THE CHEMICAL TREATMENT OF COOLING WATER

(Second Edition)

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Preface to the Second Edition

Engineers, chemists, and other technicians having the temerity to write books, are seldom able to satisfy the demands of academics. Most of us, however, find that we can live with their scorn, especially if our efforts are well received by those to whom they are directed. The enthusiastic reception with which the first edition of my book on cooling water treatment was received by the industrial community has encouraged me to undertake its revision, herewith presented.

Approximately one-third of this revised edition is new or expanded material. New topics include the reuse of cooling water, the recovery of chromate, the pros and cons of automatic blowdown controllers, and the benefits of side-stream filtration. Calculations have been included for solubilities of slightly soluble salts, the concentration of chemicals introduced by incremental addition, and the performance of side-stream filters. An exceptionally promising new microbicide containing bromine is discussed, as is the proper method for applying stabilized chlorine dioxide. In addition, 40 numerical problems have been added in an appendix that will enable the reader to check his comprehension of the quantitative aspects of cooling water treatment.

Topics that have been extensively revised and expanded include chemical treatments, chemical cleaning, and the deoiling and passivation of new cooling systems. Also revised, are the discussions of corrosion measurement, passivation and pretreatment, cooling tower maintenance, electrochemical devices, pH control, and environmental considerations related to water treatment. Finally, a large number of chemicals used or proposed for treating cooling water have been classified with respect to their functions and relative performance; an estimate has also been made of the performance to be expected of 14 chromate and nonchromate programs.

As usual, the views expressed in this book relating to methods of treating cooling water are my own, and no other individual or organization is in any way responsible for them. My wife, Dolores, has provided her customary assistance during the preparation of this work for publication.

Richmond, California
November 18, 1982

James W. McCoy

In Chapt. V several complete treatment programs are evaluated, and suggestions are given for purchasing chemicals, estimating costs, and controlling water systems. Chapt VI includes routine and emergency operating procedures, methods of chemical cleaning, and safety suggestions. Finally, Chapt. VII contains methods for determining selected minerals and gases that are useful for routine chemical control of cooling systems; a detailed procedure is also provided for making viable plate counts to check the efficacy of microbiocides.

I presume that no one has any quarrel with the dictum that if it is possible to discuss a subject quantitatively it is desirable to do so. Accordingly, the principles of physical chemistry are used as the basis for my interpretation of water treating procedures. Furthermore, exact equations have been derived to express the depletion of treating chemicals, the concentration of minerals added in the makeup water, and the degree of hydrolysis of polyphosphates.

Throughout the book I have given specific operating conditions and procedures for treatments with which I have had personal experience. Without exception these are my own views of how these programs should be managed, and no other person, organization, or Company is responsible for them, nor indeed for anything else in this book. Moreover, the specific information given here is for the purpose of illustrating principles, and does not necessarily constitute a do-it-yourself handbook. Obviously it will not be possible to follow exactly every procedure given because of special operating conditions, local environmental regulations, or lack of facilities.

Acknowledgements are tedious to the reader so I will limit these to three of the many people who (one way or another) have improved my understanding of water treatment. My colleague, Mr. Robert E. Kreider, is specially competent in the field of wastewater management, and he has made many contributions to this book. I know no more able mathematician than Mr. L. J. Painter, who has been of great help with the mathematical portion of this account. Over a number of years it has been my privilege to have participated in many informative discussions on various aspects of water treatment with Dr. Charles

Preface

The increasing urgency to conserve water and reduce thermal pollution has produced in recent years an enormous demand for new cooling towers. Thus, the current annual market is estimated at more than sixty million dollars, and it is expected to increase to about eighty million dollars by 1980*. Concomitantly, the market for water treating chemicals is expanding, and with it an interest in the principles of cooling water treatment. This book has been prepared for the benefit of chemists and engineers charged with the responsibility for selecting or administering water treatment programs, who would like to improve their understanding of the principles upon which the treatment of cooling water is based.

