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STATE OF ILLINOIS  
DEPARTMENT OF REGISTRATION AND EDUCATION



*Selected Papers on  
Cooling Tower Water Treatment*

ILLINOIS STATE WATER SURVEY  
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## FOREWORD

This circular includes selected papers pertaining to the chemical treatment and its control for cooling tower water and systems. These papers were presented at the Symposium on Cooling Tower Materials and Water Treatment as the program of the Division of Water, Air, and Waste Chemistry of the American Chemical Society held at Detroit, Michigan, April 6-7, 1965.

The purpose of this symposium was to describe the modern methods, mechanisms, and techniques for the control of corrosion, scale, and algae to maintain cooling tower water systems. The papers included here are being published by the Illinois State Water Survey to provide wide distribution of this new information, in conjunction with its continuing research in water chemistry and water treatment.

Cooling towers are an important segment of today's world in which water needs are increasing and reuse of water is often necessary to provide industry's water requirements. By passage through a cooling tower, water may be cooled 10 F by evaporation of about 1% of the circulating water and may then be reused for cooling condensers in electric generating plants or in industrial processes. Because cooling water requirements for a large electric utility plant may be in the order of hundreds of thousands of gallons per minute, the thermal load will not always permit once-through use of water, which therefore makes the use of cooling towers a necessity.

As circulating cooling water evaporates, hardness and other mineral salts increase in concentration with resultant scale and corrosion effects. This means that water treatment must be completely effective to prevent scale and corrosion and to enable operation with minimum blowdown. Because nearly a billion dollars is invested in cooling towers in the United States today, and because industrial operations depend on their continual and

trouble-free service, interest in the maintenance of cooling towers must be of great concern.

Cooling towers operate under continuous high humidity conditions at warm temperatures in the presence of oxygen and relatively high salt contents. Such conditions are generally ideal for scale formation, corrosion of metals, deterioration of wood, and algae and bacterial growths. Stagnant (low velocity) and varied velocity conditions complicate the water treatment problem for correction of corrosion. Considering these many problem areas, one might wonder how cooling towers and their associated systems survive. After much experience, research, and evaluation, the combined efforts of the cooling tower manufacturer and the water chemist can now provide economical resistant materials and proper chemical treatment formulations. The user is therefore generally assured of adequate service life, if towers of proper specifications are purchased and chemicals of proper formulation are applied with care.

Omitted from this circular are four symposium papers on cooling tower materials that have been printed in 1966 issues of Heating, Piping, and Air Conditioning. These papers and the issue in which each appeared are as follows:

"Materials Standards and Testing of Materials Used in Water Cooling Tower Manufacture" by N. L. Bailiff, Fluar Products Company, Inc., Santa Rosa, California [v. 38(1):153].

"Materials and Coatings for Water Cooling Towers" by John A. Nelson, The Marley Company, Kansas City, Missouri [v. 38(2):109].

"Changes in Preservatively Treated Slats after Five Year's Exposure in a Cooling Tower" by R. H. Baechler, U. S. Forest Products Laboratory, Madison, Wisconsin [v. 38(3):126].

"Experiences in Inspecting Cooling Towers and Corrective Measures in Chemical Treatment and Material Selection" by James L. Willa, Lillie-Hoffmann Cooling Towers, Inc., St. Louis, Missouri [v. 38(4):121].

Of the eight papers selected for this circular, the first reports on the different laboratory and field methods of evaluating corrosion inhibitors. Evaluating corrosion inhibitors always presents a challenge

in the laboratory because the questions of length of test, method of test, and the possible need to duplicate field conditions require serious deliberation. The second paper presents a new laboratory approach to the evaluation of the corrosion inhibitors of pitting. In cooling tower systems the presence of suspended matter, crevices, and the general pitting environment makes this evaluation of a corrosion inhibitor a most important one. The third paper concerns gypsum solubility and shows that the maximum concentration for minimum blowdown must be decided by the solubility of calcium sulfate, particularly in acid-treated cooling waters. This information enables the user of this equipment to operate with minimum water and chemical usage. The fourth paper, on algae growths, points out the importance of control of organic growths in reducing inefficiencies and in controlling corrosion and deposits in the circulating water system.

The fifth paper describes the different water treatment controls which must be exercised to provide the desired scale and corrosion inhibition. The sixth paper emphasizes the necessity and describes permissible methods of isolating these open circulatory water systems from potable water systems. Besides eliminating the hazard of bacterial contamination, isolation of these systems allows the water treatment chemist to treat with toxic chemicals, which often permits more satisfactory inhibition of scale, corrosion, and organic growth problems. The seventh paper describes a method of eliminating a chromate (corrosion inhibitor) waste disposal problem. The final paper concerns the use of sewage effluent as cooling tower makeup, and discusses fully the problems and pretreatment requirements involved. This subject will find increasing application in water shortage areas, since this supply may be the most economical source of water available to industry for cooling purposes.

The authors have assisted generously in preparing these papers for publication. The material is essentially as presented at the symposium, but photographs and a few other illustrations were deleted because of space and reproduction limitations. We appreciate the interest of William C. Ackermann, Chief of the Illinois State Water Survey, and Dr.

T. E. Larson, Head of the Survey's Chemistry Section, in pursuing the publication of this material.

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LABORATORY AND FIELD EVALUATION OF CORROSION INHIBITORS FOR OPEN  
CIRCULATING COOLING WATER SYSTEMS

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Nearly completely corrosion resistant metals of construction could be used in open circulating cooling water systems. However, only in rare cases can the use of such expensive metal alloys be justified. Instead, less expensive metals are used and a corrosion control program is followed to reduce general and localized corrosion to an acceptable rate.

A corrosion control program for an open circulating cooling water system consists of such requirements as the use of the proper corrosion inhibitor, adequate pH control, control over biofouling, and proper maintenance before, during, and after operation of the system. Corrosion inhibitors for metals may be individual inorganic or organic chemicals, or combinations of these chemicals, which function as anodic or cathodic inhibitors or both.

The ability of inorganic and organic chemicals to function as corrosion inhibitors for metals cannot be accurately determined from their chemical and physical properties. Furthermore, the performance of mixtures of individual corrosion inhibitors for metals cannot be accurately predicted on the basis of data obtained from a study of the individual inhibitors.

Laboratory tests are used to determine the potential of a chemical or a combination of chemicals as a corrosion inhibitor. Field tests are used to confirm laboratory findings. This paper discusses laboratory and field evaluation methods for corrosion inhibitors in open circulating cooling water systems.

