equipment be supplied, and that the safety program be enforced at all times, in order to avoid personal injury or damage to equipment. Also, contamination of drinking water by nonpotable treated or untreated waters must be prevented by eliminating cross-connections between systems or providing approved backflow preventers.

With very few exceptions, the proper control of water treatment programs which involve the direct addition of chemicals to the water depends upon proportional feeding of the chemicals to maintain a desired concentration level at all times. Particularly in systems that have appreciable makeup rates, intermittent batch or slug feeding of water treatment chemicals cannot be relied upon to produce satisfactory results.

Because sound water treatment programs require care and consistent attention, there appear on the market from time to time, devices which allegedly prevent scale and corrosion without requiring the operator's attention. Various natural forces, such as electricity, magnetism, or catalysis, generally behaving in some *new* way are said to be responsible for the effects claimed. Independent investigations of these devices have found them to produce no significant effect in preventing or correcting corrosion and scale formation.[10,11]

Corrosion Control. Corrosion damage to water systems can be minimized by using corrosion resistant materials of construction, providing protective coatings to separate the water from the metal surfaces of the equipment, removing oxygen from the water, or altering the water composition by adding corrosion inhibitors and *pH* control chemicals. Two or more of these methods are often used in the same system.

Corrosion control by the selection of corrosion resistant materials of construction is within the province of the equipment or system designer. Although it is technically possible to build equipment which will show no significant corrosion under almost any operating conditions, economic limitations usually make this impossible. On the other hand, investigation of corrosion failures in air conditioning and heating equipment sometimes reveals design errors which show that the most elementary principles of corrosion control, discussed earlier in this chapter, have been ignored.

Protective coatings are essential for controlling corrosion on external and other surfaces not reached by treated water, but can also be very helpful as adjuncts to water treatment for controlling corrosion at particularly vulnerable locations. For example, metal pans of cooling towers or evaporative condensers operated in areas, such as larger cities, in which the air contains considerable amounts of dust or other solid matter, should be coated with paint or other suitable protective coating in order to minimize localized pitting of the bottom resulting from the *poultice effect* produced by a layer of dirt. Such attack can take place even when the circulating water in the system is adequately treated with corrosion inhibitors.

In the control of corrosion by the treatment of the water, the removal of oxygen is effective for closed systems in which opportunities for the pickup of additional oxygen are small. Thus, boiler feedwater may be mechanically deaerated in an open heater or deaerating heater. This process is based upon the reduced solubility of oxygen in water at higher temperatures (Table 9) and is made more effective by equipment design features which reduce the partial pressure of oxygen in the gas above the water. The last traces of oxygen are generally removed chemically by the addition of sodium sulfite or, at higher temperatures, hydrazine.

$$\text{Sulfite: } 2\,Na_2SO_3 + O_2 \rightarrow 2\,Na_2SO_4$$

$$\text{Hydrazine: } N_2H_4 + O_2 \rightarrow N_2 + 2\,H_2O$$

Table 9 .... Solubility of Oxygen From Air in Water at Different Temperatures[4]

Temperature		Milliliters per Liter (ml/l)				
C deg	F deg	Air	=	Oxygen	+	Nitrogen
0	32	28.64	=	10.19	+	18.45
5	41	25.21	=	8.91	+	16.30
10	50	22.37	=	7.87	+	14.50
15	59	20.11	=	7.04	+	13.07
20	68	18.26	=	6.35	+	11.91
25	77	16.71	=	5.75	+	10.96
30	86	15.39	=	5.24	+	10.15
40	104	13.15	=	4.48	+	8.67
50	122	11.40	=	3.85	+	7.55
60	140	9.78	=	3.28	+	6.50
80	176	6.00	=	1.97	+	4.03
100	212	0.00	=	0.00	+	0.00

Undesirable side reactions can occur at higher temperatures leading to acidic gases when sulfite is used, or to ammonia when hydrazine is used.

