

A Rational Analysis of Cooling Water For Material Protection

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Abstract

The chemical and physical properties of certain cooling water are discussed and analyzed. The determination of its saturation pH_s value to evaluate the possible corrosive or scale-forming tendency of the water, before and after chemical treatment of the cooling water is derived. A rational method of using both Langelier and Ryzner approaches is proposed and tested by the author. Some illustrations are given in the paper.

Introduction

In the treatment of cooling water for the protection of piping material or heat-exchange equipment against scale formation or corrosion, two outstanding analytical methods of evaluation have been well recognized^(1,2,3) and are quite useful to water chemists and process engineers. One is the Langelier's Index and the other is the Ryzner's Index.

The basic reasoning is the calculation of the saturation pH value (or pH_s) from the analytical determination of the activity coefficients of the water (K_s and K_2), the calcium ion concentration $[\text{Ca}^{++}]$, the concentration of total alkalinity $[\text{A}] = [\text{OH}^-] + [\text{HCO}_3^-] + [\text{CO}_3^-]$ and the ionic strength coefficient of all the dissolved salts $[\text{S}] = 2.5\sqrt{\mu}/(1 + 5.3\sqrt{\mu} + 5.5\sqrt{\mu})$, according to Larson and Buswell⁽²⁾. The value of pH_s can be written in the following simplified form:

$$\text{pH}_s = 9.30 + \text{S} + \log \frac{K_s}{K_2} - \log [\text{Ca}^{++}] - \log [\text{A}] \quad (1)$$

or, in a simpler form,

$$\text{pH}_s = 9.30 + \text{A} + \text{B} - \text{C} - \text{D} \quad (2)$$

where $\text{A} = \text{S}$, $\text{B} = \log \frac{K_s}{K_2}$, $\text{C} = \log [\text{Ca}^{++}]$ and $\text{D} = \log [\text{A}]$

B, the activity coefficient ratio term is greatly governed by the temperature. These factors have been studied by Larson, et al.^(2,3) and they can be obtained from Figure One⁽⁴⁾.

The Langelier's Saturation Index is written as:

$$\text{L.I.} = \text{pH} - \text{pH}_s \quad (3)$$

where pH_s is described in equation (1) and pH is the actual value measured of the water.

A negative (—) value of L.I. indicates the *presence* and a positive (+) of L.I. indicates the *deficiency* of excess dissolved CO_2 in the water. A negative value of L.I. thus also indicates the degree of corrosive tendency of the water and a positive value indicates the scaling tendency⁽¹⁾.

The Stability Index as advanced by Ryzner is described as:

$$\text{R.I.} = 2\text{pH}_s - \text{pH} \quad (4)$$

A water having a value of R.I. of less than 6.0 is very definitely scale-forming, and that having a value of R.I. of higher than 7.0 is corrosive in nature⁽²⁾.

With the consolidation of both indices, Howe⁽⁴⁾ has developed a simple rational method of interpretation through simple orientation of the two systems and to evaluate the water quality by the joint relationship of R.I., L.I., and pH of the water:

$$\text{R.I.} = \text{pH} - 2 \text{ L.I.} \quad (5)$$

$$\text{and pH} = \text{R.I.} + 2 \text{ L.I.} \quad (6)$$

Equations (5) and (6) explain that the Langelier's Saturation Index, pH and the Ryzner's Stability Index are dependent on each other, in terms of their meanings. It also indicates that the pH of the stabilized water should be equal to the sum of Ryzner's Index plus two (2) times of Langelier's Index! If the pH is increased, the pH_s also increases in order to maintain the same L.I. or R.I. values of the water, other factors unchanged. In the meantime, when the pH is lowered, the pH_s is also lowered for the same L.I. or R.I. values of the water with other factors unchanged.

To produce a "stabilized" water in order to minimize its corrosion and scaling tendency on carbon steel, wrought iron, or cast iron, etc., it is desirable to maintain the L.I. within 0 to 0.5-, and the R.I. between 7.0 and 8.0. Using a specific water of which the properties are given in Table One, a group of control graphs of this water to be used for cooling are developed for all illustrations. It must be known that any chemical treatment to change pH_s would cause changes in the chemical factors responsible for the pH_s value.