The literature of water treatment, unlike that of most other branches of applied chemistry, tends to be amorphous with a generality verging on the inscrutable. It would be fatuous to claim expertise in all of the subjects germane to treating water, namely, chemistry, engineering, mathematics, and microbiology, but I believe there is a need for a comprehensive, detailed account of cooling water treatment. This book is an attempt, insofar as I understand the subject, to fulfill that need.

Chapt. I contains a description of the structure and operation of open recirculating cooling water systesm, including the development of mathematical relationships among operating variables in these systems. In Chapt. II various types of corrosion and corrosion inhibitors are discussed, while in Chapt. III the closely related subject of scaling and fouling in aqueous cooling systems is considered.

More nonsense circulates about the microbiology of cooling water than any other aspect of water treatment. Chapt. IV, therefore, is an attempt to show the reader how to use microbiocides rationally, how to evaluate their effects, and how to avoid wasting these expensive chemicals.

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*Gene Smith, "Boom in Cooling Towers", The New York Times, Sunday, Feb. 20, 1972.

F. Hinz; in a field sometimes reminiscent of the medicine show his professionalism is always most refreshing. Finally, I wish to thank my wife, Dolores, for her now expert help with proofreading.

James W. McCoy

San Francisco
February 1974

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CHAPTER I

Principles of Open Recirculating Cooling Water Systems

The mechanical operation of a recirculating cooling system with a tower will first be described to establish a background for discussing the chemical treatment of cooling water, and also to derive some exact mathematical expressions for the processes. For purposes of discussion the existence of a cooling system is assumed, and some of the principles upon which its operation is based are considered.

I.1 THE COOLING TOWER

Fig. I.1 is a schematic drawing of a counterflow evaporative cooling tower with induced draft provided by one, or several fans. The system is put into operation by filling it with V gallons of fresh water. A supply of water, S, is pumped from the basin through a heat exchanger, C, cooling some process, and being itself warmed. The warm water return, R, is pumped to the plenum at the top of the cooling tower, and distributed uniformly over the cross-sectional area through an assembly of nozzles.

The interior of the structure contains splash packing, or fill material, constructed of slats stacked in decks and spaced in staggered rows. Water splashes from row to row, breaking into droplets, at the rate of 2-4 gpm/ft^2. This rate is called the "water loading" of the tower. Film packing is also used, which exposes water to air in thin films over the surface of the fill. Fill is made of wood, cellulose sheets, molded polystyrene, or asbestos sheets. It is essential that the fill material wets well, otherwise water forms in rivulets instead of droplets.

The most efficient and economical cooling tower is one with mechanical draft as depicted in Fig. I.1, in which air, *A*, is drawn in through louvers just above the basin, and then upward counterflow to the descending rain of water. The velocity of the air is 300–700 fpm.

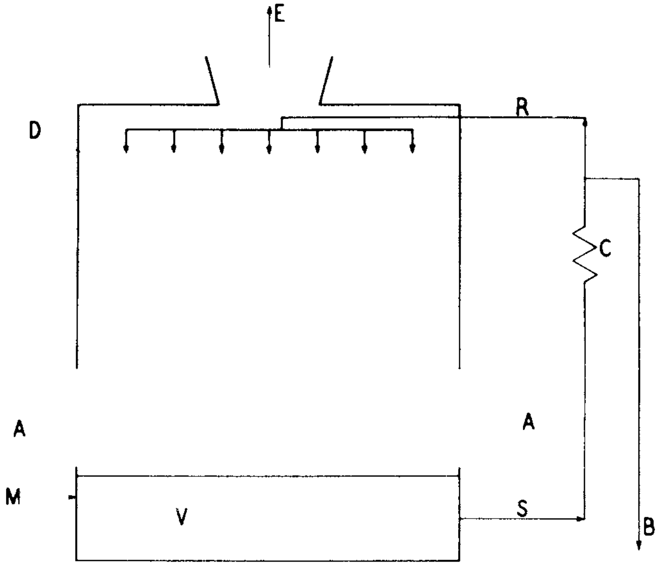


Fig. I.1 Recirculating cooling system with cooling tower

(A) Air; (B) Blowdown; (C) Heat exchange; (D) Drift or windage loss; (E) Evaporation; (M) Make up; (R) Return water; (S) Supply water; (V) Volume of system.

