

Chapter 1

CALCIUM CARBONATE FOULING

The starting point for a study of calcium carbonate fouling is the need for a method possessing the thermodynamic integrity of physical-chemistry; a method which is easily applied and will allow the amount of calcium carbonate deposited to be estimated, or forecast, from an inspection of the chemical analysis of a water supply.

At present, the literature offers only one parameter linking water analysis and the amount of calcium carbonate deposited: that parameter is the Ryznar Index. A study of that Index is, therefore, the logical starting point for the development of methods for forecasting fouling by calcium carbonate.

1.1. THE RYZNAR INDEX

The Ryznar Index [1] is formally defined as:

$$R = 2\text{pH}_S - \text{pH} \quad (1)$$

where pH_S is the equilibrium pH described by Langelier [2].

But to understand the significance of the Ryznar Index in relation to the amount of calcium carbonate deposited, it is necessary to go back to the origin of Ryznar's work and make a reappraisal in the light of recent information that was not available to him.

1.1.1. Origin of Ryznar's Work

Ryznar was investigating, in the laboratories of the National Aluminate Corporation, Chicago, the effect of scaling inhibitors in reducing, or preventing, calcium carbonate deposits in industrial water systems. The work involved the use of a test rig described by Thompson and Ryznar [3]. The basis of the test rig is shown in Fig. 1. A sample of water to be tested is contained in the header tank. A fixed volume of water is allowed to flow at a fixed rate through the coil in the heater tank, which is controlled at any desired temperature. The coil is detached from the test rig and weighed before and after each run. In this way,

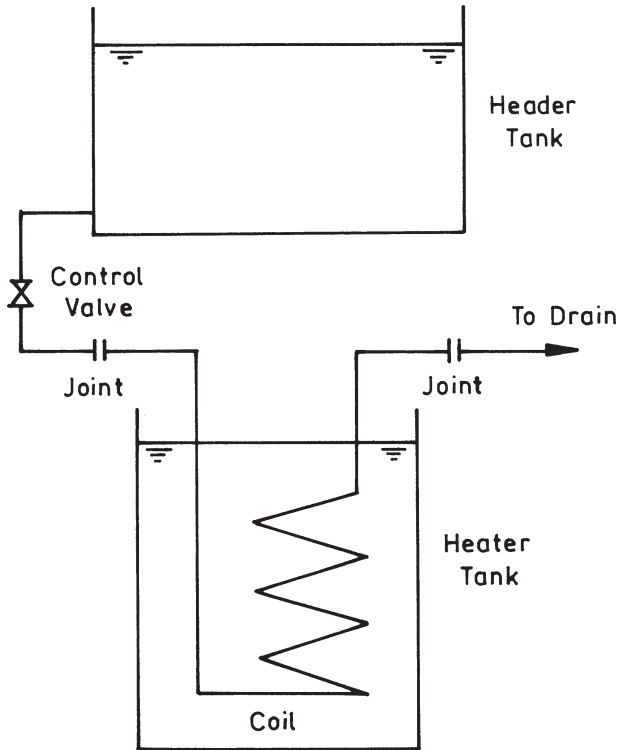


Fig. 1. Basis of Thompson-Ryznar test rig.

the weight of calcium carbonate deposited is determined, at any selected temperature, under fixed operating conditions.

At this point it must be emphasised that the conditions existing in the test rig restricts the application of Ryznar's work to those industrial water systems in which similar conditions apply. That is, once-through, closed systems in which water enters, passes through to drain, and is subjected only to a temperature rise. Apart from deposition of calcium carbonate there are no other changes: for example, incidental ingress of chemicals by contamination, or loss of dissolved gases by venting to atmosphere. The only chemical changes permitted are those resulting from the deliberate addition of known reagents to the header tank before the run starts.

These restrictions apply to all the discussions which follow in this book, unless there is a direct statement to the contrary.

Using the procedure outlined above, Ryznar determined the weight of calcium carbonate deposited by a sample of raw water, and compared it with the same water treated with various inhibitors. In this way he was able to list the inhibitors

in their order of merit. By repeating the process for different raw waters Ryznar was able to provide a more extensive and more informative list of merit for a range of inhibitors.

Because Ryznar's method required only comparative weights of calcium carbonate, and each experiment was run under fixed conditions, his data records only the weights of calcium carbonate deposited and not the volume of water from which they were produced.

Another important point to be taken into account is Ryznar's method of preparing water samples. In the earlier stages of his work he found that the experimental runs had to be extended over a protracted time, and use large volumes of water, in order to deposit sufficient calcium carbonate in the coil to produce a significant weight change.

In order to reduce the time of each run to a manageable length, Ryznar increased the scaling potential of the waters by increasing their alkalinity. Sodium carbonate or sodium bicarbonate was added for this purpose. The significance of this step is discussed later. See Sec. 1.1.4.

1.1.2. Emergence of the Ryznar Index

In the procedures followed by Ryznar it would be an advantage to be able to forecast, or estimate, from an inspection of the chemical analysis of the water, the weight of calcium carbonate deposited from a given volume of water at a given temperature. This information would facilitate the preparation of raw water samples that would yield a weight of deposit within a range required for a specific sector of Ryznar's investigations.

In pursuit of this objective Ryznar prepared 21 raw water samples which were passed through the Thompson–Ryznar test rig and the weights of calcium carbonate deposits recorded. The results are set out in Table 1.

The chemical analyses of the water samples were made at atmospheric temperature (assumed to be a nominal 15 °C). From these data Ryznar calculated, for the temperature (T) in the test rig the equilibrium pH (pH_S) as described by Langelier (loc.cit.).

The equilibrium pH is defined as:

$$\text{pH}_S = \text{p}[\text{Ca}^{2+}] + \text{p}[\text{Alk}] + \text{p}K'_2 - \text{p}K'_S \quad (2)$$

$$\text{where } K'_2 = \frac{[\text{H}^+][\text{CO}_3^{2+}]}{[\text{HCO}_3^-]} \quad (3)$$

$$\text{and } K'_S = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \quad (4)$$

pH_S was evaluated from tables by Larson and Buswell [4].

From the values of pH_S (at T) and the values of pH (at 15°C) Ryznar calculated the values of the calcium carbonate saturation index, described by Langelier (loc.cit.).

$$I = \text{pH} - \text{pH}_S \quad (5)$$

The calculated parameters are set out in Table 2.

Because the values of pH_S had been adjusted to (T), the temperature in the test rig, but the values of pH had not (being recorded for 15°C) Ryznar had broken thermodynamic integrity. But he had no choice since in 1944 there was no published method for adjusting pH for temperature changes.

