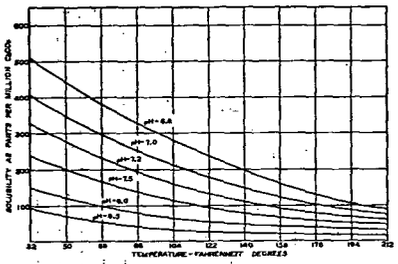


Fig. 2 Adapted from (1) *Ind. & Eng. Chem.*, 20 (1928) 1197—by Balis. (2) J.A.C.S. 50 (1929) 2088—Frear & Johnson.

Fig. 2 .... Solubility of Calcium Carbonate in Distilled Water Containing Carbon Dioxide

(pH Values at Approximately 73 F)

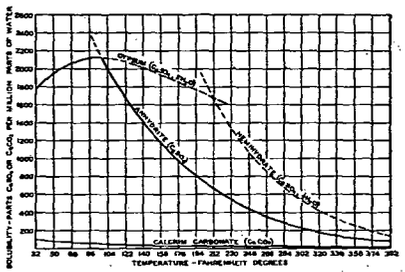


Fig. 3 Adapted from Bull. No. 15, Univ. of Mich. *Formation and Properties of Boiler Scales* by P. E. Partridge.

Fig. 3 .... Solubility of Calcium Sulfate and of Calcium Carbonate for Comparison

($CaCO_3$ in Equilibrium with Normal CO_2 Content of the Atmosphere)

coolers, are more susceptible to scale and sludge formation than are the cold parts of the same system using the same water.

The most common of the unstable soluble salts are the bicarbonates of calcium, magnesium, and occasionally iron. Under conditions favoring the removal of carbon dioxide, as when the water is strongly aerated or when it is boiled, the bicarbonates are readily converted to the relatively insoluble carbonates. The type of scale most usually encountered is calcium carbonate (often called alkalinity) from the decomposition of calcium bicarbonate according to the following chemical reaction:

$$Ca(HCO_3)_2 + \text{heat} \rightarrow CaCO_3 + CO_2 + H_2O$$

$$\underset{\text{Bicarbonate}}{\text{Calcium}} + \text{heat} \rightarrow \underset{\text{Carbonate}}{\text{Calcium}} + \underset{\text{Dioxide}}{\text{Carbon}} + \text{water}$$

Conversely, carbonates are readily converted to the more soluble bicarbonate by the addition of carbon dioxide or other acidic materials. This explains the increase in the apparent solubility of calcium carbonate at decreasing *pH* values (increasing concentration of hydrogen ion) shown in Fig. 2, the carbonate really going into solution largely as bicarbonate.

In special cases, primarily with well waters possessing a high natural iron content, deposition of iron oxide from the decomposition of ferrous bicarbonate takes place according to the following reaction:

$$4\,Fe(HCO_3)_2 + O_2 \rightarrow 2\,Fe_2O_3 + 8\,CO_2 + 4\,H_2O$$

$$\underset{\text{Bicarbonate}}{\text{Ferrous}} + \text{Oxygen} \rightarrow \underset{\text{Oxide}}{\text{Iron}} + \underset{\text{Dioxide}}{\text{Carbon}} + \text{water}$$

Low water velocity in heat transfer equipment often causes sludges to settle out in the tubes. This has the same effect on heat transfer as scale formation. When this occurs, increasing the water velocity often cures the condition.

It is sometimes desired to evaluate the tendency in a particular water toward the separation of calcium carbonate, which may be desirable as a means of establishing a corrosion-resistant film on metal surfaces, or in other circumstances may be undesirable because of the impedance of the calcium carbonate film to heat transfer. This tendency is indicated approximately by the Langelier Index,[9] which is obtained by subtracting the actual *pH* of a particular water from the *pH* at which it is estimated precipitation of calcium carbonate would just begin. This estimate may be made by the use of Fig. 4.

There are various expedients which may be employed for avoiding or mitigating difficulties due to scales:

a. The water may be treated before use to remove elements such as calcium, magnesium, and iron, which form relatively insoluble compounds. In the various softening processes this removal of these elements is accompanied by the addition of other elements, particularly sodium, the compounds of which are relatively soluble.

b. The water may be treated within the equipment to promote the separation of dissolved solids as sludges, rather than as scale which is, in most cases, more objectionable.

c. The increase in total solids, due to the evaporation of water, may be controlled by the displacement, continuously or intermittently, of some of the used water by fresh supply.