## SELECTION OF CHEMICALS

Several factors must be taken into consideration when selecting a chemical for evaluation as a corrosion inhibitor. Among the most important of these factors are:

- 1) Cost
- 2) Availability in commercial quantities
- 3) Ease of feeding
- 4) Compatibility with constituents normally encountered in water
- 5) Suitable means of testing
- 6) Stability at temperatures normally encountered in heat exchangers
- 7) Toxicity
- 8) Effect on waste disposal systems
- 9) Resistance to bacterial decomposition
- 10) Solubility in water

## LABORATORY EVALUATION

Much time, work, and money could be saved if the structure of inorganic and organic compounds could be studied and their potential as corrosion inhibitors determined. Unfortunately, such an optimum means of screening is not realistic.

It is not necessary in evaluating corrosion inhibitors to duplicate all field conditions in the laboratory. Short time laboratory tests indicate whether an inhibitor deserves further consideration. Extended laboratory tests under closely controlled conditions provide data on the corrosion prevention effectiveness of the inhibitor.

The ideal short time test is one where the least amount of time is required, and results are reproducible. Many short time test methods have been investigated. Several of these are discussed below.

### 1) Static Test

This test consists merely of suspending a corrosion test specimen in a container of the test solution containing a measured concentration of the corrosion inhibitor. This method has very little value, since the corrosion data is neither reliable nor reproducible. Reasons why this

method is unsatisfactory are: the film of water adjacent to the specimen is motionless, and therefore the desirable corrosion protection reactions cannot properly occur; there is no temperature control; there is no control over pH; there is no control over the concentration of dissolved oxygen in the water contacting the specimen.

## 2) Rotating Rod Test

Bregman and Newman<sup>9</sup> used a rotating rod test as a quick means of screening corrosion inhibitors. In this test, polished mild steel rods 1/4 inch in diameter and 3 inches long are rotated at 1750 rpm, corresponding to a peripheral velocity at the surface of the specimen of 1.9 feet per second, in 500 ml of test water at about 75 F for 24 hours. The composition of the test water used is shown in table 1.

After testing, rods are air dried, examined, and scored. Results are judged to be semiquantitative in view of the visual-only nature of the test.

Puckorius and Ryzner<sup>15</sup> modified Bregman and Newman's testing apparatus so that the test water was stirred and aerated. Coupon type specimens and a corrosometer probe were used to obtain quantitative data. Figure 1 illustrates the apparatus.

## 3) Circulation Tests

Many types of circulation systems have been devised to obtain reliable and reproducible corrosion data. These systems range from small laboratory systems incorporating control of flow rate, temperature, pH, and concentration of dissolved oxygen to small pilot plant open circulating cooling water systems. In running a laboratory recirculating system in which corrosion test specimens have been installed, generally approximately 250 ml of test solution is used for each square inch of specimen area.

Figure 2 shows a schematic illustration of laboratory apparatus used by Fisher and Jeter.<sup>10</sup> The water capacity of the system is 21 liters.

Table 1. Composition of Test Water Used by Bregman and Newman

<u>Constituent</u>	<u>Concentration (ppm)</u>
Hardness (as CaCO <sub>3</sub> )	400
Calcium (as CaCO <sub>3</sub> )	250
Magnesium (as CaCO <sub>3</sub> )	150
Total alkalinity (as CaCO <sub>3</sub> )	5
Sulfate (as Na <sub>2</sub> SO <sub>4</sub> )	1400
Chloride (as NaCl)	500
pH	7.0

Table 2. Composition of Test Water Used by Fisher and Jeter

<u>Constituent</u>	<u>Concentration (ppm)</u>	
	<u>St. Louis tap water</u>	<u>Plant Tower water</u>
Hardness (as CaCO <sub>3</sub> )	128	336
Calcium (as CaCO <sub>3</sub> )	62	168
Magnesium (as CaCO <sub>3</sub> )	66	168
P. alkalinity (as CaCO <sub>3</sub> )	4	-
Total alkalinity (as CaCO <sub>3</sub> )	74	24
Carbonate (as CO <sub>3</sub> )	-	-
Bicarbonate (as HCO <sub>3</sub> )	-	22
Sulfate (as SO <sub>4</sub> )	98	332
Chloride (as Cl)	22	140
Silica (as SiO <sub>2</sub> )	10	18
Nitrate (as NO <sub>3</sub> )	-	62
Fluoride (as F)	-	15
Total iron (as Fe)	-	0.2
Total dissolved solids	396	1090
pH	8 . 8 7 . 2 - 8 . 2	