In this present reappraisal of Ryznar's original work, Eq. (2) has been used in the modified form:

$$\text{pH}_S = \text{p}[\text{Ca}^{2+}] + \text{p}[\text{Alk}] + \text{p}K_2 - \text{p}K_S + (\text{DS})^{0.5}/100 \quad (6)$$

described by Emerson [5].

$$\text{Where } K_2 = \frac{(\text{H}^+)(\text{CO}_3^{2-})}{(\text{HCO}_3^-)} \quad (7)$$

$$\text{and } K_S = (\text{Ca}^{2+})(\text{CO}_3^{2-}) \quad (8)$$

Values of $\text{p}[\text{Ca}^{2+}]$ and $\text{p}[\text{Alk}]$ have been taken from tables by Manning [6] and values of $\text{p}K_2$ and $\text{p}K_S$ from tables on pp. 416 and 424 of Hamer *et. al.* [7].

For this reason the values of pH_S , I , and R in Tables 2 and 3 may differ slightly from those in Ryznar's original paper.

A plot of the values of calcium carbonate saturation index (I) against weight of calcium carbonate (Q) from Table 2 is shown in Fig. 2.

The plot shows a ragged scattering of points with no apparent relationship between the two quantities. The scattered pattern may be due to:

- (i) Absence of any fundamental relationship between I and Q .
- (ii) Errors introduced by Ryznar breaking thermodynamic integrity.
- (iii) Experimental errors in the test rig.
- (iv) A combination of two or more (i) to (iii).

These matters are discussed later in Secs. 1.1.3 and 1.1.4. But Ryznar assumed that only (i) was applicable. He abandoned any further investigation of a relationship between I and Q and began to search for a new, empirical index that was directly linked to the weight of calcium carbonate deposited. Ryznar's further investigations produced an empirical index:

$$R = 2\text{pH}_S - \text{pH} \quad (1)$$

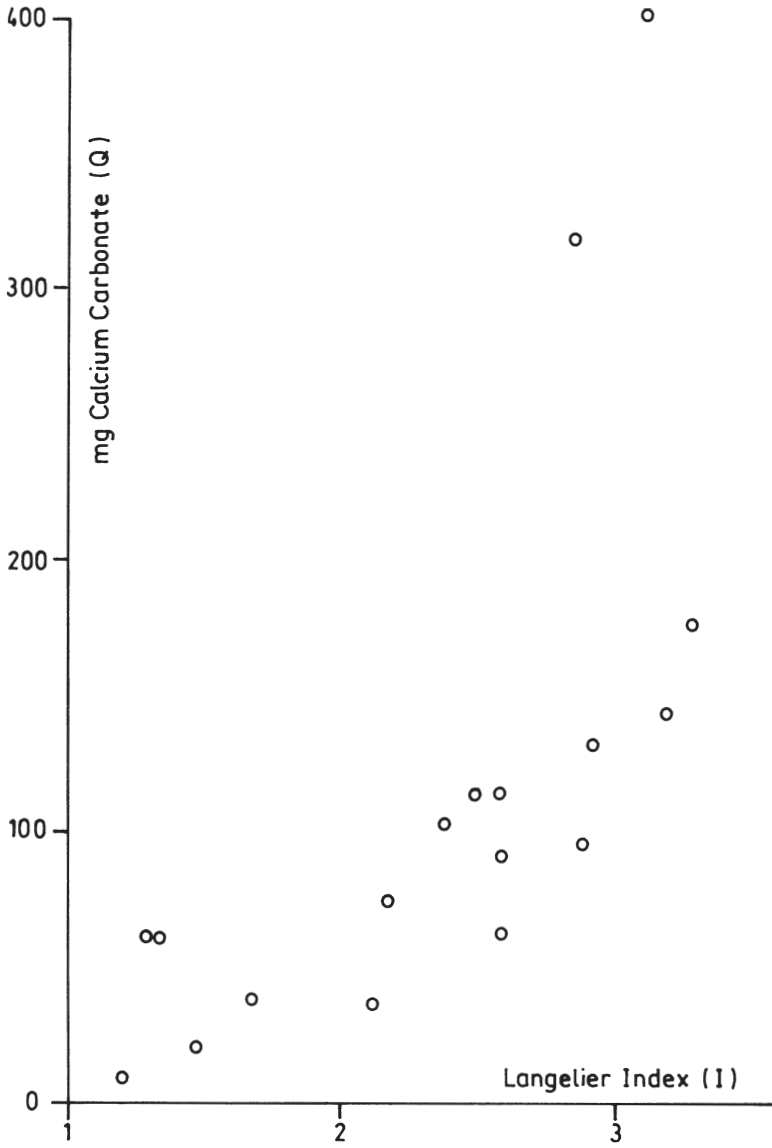


Fig. 2. Plot of Langelier index(I)-v-weight of calcium carbonate(Q).

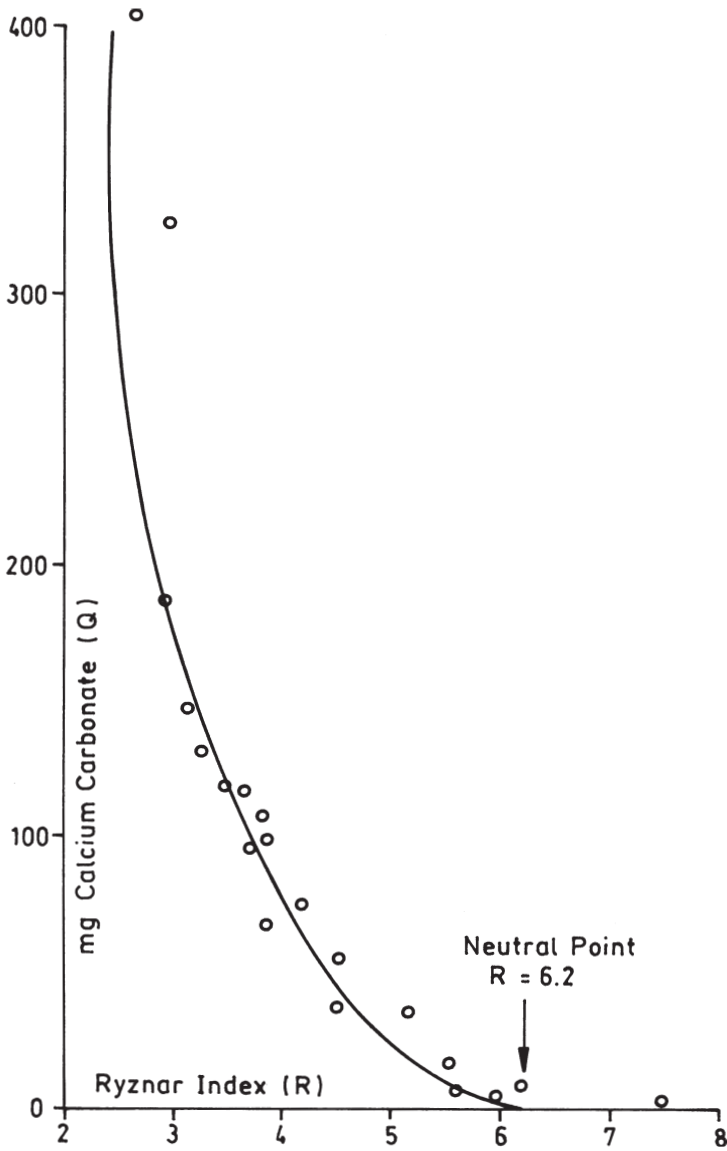


Fig. 3. Plot of Ryznar index(R)-v-weight of calcium carbonate(Q).

