

Indexes for Calcium Carbonate

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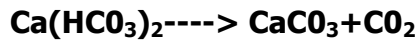


**Langelier Index**  
**Ryznar Index**  
**etc**

## CALCIUM CARBONATE

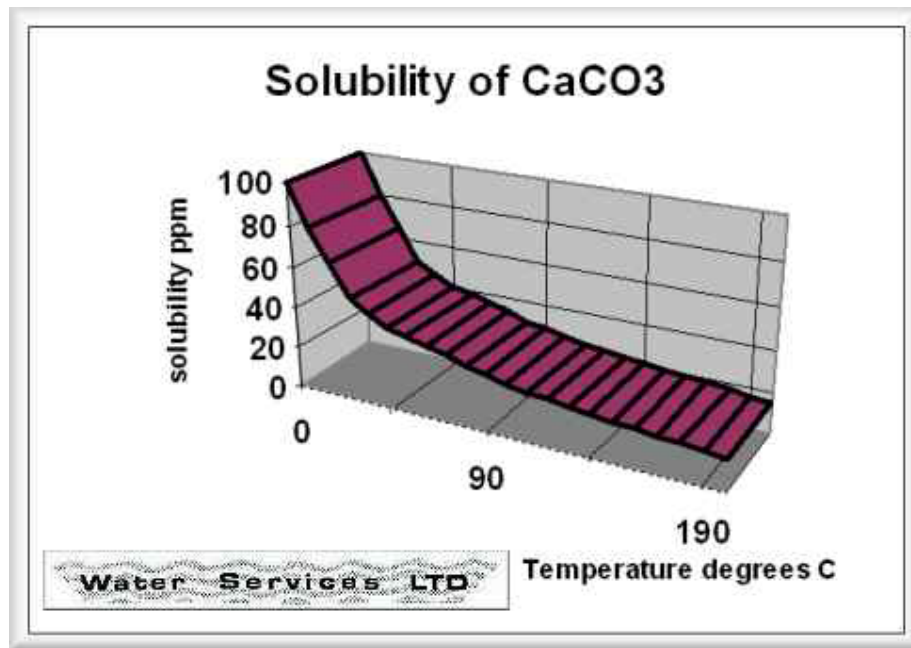
Calcium carbonate is probably the most common type of scale found in cooling water systems; it forms an extremely tenacious heat insulating deposit.

Calcium and bicarbonate alkalinity are found in almost all cooling waters. The addition of heat, or a sharp rise in pH, will cause calcium bicarbonate to decompose and form carbon dioxide and calcium carbonate.



Although the bicarbonate salt is moderately soluble, the carbonate salt has very low solubility. The figure below shows the relationship of temperature to the solubility of calcium carbonate.

Note that calcium carbonate is extremely low in solubility at any temperature. It is logical that the deposition of calcium carbonate is found along heat transfer surfaces where cooling water is subjected to the highest temperatures.



Due to problems associated with calcium carbonate scale formation, it is important that the cooling water control parameters be such that the potential for CaCO3 formation is minimized. Probably the best way to qualitatively predict the formation of CaCO3 scale is through the use of the [Langelier Saturation Index](#) or the [Ryznar Stability index](#), both of which are discussed in more detail in link.

## Langelier Saturation Index

Work done by Professor Langelier, published in 1936, deals with the conditions at which a given water is in equilibrium with calcium carbonate. The equation developed by Langelier makes it possible to predict the tendency of water either to precipitate or to dissolve calcium carbonate. The equation expresses the effects of pH, calcium, total alkalinity, dissolved solids and temperature as they relate to the solubility of calcium carbonate for waters in the 6.5 - 9.5 pH range. The equation is written:

$$pH_s = (pK_2 - pK_s) + pCa + pAlk.$$

The left side of the equation represents the pH at which water with a given calcium content and alkalinity is in equilibrium with calcium carbonate. The terms  $K_2$  and  $K_s$  symbolize the second dissociation constant and the solubility product constant for calcium carbonate, respectively. These terms are functions of temperature and total mineral content. Their values for any given condition can be computed from the known thermodynamic constants. Both the calcium and the alkalinity terms are the negative logarithms of their respective concentrations. The calcium content is molar, while the alkalinity is an equivalent concentration. That is, it is the titratable equivalence of alkaline base per liter.