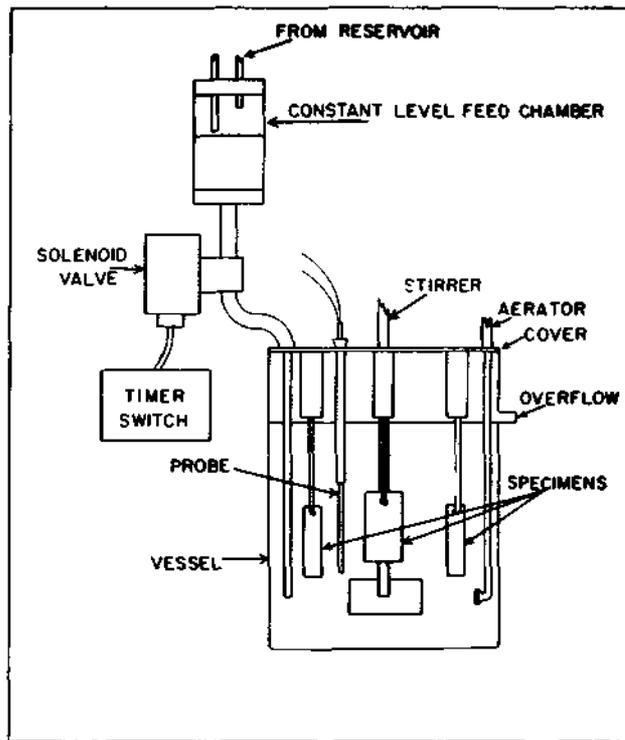


Figure 1. Corrosion test apparatus used by Puckorius and Ryzner

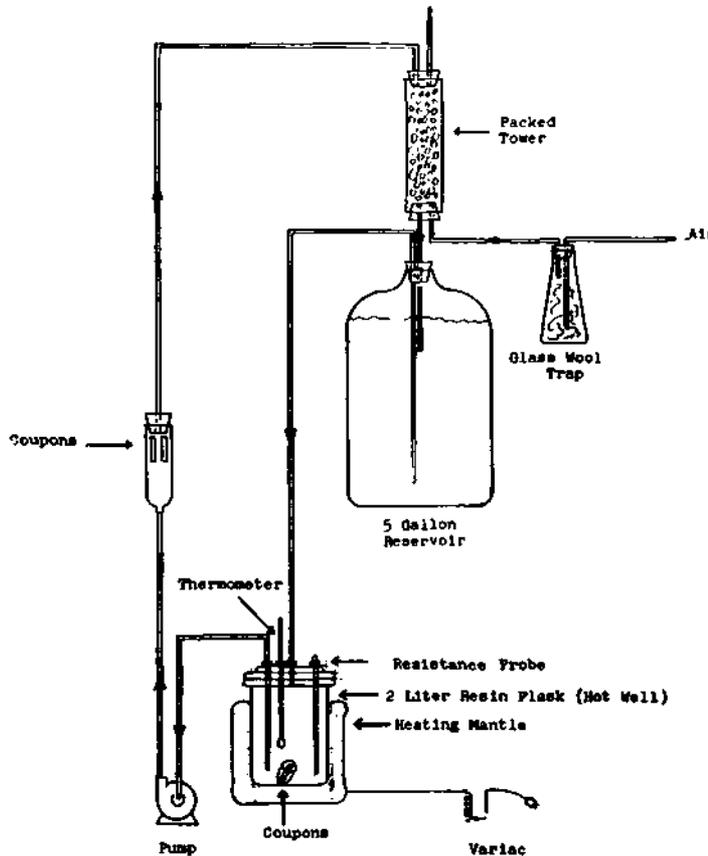


Figure 2. Corrosion test apparatus used by Fisher and Jeter

The water is saturated with oxygen in the aeration column to simulate cooling tower operation. The velocity in the hot well is essentially static, while the velocity past the 1-inch by 2-inch by 1/2-inch steel coupon type corrosion test specimens in the tower line is approximately 0.1 foot per second as calculated from the 0.6 gpm flow rate of water through the system. The temperature of the water is maintained at 140 F during a four-week duration test period. Coupon corrosion rates are calculated from weight loss data. An electrical resistance corrosion probe is installed in the system to obtain additional data.

Chemical analyses of the waters used in the screening tests are shown in table 2.

After the laboratory evaluation tests, Fisher and Jeter ran many field tests. Some of the several conclusions they reached are:

- A) Coupon data reveal excellent correlation between laboratory and field tests on the same inhibitor despite differences in water analyses.
- B) Corrosion data using resistance probes correlate very well with that obtained on standard coupons having a 120-grit surface.

In our laboratory we use a screening system where 3-inch by 1/2-inch by 1/16-inch steel coupon type corrosion test specimens are attached to a rotating disc in a temperature controlled aerated test solution. The calculated water velocity is 1.5 feet per second. Water temperature is thermostatically controlled at 120 F  $\pm$  2 F by a heating mantle surrounding the glass container holding the test water. Water capacity of the container is 3.5 gallons. A multi-container system is employed so that several corrosion tests can be run at one time. The pH of the test water is adjusted by feeding carbon dioxide as needed through a sparger tube arrangement.

Analysis of the test solution is shown in table 3.

The desirable test period is about one week. This period of time allows for protective film formation on the corrosion test specimens. Results are reproducible and reliable for the temperature employed.

Table 3. Composition of Test Water Used by Drew

<u>Constituent</u>	<u>Concentration (ppm)</u>
Hardness (as CaCO <sub>3</sub> )	400
Calcium (as CaCO <sub>3</sub> )	300
Magnesium (as CaCO <sub>3</sub> )	100
Total alkalinity (as CaCO <sub>3</sub> )	20
Chloride (as Cl)	500
Sulfate (as SO <sub>4</sub> )	500
Copper (as Cu)	0.2
Iron (as Fe)	0.5
Total dissolved solids	1646
pH	6.8
Langelier's Index at 120 F	-0.92

Table 4. Composition of Test Water Used by Kerst

<u>Constituent</u>	<u>Concentration (ppm)</u>
Hardness (as CaCO <sub>3</sub> )	1276
Calcium (as Ca)	352
Magnesium (as Mg)	158
P. alkalinity (as CaCO <sub>3</sub> )	0
Total alkalinity (as CaCO <sub>3</sub> )	44
Bicarbonate (as HCO <sub>3</sub> )	54
Chloride (as Cl)	79
Sulfate (as SO <sub>4</sub> )	1170
Total dissolved solids	1960
pH	7.4

**HAIR PIN SPECIMEN  
FOR USE WITH HIGH TEMPERATURE CORROSION TESTER  
(SECTION)**

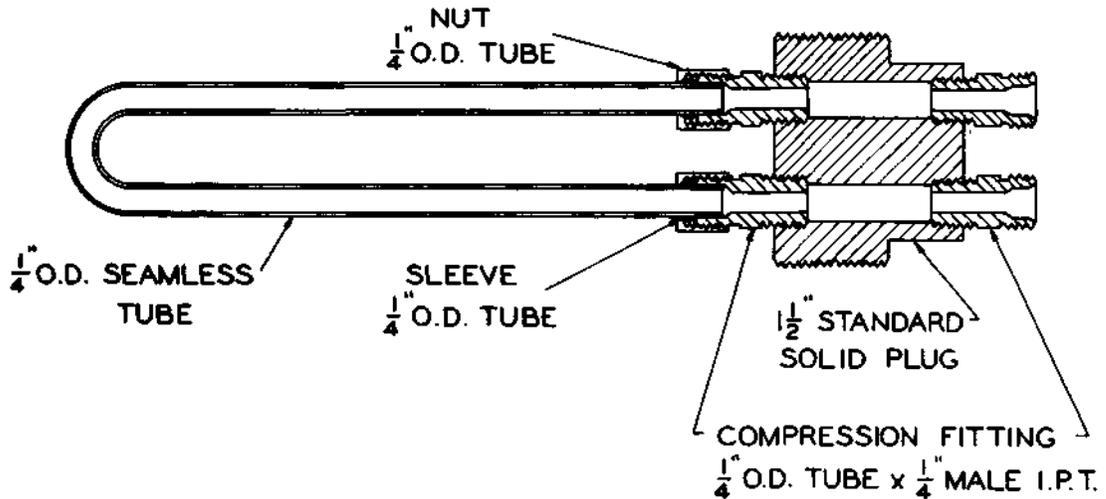


Figure 3. Hairpin specimen for use with high temperature corrosion tester (section) used by Kerst

