867 1372 951">1 This provides data specific to the sample under its specific sampling temperature. This table calculates all the indices that apply. Some warnings are given based upon input data and the potential for scale formation.</li> <li data-bbox="467 989 1372 1041">2 Sample ID: These cells provide the labels for the tables and graphs. The term "SAMPLE ID ...." can be changed as can anything that is blue.</li> <li data-bbox="467 1079 1372 1194">3 Temperatures can be entered as C or F. This is the actual temperature at which the measurement is made. Enter a numerical value in the first cell and either an upper or lower case C/F in the second. A warning appears if an invalid character is entered.</li> <li data-bbox="467 1232 1372 1379">4 Both the methyl orange (M) and phenolphthalein (P) alkalinities are requested in units of ppm as <math>CaCO_3</math>. An error message will appear if the combination of values for the two alkalinities and the pH are invalid. M-ALK is used to determine the scaling indices and the calculation will proceed. The P-ALK is required to make a high-pH correction to the equilibrium diagram.</li> <li data-bbox="467 1417 1372 1501">5 A value for the P-ALK is expected if the pH is greater than 8.00 and a warning will appear. The various indices will still be calculated for the table on this sheet. There may be some small error in the temperature effects if it isn't there.</li> <li data-bbox="467 1539 1372 1623">6 Calcium hardness in ppm as <math>CaCO_3</math> is used for the calculation. If your value is in mg/L as Ca, enter this as 2.5*the value in mg/L. This will apply the correction.</li> <li data-bbox="467 1661 1372 1692">7 The pH is the measured pH at the temperature specified above.</li> <li data-bbox="467 1730 1372 1801">8 The chloride and sulfate are required in mg/L as Cl or <math>SO_4</math>. Both are used for calculating the Larson-Skold Index. The sulfate is used to calculate the Skillman Sulfate Index.</li> </ol>

Worksheet	Notes
Temperature	<ol style="list-style-type: none"> <li>1 This worksheet shows the variations of the sample with temperature. It is valid for pH &lt; 10.3 which covers most cooling and domestic waters. A warning will appear if the pH goes above 10.2.</li> <li>2 It is interesting to note that the scaling potential changes very little with temperature over the delta-T common to most cooling systems. A 10 C° temperature range changes the LSI by about 0.2. This is hardly enough to promote scaling.</li> <li>3 When designing a system or treatment program, it should be recognized that if a water is already scaling, it will tend to drop out calcium carbonate at the hottest surface. It should also be noted that the delta-T of the system is an averaged temperature rise. A given heat exchange surface may be much higher, e.g., the surface of the mould in a continuous casting machine for steel production may be as high as 120-140 °C in spite of the overall cooling water stream having a delta-T of 5-10 C°.</li> </ol>
Hi-pH	<ol style="list-style-type: none"> <li>1 This worksheet shows temperature variations for pH &gt; 10.4 as might be found in ash-transport, mining and basic oxygen scrubbers. A warning will appear if the pH is below 10.2.</li> <li>2 W-index was able to show that all the <i>normal</i> treatments applied to minimize scaling in the system, from which the pipe section on the cover had been taken, were inappropriate and how to keep the system from scaling as badly as it had been doing.</li> </ol>
CTower	<ol style="list-style-type: none"> <li>1 This worksheet makes an estimate of the changes that might occur when the water sample is cycled in a cooling tower.</li> <li>2 As the first step, the system is equilibrated with the carbon dioxide in the atmosphere.</li> <li>3 The start, stop and step range is selected on the Setup worksheet.</li> </ol>
RO	<ol style="list-style-type: none"> <li>1 This worksheet does a similar calculation to those in CTower, but without the equilibration step.</li> <li>2 The calculation provides an estimate of the likelihood of scaling on the reject side when the water sample is passed through an RO membrane.</li> <li>3 The reject/throughput ratios are preset in 10% steps.</li> </ol>
Composition	<ol style="list-style-type: none"> <li>1 This worksheet calculates the composition of the three carbonate species and the hydrogen and hydroxide ions from self ionization of water.</li> <li>2 They are provided in several units over the range specified in the setup menu. using the water on the Input worksheet.</li> <li>3 Both tables and graphs are provided.</li> </ol>
pK	<ol style="list-style-type: none"> <li>1 This gives the values of the constants used to do the calculations over the selected temperature range.</li> </ol>
Xtra	<ol style="list-style-type: none"> <li>1 This provides a selection of graphs that were made as W-index was developed. These didn't make the cut for the final version. Rather than discard them, they are available for use.</li> <li>2 This worksheet is also a good place to store any graphs made by the user.</li> </ol>

## **Technical Support**

### **FAQs**

This section is a summary of questions that have popped up over the years. Users are encouraged to supply additional questions as the user is the one with the questions. The developer can almost see things in their sleep and can miss some critical points.

1. Why do these values differ from some other calculations?

W-index does a rigorous calculation using the detailed quadratic equation that relates the various carbonate equilibria. Many other calculations are based upon approximations to simplify the calculations. These may or may not be totally valid. The end result is dependent upon the nature of the polynomials used to fit the various constants. When W-index was updated to version 4.0, the polynomials were updated to those recommended in Standard Methods. The provision was included to include a switch for substitute some of the constants to match those issued with an AWWA publication. There are, of course, others.