The data in Table 2 has been rearranged to show values of R and the new parameters are set out in Table 3.

A plot of the values of the Ryznar Index (R) against the weight of calcium carbonate (Q) from Table 3 is shown in Fig. 3. It will be seen that a smooth curve can be drawn through the plot to give a neutral point (zero deposit) at $R = 6.2$. Ryznar's original graph gave the neutral point as $R = 6.0$. The slight difference is due to the difference in evaluation mentioned earlier in this section.

A number of proprietary water treatment suppliers have accepted the criterium ($R = 6.0$) as a basis for the routine control of systems using their treatment.

There is still a moderate amount of scattering of points in Fig. 3 which may be due to:

- (v) Ryznar breaking thermodynamic integrity.
- (vi) Experimental errors in the test rig.
- (vii) A combination of both.

Ryznar did not proceed beyond Fig. 3. Having established that a smooth curve could be drawn linking R and Q , and that a neutral point existed at $R = 6.0$, he allowed the matter to rest. He did not, for example, publish any further work on methods of forecasting, or estimating, the weight of calcium carbonate deposited using calculations based on his index R .

The objective of this section of this book is to provide methods of forecasting, or estimating, the weight of calcium carbonate deposited in systems: then clearly further work must be done on the Ryznar Index if it is to be included in the methods which follow in this book. It is therefore important to investigate, and if possible eliminate, errors which may be arising from (v) and (vi) above.

1.1.3 Revised Evaluation of the Ryznar Index

The first step in a revised evaluation of the Ryznar Index is to restore, as far as possible, the thermodynamic integrity. This can be achieved by using values of pH_S and pH that have both been adjusted to the temperature (T) in the test rig.

The values of pH_S have already been adjusted. The values of pH at 15°C in Tables 1–3 are converted to temperature T using the method described by Emerson on pp. 20–21 of Ref. [8]. The new values of pH are set out in Table 4, which is a revised version of Table 3.

A plot of the revised data in Table 4 is shown in Fig. 4. It will be seen that a smooth curve can be drawn through the plot. This curve is very similar to that obtained in Fig. 3 (which has been inserted in Fig. 4 as a dotted line for comparison) but has been displaced to the right in the diagram to give a new neutral point at $R = 7.5$.

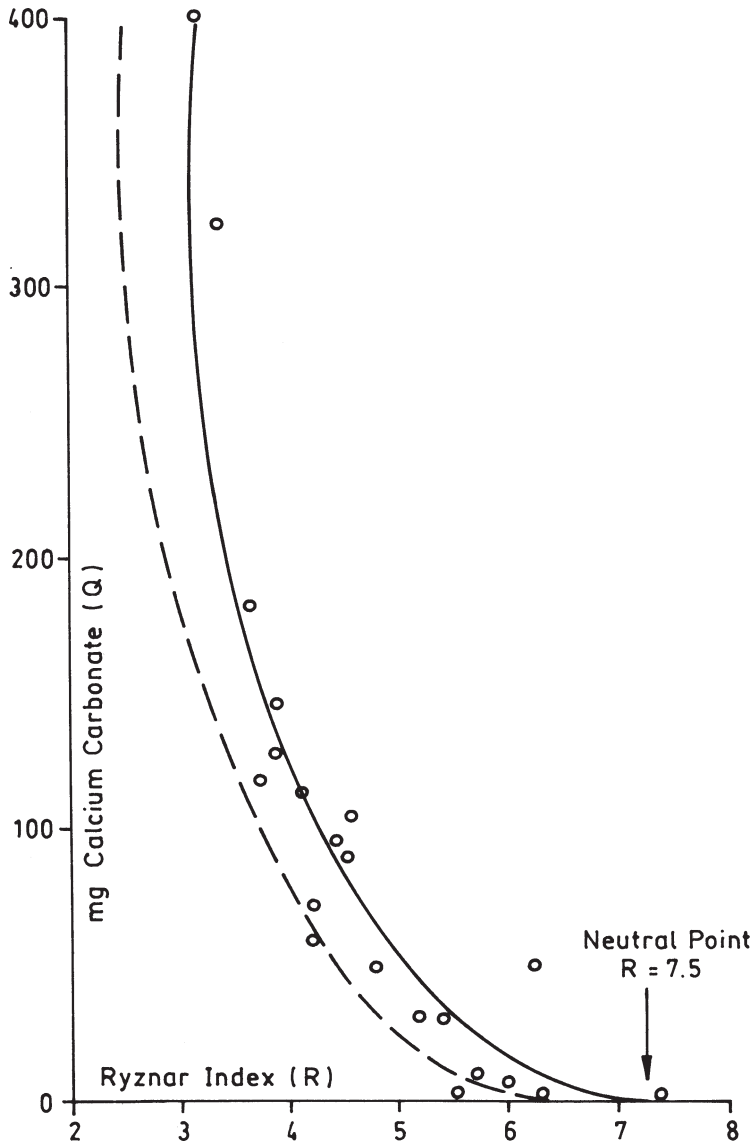


Fig. 4. Plot of revised Ryznar index(R)-v-weight of calcium carbonate(Q).

It will be a matter for individual water treatment suppliers and plant operators to decide whether to accept the thermodynamically improved neutral point of $R = 7.5$ as a basis for plant control instead of the older, more familiar $R = 6.0$ discussed in Sec. 1.1.2.

There is still a moderate amount of scattering of points in Fig. 4. In this respect, Fig. 4 offers no improvement over Fig. 3. This leads to the conclusion that the scattering is not due to the thermodynamic status of the data. If the thermodynamic status was a significant explanation there would have been a marked improvement in the closeness of the “fit” of the points to the curve on moving from Fig. 3 to Fig. 4. This conclusion is not altogether unexpected since the Ryznar Index in Eq. (1) is empirically derived and not the result of a rigid thermodynamic calculation.

Leading on from this conclusion the next logical step is to consider possible experimental errors in the test rig.

1.1.4 Experimental Errors

It is considered possible for experimental errors to arise in the test rig for the following reasons:

- (viii) In Sec. 1.1.1, it was explained that Ryznar increased the alkalinity of water samples by the addition of alkali (sodium carbonate or sodium bicarbonate). Following such additions time will be required for the ionic species contributing to the alkalinity and pH of the water to undergo internal rearrangement and achieve equilibrium. Very little is known about this time interval, but it introduces the possibility of the onset of precipitation being delayed. This delay could vary from one water to another and thus introduces an error when comparing results. Thus the “fixed” conditions of the test runs may, in fact, be open to some variation.
- (ix) When a water is treated with alkali, to increase the scaling potential, it passes through a metastable stage where actual precipitation does not take place. This metastable stage continues until the water is disturbed and passes into a labile (precipitating) stage by an increase in alkalinity and/or temperature. Here again, the onset of precipitation may be delayed leading to a variation in the conditions of the test run. The existence of the metastable stage is demonstrated in many natural occurring waters, which have a positive calcium carbonate saturation index (scaling) but remain stable without precipitation over long periods until the temperature is raised.