**DREW SINGLE TUBE HEAT EXCHANGER  
FLOW DIAGRAM**

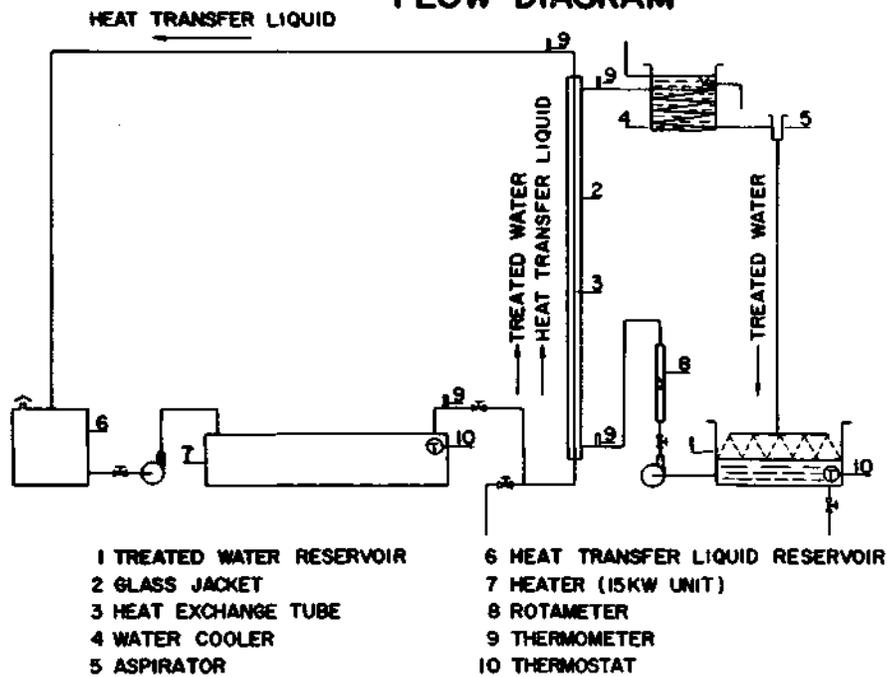


Figure 4. Schematic flow diagram of Drew single tube heat exchanger

However, as in previous systems described, there is the disadvantage that there is no heat transfer between the metal and the test solution. The results obtained with this system are considered quantitative. General corrosion rates are determined from the weight losses of the specimens. Pit depths are determined with a measuring microscope. Shorter time evaluation tests can be used to give an indication if longer tests should be considered.

Kerst<sup>14</sup> used hairpin-shaped specimens, with which heat transfer was obtained in running corrosion tests. The specimen consists of approximately 13 inches of 1/4-inch seamless steel tubing bent on a 7/8-inch radius to give a hairpin-shaped specimen, and mounted on a pipe plug by means of compression fittings. Hot fluid at about 350 F is circulated through the tube. Water flow rates vary from 1.5 to 2.5 feet per second. The composition of the test water used is shown in table 4. Figure 3 illustrates the specimen.

Specimens are screwed into 1-1/2 inch tees in the circulating water piping of an experimental cooling tower system. At the end of a ten-day run, specimens are removed, photographed, cleaned, and weighed and the corrosion rates determined. Kerst points out that with a provision for temperature control, the results obtained by the use of hairpin-type specimens make it possible to estimate apparent skin temperatures at the corroding surface, and that this is important insofar as corrosion rates are concerned, since at high temperatures corrosion rates may be much higher than encountered at lower temperatures.

The use of a test heat exchanger with provision for heat transfer between a heating medium and the test solution is the best means of evaluating corrosion inhibitors. We<sup>11</sup> have built a single tube heat exchanger, consisting of a 3/8-inch center tube over which from one to nine low carbon seamless steel tube corrosion test specimens (3/4-inch diameter by 3.5 inches long) separated by teflon ring gaskets are installed. Ends of outer specimens are tightened. One or more corrosion test specimens may be replaced with stainless steel dummies equipped with thermocouples to collect heat transfer data. Dow Corning 550 Fluid, the temp-

erature of which can be increased to 450 F and thermostatically held there in only a few minutes with a 15 kw heater, is pumped through the tube while cooling water with an inlet temperature of 116 F  $\pm$ 0.05 F is pumped concurrently through the exchanger on the outside and over the specimens at 2.2 gpm or 2.04 feet per second. Water temperature differential is 4.5 F with a heat exchange of 8323 Btu/hr/ft<sup>2</sup> occurring through a total heat exchange surface area of 0.589 sq ft. The overall heat exchange coefficient is 18.3 Btu/hr/ft<sup>2</sup>/°F.

A schematic flow diagram of the heat exchanger is shown in figure 4. The composition of Standard Test Solutions used in running corrosion tests is the same as in table 3.

Experimental data has shown that corrosion tests can be reproduced with a  $\pm$ 3% error.

#### FIELD EVALUATION

Important factors that must be considered in the field evaluation of corrosion inhibitors in open circulating cooling water systems are:

- 1) Metals of construction in the system
- 2) Composition of the makeup and cooling water
- 3) Possibility of and type of product contamination
- 4) Possibility of and type of air borne contamination
- 5) Maximum skin temperatures in heat exchangers
- 6) Amount of water contained in the systems
- 7) Amount of makeup water used
- 8) Control of biofouling
- 9) Interference with waste disposal
- 10) Testing methods and controls
- 11) Method and location of feeding

If all of the above factors are favorable for the evaluation of an inhibitor in a system, plans can be made for a change over from the inhibitor currently being used to the inhibitor to be tested.

Methods that are used for the field evaluation of corrosion inhibitors are:

- 1) Installation of corrosion test specimens
- 2) Use of test heat exchangers
- 3) Use of electrical resistance corrosion measurements
- 4) Inspection of equipment

Each of these methods is discussed below.

#### 1) Installation of Corrosion Test Specimens

Metals that may be used in the construction of heat exchangers are steel, inhibited admiralty, admiralty, brass, copper, aluminum, and stainless steel. The metals of construction generally encountered are steel and inhibited admiralty. In such cases, generally only steel corrosion test specimens are used, since inhibited admiralty is more corrosion resistant than steel. Where other metals of construction are used, corrosion test specimens made of the metals involved generally are used.

Various shapes and sizes of corrosion test specimens are used. The shapes generally encountered are coupons and nipples. Several recommendations have been made by various organizations for standardization and processing of corrosion test specimens. A Task Group of the National Association of Corrosion Engineers and a committee of the American Society for Testing Materials are working on this. However, no standards have been adopted as yet.