Two kinds of heat transfer occur within the tower between warm water and air. Some of the liquid changes to vapor with the absorption of heat. This energy, called the latent heat of vaporization, is that necessary to overcome the attractive forces between molecules in the liquid state. This heat, about 1000 Btu/lb, is abstracted from the liquid water remaining, and lowers its temperature. Absorption of latent heat accounts for 75–80 percent of the heat transferred in cooling towers. As long as the wet-bulb temperature, which is a measure of the heat content of the atmospheric air, is lower than the water temperature heat is transferred from the water to the air, raising its temperature and lowering that of the water. This is called sensible heat; it accounts for the remaining 20-25 percent of heat transferred.

The stream of air and water vapor containing entrained droplets, is drawn upward through the tower by the fans, and passes through a "drift eliminator"–an arrangement of baffles that produces sudden changes of direction of the stream. Water droplets are thus separated from the vapor stream, and fall with the bulk of the water into the basin. Water vapor, E, and air pass out through the fan stack to the atmosphere. A small amount of liquid water, D, is blown out of the tower by wind. This is called drift or windage loss; in a well-designed tower it amounts to 0.1-0.2 percent of the recirculation rate.

For reasons to be developed later, a volume of water, B, is continuously withdrawn from the system, and another volume of fresh water, M, is added to the basin to maintain the total volume of water, V, constant. It will be readily apparent that

$$M = E + B + D \tag{I-1}$$

I.2 VARIABLES AFFECTING PERFORMANCE

a. Heat Transfer in the Tower

The rate at which heat is transferred in a cooling tower depends upon four factors: (1) the area of the water surface in contact with air; (2) the relative velocity of air and water; (3) the time of contact between air and water; (4) the difference between the wet-bulb temperature of the inlet air, A, and the temperature of the returned water, R. Item (1) depends upon the construction of the fill; (2) can be controlled within limits by regulating the speed of the fans; (3) is a function of (2) and the height of the tower; (4) is fixed by climate.

The wet bulb temperature can be measured with a sling psychrometer. The bulb of a thermometer is encased in wicking saturated with water, and the thermometer in a suitable holder is whirled through the air for about two minutes. If the air is not saturated, water evaporates from the wick cooling the bulb, and the wet-bulb temperature is indicated by the thermometer. The drier the air the greater the difference between the wet-bulb temperature, and the temperature of the air as measured by an ordinary thermometer. At 100 percent relative humidity the two temperatures are equal.

Under ideal conditions, when a stream of unsaturated air passes over a wetted surface water evaporates saturating the air and lowering the temperature of the remaining water. When the water becomes cooler than the air, sensible heat flows from the air to the water, eventually reaching equilibrium at the wet-bulb temperature, where the loss of heat from the water by evaporation is equal to the sensible heat passing from the air to the water. Thus, as water falls through a cooling tower, the latent heat of vaporization and the sensible heat approach each other so that in an infinitely high structure the temperature of the bulk water would be equal to the wet-bulb temperature of the entering air. In a finite tower, however, it is impossible to achieve zero approach, because not all of the water falling through the structure can contact fresh cool air.

One measure of the efficiency of a cooling tower is its approach, which is the difference between the temperature of the cooled water in the basin of the tower and the wet-bulb temperature of the atmosphere. The design approach determines in large measure the cost of constructing a cooling tower. A tower with a 5°F approach, for example, costs 60-70 percent more than one with a 10°F approach under the same heat load. A 5°F approach would require a tower perhaps 35-40 ft high, whereas a 10°F approach could be obtained in a tower around 25 ft high. The average design approach in industrial cooling towers is 8-15°F.