The algebraic difference between the actual pH of a sample of water and its computed  $pH_s$  is called the Calcium Carbonate Saturation Index. Hence, Saturation Index equals pH minus  $pH_s$ .

$$\text{Langelier Index (LSI)} = pH - pH_s$$

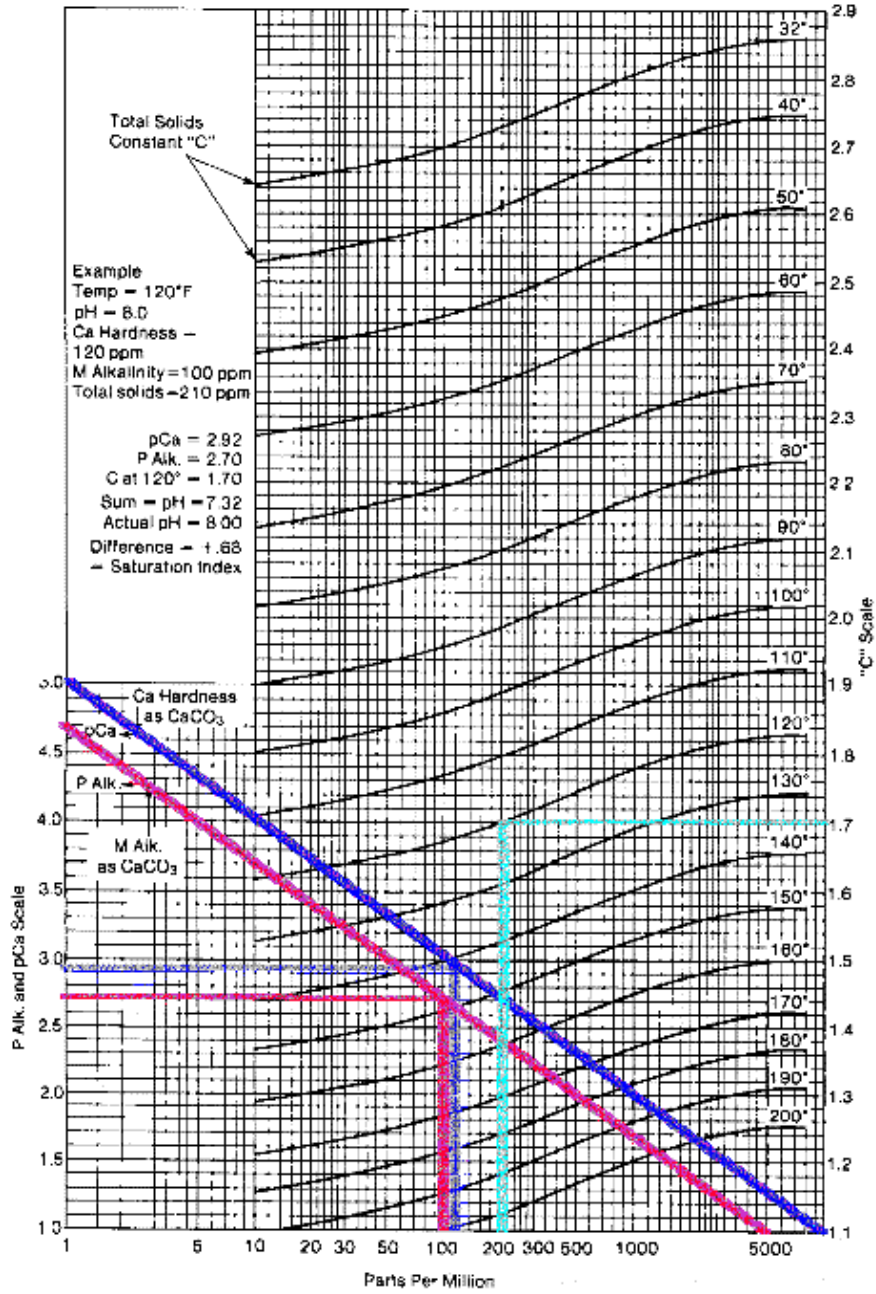
This index is a qualitative indication of the tendency of calcium carbonate to deposit or dissolve. If the index is positive, calcium carbonate tends to deposit. If it is negative, calcium carbonate tends to dissolve. If it is zero, the water is at equilibrium.

The LSI **was not intended** as an indicator of corrosivity towards mild steel or other metals of construction. The LSI describes only the corrosivity of a water towards an existing calcium carbonate scale, or other calcium carbonate bearing structure.

The LSI does describe the tendency of a water to dissolve (corrode) calcite scale. It has also been used to control the "corrosion" of asbestos-concrete-board (ACB) fill which uses calcium carbonate as part of the binder. But the interpretation of corrosivity towards metals is not explicit in the LSI.

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The calculation of  $pH_s$  has been simplified by the preparation of various nomographs. A suitable one is shown in the picture of the image below.