When coupon type corrosion test specimens are used, it is important to have the ratio of surface to edge area large. Coupons may be 1 inch to 4 inches long, 1/2 inch to 1 inch wide, and around 1/16 inch thick. The nipple type specimens generally are 3/4 inch to 1 inch in diameter and from 3 inches to 10 inches long. Before installation specimens are thoroughly cleaned and weighed. Table 5 describes a suitable method for preparing specimens before installation. Specimens are generally attached to assemblies for installation and are installed in locations where the cooling water is the hottest. Figure 5 illustrates the installation of specimens in a by-pass line. In some cases specimens are suspended in a tower basin or spray pond, but this practice is avoided where possible because of the slow velocity and low temperature of the

Table 5. Suitable Method for Preparing Specimens  
Before Installation

- 1 Stamp identification number on coupon before cleaning.
- 2 Immerse coupon in carbon tetrachloride or chloroform to remove any grease.
- 3 Immerse coupon in a solution of 10 ml of concentrated hydrochloric acid and 90 ml of distilled water at 125 F for 15 to 20 minutes to remove corrosion products and mill scale.
- 4 Immerse coupon in a 1% sodium hydroxide solution.
- 5 Scrub coupon thoroughly with a nylon brush under flowing water.  
Dry with tissue paper.
- 6 Using rubber gloves to prevent direct contact of fingers with coupon, immerse the coupon in alcohol and then acetone.
- 7 Put glass rod through hole of specimen, suspend in a beaker, and put in a constant temperature oven at 105 C. Remove coupon and store in desiccator containing silica gel.
- 8 Weigh coupon, record weight, and insert in Vapor Phase Inhibited bag with identification number. Seal bag and store for shipment as needed.

Table 6. Suitable Method for Cleaning Specimens After Exposure

- 1 Using a nylon brush, scrub coupon thoroughly with soap under flowing water to remove loose deposits.
- 2 Rinse coupon with distilled water and dry with a clean towel.
- 3 Immerse coupon in a mixture of 95 ml glacial acetic acid and 5 ml Rodine No. 41 at 120 F for 20 to 30 minutes.
- 4 Wash coupon with soap under flowing water. If all corrosion products are not removed, repeat steps 2, 3(for 10 to 15 minutes), and 4.
- 5 If any corrosion products still remain, dip the coupon in a solution of 1:1 hydrochloric acid for 30 seconds. Wash coupon with soap and tap water.
- 6 Rinse coupon with distilled water and then immerse in alcohol. Dry with a clean towel.
- 7 Immerse coupon in acetone and put in constant temperature oven at 105 C for several minutes.
- 8 Place coupon in desiccator containing silica gel until constant temperature is reached.
- 9 Weigh the specimen, record the weight, and calculate the corrosion rate.
- 10 Measure plit depths with a measuring microscope.

Table 7. Methods for Determining General Corrosion Rate

Coupon specimens

$$I = \frac{t_1}{2} \times \frac{(W_1 - W_2)}{W_1} \times \frac{365}{D}$$

where

I = corrosion rate in mils per year  
t<sub>1</sub> = original thickness in inches  
W<sub>1</sub> = original weight in grams  
W<sub>2</sub> = final weight in grams  
D = exposure time in days

Tubular specimens

$$I = \frac{15,150 \times L}{\bar{W} \times P}$$

where

I = corrosion rate in mils per year  
L = average weight loss in grams  
P = duration of test in days  
W = average original weight in grams

CORRECT METHOD FOR INSTALLING DREW PLUG-MOUNTED  
CORROSION TEST COUPONS IN PIPE LINES

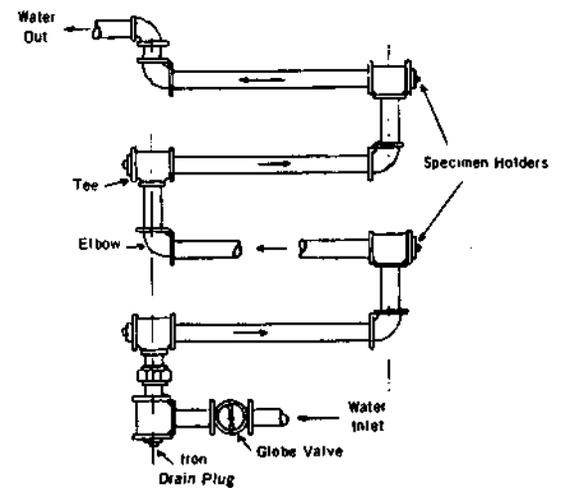
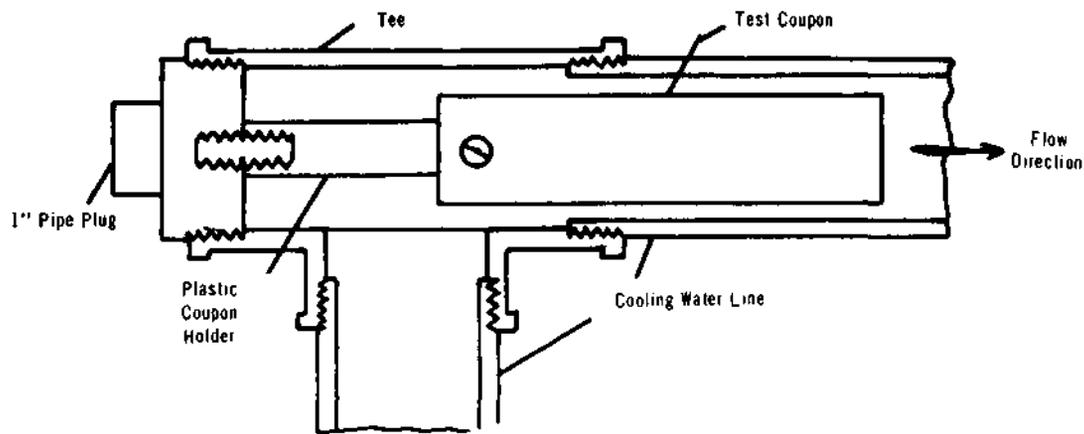


Figure 5. Typical installation of corrosion test specimens in a by-pass line

cooling water. Generally several specimens are installed and then removed at planned intervals, such as 7, 14, 21, 30, 60, and 90 days. After specimens are removed, they often are photographed and then are cleaned, reweighed, and photographed again. Table 6 describes a suitable method for cleaning corrosion test specimens after installation.

The rate of general corrosion is calculated from an empirical expression which includes period of exposure and weight loss, and generally is expressed in mils per year or milligrams per square decimeter per day. Table 7 gives methods for determining the general corrosion rate.

The depth of any pits can be determined with a measuring microscope. The data obtained are interpreted to express the performance of the corrosion inhibitor in providing protection against general and pitting types of corrosion. Various values have been suggested in interpreting data. Examples are:

Rate of general corrosion in mils per year		Interpretation				
		excellent	very good	good	fair	poor
Less than 2						Excellent
2-3						Very good
3-5						Good
5-7						Fair
7-10						Poor
Over 10						Very poor

Number and type of pits	Interpretation					
	excellent	very good	good	fair	poor	very poor
None	x					
Few wide shallow	x					
Few wide deep						x
Few narrow shallow		x				
Few narrow deep						x
Small wide shallow			x			
Small wide deep						x
Small narrow shallow				x		
Small narrow deep						x
Many wide shallow					x	
Many wide deep						x
Many narrow shallow					x	
Many narrow deep						x

## 2) Use of Test Heat Exchangers

Test heat exchangers of various designs using one or more metals of construction have been installed at plant sites to field evaluate corrosion inhibitors. Heat exchangers generally are of mono-tube design with plant cooling water passing through one side of the tube and a controlled heating medium on the other side. Heat exchangers are designed so as to provide heat transfer and a flow rate similar to those in plant heat exchangers. Before installation, the tube specimen is cleaned for removal of any scale and grease. The concentration of the corrosion inhibitor applied to the cooling water depends upon the type of inhibitor used.