A second measure of performance is the cooling range, which is the difference between the temperature of the supply water, S, and the return water, R. The cooling range in most industrial towers is 15-30°F. The amount of heat rejected by a cooling tower can be calculated from the cooling range and the recirculation rate. The latter is usually indicated, in gallons per minute, on a water meter. One British thermal unit is the amount of heat required to raise the temperature of one pound of water one degree Fahrenheit. Therefore:

$$\begin{aligned}\text{Heat duty, Btu/h} &= \text{gpm} \times 60\ \text{min/h} \times 8.34\ \text{lb/gal} \times \Delta t\,^{\circ}\text{F} \\ &= \text{gpm} \times 500 \times \Delta t \qquad \text{(I-2)}\end{aligned}$$

The total heat theory of Merkel(1) satisfactorily explains the transfer of heat from water to air in a counterflow evaporative cooling tower. Total heat (enthalpy) includes the sensible heats of air and water vapor plus the latent heat of vaporization of water. Merkel's theory states that the total heat transfer occurring at any particular location in a cooling tower is proportional to the difference between the enthalpy of the air at that location, and that of saturated air at the temperature of the water at the same location in the cooling tower. This statement is more concisely expressed by Merkel's equation.

$$Ldt = Gdh = KadV\,(h' - h) \tag{I-3}$$

where:

L = water flow rate (lb/h)
t = bulk water temperature (°F)
G = air flow rate (lb dry air/h)
K = heat transfer coefficient
a = area of contact between air and water (ft^{-1})
V = active tower volume (ft^3/ft^2 plan area)
h = enthalpy of moist air (Btu/lb)
h' = enthalpy of moist air at bulk water temperature (Btu/lb)

To calculate the total heat transfer it is necessary to integrate Merkel's equation.

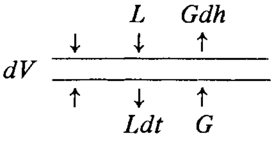
$$\frac{KaV}{L} = \int_{t_1}^{t_2} \frac{dt}{h' - h} \tag{I-4}$$

$$\frac{KaV}{G} = \int_{h_1}^{h_2} \frac{dh}{h' - h} \tag{I-5}$$

where:

t_1 = temperature of warm water entering (°F)
t_2 = temperature of cold water in basin (°F)
h_1 = enthalpy of cool air entering (Btu/lb)
h_2 = enthalpy of warm air leaving (Btu/lb)

The process of evaporative cooling in an infinitesimal volume may be depicted in terms of differentials, as follows:



Water falling through a vertical element (dV) continuously encounters cooler air and approaches the inlet air's wet-bulb temperature as a limit. Air rising through the vertical element continuously moves toward warmer water and approaches the temperature of the returned water as a limit. If the initial temperature of the water is higher than the wet-bulb temperature, the water will cool toward that temperature by convective transfer of sensible heat; if below the wet-bulb temperature, the water will warm toward that temperature.

Eq. (I-5) shows that water is cooled at a rate proportional to the difference in total heat per pound between saturated air at the temperature of the water, and that of the atmosphere. Woods and Betts(2) have devised an arithmetical method for integrating the equation, an otherwise time-consuming task.

Still another important characteristic of a cooling tower's performance is L/G, the liquid-gas mass transfer ratio.

$$L/G = (\text{water, lb/h})\,/\,(\text{air, lb/h})$$

In open recirculating towers with mechanical draft, L/G is 0.75-1.50.

The reader interested in a more detailed account of heat transfer theory and methods of calculation should refer to the book by Stanford and Hill.(3)

b. Heat Transfer Within the Cooling System

The process represented by C in Fig. I.1 is one in which a hot fluid is cooled by water, which is itself heated without any loss of exchanged heat. Industrial heat exchangers consist of a number of tubes enclosed in a shell. Exchangers with cooling water in the tubes, and hot product in the shell are the most satisfactory. Fouling often occurs if water is circulated through the shell, because the velocity of the water stream is lower in this design. Tubes are much easier to clean than the shell. The latter contains fixed internal baffles to produce turbulent flow that make it difficult, if not impossible, to clean the inside of the shell effectively. Matters are also so arranged that the pressure of the product being cooled is higher than that of the water, so that water cannot leak into the hot product, and damage equipment.