- (x) The precipitation of calcium carbonate when water is heated takes place in the bulk of the water. Some precipitate then becomes attached to the heat exchange surface. (This is in direct contrast, for example, to calcium sulphate which crystallises on the heat exchange surface). Under these conditions some of the precipitate may be carried forward with the flow of water and pass to drain. Thus some of the precipitated calcium carbonate may be lost and not recorded when the test coil is weighed. Variations in the recorded weight of calcium carbonate for the reasons just discussed may be small. But they are significant in comparison with the recorded weights which amount to a modest number of milligrams.

It may be argued that items (viii), (ix), and (x) are only hypotheses, and pose the question “Can errors of this type actually arise?”. The short answer is “Yes”. Edwards [9], working in the laboratories of Imperial Chemical Industries Ltd., in London, was carrying out investigations very similar to Ryznar using a very similar test rig. He found that the reproductivity of results was poor. Samples of water, prepared to the same specification, and put through the test rig on successive days, gave variable weights of calcium carbonate. It was necessary to run 5 or 6 tests and take a mean value in order to obtain meaningful results.

Again, a sample of water, treated with inhibitors A, B, C and D, gave results indicating an order of merit:

A
B
C
D

but on subsequent runs the order changed:

B	A	A	
A	B	C	etc.
C	D	B	
D	C	D	

Again, it was necessary to run 5 or 6 tests and take mean values in order to obtain meaningful results.

It will be seen from Edwards results that the use of the test rig provides a screening test capable of indicating broad trends in the amount of calcium carbonate precipitated (and its reduction by using various inhibitors). But the results are not sufficiently finely tuned to match parameters calculated on an accurate thermodynamic basis.

To overcome this difficulty the next logical step is to investigate a method for calculating the weight of calcium carbonate deposited on a thermodynamic basis.

1.2. NEW DATA

The discussions in Sec. 1.1 have extracted from Ryznar's work with the test rig all the information likely to be of value in estimating calcium carbonate deposition. The next step forward is to provide a method of calculating the weight of calcium carbonate deposited, instead of using weights obtained from a test rig. Such a method was not available to Ryznar or Edwards, but is available now. It has been applied in the following way:

Ten water analyses have been selected which are typical of the raw waters likely to be available from natural sources, or municipal supplies, for industrial use. The analyses are set out in Table 5.

The analyses cover the same broad characteristics as the waters used by Ryznar, with one important exception. Because Ryznar increased the alkalinity of his waters, his pH values are high (in the 8.0 to 9.0 range, with a few exceptions). These pH values are higher than those normally found in the natural waters and municipal supplies available to industry. Therefore in Table 5 a lower pH range (7.0 to 7.9) has been used.

In the original Ryznar test rig waters were maintained at a temperature of 95 °C in 13 cases, at 70 °C in 3 cases, and at 50 °C in 5 cases. This range of temperatures is too narrow to cover the range likely to be encountered in actual plant practice. Therefore in this discussion a temperature range of:

30 °C 40 °C 50 °C 60 °C 70 °C 80 °C

has been selected.

For each of the ten waters at each of the six temperatures the values of pH_s , pH, I , and R have been calculated as described in Secs. 1.1.2 and 1.1.3. From the values of I , the weights of calcium carbonate (W) have been calculated by the method described by Emerson on p. 26 of Ref. [8].

W is expressed as mg/l, a unit which is more useful than the original Q (in mg). Values of W allow weights of calcium carbonate deposits to be calculated for any volume throughput of water. The results of the above calculations are set out in Table 6.

In order to obtain a preliminary insight into the relationship between R and W a plot of values at 30 °C, 50 °C, and 80 °C was made in Fig. 5. It will be seen that a smooth curve can be drawn for each temperature, and the whole temperature range covered by a family of curves. It is therefore worthwhile

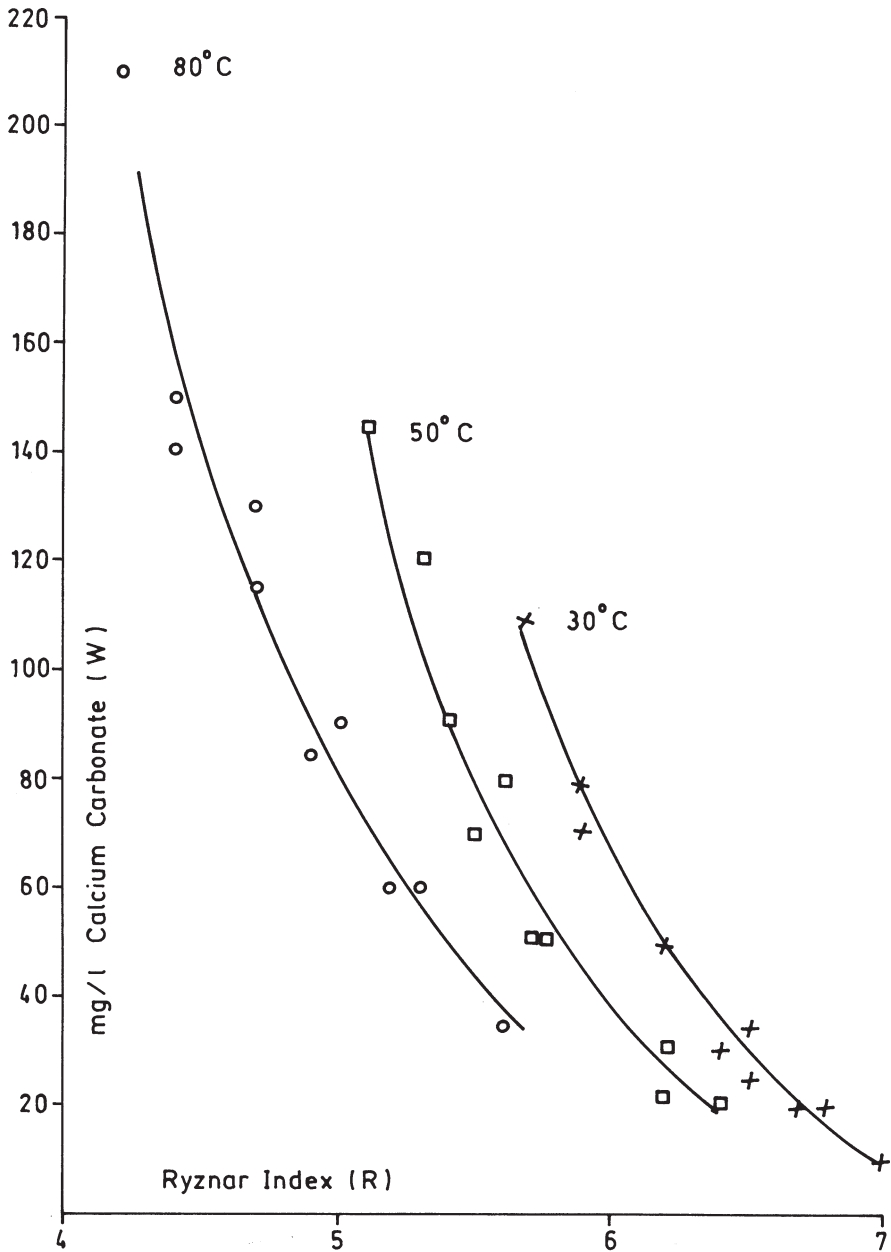


Fig. 5. Plot of revised Ryznar index(R)-v-weight of calcium carbonate(W).