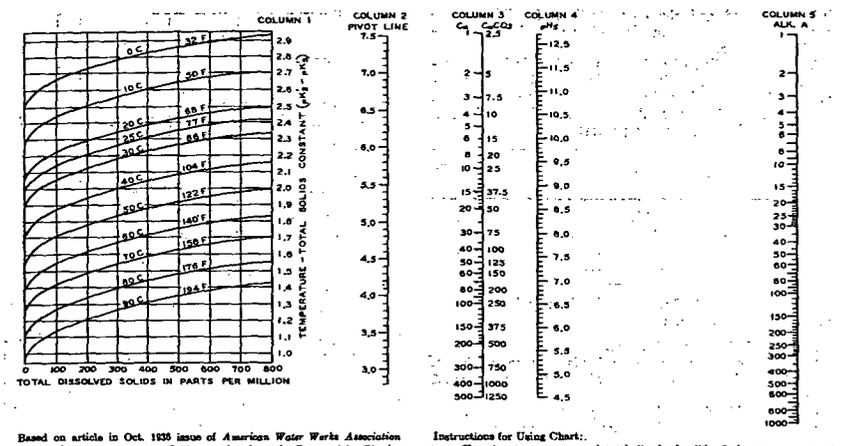
d. Substances, such as the polyphosphates, having the property of inhibiting the precipitation of calcium carbonate from solutions supersaturated with it, may be added.

e. The *pH* of the water may be lowered (hydrogen ion concentration raised) to reduce the tendency for precipitation of carbonate. This is permissible only to such an extent as will not cause a serious increase in rate of corrosion.

The choice of the best expedient or combination of expedients must be made for each type of equipment, and will be affected by operating and water considerations. Item c above must be used, regardless of which other items are used, for all recirculating water systems from which evaporation takes place.

Once-Through Equipment

Where abundant supplies of water are available at low cost, the cooling water may pass through the equipment once, undergoing a rise in temperature. Little difficulty from scale should be encountered if the Langelier Index is lower than +0.5, based on the highest water temperature encountered in the system. This often corresponds to a carbonate hardness of less than 200 ppm when water temperatures are lower than 100 F. However, since many municipal supplies are softened so that incipient calcium carbonate



Based on article in Oct. 1935 issue of *American Water Works Association Journal* and later corrections for Tables 2 and 4 of article. Prepared for Charles P. Hoover of the Columbus, Ohio, Water Softening and Purification Plant by M. L. Riehl.

(Data required for determining pH saturation)

(1) Total alkalinity, as parts per million of $CaCO_3$.
(2) Calcium in parts per million.
(3) Total dissolved solids, in parts per million.
(4) Temperature, Centigrade, at which *pH* saturation desired.

Instructions for Using Chart:

1. Knowing temperature and total dissolved solids, find temperature and total solids constant on Col. 1.
2. Align this constant with given value of calcium on Col. 3 of Chart, then locate point in Col. 2 of Chart (Pivot Line).
3. Align this point on Pivot Line with given alkalinity on Col. 5; read *pH* saturation on Col. 4.

Saturation index is *pH* actual minus *pH* saturation.

e.g.—*pH* actual,	*pH* saturation.	Saturation index.
7.6	8.1	−0.5 (corrosive)
8.4	7.8	+0.6 (scale forming)

(Applicable within pH Range 7.0–9.5)

Fig. 4 .... Graph and Nomogram for Determination of *pH* Saturation by Langelier's Formula

precipitation is induced, the Langelier Index is a more reliable indication of scaling tendency.

Prevention of scale in once-through systems is based primarily on the adjustment of *pH*, the application of surface-active agents, or a combination of the two. Normally the addition of a few parts per million of a surface-active agent such as a polyphosphate[10] fed proportionately to a water with a scaling tendency is all that is required to control scale.

Where a given water does not respond satisfactorily to surface-active agents, reduction of *pH* with sulfuric acid or carbon dioxide is often employed. The *pH* is reduced only sufficiently to have it fall within the effective range of the surface-active agent. The use of acid or carbon dioxide is sometimes permitted without polyphosphates when corrosion will not be severe. In this case the *pH* is reduced so that the Langelier Index is less than +0.5. The acid or carbon dioxide must be added with care. Use of automatic *pH* controllers is required if corrosion is to be prevented.

A special case of scale from ferrous bicarbonate decomposition was mentioned previously. Ferrous bicarbonate is considerably less stable than calcium bicarbonate. The prevention of this decomposition can be accomplished by the addition of polyphosphate in low concentrations.[11] The use of polyphosphate in the ratio of two parts by weight to one part by weight of iron is usually most effective. The polyphosphate must be added to the water before exposure of the water to air or chlorine if effective stabilization of the iron is to occur.

Closed Recirculating Systems

The closed recirculating system is one in which water circulates through one heat exchanger where it absorbs heat, has its temperature elevated, and circulates through another heat exchanger in which its temperature is lowered. In cold water or chilled water systems scaling is seldom a problem. In hot water systems scaling is seldom a problem unless there is a large amount of make-up water.[12]

Open Recirculating Systems

Where water from condensers and similar equipment is passed through a spray pond or cooling tower and then returned to the equipment, there is an increase in the concentration of solids because of the evaporation of some of the water into the cooling air, and, moreover, the aeration removes carbon dioxide. Both factors promote the tendency to deposit scale.

The corrosive properties of the water can also be increased through the absorption of acid gases such as sulfur dioxide (SO_2), from the air.[13] The absorption of gases from the air