After the test heat exchanger is in service for a predetermined period of time, the tube specimen is removed and processed. Processing includes such procedures as photographing, splitting the tube specimen longitudinally, analysis of any deposit present, cleaning, examination and photographing of the cleaned portion. The performance of the corrosion inhibitor is based on the results of an examination of the tube specimen.

## 3) Use of Electrical Resistance Corrosion Measurements

The corrosion rate of a metal in a corrosive solution can be rapidly determined with instruments and probes which measure the change in electrical resistance of the metal.

The principle of operation in making corrosion rate measurements by the above means is that the electrical resistance of a probe, such as a wire exposed in a corrosive solution, varies inversely with its cross-sectional area and will increase as its diameter decreases. Hence, as the probe corrodes, the electrical resistance increases. By using a reference element of the same metal protected by a coating, changes in the resistance ratio of the measuring element can be measured and converted to the rate of corrosion expressed in terms such as mils per year. One manufacturer<sup>7</sup> claims that qualitative measurements of the pitting tendency of a corrosive liquid can be made with this company's instrument.

The specific sensitivity of this method depends primarily on the shape of the test probe. Probes are available in the shape of a wire, a thin metal strip, or a small diameter tube.

Recording instruments are available which measure both the corrosion rate and total corrosion.

In the field, probes may be installed in any suitable location in the cooling system. Up to two weeks of exposure of the probe may be required before readings having value are obtained. After this period, readings are taken one or more times each day and at times when conditions develop that may change the corrosion rate. Examples of these conditions are loss of control over application of the corrosion inhibitor or pH, and process contamination.

#### 4) Inspection of Equipment

Although inspection of heat exchange equipment, piping, etc. is the most positive means for field evaluation of a corrosion inhibitor, this means usually is not practical in the majority of cases because heat exchange equipment generally is not available for inspection until a turn-around, which may be in one or more years. In those cases where heat exchangers can be removed from service without losing production, this means certainly is the most desirable. Where this means is used, other means, such as the ones described above, also are used to obtain additional information.

Inspection of heat exchange equipment provides valuable information. For example, the effects of water velocity, temperature, suspended matter in the cooling water, and biofouling on general and localized corrosion are determined only by inspection of the equipment.

#### SUGGESTED STANDARD METHODS

It is the authors' opinion that standard methods used for laboratory and field evaluation of corrosion inhibitors should be those that provide reliable and reproducible corrosion data in the shortest period of time.

Water test solutions similar to those shown in the tables are satisfactory for corrosion testing.

Suggested standard methods are given below.

<u>Type of evaluation test</u>	<u>Suggested method</u>
Short time laboratory evaluation test	Fisher and Jeter's shown in figure 2 and Drew's screening system test previously described
Extended laboratory evaluation test	Test heat exchanger similar to Drew's shown in figure 4
Field evaluation test	Installation of corrosion test specimens supplemented by resistance probe measurements

#### SUMMARY

The authors have discussed several methods that are used for evaluating corrosion inhibitors in the laboratory and in the field and have pointed out advantages and disadvantages of each.

Suggested standard methods for laboratory and field evaluation of corrosion inhibitors are proposed.

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MAXIMUM SELF-GENERATED ANODIC CURRENT DENSITY AS AN INHIBITOR  
PITTING INDEX

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Localization of attack and pitting long have been a major concern to those who contemplate the use of inhibitors in water systems. While these problems are not unique to inhibited systems, their occurrence therein frequently has been stressed, perhaps overly so. Hence, evaluation of the pitting tendencies of inhibitors continues to be quite relevant.

Pitting tendencies of inhibitors frequently have been attributed to their influence on anodic polarization. Shortcomings of the latter as a criterion of this tendency have been recognized in recent years.<sup>1</sup> Further, numerous inhibitors which promote pitting fail to affect polarization of the anodes of differential aeration cells appreciably.<sup>3,4</sup>

Differential aeration conditions prevail in a pitting situation, particularly during the propagative stages thereof. The latter are of primary interest in the present investigation. They also are of major concern with regard to the useful life of lines and equipment.

Localization of attack and pitting involve a pronounced decrease in the normal anodic:cathodic area ratio. The decrease in this ratio tends to increase the anodic current density. As a consequence, it tends to raise the anodic polarization. The latter is a result of a pitting situation rather than the cause.

Anodic:cathodic area ratios generally remain essentially constant in most experimental differential aeration cells. They do not reflect the pronounced decrease in this ratio which is encountered in a pitting situation. As a consequence, the high anodic current densities characteristic of pitting attack are not attained by the self-generated currents

from such experimental cells.

In most cases the maximum self-generated current density, and consequently the maximum rate of penetration, will be obtained with an infinite cathodic:anodic area ratio. Thus, the maximum self-generated anodic current density generally will correspond to that required to bring the potential of the anode to the open-circuit value of the cathode. Occasionally, however, discontinuities in the anodic polarization curve lead to attainment of maximum anodic current density before the potential of the anode reaches the open-circuit value for the cathode.

#### EXPERIMENTAL

The maximum self-generated anodic current density can be determined with cells of equal anodic and cathodic areas (i.e., 1:1 cells) -- such as were used in the present investigation -- by application of an external emf in series with the cells. Stepwise increase of the external emf permits determination of the maximum anodic current density, whether it occurs when the anode potential reaches the open-circuit value of the cathode or before.

The differential aeration cells which were used differed from those previously described<sup>5,6</sup> only in the substitution of polystyrene spacers for Micarta. Briefly, they consisted of two steel (AISI 1010) electrodes, one of which (i.e., the anode) was wrapped with Whatman No. 120 paper to restrict access of dissolved oxygen.

The cells were operated for a period of two days (at 35 C) to permit attainment of reasonably steady conditions before polarization measurements were made.<sup>3</sup> A 100 ohm potentiometer across a 1-1/2 volt dry cell sufficed for control of the external emf which was applied in series with the differential aeration cells during the course of the polarization measurements.

Analyses of the water which served for the test media are included in table 1.