exploring the mathematics of Table 6 in further detail. It can be shown by a detailed mathematical analysis of Table 6 that the relationship between R and W can be expressed as:

$$W = \exp(AR + B) \quad (9)$$

and that for individual temperatures the “best fit” equations are:

$$30\text{ }^{\circ}\text{C} \quad W = \exp(-1.75R + 14.79) \quad (10)$$

$$40\text{ }^{\circ}\text{C} \quad W = \exp(-1.66R + 13.80) \quad (11)$$

$$50\text{ }^{\circ}\text{C} \quad W = \exp(-1.47R + 12.54) \quad (12)$$

$$60\text{ }^{\circ}\text{C} \quad W = \exp(-1.13R + 10.28) \quad (13)$$

$$70\text{ }^{\circ}\text{C} \quad W = \exp(-1.17R + 10.33) \quad (14)$$

$$80\text{ }^{\circ}\text{C} \quad W = \exp(-1.24R + 10.65) \quad (15)$$

A further examination of Eqs. (10) to (15) shows that the values of A are linear in relation to temperature and the “best fit” equation is:

$$A = 0.015T - 2.22 \quad (16)$$

Similarly, the values of B are linear in relation to temperature and the “best fit” equation is:

$$B = -0.11T + 18.21 \quad (17)$$

Substituting Eqs. (16) and (17) in Eq. (9) gives a universal equation:

$$W = \exp[(0.015T - 2.22)R - 0.11T + 18.21] \quad (18)$$

For practical purposes it may be easier to use Eq. (18) in the logarithmic form:

$$\ln W = (0.015T - 2.22)R - 0.11T + 18.21 \quad (19)$$

$$\text{or} \quad \log W = (0.007T - 0.97)R - 0.048T + 7.92 \quad (20)$$

1.2.1. Use in the Field

When applied to practical problems in the field, Eqs. (18) or (19) or (20) will give the best value of W calculated on the basis of R . The calculated value of W is the maximum weight of calcium carbonate that can be deposited from 1 litre

of water. But in practice in an actual system it could be less for the following reasons.

- (xi) If the water velocity is high, the retention time in the system may be too low to allow all deposition to be completed within the system.
- (xii) Because the precipitation of calcium carbonate takes place in the bulk of the water (rather than on the heat exchange surfaces) precipitated calcium carbonate may be carried out of the system by the flow of water.
- (xiii) Retention of precipitated calcium carbonate can be influenced by the roughness of the metal surfaces, and the geometry of the system (e.g. sharp bends).
- (xiv) There may be temperature variations within the system, so that some parts may not be as high as T . In these lower temperature regions precipitation will be reduced.

Having listed these points it may be stated that the calculated value of W represents the highest weight of calcium carbonate that can be deposited, and thus represents the maximum fouling likely to be encountered.

Another practical aspect that must be considered is the speed and ease with which Eq. (18), or (19), or (20) can be used by a water technologist. Whether the technologist is advising a design team on the choice between several possible water supplies, or carrying out site tests with portable analytical equipment, the ability to produce a quick answer has obvious advantages. To assist in this, a table giving values of W against R is set out in Table 7. It is used as follows:

- (xv) From a water analysis at atmospheric temperature (15 °C) take the values of Ca, Alk, and DS. Use them to calculate the value of pH_S at T by using Eq. (6) evaluated as described in Sec. 1.1.2. To assist in this evaluation values of:

$p[Ca^{2+}]$ are given in Table 8

$p[Alk]$ in Table 9

pK_2 and pK_S in Table 10.

Values of $(DS)^{0.5}/100$ are calculated by simple arithmetic.

- (xvi) From a water analysis at atmospheric temperature (15 °C) take the values of pH and Alk and use them to convert pH to the pH at T , using the method described by Emerson on p. 20 of Ref. [8].
- (xvii) From (xv) and (xvi) calculate the Ryznar Index at T .

$$R = 2pH_S - pH \quad (1)$$

- (xviii) In Table 7, locate the sector containing the value of R obtained in (xvii). Scan the sector heading horizontally and locate the column headed with the value of R .
- (xix) At the left hand edge of the table scan vertically to find T . Now scan horizontally to meet the column selected in (xviii).
- (xx) Where the two intersect is the value of W .

Example

Water analysis at 15 °C

$$\text{Ca} = 300 \text{ mg/l CaCO}_3$$

$$\text{Alk} = 250 \text{ mg/l CaCO}_3$$

$$\text{DS} = 450 \text{ mg/l as such}$$

$$\text{pH} = 7.8.$$

Temperature in system = 60 °C.

Evaluate Eq. (6) as:

$$\text{p}[\text{Ca}^{2+}] = 2.53 \text{ from Table 8}$$

$$\text{p}[\text{Alk}] = 2.30 \text{ from Table 9}$$

$$\text{p}K_2 - \text{p}K_S = 1.40 \text{ (10.14} - 8.74 \text{ @ } 60^\circ\text{C from Table 10)}$$

$$\frac{(\text{DS})^{0.5}}{100} = 0.21$$

$$\text{pH}_S = 6.44 \text{ @ } 60^\circ\text{C}$$

From Table 20 at 15 °C in Ref. [8]

$$\text{Alk} = 250 \quad \text{gives } C = 520.$$

$$\text{pH} = 7.8.$$

From Table 74 at 60 °C in Ref. [8]

$$\text{Alk} = 250 \quad \text{gives pH} = 7.6 \text{ @ } 60^\circ\text{C}.$$

$$C = 520$$

Evaluate Eq. (1) as:

$$\begin{aligned} R &= 2\text{pH}_S - \text{pH} = 2 \times 6.44 - 7.6 = 12.88 - 7.6 \\ &= 5.28 \text{ @ } 60^\circ\text{C}. \end{aligned}$$

In Table 7, locate the sector headed R 5.0 to 5.9.

Select the column headed 5.3.

At the left hand edge find $T = 60\text{ }^{\circ}\text{C}$.