2. My LSI, RSI and PSI don't agree. The LSI says it should scale and the RSI and PSI say it won't. Which should I believe?

The LSI calculates the potential for scaling based upon thermodynamics. There is a kinetic factor that determines whether or not it actually does scale. That is almost impossible to predict. The RSI and PSI are based upon experience with a limited number of waters. Will your system behave in the same manner? Not necessarily. Look at the reference to Feitler's  $pH_c$  on page 3 and the list comparing some of the author's results on page 5. Now use your own judgement.

3. You may contact us at the following addresses:

Mail: Marvin Silbert and Associates  
23 Glenelia Avenue, Toronto, Ontario, Canada, M2M 2K6  
Telephone: 1-416-225-0226  
Fax: 1-416-225-2227  
E-mail: [marvin@silbert.org](mailto:marvin@silbert.org)  
WWW: <http://www.silbert.org>

4. Additional Reference Material

For further reference, see Miyamoto and Silbert, A new approach to the Langelier stability index, Chemical Engineering 93 #8, pp 89-92 (28 April 1986).

The polynomials used within the calculations come from the 1995 edition of Standard Methods for the Examination of Water and Wastewater, procedure 2330, Calcium Carbonate Saturation. The option is provided to select the values for  $pK_2$  and  $pK_s$  used by the American Water Works Association

## **Sample Output**

The pages that follow are printouts of the various worksheets showing the inputs and outputs when a water sample has been entered into W-index. The test sample is Lake Ontario, one of the Great Lakes that forms the Canada-USA border. Lake Ontario sits on a limestone base and is a moderately hard water. The Canadian province of Ontario and the US state of New York use vast quantities of this water for a multitude of domestic and industrial applications.

# W - I N D E X

## Water INDEX calculations, version 5.0, (C) 1990, 94, 99, 2006

Developed by: **MARVIN SILBERT and ASSOCIATES**

W-index uses calculations found in the literature to determine the various scaling indices. To interpret the results, it should be recognized that the various indices are based upon thermodynamic principles. While these principles may provide the driving force, the process may not move and scaling may not occur as predicted unless the kinetics "cooperate". This should not be considered as a validation of the superiority of one index over another. It may only take a small jolt to the system, such as a sudden flow change or a bit of turbulence to set it off.

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**Enter User's Affiliation here**

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### Instructions:

- |        |   |
|--------|---|
| Setup  | This tab provides the set-up parameters. Those marked in blue can be adjusted to meet the users needs.  |
| Input  | Enter the sample identification and the water analyses in the blue spaces. This information will be used in the subsequent worksheets. This page will calculate the various scaling indices for the water. For high-pH (>10.3) water systems the negative root calculation will be used for the LSI and the RSI and PSI will no longer have any validity. The Larson-Skold Index will disappear if the water is outside the applicable range. |
| Temp   | This page takes the water through the temperature range selected in the Setup page. It provides plots of the LSI and RSI as well as the pH and the various carbonate and water constants. These calculations are valid for pH<10.3 as might be encountered in most water systems that use natural waters.   |
| Hi-pH  | This page takes the input water through the temperature range selected in the Setup page. This page is valid only when the pH >10.3 as might occur in clarifiers, alkaline wastes, alkaline scrubbers and hydraulic ash-transport systems.  |
| Ctower | This page simulates the changes that might be expected to occur if the water was used in a cooling tower. The number of cycles of concentration over which it operates is entered into the Setup page.  |
| RO     | This page does a simulation of the changes that might occur if the water was passed through a reverse-osmosis system and calculates the scaling potential of the reject stream for different throughput/reject rates.   |
| Comp   | This page calculates the variation of carbonate species and hydroxide across the pH range from acidic to alkaline. It includes tables and graphs based upon the activity and concentrations calculated from the sample. The carbonate equilibrium diagram shows where the input water sits and a second graph takes a cross section through the sample region.  |
| Xtra   | This page contains a collection of additional graphs that were made during the development of W-index. You are free to use them if you find them useful.  |

For more info: **MARVIN SILBERT and ASSOCIATES**  
**23 Glenelia Avenue, Toronto, ON, Canada, M2M 2K6**  
Tel: 1-416-225-0226, FAX: 1-416-225-2227, e-mail: [software@silbert.org](mailto:software@silbert.org)

**SETUP instructions:** Enter appropriate values **ONLY** in the blue blocks. Do not enter values in any other location.  
Do not enter values in any other location.

Experience shows that scale does not always form when the LSI exceeds 0. Values of 0.5 -1.0 have been suggested  
You may enter your choice in the boxes on the right.