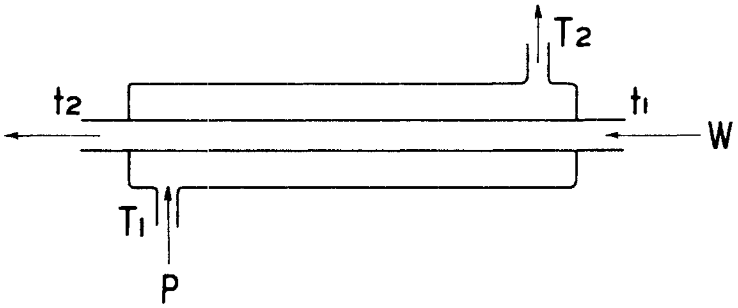


Fig. I.2 Simple water-cooled heat exchanger–(P) Hot product to be cooled; (W) Cooling water; (t_1) Temperature of cold water; (t_2) Temperature of warmed water; (T_1) Temperature of hot product; (T_2) Temperature of cooled product

Fig. I.2 illustrates the cooling process in a single-pass, counterflow heat exchanger consisting of a single tube in a shell, an arrangement similar to a Liebig condenser. The transfer of heat from P to W is described approximately by Eq. (I-6):

$$U = \Delta Hp/\Delta t_m A \qquad \text{(I-6)}$$

where:

U = net effective overall heat transfer coefficient (Btu/°F-h-ft^2)
ΔH = difference in enthalpy of P at T_1 and T_2 (Btu/lb)
p = flow rate of product (lb/h)
A = area of heat transfer surface (ft^2)
Δt_m = the average of the temperature differences at both ends of the exchanger (°F)

$$\Delta t_m = \frac{(T_1 - t_2) + (T_2 - t_1)}{2}$$

Here it is assumed that the temperature of the fluid in the shell falls continuously and uniformly from T_1 to T_2, while that of the water inside the tube rises similarly from t_1 to t_2. With this assumption it is permissible to use the average of the terminal differences for the mean temperature difference. In more complicated heat exchangers, however, it is necessary to use the log mean temperature difference, and when calculating the value for multipass exchangers correction factors also must be applied to $(\Delta t)_m$.

$$(\Delta t)_{\log_e} = \frac{(\Delta t)_{\max} - (\Delta t)_{\min}}{\log_e \left[\dfrac{(\Delta t)_{\max}}{(\Delta t)_{\min}}\right]} = \frac{(T_2 - t_1) - (T_1 - t_2)}{\log_e \left[\dfrac{(T_2 - t_1)}{(T_1 - t_2)}\right]}$$

Jacob and Hawkins$^{(4)}$ have given a derivation of the log mean temperature difference, and Nagle$^{(5)}$ describes a method for calculating the value for various kinds of heat exchangers.

In a water-tube exchanger U is likely to decrease gradually because of accumulating deposits, or because of scale forming on the tubes. Referring to Fig. I.2, the effect of these events on the heat transfer coefficient can be predicted qualitatively. If a thin layer of insulating scale forms on either side of the tube T_2 rises and t_2 falls as less heat passes from P to W through the insulating layer. Thus, ΔH decreases, and as both t_1 and T_1 are unaffected by conditions within the exchanger, Δt_m increases. The net result is that the heat transfer coefficient becomes smaller.

If the flow of water is slowed by deposits, t_2 and T_2 both rise. In this event, however, Δt_m may increase and ΔH may decrease by such small amounts that the effect on U may not be significant.

The reciprocal of the heat transfer coefficient is called the "fouling resistance;" this number multiplied by one thousand is the "fouling factor." Except in unusual circumstances the effect of fouling resistances can never be exactly known, as fouling within an actual heat exchanger is seldom uniform, and also the net effect is a combination of conditions on both sides of the heat transfer surface.

I.3 RELATIONSHIPS AMONG OPERATING VARIABLES

Fig. I.1 shows that an amount of water, E, evaporates continuously from the system, depleting the total volume, V. Make-up water, M, must be added continuously to replace that lost by evaporation. It can readily be seen that as this process continues salts in the make up increase in concentration in the recirculating water. Because of considerations explained later in Chapter V, a certain maximum value is selected for the concentration of total dissolved solids in the recirculating water. When this concentration has been reached a valve in the return line is opened allowing a certain

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