**pH<sub>s</sub> is the pH at saturation in calcite or calcium carbonate and is defined as:**

$$\text{pH}_s = (9.3 + A + B) - (C + D)$$

Where:

- A = (Log10 [TDS] - 1) / 10
- B = -13.12 x Log10 (°C + 273) + 34.55
- C = Log10 [Ca<sup>2+</sup> as CaCO<sub>3</sub>] - 0.4
- D = Log10 [alkalinity as CaCO<sub>3</sub>]

### Ryznar Stability index

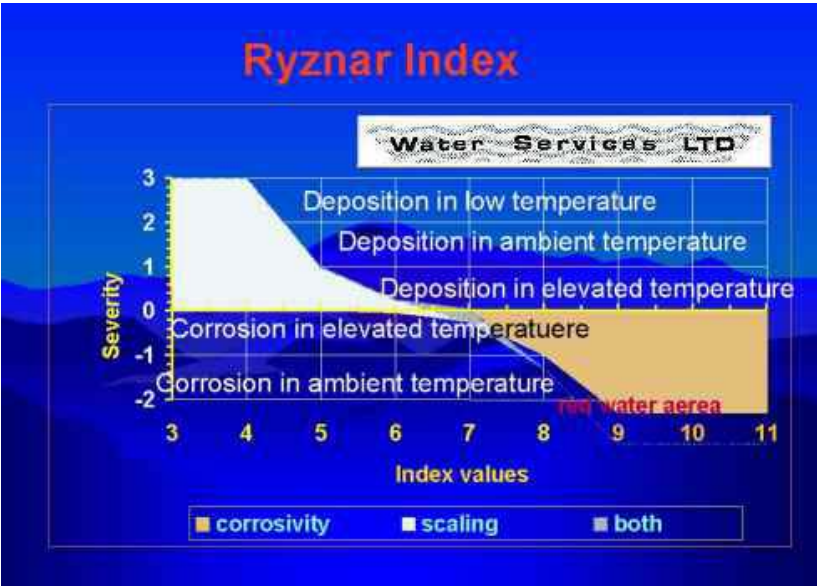
The Ryznar Stability index is an empirical method for predicting scaling tendencies of water based on a study of operating results with water of various saturation indices.

$$\text{Stability index} = 2\text{pH}_s - \text{pH} = \text{pH}_s - \text{Langelier's Saturation pH}$$

This index is often used in combination with the Langelier index to improve the accuracy in predicting the scaling or corrosion tendencies of a water. The following chart illustrates how to use this index.

Ryznar Stability index	Tendency of Water
4.0-5.0	heavy scale
5.0-6.0 6.0-7.0	light scale little scale or corrosion
7.0-7.5	corrosion significant
7.5-9.0 9.0 and higher	heavy corrosion corrosion intolerable

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The calculation of  $pH_s$  has been even simplified by the use of computers. A spreadsheet for computer calculation is listed below, and can be used on-line at our website.

Water Data		
pH	8,20	
Total dissolved solids	250,00	ppm CaCO3
m Alkalinity	150,00	ppm CaCO3
Calcium Hardness	120,00	ppm CaCO3
Temperature :	85,00	degrees C
Indexes		
Ryznar:	5,45	
Langelier:	1,37	

**Spreadsheet for Indexes calculation**

**Puckorius Scaling Index (PSI)**

Other indices do not account for two other critical parameters: the buffering capacity of the water, and the maximum quantity of precipitate that can form in bringing water to equilibrium. The PSI attempts to quantify the relationship between saturation state and scale formation by incorporating an estimate of buffering capacity of the water into the index.

Water high in calcium, but low in alkalinity and buffering capacity can have a high calcite saturation level. The high calcium level increases the ion activity product.

A plot of ion activity product versus precipitate for the water would show a rapid decrease in pH as calcium precipitated due to the low buffering capacity. Even minuscule decreases in carbonate concentration in the water would drastically decrease the ion activity product due to the small quantity present prior to the initiation of precipitation.

Such water might have a high tendency to form scale due to the driving force, but scale formed might be of such a small quantity as to be unobservable. The water has the driving force but not the capacity and ability to maintain pH as precipitate matter forms.

The PSI index is calculated in a manner similar to the Ryznar stability index. Puckorius uses an equilibrium pH rather than the actual system pH to account for the buffering effects:

$$\text{PSI} = 2 (\text{pHs}) - \text{pHeq}$$

Where:

- pHs is the pH at saturation in calcite or calcium carbonate
- $\text{pHeq} = 1.465 \times \log_{10}[\text{Alkalinity}] + 4.54$
- and  $[\text{Alkalinity}] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-]$

Coming in more details into PSI, we can conclude that PSI is actually the Ryznar index, in which the actual pH is replaced by the corrected pHeq. But the above formulae is valid only for pH values below 8,3 (the phenolphthalein reversion point).

So the use of PSI in pH values over 8,3 is best to be avoided.