TABLE 1. *The analytical data of a cooling water.*

| | Sample | | | | Average | | |
|--|--------|------|------|------|---------|------|------|
| | 1 | 2 | 3 | 4 | Av. | Term | |
| Temp °C | 40 | 60 | 50 | 50 | 50 | | |
| Temp °F | --- | --- | --- | --- | (122) | B | 1.50 |
| Total Diss. Solids, mg/2 | 380 | 380 | 405 | 400 | 391 | A | 0.16 |
| Ca Hardness, mg/1 | 277 | 332 | 274 | 227 | 278 | C | 2.04 |
| Total Diss. Solids, mg/1 (CaCO ₃) | 258 | 268 | 268 | 247 | 280 | D | 2.40 |
| pH | 7.85 | 7.95 | 8.01 | 7.81 | 7.91 | -- | --- |

The values A, B, C, and D are obtained from Figure 1 and the pH_s value can thus be calculated. Also, the relationship of pH, L.I., R.I. at different pH values is illustrated in Figure 2.

$$\text{pH}_s = 9.30 + (1.5 + 0.16) - (2.04 + 2.40) = 6.52$$

At pH = 7.91, we have

$$\text{L.I.} = 7.91 - 6.52 = +1.39$$

$$\text{R.I.} = 2 \times 6.52 - 7.91 = +5.13$$

From Figure 2 it can be seen that the water is quite scaling even at a temperature slightly higher than 60°F. In order to protect the piping

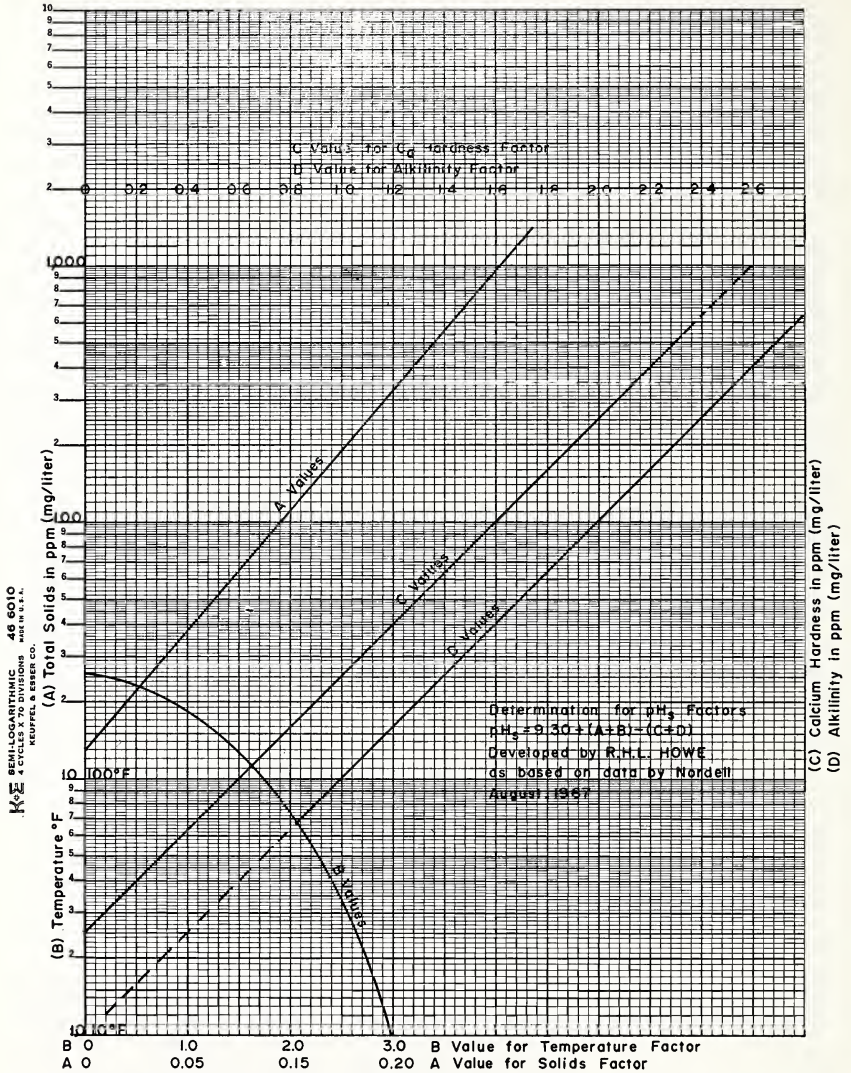
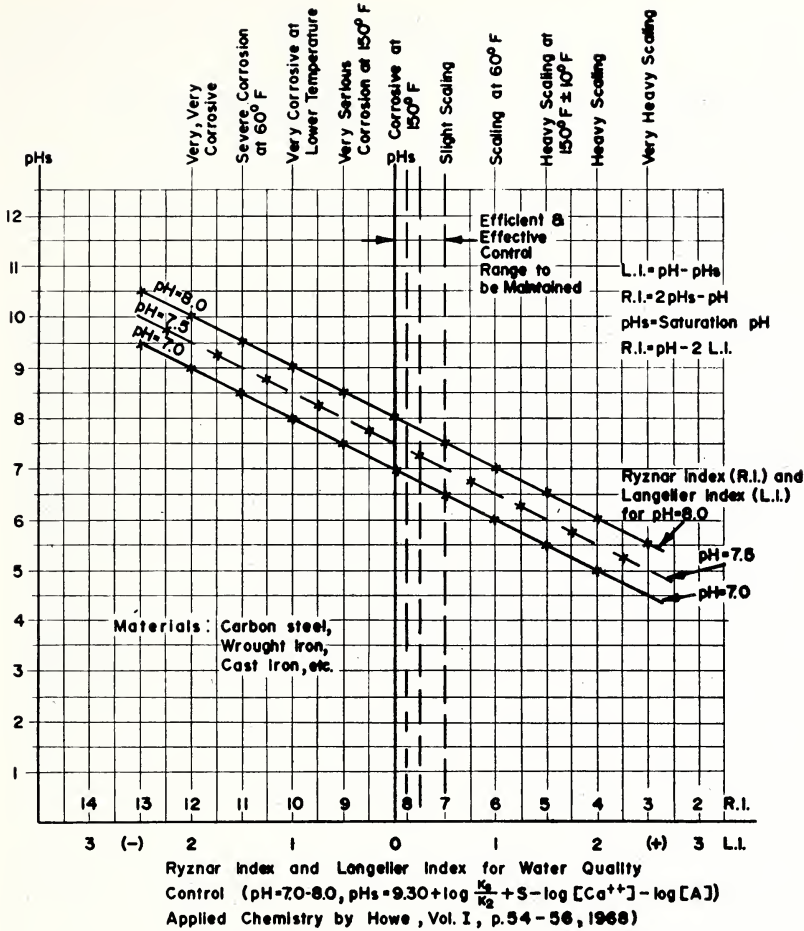