Table 1. Composition of Water Used in Tests

Bicarbonate ( $\text{HCO}_3$ )	11 ppm
Chloride (Cl)	18 ppm
Sulfate ( $\text{SO}_4$ )	78 ppm
Calcium (Ca)	20 ppm
Magnesium (Mg)	6 ppm
Total Hardness ( $\text{CaCO}_3$ )	76 ppm

#### Influence of pH

The utility of the maximum self-generated anodic current density as a criterion of pitting tendency is illustrated by its application to the problem of the localization of corrosion frequently observed on elevation of the pH. Corrosion products tend to precipitate closer to the point of attack as the pH is raised, and this leads to increased tuberculation and pitting. These features become quite pronounced as the pH rises appreciably above 7.

The influence of elevation of the pH from 7 to 8.2 on the polarization of differential aeration cells is shown in figure 1. This increase was accomplished by treatment with sodium bicarbonate equivalent to 200 ppm bicarbonate.

Intersections of the two arms of the individual curves denote the short circuit conditions of the corresponding cells. They show the maximum self-generated current densities attainable from the respective 1:1 cells. (Higher levels require application of an external emf.)

The horizontal broken line on each curve denotes the open-circuit potential of the respective cathode; its intersection with the anodic arm of the corresponding curve denotes the maximum self-generated anodic current density.

The moderate rise in pH from 7 to 8.2 does not alter the rate of development of the polarization of either the anode or cathode appreciably,

but it does increase the potential difference of the cell. The latter is responsible for the higher current density level at the higher pH.

Elevation of the pH is accompanied by a pronounced increase in the maximum self-generated anodic current density. This is in accord with the increased localization of attack which accompanies the pH elevation. Increased potential difference of the cell is primarily responsible for this increased maximum anodic current density.

The rather pronounced tuberculation characteristic of high pH attack encourages enlargement of the covered areas -- the anodes. This is reflected by the rather broad saucer-shaped pits frequently encountered at the higher pH levels. It generally prevents attainment of the extremely high cathodic:anodic area ratios required for maximum pit propagation.

Two rather widely different inhibitive systems -- zinc sulfate and sodium nitrite -- were chosen for further investigation of the significance of maximum self-generated anodic current density. Zinc salts rarely lead to localization of attack, whereas low levels of nitrite frequently encourage pit propagation.

#### Zinc Sulfate

The influence of several levels of zinc sulfate on the maximum self-generated anodic current density of differential aeration cells at pH 7 is shown in figure 2. Concentrations are given in terms of zinc since this appears to be the active inhibitive portion of the salt.

Only the anodic arms of the polarization curves are included in this figure. Open-circuit values for the cathodes are designated by the solid points; short circuit values for the 1:1 couples by the X's. The position of the arrow designates the point where the anodic polarization curve attains the maximum self-generated anodic current density.

Zinc does not affect the slope of the anodic polarization curve to a significant degree. The determinant factor with respect to the maximum self-generated anodic current density is the potential difference of the cell.

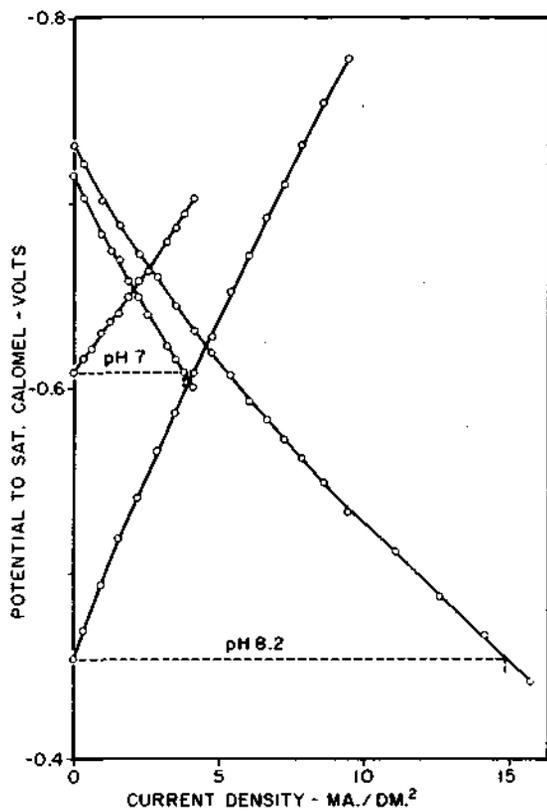


Figure 1. Polarization of differential aeration cells in neutral and alkaline waters

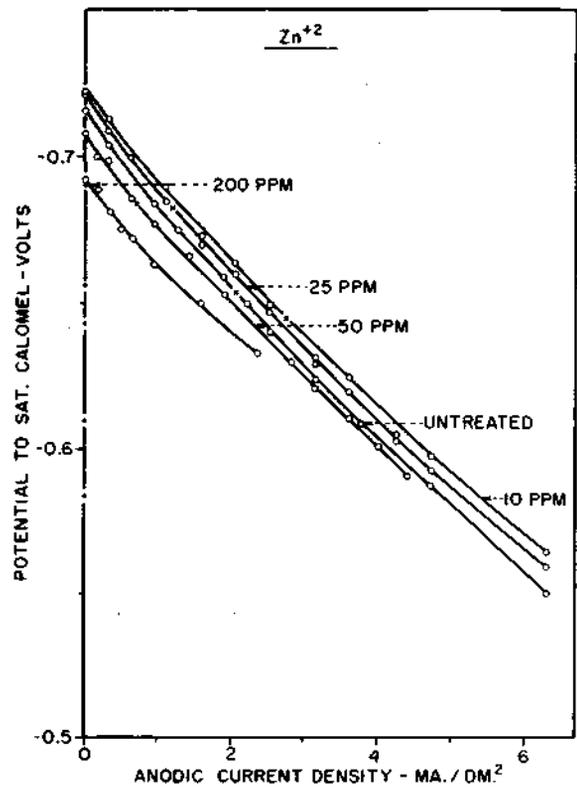


Figure 2. Polarization of anodes of differential aeration cells in zinc (sulfate) treated waters

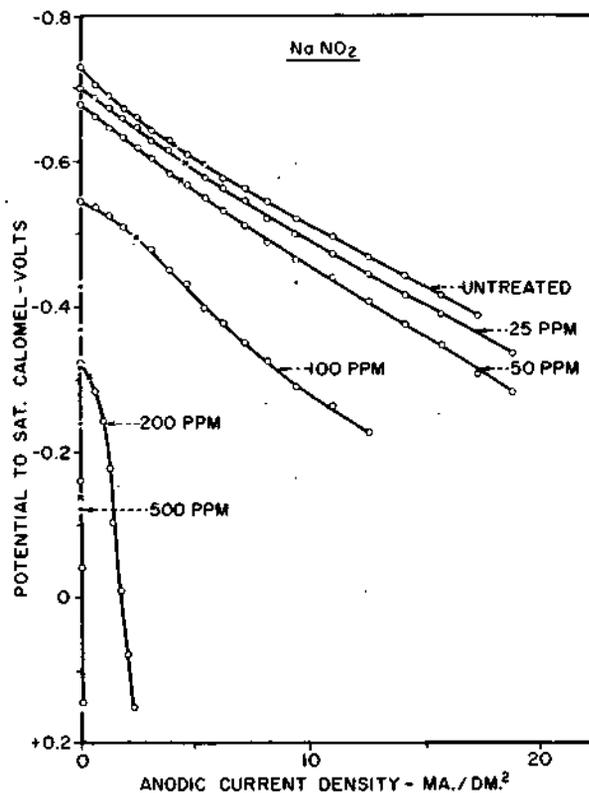


Figure 3. Polarization of anodes of differential aeration cells in sodium nitrite treated waters

