

QUANTITATIVE FORECASTING
OF PROBLEMS IN
INDUSTRIAL
WATER SYSTEMS

A G D EMERSON

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FOREWORD

Some calculations in Sections 1.2.1, 1.3.1, 1.5.2, 3.3, 3.4, 4.1.1, 4.4.4, 4.4.6, 4.4.7, and 5.1.4 require the use of tables published in an earlier work cited as Ref. [8] in the References.

Readers will therefore need to have a copy of that earlier work to hand before using this book.

Unfortunately, after this book had been drafted, the publishers of Ref. [8] stated that this earlier work was now out of print. Readers may therefore have difficulty in obtaining a copy.

To overcome this situation Ref. [8] has been reprinted as a Supplement at the end of this book. Readers will therefore have all the tables needed, both from this book and from the supplement, available under one cover.

SYNOPSIS

The operating problems most likely to be encountered in industrial water systems are:

- Fouling by calcium carbonate.
- Fouling by calcium sulphate.
- Fouling by calcium phosphate.
- Corrosion of mild steel.
- Corrosion of copper.

Methods are described for calculating the amount of fouling likely to occur, and the rate at which corrosion is likely to proceed.

These data enable a quantitative forecast to be made of the problems likely to be encountered in an industrial water system, while the project is still at the design stage. The information will also be of assistance in investigating problems experienced in existing systems.

The data are presented in the form of tables to assist operators who are working on site with portable testing equipment.

The methods described introduce new concepts for the saturation indices of calcium carbonate, calcium sulphate, and calcium phosphate; for buffer capacity; and the pitting propensity index.

NOMENCLATURE

- () Thermodynamic activities, expressed as mol/l.
- [] Stoichiometric concentrations, expressed as mol/l.
- a* Fraction of molecules remaining after precipitation.
- Alk Total alkalinity } expressed as
 - Alkalinity to Methyl Orange } mg/l in terms
 - Alkalinity to pH 4.5 } of CaCO_3 .
- b* Fraction of molecules remaining after precipitation.
- B* Buffer Capacity
- C* Total carbon dioxide expressed as mg/l in terms of CaCO_3 .
- C* Corrosion rate
- Ca* Calcium hardness expressed as mg/l in terms of CaCO_3 .
- Cl_R Chlorine residual expressed as mg/l Cl_2 .
- DS* Dissolved solids expressed as mg/l as such.
- exp Exponential exp (*a*) = e^a .
- E* Summation of equilibrium constants.
- E* Constant for Suzuki's equation.
- f* Activity coefficient.
- I* Calcium carbonate saturation index. (Langelier Index)
- I_L Copper pitting propensity index. (Lucey Index)
- I_p Calcium phosphate saturation index.
- I_s Calcium sulphate saturation index.
- K* Thermodynamic equilibrium constants.
- K'* Stoichiometric equilibrium constants.
- ln Logarithm to base e.
- log Logarithm to base 10.
- n* Number of concentrations.
- p Negative log.
- pH_s Equilibrium pH.
- Phos Total phosphate expressed as mg/l in terms of PO_4 .
- Q* Weight of calcium carbonate expressed as mg CaCO_3 .
- R* Ryznar Index.

- SO_4 Sulphate expressed as mg/l in terms of Na_2SO_4 .
 T Temperature $^{\circ}\text{C}$.
 μ Ionic strength.
 V Vectors.
 W Weight of calcium carbonate expressed as mg/l CaCO_3 .
 Z Valency.

INTRODUCTION

This book has been written as a contribution to changing the attitude of mind when considering problems in industrial water systems. The need for such a change has been brought about by changes in prevailing economic conditions.

Industrial systems using water for heating or cooling purposes frequently encounter problems which are associated with the quality of water used. In former times, when both labour and materials were cheap, it was a relatively simple matter to discard a system that had encountered problems and build a new one designed in the light of the experience gained from an old system: in this way it was hoped to avoid the difficulties previously experienced.

If discarding the system was not considered necessary, some form of chemical treatment and monitoring might be introduced. If this was not entirely satisfactory then, with cheap labour available, it was, again, a relatively simple matter to arrange for periodic manual cleaning of the system to make good the deficiencies of the treatment. In fact some operators used to boast of the quantity of deposit removed during such manual cleaning operations. As though it was a matter of pride, instead of a reflection on the manner in which the system had been controlled and operated.

But under present day economic conditions such a leisurely approach is no longer feasible. In the design and operation of industrial water systems it is important to know in advance what problems are likely to be encountered, and to be able to give a forecast in quantitative terms.

For one type of system, the steaming boiler, the problem is not too difficult. For example, a boiler feed water contains X mg/l of hardness salts: since all the water entering the boiler is evaporated as steam, all the hardness salts must remain behind to form scale. Therefore X mg of scale will be formed for each litre of water evaporated. Expressing the problem in quantitative terms is therefore a matter of simple arithmetic. For this reason steaming boilers have been excluded from the discussions in this book.