The vertical column and horizontal line meet at $W = 101\text{ mg/l CaCO}_3$.

This figure may be multiplied by the rate of water flow and the time the plant is on load to give total calcium carbonate fouling.

1.2.2. Margin of Error

Before concluding the discussion of the use of Table 7 it will be useful to try to access the margin of error likely to be encountered

To make this assessment five waters from Table 5 have been selected as representative of the range of waters examined. They are Nos: 22, 25, 26, 29 and 30.

Similarly, three temperatures from Table 6 have been selected as representative of the range of temperatures examined. They are $30\text{ }^{\circ}\text{C}$, $60\text{ }^{\circ}\text{C}$, and $80\text{ }^{\circ}\text{C}$.

Combining these two pieces of data, the values of R and W as recorded in Table 6 have been listed. The corresponding values of W from Table 7 have been added alongside. The difference between corresponding values of W have been listed and expressed as a percentage. The details are set out in Table 11.

In setting up Table 11 the values of W from Table 6 have been taken as the true value, since they were calculated direct from individual water analyses on a sound thermodynamic basis.

It will be seen from Table 11 that the errors vary between +50% and -27%. In an ideal situation the error should be zero. How do the errors arise and what is their significance?

Equation (18), on which Table 7 is based, is a “best fit” derived from Eqs. (10) to (17) which are themselves a “best fit” to a set of data. Therefore, there will be cases where the value of a parameter calculated from one of the equations will be different from the true value.

The errors may be positive or negative, and they will also be cumulative because any error arising from Eqs. (10) to (15) will be combined with any errors arising from Eqs. (16) and (17).

It can be shown that the error of +50% mentioned above can be caused by an error of -0.2 in the value of R , and the error of -27% caused by an error of +0.5 in the value of R . Errors of this magnitude can be caused by errors of the order of 0.15 in the values of pH_S and pH : errors which are within the tolerance applicable to normal plant practice.

To assess the significance of the errors in Table 11 it is necessary to compare them with errors which arise from variations in water analyses due to natural

causes. To investigate this aspect, water analyses from two different locations have been selected. Each water supply possesses characteristics that are likely to lead to scaling. For each supply, the mean, maximum and minimum analyses have been recorded. During the progress of any project the normal procedure is to base calculations for design, operation, and control of a system on the mean water analysis. But during the working life of the system it will receive water varying between the minimum and maximum analyses.

To represent these real-life conditions W has been calculated at 30 °C, 50 °C, and 80 °C for the mean, maximum, and minimum analyses of both supplies. The difference in values between mean and maximum analyses, and between mean and minimum analyses have been recorded as errors. The results are set out in Table 12.

It will be seen that the errors recorded in Table 12 vary between +190% and -95%. This range is much greater than those recorded in Table 11. Therefore Table 7 may be used as a useful working estimate since any errors it may produce will be far outweighed from those arising from natural causes.

1.3. THE LANGEЛИER INDEX

It was stated earlier in Sec. 1.1.2 that Ryznar had investigated a possible relationship between Q and I , but had abandoned this line of investigation. In view of the relationship between R and W subsequently produced in Sec. 1.2 the question arises "Is it possible to produce a similar relationship between I and W ?"

To explore this possibility a plot of values for I and W at 30 °C, 50 °C, and 80 °C (as recorded in Table 6) was made in Fig. 6. It will be seen from the plot in Fig. 6 that a smooth curve can be drawn for each temperature, and that the whole range can be covered by a family of curves. It is therefore worth exploring the mathematics of the relationship between I and W in further detail.

It can be shown by a detailed mathematical analysis that the relationship between I and W can be expressed as:

$$W = \exp(YI + Z) \quad (21)$$

and that for individual temperatures the "best fit" equations are:

$$30 \text{ °C} \quad W = \exp(4.30I + 0.71) \quad (22)$$

$$40 \text{ °C} \quad W = \exp(3.73I + 0.69) \quad (23)$$

$$50 \text{ °C} \quad W = \exp(3.50I + 0.69) \quad (24)$$

$$60 \text{ °C} \quad W = \exp(2.23I + 1.70) \quad (25)$$

$$70 \text{ °C} \quad W = \exp(2.92I + 0.69) \quad (26)$$

$$80 \text{ °C} \quad W = \exp(2.97I + 0.37) \quad (27)$$

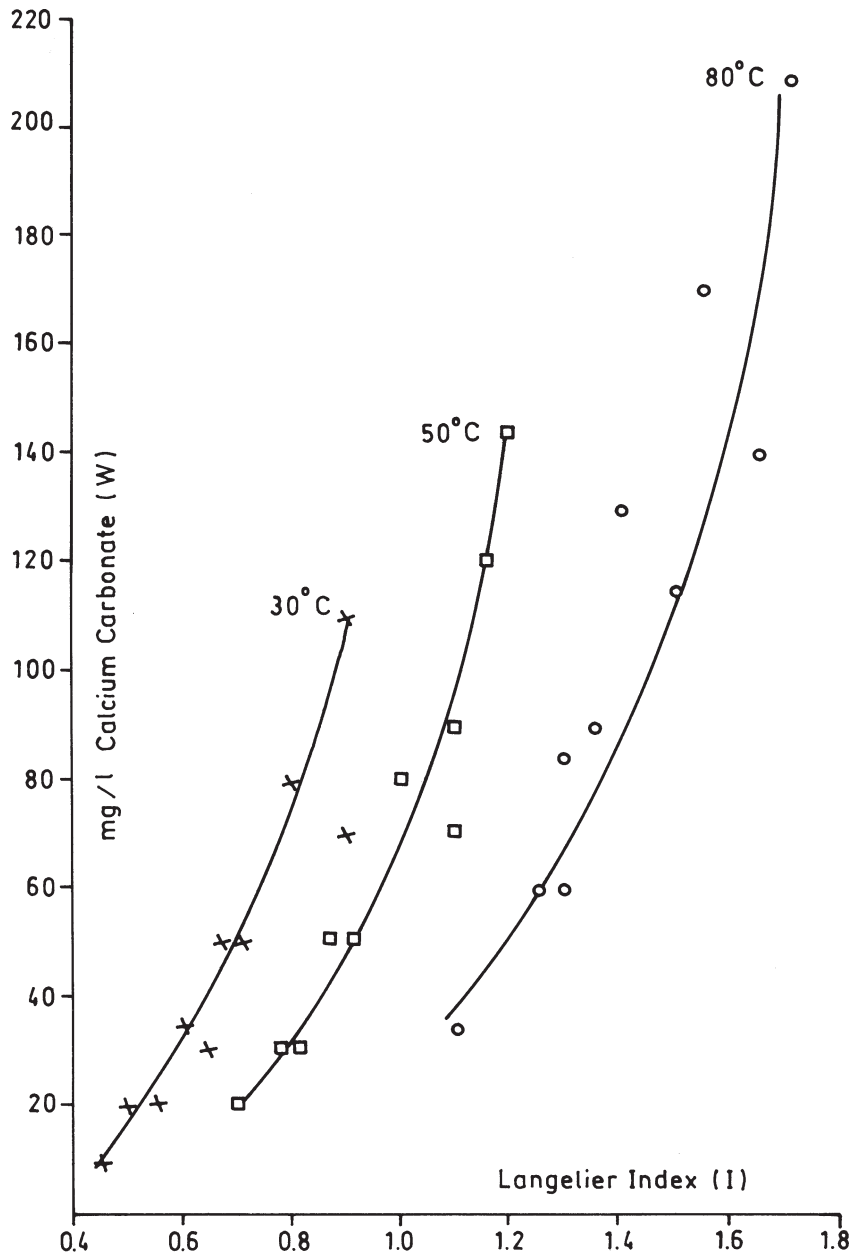


Fig. 6. Plot of Langelier index(I)-v-weight of calcium carbonate(W).