	Caution	Warning
LSI	0.00	0.60
RSI	6.00	5.00

	MW	ppm to CaCO3	CaCO3 to ppm
HYDROGEN	1.008	50	0.02
CARBON DIOXIDE	44.010	1.140	0.440
BICARBONATE	61.017	0.820	1.220
CARBONATE	60.009	1.660	0.600
HYDROXIDE	17.008	2.940	0.340

Polynomials for constants	2	1. From Standard Methods for Water and Wastewater	
		2. Use AWWA values for pK2 and pKs	
Equation used for pH calcs.	3	1. Puckorius	1.465 log(M Alk) + 4.54
		2. Kunz	1.60 log(M Alk) + 4.44
		3. Caplan	1.645 log(M Alk) + 4.477
Concentration range	2	Decimal points to be displayed	
	3	Minimum COC for cooling tower	
	0.25	Step	
	5.00	End COC	
Temperature range	0	Starting Temperature	0.0
Sample temperature is 25°C	10	Step	10.0
	100	End Temperature	100.0
	C	Enter "C" or "F" to select units	Display (°C)

Notes

- 1 W-index uses the Puckorius Scaling Index or PSI only on the Input worksheet. The author's experience with the PSI has show it to give an overly optimistic value in a large grouping of waters that were indeed scaling.
- 2 The user has the complete range of editing features available with Microsoft Excel and should feel free to change the appearance of any graph to meet your own needs. It is highly recommended that a back-up copy of this spreadsheet be made. This provides a means to get back to the starting point should anything be changed beyond the point of recovery or otherwise lost.
- 3 Microsoft Excel has a number of idiosyncrasies with respect to autoscaling of graph axes. It was impossible to overcome all of them. The user should make adjustments as needed to enhance the appearance of the graph.
- 4 To copy a graph and insert it in Word, PowerPoint or other programs, click on the edge of the graph to make it active. Push Ctrl-C to copy and then go to the place you want that graph to appear in the other program. Push Ctrl-V and a copy will appear in that other program.

**W-index**

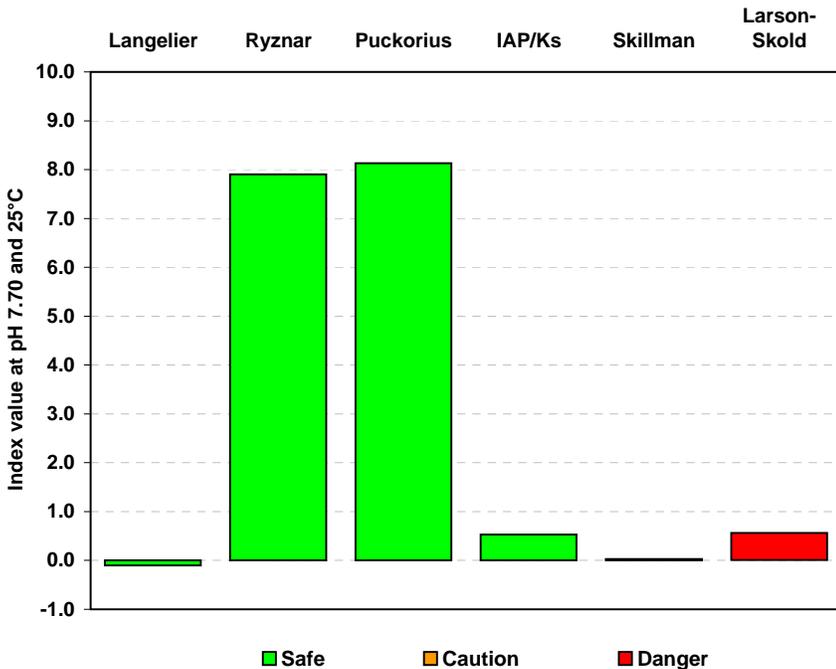
**Calcium Carbonate Scaling Index Calculations**

Sample ID:

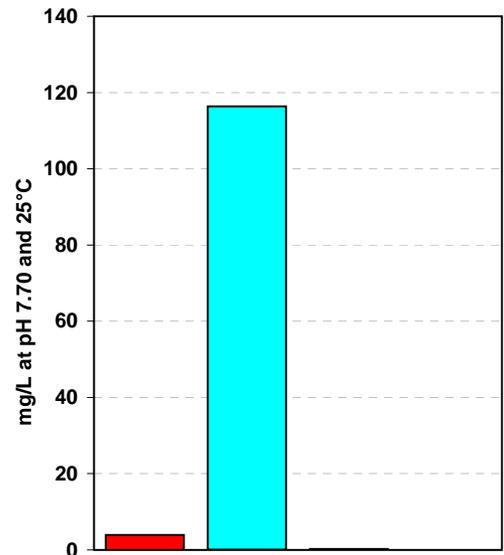
**Lake Ontario**

INPUT DATA						
Temperature	25 °C					
TDS	180 ppm					
M - Alkalinity	100 ppm CaCO3					
P - Alkalinity	0 ppm CaCO3					
Ca Hardness	100 ppm CaCO3					
pH @ Temperature	7.7 <span style="color: red;">pH&lt;10.3 Positive Root Applies</span>					
Chloride	28 mg/L Cl					
Sulfate	32 mg/L SO4					
Ionic Strength	0.0045 Moles/L					
DISTRIBUTION	Traditional as ppm CaCO3	Moles/L	mg/L	ppm CaCO3	Mole %	
Hydrogen Ions		2.0E-08	0.00	0.00	0.00	
Carbon Dioxide		8.8E-05	3.89	4.43	4.42	
Bicarbonate	100 M	1.9E-03	116.37	95.42	95.33	
Carbonate		4.5E-06	0.27	0.45	0.22	
Hydroxide Ions		5.1E-07	0.01	0.03	0.03	
INDICES	Positive Root	Negative Root				
pHs	7.80	11.29				
Langelier Saturation	-0.10	3.59 <span style="color: red;">DANGER</span>				
Ryznar Stability	7.90	-NA-				
Puckorius Practical	8.13	-NA-				
IAP/Ksp		0.53	<span style="color: red;">Undersaturated</span>			
Caplan pH		7.77				
Kunz		7.64				
Puckorius Equilibrium pH		7.47				
Skillman Sulfate		0.03	<span style="color: red;">Undersaturated</span>			
Larson-Skold		0.56	<span style="color: red;">** CARBON STEEL CORROSION **</span>			
CONSTANTS			K	pK		
Dissociation of Water		Kw	1.0E-14	13.99		
Solubility Product for Calcite		Ks	4.7E-09	8.33		
Carbon Dioxide - Bicarbonate Equivalence		K1	4.4E-07	6.35		
Bicarbonate - Carbonate Equivalence		K2	4.7E-11	10.33		