FIGURE 1.

or equipment, it is obvious that water needs treatment for its stabilization. Now, the water mentioned in Table One has been treated with 5.0 ppm of polyphosphates for moderate cooling (maximum temperature 120°F). For high temperature cooling (maximum 212°F), additional treatment with a preparation of combined organic-inorganic-dispensant-stabilizers (50 ppm) has to be used. The analytical results of treated water are in Table Two.



Example of a Special Group of Water Quality Control Graphs Developed by R.H.L. Howe

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FIGURE 2.

TABLE 2. *Treated water analysis.*

| | | Term | |
|---|-------|------|------|
| Temperature | 122°F | B | 1.50 |
| Total Dissolved Solids, mg/1 | 467 | A | 0.17 |
| Ca Hardness, mg/1 | 279 | C | 2.05 |
| Total Alkalinity | 80 | D | 1.90 |
| pH | 7.1 | | |
| $pH_s = 9.30 + (1.50 + 0.17) - (2.05 + 1.90) = 9.30 + 1.67 - 3.95 = 7.02$ | | | |
| $L.I. = 7.2 - 7.02 = +0.18$ | | | |
| $R.I. = 2 \times 7.02 - 7.02 = +6.84$ | | | |
| $L.I. = \frac{7.2 - 6.84}{2} = \frac{0.36}{2} = +0.18$ | | | |

From these numbers to fit into Figure 2, it can be noted that the water has now only a slightly scaling tendency, and it is well within the regime of "effective control."

Indeed, it is hoped that this simple rational approach may assist chemists and/or engineers in their daily endeavor of protecting materials and equipment against damages by corrosion or scale formation due to improper or inadequate water treatment, either internally or externally!

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