But for systems involving heat-exchangers (whether for heating or cooling) a more complex situation exists, depending on the chemical reactions taking place in the water at various temperatures. The study in this book has been restricted to heat exchange systems where there is no loss of water by evaporation, or

other means, unless specifically mentioned in special cases. It is also assumed that there is no change in the chemical characteristics of the water by accidental ingress of contaminants, or by the loss of dissolved gases by venting to atmosphere, unless addition of chemicals or loss of gases are specifically mentioned in special cases. Changes in the chemical characteristics of the water are limited to those induced by a change of temperature.

The problems most likely to be encountered in the types of systems outlined above are fouling and corrosion. Fouling is caused by:

Deposition of calcium carbonate.

Deposition of calcium sulphate.

Deposition of calcium phosphate.

These are studied by physical-chemistry methods.

It is appreciated that some fouling may occur by the formation of organic slimes, which may act as binders for the inorganic deposits mentioned above. But organic slimes have been excluded from the discussion as their formation is not amenable to physical-chemistry methods.

The metals of construction most likely to be used in industrial water systems are mild steel and copper: their rates of corrosion have therefore been included in the discussion. Other metals may be used from time to time, but mild steel and copper are regarded as basic: other (often more expensive) metals are introduced when justified on technical and economic grounds by the operating conditions existing in an individual system.

Manufacturers of special alloys are sometimes able to indicate how the rate of corrosion of their materials compare with mild steel or copper under given operating conditions. Thus, a knowledge of the probable rate of corrosion of the basic metals can be of assistance in selecting special alloys.

The purpose of the data offered in this book is to enable quantitative forecasts to be made of the fouling or corrosion likely to be encountered in an industrial water system, while the project is still at the design stage. A decision can then be made on the type of water treatment to be adopted, commensurated with the purpose for which the system is to be used, and its life expectancy.

A discussion on the various types of water treatment that might be considered is beyond the terms of reference of this book. It is a diagnostic tool utilising the basic physical-chemistry of water supplies. Water treatment methods may change from time to time, but the basic physical-chemistry remains unchanged.

However, a forecast of probable operating problems may be used to influence the choice of a water supply, if several alternatives are available on any given site.

In the case of a small project, or one handling a low grade product, a forecast of problems as outlined in this book may suffice. But for a large project, or one handling a sophisticated and expensive product, a trial run on a scale model may be undertaken before final design details are settled. In such a case an initial forecast of the problems will enable the trial run to focus on the most critical conditions likely to be encountered.

In addition, to work at the design stage of a project, the methods described in this book may be used to assist operators in investigating problems on an existing system. As this often involves working with portable testing equipment, the data are presented in the form of tables to facilitate site work.

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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,

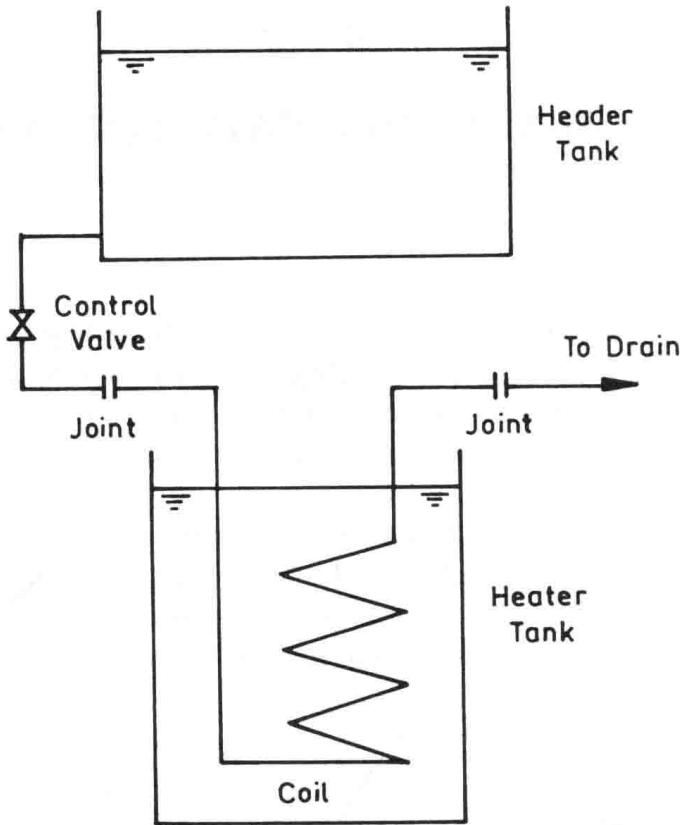


Fig. 1. Basis of Thompson-Ryznar test rig.

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 $15^\circ C$) Ryznar calculated the values of the calcium carbonate saturation index, described by Langelier (loc.cit.).

$$I = pH - pH_S \quad (5)$$

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 $15^\circ C$) 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:

$$pH_S = p[Ca^{2+}] + p[Alk] + pK_2 - pK_S + (DS)^{0.5}/100 \quad (6)$$

described by Emerson [5].

$$\text{Where } K_2 = \frac{(H^+)(CO_3^{2-})}{(HCO_3^-)} \quad (7)$$

$$\text{and } K_S = (Ca^{2+})(CO_3^{2-}) \quad (8)$$

Values of $p[Ca^{2+}]$ and $p[Alk]$ have been taken from tables by Manning [6] and values of pK_2 and pK_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:

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