**Summary of Indices**



**Carbonate Species**



■ Carbon Dioxide ■ Bicarbonate ■ Carbonate ■ Hydroxide

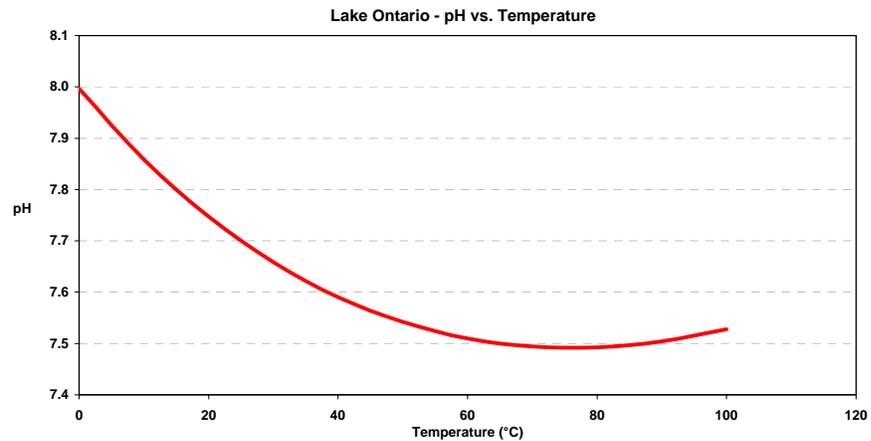
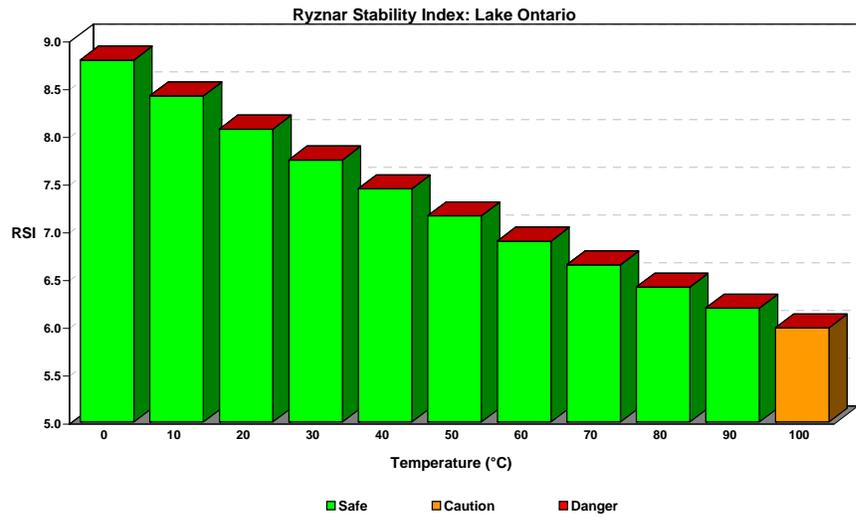
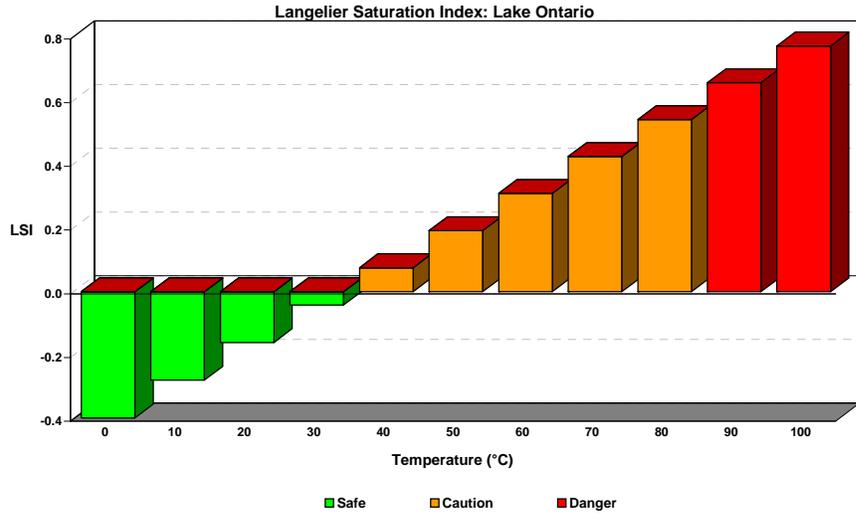
**W-index Temperature Effects Upon Scaling Indices**