Chemical removal of oxygen is used less often for cold water circuits because of the slow rate of reaction of the sodium sulfite with the dissolved oxygen, although the addition of a very small amount of a cobalt salt acts as a catalyst to greatly speed the reaction.[12] When economically feasible, catalyzed sodium sulfite can be used to control corrosion in once-through cooling systems. In open-spray systems, of course, chemical removal of oxygen would be too expensive because the circulating water would be thoroughly oxygenated again with each passage through the spray equipment.

Oxygen removal by vacuum deaeration can be used to minimize corrosion in once-through cooling systems. It is particularly applicable when the water contains an appreciable carbon dioxide concentration because the deaeration removes this as well as the oxygen.

Corrosion control treatment of heating and cooling waters is most often carried out by *pH* control or by a combination of *pH* control and the maintenance of a corrosion inhibitor in the water. Contrary to a widely held belief, adjustment of the *pH* to 7.0 is *not* sufficient to stop corrosion. When the oxygen concentration is low, control of *pH* at certain levels is frequently adequate, as in the case of low pressure heating boilers maintained at a *pH* above 10.5. In most other cases, the adequate minimization of corrosion requires the use of an inhibitor in addition to *pH* control.

Chromates are by far the most effective and universal corrosion inhibitors known for water systems. Depending upon the water temperature and the effectiveness of treatment control, the minimum concentration required may be from 200 ppm (as sodium chromate) to 2000 ppm. The minimum concentration must be carefully maintained because with chromates, as with other anodic inhibitors, pitting may develop if the inhibitor concentration is allowed to drop very low. Higher than minimum concentrations are maintained in closed systems because the cost is low, in view of the small water losses, and an extra safety factor is thus provided. The chromates are effective inhibitors over a very wide *pH* range from about 6.5 up. An upper *pH* limit is frequently established for purposes of scale control.

When economy of treatment is of primary importance, as in very large cooling towers, it is possible to use low concentration mixtures of several inhibitors. A number of combinations are in use, such as chromate-polyphosphate, zinc-chromate, chromate-polyphosphate-zinc, and chromate-ferrocyanide. Total inhibitor concentrations of 60 ppm and less are effective with such mixtures, but close *pH* control is essential for good corrosion control. Depending upon the mixture used, the desirable *pH* range may be 6.0 to 6.5, 6.5 to 7.5, 6.0 to 7.0 or other range. Unless tower operating conditions are constant and continuous, an acid feeder and automatic *pH* controller is required to maintain the necessary *pH* control.

The chromates are sometimes undesirable because of their yellow color, disposal problems, and potential hazard if used carelessly. Sodium nitrite has been used in place of chromate as an inhibitor. With ferrous metals it is nearly as effective as chromate but must be maintained at a *pH* above 7.0 to avoid breakdown and at a minimum concentration of about 500 ppm. It is also necessary to check for both nitrite and nitrate concentrations at frequent intervals because the nitrite is subject to rapid bacterial oxidation and conversion to nitrate, which has no corrosion inhibiting properties. Sodium nitrite has little or no protective effect on nonferrous metals, and other inhibitors must be added with it, to provide protection. A commonly used nitrite-base inhibitor includes borax as a *pH* buffer, and the sodium salt of mercaptobenzothiazole as an inhibitor, for nonferrous metals.

Under the proper conditions polyphosphates have been effective in reducing tuberculation and pitting. For this purpose polyphosphate concentrations higher than those used for scale control must be provided, as must close *pH* control, in the 6.0 to 7.0 range.

Corrosion control treatment of once-through cooling water is practical only with very inexpensive chemicals. *pH* adjustment with caustic soda or lime is sometimes used in an attempt to form and maintain a thin protective film of calcium carbonate on the metal surfaces by adjusting the Langelier Index of the water to about +0.5 to +1.0. Sodium silicate (water glass) is also fairly effective for corrosion control in once-through systems, including potable water systems. Sufficient silicate is fed to increase the silica content of the water by about 8 ppm.

Other chemicals used for corrosion control in heating and cooling systems include volatile amines (such as morpholine and cyclohexylamine) and filming amines (such as octadecylamine) used for steam condensate line protection. Various mixtures are used for glycol or alcohol antifreeze solutions in chilled water or snow melting systems, where the inhibitor must be chemically compatible with the antifreeze agent.