## Larson-Skold Index

The Larson-Skold index describes the corrosivity of water towards mild steel. The index is based upon evaluation of in-situ corrosion of mild steel lines transporting Great Lakes waters. The index is the ratio of equivalents per million (epm) of sulfate (SO<sub>4</sub><sup>2-</sup>) and chloride (Cl<sup>-</sup>) to the epm of alkalinity in the form bicarbonate plus carbonate:

$$\text{Larson-Skold index} = (\text{epm Cl}^- + \text{epm SO}_4^{2-}) / (\text{epm HCO}_3^- + \text{epm CO}_3^{2-})$$

The Larson-Skold index has been correlated to observed corrosion rates and to the type of attack in a study of Great Lakes waters. Extrapolation to other waters, such as those of low alkalinity or extreme alkalinity, goes beyond the range of the original data. The index has proven a useful tool in predicting the aggressiveness of once through cooling waters.

It is particularly interesting due to the preponderance of waters of composition similar to the Great Lakes waters and to its usefulness as an indicator of aggressiveness in reviewing the applicability of corrosion inhibition treatment programs that rely on the natural alkalinity and film forming capabilities of a cooling water.

The Larson-Skold index might be interpreted by the following guidelines:

- Index << 0.8 chlorides and sulfate probably will not interfere with natural film formation
- 0.8 << index << 1.2 chlorides and sulfates may interfere with natural film formation. Higher than desired corrosion rates might be anticipated
- Index >> 1.2 the tendency towards high corrosion rates of a local type should be expected as the index increases



### Stiff-Davis Index

The Stiff-Davis index attempts to overcome the shortcomings of the Langelier Index with respect to high total dissolved solids' waters and the impact of "common ion" effects on the driving force for scale formation.

Like the LSI, the Stiff-Davis index has its basis in the concept of saturation level. The solubility product used to predict the pH of saturation (pHs) for a water is empirically modified in the Stiff-Davis index.

Stiff-Davis indices will predict that a water is less scale forming than the LSI calculated for the same water chemistry and conditions. The deviation between the indices increases with ionic strength. Interpretation of the index is by the same scale as for the Langelier Saturation index.

Stiff-Davis Index is calculated by an ASTM standard method.

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**D4582-91(2001) Standard Practice for Calculation and Adjustment of the Stiff and Davis Stability Index for Reverse Osmosis**

Developed by Subcommittee: [D19.08](#)  
See [Related Work](#) by this Subcommittee  
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**Drawbacks of the use of Indexes**

The Saturation Index, however, measures only the directional tendency or driving force of a water. It cannot be used as a quantitative measure. Two different waters, one of low hardness and thus corrosive, and the other of high hardness and thus scale forming, can have the same Saturation Index.

**The most important drawback related to the Langelier (and all other indexes) is that it calculates the current situation of the specific sample.**

**So, if it was originally a matter of a scaling forming water, and deposition has already took place, calcium, alkalinity and total solids are missing from the sample, while pH has been modified.**

**So the sample is not any more scale forming, but balanced.**

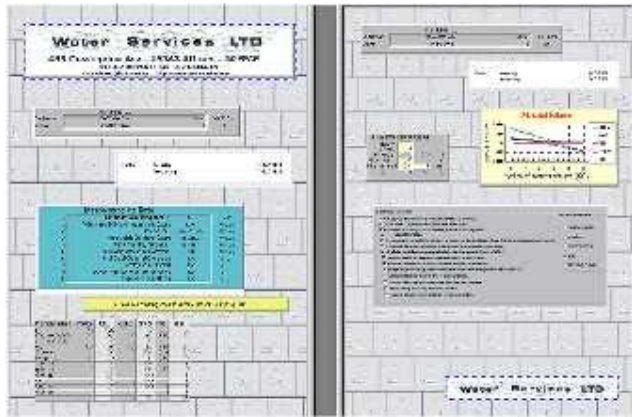
**Modifications also occur in an originally corrosive water, after corrosion is taking place.**

If we calculate the index under such conditions, we will conclude erroneously.

Water Services Ltd has developed an extremely accurate recalculation method, based upon the Langelier Index and computer analysis, available to its customers.

By this procedure, the user can define not only the current situation, but also the history of the water into the system (p.e. if deposition or corrosion has already take place, and in which level).

Please [contact us](#) for more details, or download from our site a sample report.



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 <b>Iran</b>	<p style="text-align: center;"><b>رہبیت افسردنه</b></p> <p style="text-align: center;"> <small>                             RAHBEH ENI &amp; CONSUL CU                              ADD. NO. 912 1ST FLOOR, KARIMZADEH LAND AVE                              TEHRAN                         </small> </p>
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