Sample ID: **Lake Ontario**

TEMPERATURE EFFECTS - from positive root and valid for pH <10.3

Temp (°C)	0	10	20	30	40	50	60	70	80	90	100
pH	8.00	7.86	7.75	7.66	7.59	7.54	7.51	7.49	7.49	7.50	7.53
pHs	8.39	8.14	7.91	7.70	7.52	7.35	7.20	7.07	6.95	6.85	6.76
LSI	-0.40	-0.28	-0.16	-0.04	0.07	0.19	0.31	0.42	0.54	0.66	0.77
RSI	8.79	8.41	8.07	7.74	7.44	7.16	6.89	6.65	6.41	6.19	5.99

Sample Temperature = 25 °C



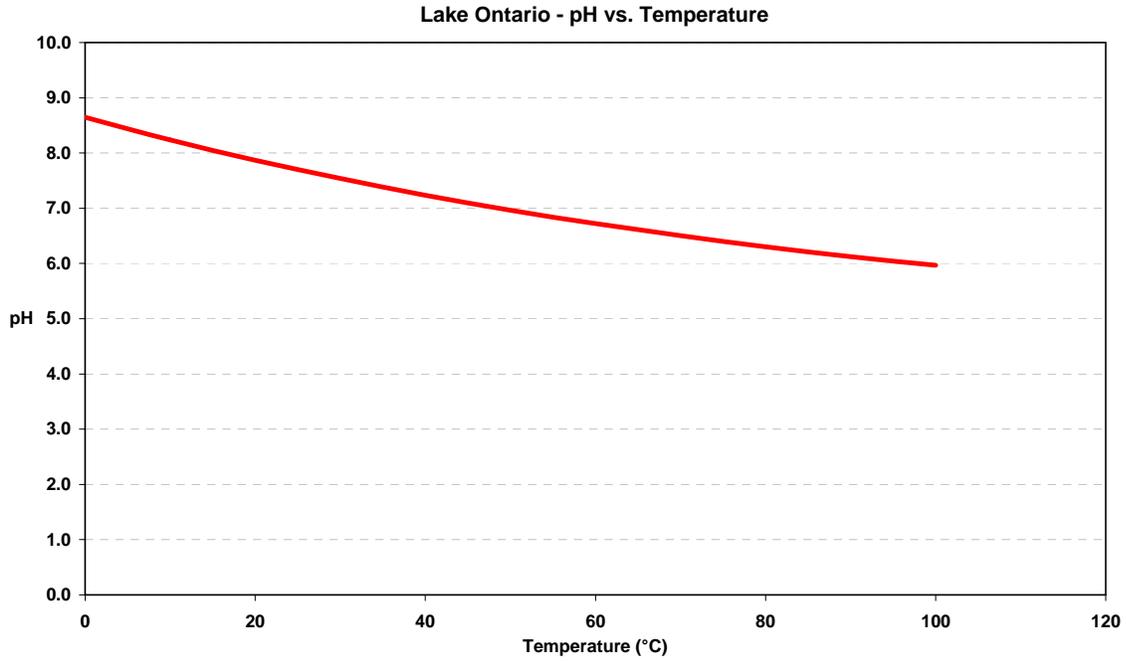
**W-index      Temperature Effects Upon Scaling Indices**

Sample ID:      **Lake Ontario**

**TEMPERATURE EFFECTS - from negative root and valid for pH >10.3**

Temp (°C)	0	10	20	30	40	50	60	70	80	90	100
pH	8.65	8.24	7.87	7.54	7.24	6.97	6.72	6.50	6.30	6.12	5.97
pHs	12.23	11.83	11.46	11.13	10.83	10.56	10.32	10.10	9.90	9.72	9.56
LSI	3.59	3.59	3.59	3.59	3.59	3.59	3.59	3.59	3.59	3.59	3.59