A further examination of Eqs. (22) to (27) shows that the values of Y are linear in relation to temperature and the “best fit” equation is:

$$Y = -0.03T + 5.17 \quad (28)$$

Similarly, the values of Z are linear in relation to temperature and the “best fit” equation is:

$$Z = -0.0004T + 0.714 \quad (29)$$

Substituting Eqs. (28) and (29) in Eq. (21) gives a universal equation:

$$W = \exp[(-0.03T + 5.17)I - 0.0004T + 0.714] \quad (30)$$

For practical purposes it may be easier to use Eq. (30) in the logarithmic form:

$$\ln W = (-0.03T + 5.17)I - 0.0004T + 0.714 \quad (31)$$

$$\text{or } \log W = (-0.014T + 2.41)I - 0.0002T + 0.333 \quad (32)$$

1.3.1. Use in the Field

When applied to practical problems in the field Eq. (30), (31), or (32) will give the best values of W calculated on the basis of I . The calculated value of W is the maximum weight of calcium carbonate that can be deposited from 1 litre of water.

But in practice, in a actual system it could be less for the reasons already given in items (xi) to (xiv) in Sec. 1.2.1.

Also, as in Sec. 1.2.1, there is a need for a fast and easy method for evaluating Eq. (30), or (31), or (32). To assist in this, a table giving values of W against I is set out in Table 13. It is used as follows:

- (xxi) From a water analysis at atmospheric temperature (15 °C) take the values of Ca, Alk, and DS. Use them to calculate the value of pH_S at T as already described in item (xv) of Sec. 1.2.1.
- (xxii) From a water analysis at atmospheric temperature (15 °C) take the values of Alk and pH and use them to convert the pH to the value at T as already described in item (xvi) of Sec. 1.2.1.
- (xxiii) From (xxi) and (xxii) calculate the Langelier index at T .

$$I = \text{pH} - \text{pH}_S \quad (5)$$

- (xxiv) In Table 13, locate the sector containing the value of I obtained in (xxiii). Scan the sector heading horizontally and locate the column headed by the value of I .
- (xxv) At the left hand edge of the table scan vertically to find T . Now scan this line horizontally to meet the column selected in (xxiv).
- (xxvi) Where the two intersect is the value of W .

Example

Water analysis at 15 °C

$$\begin{aligned} \text{Ca} &= 300 \text{ mg/l CaCO}_3 \\ \text{Alk} &= 250 \text{ mg/l CaCO}_3 \\ \text{DS} &= 450 \text{ mg/l as such} \\ \text{pH} &= 7.8. \end{aligned}$$

Temperature in system = 60 °C.

Evaluate Eq. (6) as:

$$\begin{aligned} \text{p[Ca}^{2+}] &= 2.53 \text{ from Table 8} \\ \text{p[Alk]} &= 2.30 \text{ from Table 9} \\ \text{p}K_2 - \text{p}K_S &= 1.40 \text{ (10.14 - 8.74 @ 60°C from Table 10)} \\ \frac{(\text{DS})^{0.5}}{100} &= \underline{0.21} \\ \text{pH}_S &= 6.44 \text{ @ 60°C} \end{aligned}$$

From Table 20 at 15 °C in Ref. [8]

$$\begin{aligned} \text{Alk} = 250 & \quad \text{gives } C = 520. \\ \text{pH} = 7.8 & \end{aligned}$$

From Table 74 at 60 °C in Ref. [8]

$$\begin{aligned} \text{Alk} = 250 & \\ C = 520 & \quad \text{gives pH} = 7.6 \text{ @ 60°C.} \end{aligned}$$

Evaluate Eq. (5) as:

$$I = 7.6 - 6.44 = 1.16.$$

In Table 13, find the sector headed 1.1 to 2.0 and select the column headed 1.2. At the left hand edge find $T = 60\text{ }^{\circ}\text{C}$ The vertical column and horizontal line meet at:

$$W = 114\text{ mg/l CaCO}_3.$$

This number, multiplied by the rate of water flow and the time the plant is on load, will give the total calcium carbonate fouling.

1.3.2. Margin of Error

Before concluding the discussion on the use of Table 13, it will be useful to try to assess the margin of error likely to be encountered. To make this assessment the procedure already described in Sec. 1.2.2 has been adopted. Analyses Nos. 22, 25, 26, 29 and 30 from Table 5 have been taken and temperatures $30\text{ }^{\circ}\text{C}$, $50\text{ }^{\circ}\text{C}$, and $80\text{ }^{\circ}\text{C}$ from Table 6.

Combining these two pieces of data, the values of I and W as recorded in Table 6 were listed. The corresponding values of W from Table 13 were added alongside. The difference between corresponding values of W were then listed and expressed as a percentage. The details are set out in Table 14.

In setting up Table 14 the values from Table 6 were regarded as the true values, since they were calculated direct from individual water analyses on a sound thermodynamic basis.

It will be seen from Table 14 that the error varies between $+36\%$ and -26% . This is a narrower range than that exhibited by R in Sec. 1.2.2. How do these errors arise and what is their significance?

The discussion in Sec. 1.2.2 concerning Eqs. (10) to (18), Table 7, and the errors recorded in Table 11, also apply here concerning Eqs. (21) to (30), Table 13, and the errors recorded in Table 14. It can be shown that the errors of $+36\%$ and -26% mentioned above, can be caused by errors of -0.04 and $+0.06$ in the evaluation of I . These errors can arise from errors of the order of 0.03 in the values of pH and pH_S : errors which are well within the tolerance applicable to the evaluation of these parameters.

As already stated in Sec. 1.2.2 this is an important point which must not be overlooked when considering the magnitude of errors in the value of W , as a means of assessing the magnitude of errors in the procedure under discussion.

To assess the significance of errors in Table 14 the procedure already described in Sec. 1.2.2 has been adopted. The same two waters listed in Table 12 have been used again and the values of W for values of I at $30\text{ }^{\circ}\text{C}$, $50\text{ }^{\circ}\text{C}$, and $80\text{ }^{\circ}\text{C}$ are recorded. The results are set out in Table 15.