The delignification of wood in cooling towers, while not strictly corrosion, is a related deterioration of materials of construction. Several distinct types of failure have been noted, one of which is biological in nature and the other chemical. Prevention of this deterioration may be effected by treating the wood, either prior to construction or in place.

Solutions of copper salts and of chromates are among those used for this purpose. Chemical delignification, usually a significant problem where the circulating water is high in alkalinity and low in hardness, can be minimized by keeping the circulating water *pH* low (about 7.0) and by limiting chlorine to a maximum of 1.0 ppm.

Scale Control—The methods used for scale control in heating and cooling systems include a variety of both *internal* and *external* treatment procedures. The selection of an appropriate method for any one system requires the evaluation of a considerable number of factors. Smaller systems tend to utilize internal treatment methods in which the chemicals are added directly to the water, whereas larger systems may use external treatment if financially justifiable.

Each of these scale control methods attempts to minimize the opportunity for precipitation of calcium carbonate, the least soluble common constituent of waters. The solubility of calcium carbonate depends upon the *pH*, temperature, and total solids content of a water in addition to the calcium and alkalinity (bicarbonate or carbonate). From these items, by the use of one of several nomographs (such as that in Fig. 2) the pH_s, i.e., the *pH* at which any given water is in equilibrium with calcium carbonate, can be calculated. This *pH* can be used with the actual *pH* of the water in either of two calculations which will indicate whether the water has a tendency to precipitate calcium carbonate or to dissolve it.

The older of these is the Langelier Saturation Index.[13]

$$\text{Saturation Index} = pH - pH_s$$

A positive Saturation Index shows a scale-forming tendency. The larger the index, the greater this tendency. But it is a *tendency* only, other factors may inhibit scale formation under some circumstances. Usually, calcium carbonate precipitates, generally as a scale, when the Saturation Index exceeds +0.5 to +1.0. A negative Saturation Index indicates that calcium carbonate will dissolve and that bare metal will remain bare and thus accessible for corrosion.

Rysnar[14] suggested a modified method for predicting scale formation based upon operating performance. He called this the Stability Index.

$$\text{Stability Index} = 2\,pH_s - pH$$

The Stability Index is always positive. When it falls below 6.0 scale formation is possible, and it becomes more probable the lower the numerical value of the index.

Similar, but not as simple, methods have been published for estimating the scale-forming tendencies of calcium sulfate[15] and calcium phosphate,[16] but are not so commonly used. At cooling water temperatures and lower pressure boiler temperatures, calcium sulfate is far more soluble than calcium carbonate as shown in Fig. 3.

The most fool-proof method for preventing scale formation is softening the water by passage through an ion exchange (formerly called zeolite) water softener. This external treatment process removes all but 2 to 5 ppm of hardness. It is usually carried out in a closed vertical tank about ¾ filled with small beads of synthetic resin, called a cation exchange resin, that has unique chemical properties. At low concentrations, it preferentially absorbs calcium and magnesium ions from the water, yielding, in return, a chemically equivalent amount of sodium ion, which is not scaleforming.

The calcium and magnesium content of the resin ultimately rises to the point where they are no longer completely absorbed from the water passing through the resin. The flow of water is then reversed, backwashing the resin to remove any dirt particles, and the resin is then regenerated by passing a much higher concentration of salt through it. The sodium ions of the strong salt solution displace the absorbed calcium and magnesium ions restoring the resin to its initial sodium form. After rinsing out excess salt, the resin is ready for another softening cycle.

$$\underset{\text{Regenerated Resin}}{Na_2R} + Ca^{++}(\text{or } Mg^{++}) \xrightarrow[\text{Regeneration}]{\text{Softening}} \underset{\text{Exhausted Resin}}{CaR} + 2Na^{+}$$

When it is possible to accept and control the presence of suspended matter in the water, hardness may be eliminated by precipitation within the operating equipment. This is commonly done in lower pressure process steam boilers. Alkalis are commonly used to precipitate calcium carbonate in accordance with Equation 1. Phosphates are added to remove the last of the hardness, by virtue of the lower solubil-