**Sample Temperature = 25 °C**



## W-index Cooling Tower Concentration Effects Upon Scaling Indices

Sample ID: **Lake Ontario**

### EFFECTS OF CONCENTRATING WATER IN A COOLING-TOWER SYSTEM

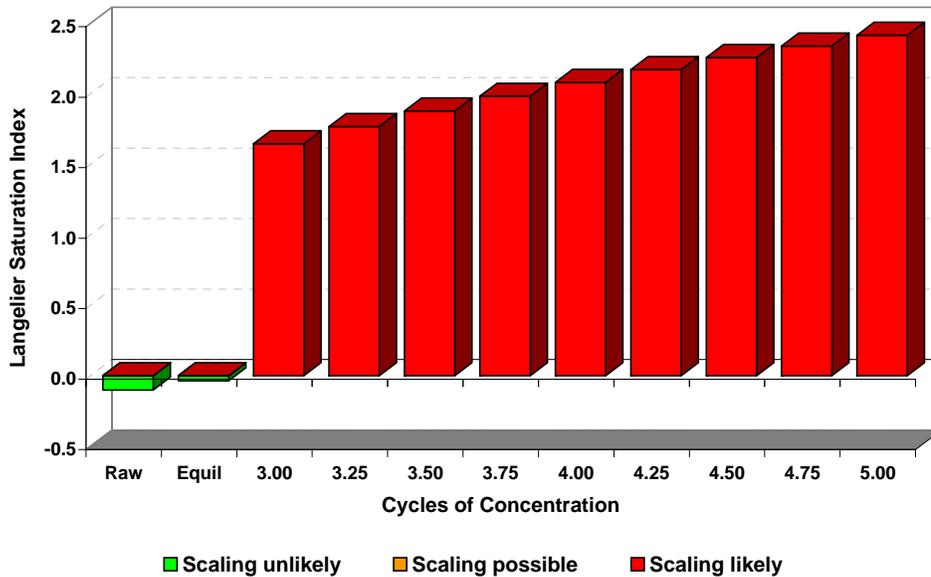
Valid for pH 7-10

Sample Temperature = 25 °C

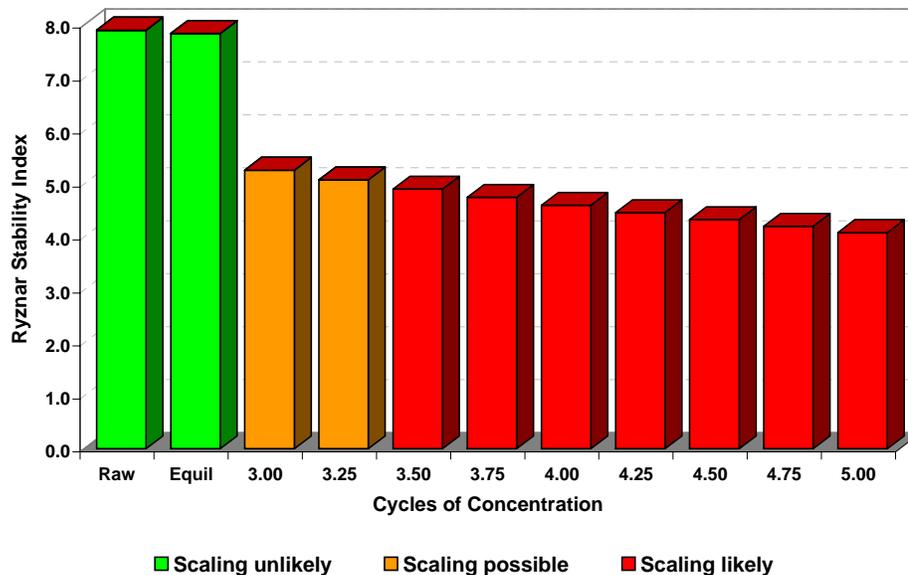
	Raw Water	Equilibrated	Cycles of Concentration								
			3.00	3.25	3.50	3.75	4.00	4.25	4.50	4.75	5.00
TDS	180	180	540	585	630	675	720	765	810	855	900
Ca	100	100	300	325	350	375	400	425	450	475	500
alk	100	100	300	325	350	375	400	425	450	475	500
pH	7.70	7.77	8.55	8.61	8.66	8.71	8.76	8.80	8.84	8.88	8.92
pHs	7.80	7.80	6.91	6.84	6.78	6.73	6.68	6.63	6.58	6.54	6.50
LSI	-0.10	-0.03	1.65	1.77	1.88	1.98	2.08	2.17	2.26	2.34	2.42
RSI	7.90	7.84	5.26	5.07	4.90	4.74	4.59	4.45	4.32	4.20	4.08

**NOTE:** Equilibration of the water within any given system will be dependent upon a the rate of carbon dioxide transfer. This will vary with such factors as flow rates, tower design and weather. The values above can at best be considered as approximations. For more precise work, measurements must be made under a variety of operating conditions.