It will be seen that the errors recorded in Table 15 vary between +463% and -100%. This range is much greater than the range recorded in Table 14. Therefore the errors arising from Table 13 can be ignored as likely to be outweighed by errors arising from natural causes.

1.4. CHOICE BETWEEN LANGELIER AND RYZNAR

In this book two methods have been developed for estimating the weight of calcium carbonate deposited in a system. One method is based on the Ryznar Index (R) and the other on the Langelier Index (I). The existence of two possible methods of estimation at once raises the question, "Which one shall be used?" for any specific problem.

To assist in answering this question selected values of W , based on R and derived from Table 7, and selected values of W , based on I and derived from Table 13, are set out together in Table 16. The values based on I have been taken as the standard: the difference between the values based on R and the values based on I have been recorded in Table 16 and expressed as a percentage.

As already stated in Sec. 1.3.1 values of W based on I are considered to be superior to values based on R . Calculations based on I have a higher thermodynamic integrity than those based on R . (R is an empirically derived parameter, and this is considered to be a weak point). Thus values based on I (Langelier) is the preferred method.

But some water treatment technologists and plant operators may have already established methods of treatment and control based on R , and would prefer to continue using R as a basis for estimating W . If this preference is followed, it will be seen from Table 16 that errors between +38% and -25% may be encountered. But these degrees of error are small compared with errors likely to be introduced by natural causes. See Secs. 1.2.2 and 1.3.2.

The final decision will depend on the degree of tolerance that can be accepted when making a forecast for any given installation.

In the case of a small project, or one handling a low grade product, a tolerance between +38% and -25% may be acceptable. A calculation for W based on the value of R would be attractive to a technologist or operator who already has embedded in his methods of treatment and control calculations based on R .

But for a large project, or one handling a sophisticated and expensive product, a more accurate value for W , based on the value for I , will be required.

1.5. THE SPECIAL CASE OF RECIRCULATING SYSTEMS

Under the proviso stated in Sec. 1.1.1 the whole of the work discussed up to this point is restricted to once-through, closed systems. However, as industrial installations often include recirculating systems, they must now be considered.

1.5.1. Closed Recirculating Systems

Some industrial cooling systems take the form of a primary closed ring in which water continuously recirculates. Heat, which needs to be dissipated, is absorbed by the water in a heat-exchanger and then discharged from the water by a second heat-exchanger which itself is cooled by a secondary cooling system.

In the primary system the volume of water used for the initial filling (or re-filling after draining for maintenance) will deposit an initial quantity of calcium carbonate according to the temperature rise experienced. Once this initial precipitation has taken place, no more calcium carbonate will be deposited.

The quantity of calcium carbonate can be estimated by the methods already described, from the analysis of the water and the temperature in the system. In the calculation, the volume of water in the closed system replaces the flow rate for a once-through system.

1.5.2. Open Recirculating Systems

The open recirculating cooling system, incorporating an evaporative cooling tower, is widely used in industry. A special feature of this type of system is the increase in the concentration of dissolved salts in the recirculating water.

The normal procedure for this type of system is to operate with a pre-determined number of concentrations in the recirculating water (by controlled purging from the system) coupled with treatment with an inhibitor. Each inhibitor varies in the quantity of calcium carbonate it can hold in solution before precipitation occurs. This factor determines the optimum number of concentrations to be maintained in the recirculating water. Therefore the number of concentrations and the dosage of inhibitor are usually given to the plant operator by the water treatment supplier.

In this context, it will be useful to estimate the weight of calcium carbonate that will be deposited by a given water in a given plant at a given temperature if the system is operated at various number of concentrations. This information will assist in selecting the most appropriate treatment to inhibit fouling, and the number of concentrations compatible with the selected treatment. Also, this

information can be used to justify the cost of treatment by giving an indication of the loss of thermal efficiency if the system is operated without treatment.

In order to estimate the fouling (whether on the basis of Table 7 or on the basis of Table 13) it is necessary to modify the methods previously described for calculating pH_S and pH .

pH_S

The value of pH_S for the make-up water at T , the temperature in the system is first calculated as in (xv) in Sec. 1.2.1. If the system is to operate with “ n ” concentrations in the recirculating water, the value of pH_S in the make-up water is converted to pH_S in the recirculating water by means of the equation described by Emerson [5]:

$$\begin{array}{l} pH_S \\ \text{(recirc.)} \end{array} = \begin{array}{l} pH_S \\ \text{(make-up)} \end{array} - 2 \log n + (n^{0.5} - 1) \frac{DS^{0.5}}{100} \quad (33)$$

pH

The value of pH in the recirculating water at T , the temperature in the system, at “ n ” concentrations is calculated from the alkalinity of the make-up water using the method described on p. 27 of Ref. [8].

With the new values of pH_S and pH new values of R or I can be calculated and a new value for W read off from Table 7 or Table 13.

Example

Make-up water analysis at 15 °C

$$Ca = 120 \text{ mg/l CaCO}_3$$

$$Alk = 80 \text{ mg/l CaCO}_3$$

$$DS = 180 \text{ mg/l as such.}$$

Temperature in system = 40 °C.

Number of concentrations in system = 3.

From Eq. (6)

$$p[Ca^{2+}] = 2.92 \text{ from Table 8}$$

$$p[Alk] = 2.80 \text{ from Table 9}$$

$$pK_2 - pK_S = 1.70 \text{ (10.22 - 8.52 at 40 °C from Table 10)}$$

$$\frac{(DS)^{0.5}}{100} = 0.13$$

$$pH_S = 7.55.$$

Convert to recirculating water

$$\begin{aligned} \text{pH}_S &= 7.55 - 2 \log 3 + 0.13(3^{0.5} - 1) \\ &= 7.55 - 0.95 + 0.13(1.73 - 1) \\ &= 7.55 - 0.95 + 0.09 \\ &= 6.69. \end{aligned}$$

Alk in make-up water = 80.

In circulating water = $3 \times 80 = 240$.

From p. 27 of Ref. [8]

$C = 2 \text{Alk} = 2 \times 240 = 480$.

From Table 63 of Ref. [8]

$\text{pH} = 8.2$

$$R = 2\text{pH}_S - \text{pH} = 2 \times 6.69 - 8.2 = 13.38 - 8.2 = 5.18.$$

From Table 7

$W = 159 \text{ mg/l CaCO}_3$ for water in system

$= 159/3 = 53 \text{ mg/l CaCO}_3$ for make-up water.

Alternatively:

$$I = \text{pH} - \text{pH}_S = 8.2 - 6.69 = 1.51.$$

From Table 13

$W = 490 \text{ mg/l CaCO}_3$ for water in system

$= 490/3 = 163 \text{ mg/l CaCO}_3$ for make-up water.

The values of W in the make-up water may be multiplied by the rate of adding water to the system and the time that the plant is on load to give the total calcium carbonate fouling.

In considering the values of W above, the comments in Sec. 1.4 are still applicable.