**Likelihood of Scaling in Cooling Tower: Lake Ontario**



**Likelihood of Scaling in Cooling Tower: Lake Ontario**



**W-index Concentration Effects Upon Scaling Indices**

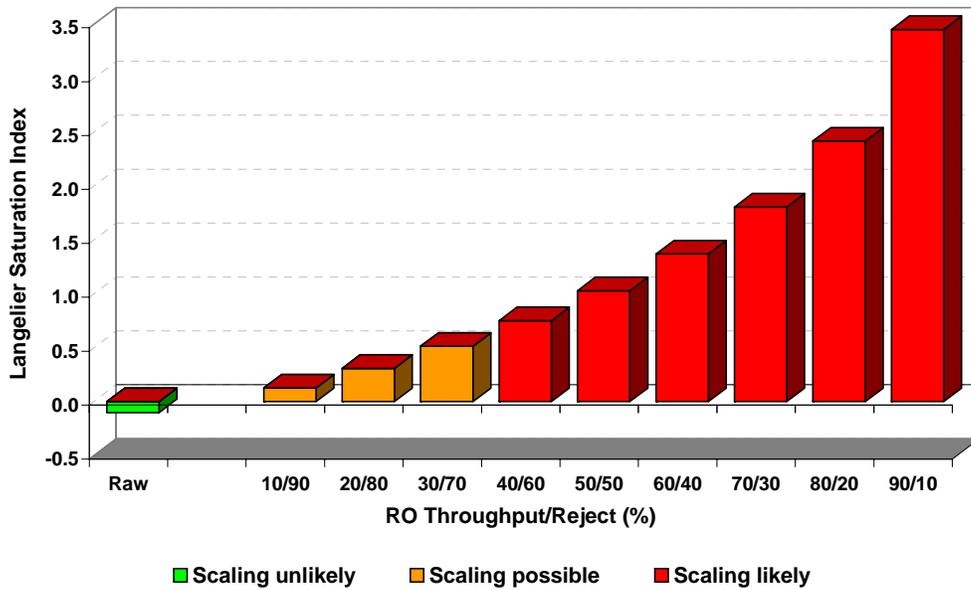
Sample ID: **Lake Ontario**

**EFFECTS OF CONCENTRATING WATER IN REVERSE OSMOSIS REJECT**  
 Valid for pH 7-10  
 Sample Temperature = 25 °C

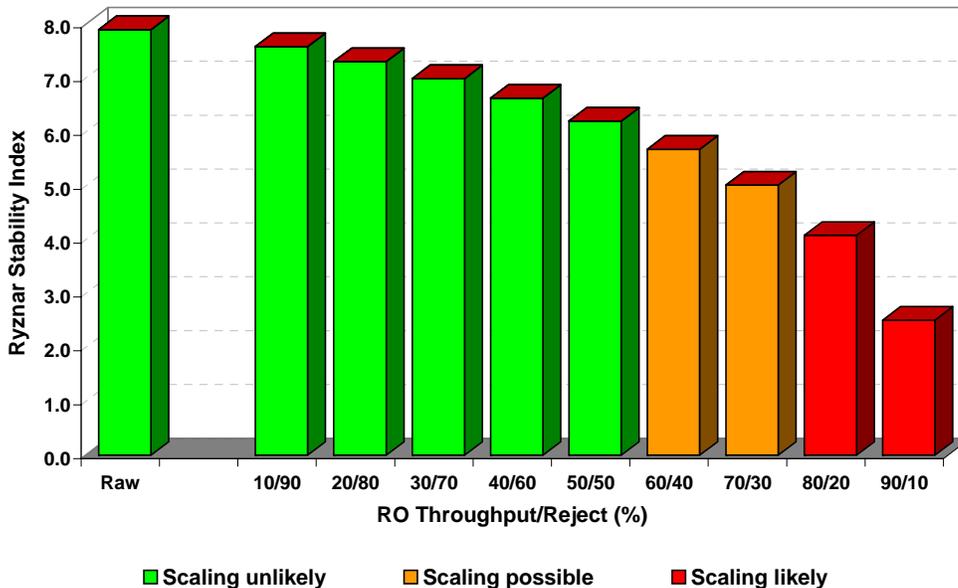
	Raw Water	RO Recovery Rate (%)								
		10	20	30	40	50	60	70	80	90
TDS	180	200	225	257	300	360	450	600	900	1800
Ca	100	111	125	143	167	200	250	333	500	1000
Talk	100	111	125	143	167	200	250	333	500	1000
pH	7.70	7.84	7.93	8.02	8.13	8.26	8.42	8.63	8.92	9.41
pHs	7.80	7.71	7.62	7.51	7.38	7.23	7.05	6.82	6.50	5.96
LSI	-0.10	0.13	0.31	0.51	0.75	1.03	1.37	1.81	2.42	3.45
RSI	7.90	7.59	7.31	6.99	6.63	6.20	5.68	5.01	4.08	2.51

NOTE: If scaling is indicated, the addition of acid or a crystal modifier to the RO feedwater may be required.

**Likelihood of Scaling in RO Reject: Lake Ontario**



**Likelihood of Scaling in RO Reject: Lake Ontario**

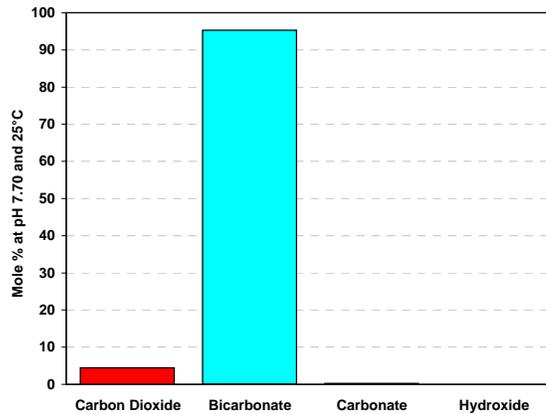
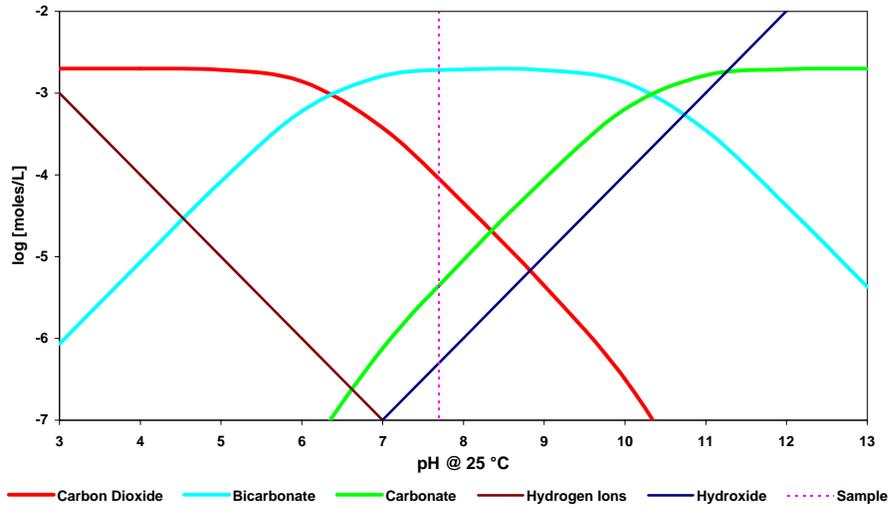


## W-index Composition of Carbonate Species vs. pH

Sample ID: **Lake Ontario**  
 Sample Temperature = 25 °C

	pH	3	4	5	6	7	8	9	10	11	12	13
Log Moles/L	Carbon Dioxide	-2.7	-2.7	-2.7	-2.9	-3.4	-4.3	-5.4	-6.5	-8.1	-10.0	-12.0
	Bicarbonate	-6.1	-5.1	-4.1	-3.2	-2.8	-2.7	-2.7	-2.9	-3.5	-4.4	-5.4
	Carbonate	-13.4	-11.4	-9.4	-7.6	-6.1	-5.0	-4.0	-3.2	-2.8	-2.7	-2.7
	Hydrogen Ions	-3.0	-4.0	-5.0	-6.0	-7.0	-8.0	-9.0	-10.0	-11.0	-12.0	-13.0
	Hydroxide	-11.0	-10.0	-9.0	-8.0	-7.0	-6.0	-5.0	-4.0	-3.0	-2.0	-1.0
Moles/L	Carbon Dioxide	2.0E-03	2.0E-03	1.9E-03	1.4E-03	3.8E-04	4.5E-05	4.4E-06	3.2E-07	8.2E-09	9.7E-11	9.9E-13
	Bicarbonate	8.6E-07	8.6E-06	8.3E-05	6.0E-04	1.6E-03	1.9E-03	1.9E-03	1.4E-03	3.5E-04	4.2E-05	4.3E-06
	Carbonate	4.0E-14	4.0E-12	3.9E-10	2.8E-08	7.6E-07	9.1E-06	8.9E-05	6.4E-04	1.6E-03	2.0E-03	2.0E-03
	Hydrogen Ions	1.0E-03	1.0E-04	1.0E-05	1.0E-06	1.0E-07	1.0E-08	1.0E-09	1.0E-10	1.0E-11	1.0E-12	1.0E-13
	Hydroxide	1.0E-11	1.0E-10	1.0E-09	1.0E-08	1.0E-07	1.0E-06	1.0E-05	1.0E-04	1.0E-03	1.0E-02	1.0E-01
Mole %	Carbon Dioxide	99.96	99.57	95.87	69.91	18.84	2.26	0.22	0.02	0.00	0.00	0.00
	Bicarbonate	0.04	0.43	4.13	30.09	81.11	97.24	94.84	64.82	11.68	0.34	0.00
	Carbonate	0.00	0.00	0.00	0.00	0.04	0.46	4.44	30.35	54.70	16.14	1.93
	Hydroxide	0.00	0.00	0.00	0.00	0.01	0.05	0.50	4.82	33.62	83.51	98.06
Mole %	Carbon Dioxide	99.96	99.57	95.87	69.91	18.84	2.26	0.22	0.02	0.00	0.00	0.00
	Bicarbonate	0.04	0.43	4.13	30.09	81.12	97.28	95.32	68.10	17.60	2.09	0.21
	Carbonate	0.00	0.00	0.00	0.00	0.04	0.46	4.46	31.88	82.40	97.91	99.79
ppm as CaCO <sub>3</sub>	Carbon Dioxide	100.30	99.91	96.20	70.15	18.91	2.27	0.22	0.02	0.00	0.00	0.00
	Bicarbonate	0.04	0.43	4.13	30.11	81.17	97.35	95.38	68.15	17.61	2.09	0.21
	Carbonate	0.00	0.00	0.00	0.00	0.08	0.91	8.89	63.52	164.17	195.06	198.81
	Hydroxide	0.00	0.00	0.00	0.00	0.01	0.05	0.51	5.07	50.65	506.51	5065.08
mg/L as species	Carbon Dioxide	87.98	87.64	84.39	61.53	16.59	1.99	0.19	0.01	0.00	0.00	0.00
	Bicarbonate	0.05	0.52	5.04	36.72	98.99	118.72	116.32	83.10	21.48	2.55	0.26
	Carbonate	0.00	0.00	0.00	0.00	0.05	0.55	5.36	38.27	98.90	117.51	119.76
	Hydroxide	0.00	0.00	0.00	0.00	0.00	0.02	0.17	1.72	17.23	172.28	1722.82

Carbonate Equilibrium Diagram



## Variation of Equilibrium Constants with Temperature

Temp (°C)	0	10	20	30	40	50	60	70	80	90	100
pKw	14.94	14.53	14.16	13.83	13.53	13.26	13.02	12.80	12.60	12.42	12.26
pKs	7.79	7.90	8.02	8.13	8.24	8.36	8.47	8.58	8.69	8.80	8.91
pK1	6.55	6.43	6.35	6.30	6.27	6.25	6.26	6.27	6.30	6.34	6.39
pK2	10.47	10.34	10.22	10.13	10.06	10.01	9.97	9.95	9.94	9.95	9.97

Sample Temperature = 25 °C