The initial increment of zinc (10 ppm) increases the maximum self-generated anodic current density as well as the current from the 1:1 cell. The extent of the increase does not appear sufficient to indicate a significant increase in the tendency to pit. This is in agreement with the known behavior of zinc salts as inhibitors. Actual pit formation seldom is encountered, although indications of incipient localization are not uncommon.<sup>7</sup>

#### Sodium Nitrite

Anodic polarization data for the sodium nitrite series are shown in figure 3. A pH of 8 or above normally is employed when nitrite is used as the inhibitor. Sodium bicarbonate equivalent to 100 ppm bicarbonate was added to the water shown in table 1 to provide such a medium (pH = 8.2).

The maximum self-generated anodic current density for the control falls at a rather high level characteristic of the elevated pH (e.g., figure 1). It rises somewhat more with the initial nitrite increments, but higher dosages reverse this trend and very low levels eventually are attained (e.g., at 200 and 500 ppm sodium nitrite).

The slopes of the anodic polarization curves do not change significantly at the lower nitrite dosages. As a result, the potential difference of the cell is the major determinant factor with regard to the maximum self-generated anodic current density at these inhibitor levels (i.e., 10-100 ppm). A rather pronounced increase in anodic polarization rate becomes an additional factor at the two higher nitrite dosages.

The intermediate stages of development of inhibition by nitrite - where relatively high maximum self-generated anodic current densities are encountered - correspond to the range where normal differential aeration attack (i.e., with no externally applied emf) of the 1:1 cells is stimulated. Both reflect the increased potential difference of the cell which results from the greater sensitivity of the cathode to the passive shift produced by this inhibitor.

These intermediate stages of protection correspond to inhibitor dosages which lead to pitting. This is illustrated by the data in figure 4

(right) which show the influence of the nitrite concentration on the attack of steel at pH 8.2. These data are the results of agitated batch tests of the type previously described. The tests were conducted for a period of five days at 35 C. The broken vertical lines show the pit penetration; the solid points denote the maximum and the X's the average of the five deepest pits.

Sodium benzoate also is a passivator, but does not appear to promote pitting regardless of its concentration. This is shown by the data in figure 4 (left) which also contains the weight loss values for a series of agitated tests with sodium benzoate at pH 6.5.

The rather abrupt drop from no appreciable inhibition to practically complete protection is of particular significance. No intermediate stages of inhibition appear. Instability of these intermediate stages appears responsible for the freedom from pitting characteristic of benzoate inhibition.

Generally, as in the above cases, the potential difference of the cell is a major determinant factor with regard to the maximum self-generated anodic current density, but this is not always the case. Sodium molybdate provides such an exception.

#### Molybdate and Citrate

Sodium molybdate and sodium citrate behaved quite similarly in the earlier differential aeration tests with 1:1 cells. In neither case did development of passivation proceed past the stimulation stage. Yet, there is considerable difference in the tendencies of the two passivators to pit as is shown by the data in figure 5.

Citrate promotes pitting throughout the range of concentrations investigated -- as might be expected. Molybdate, however, promotes pitting only at relatively low concentration levels.

Further polarization tests of differential aeration cells in molybdate treated waters were run to determine the maximum self-generated anodic current densities for such systems. The results of such a test at a sodium

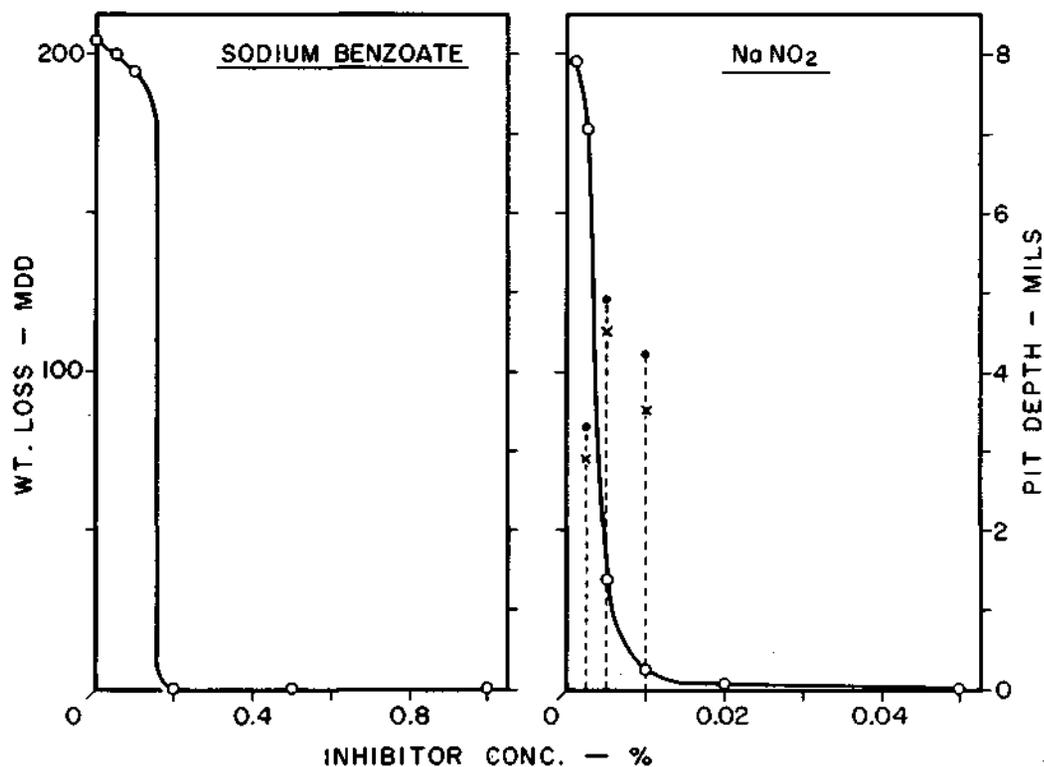


Figure 4. Influence of benzoate (left) and nitrite (right) on corrosion of steel

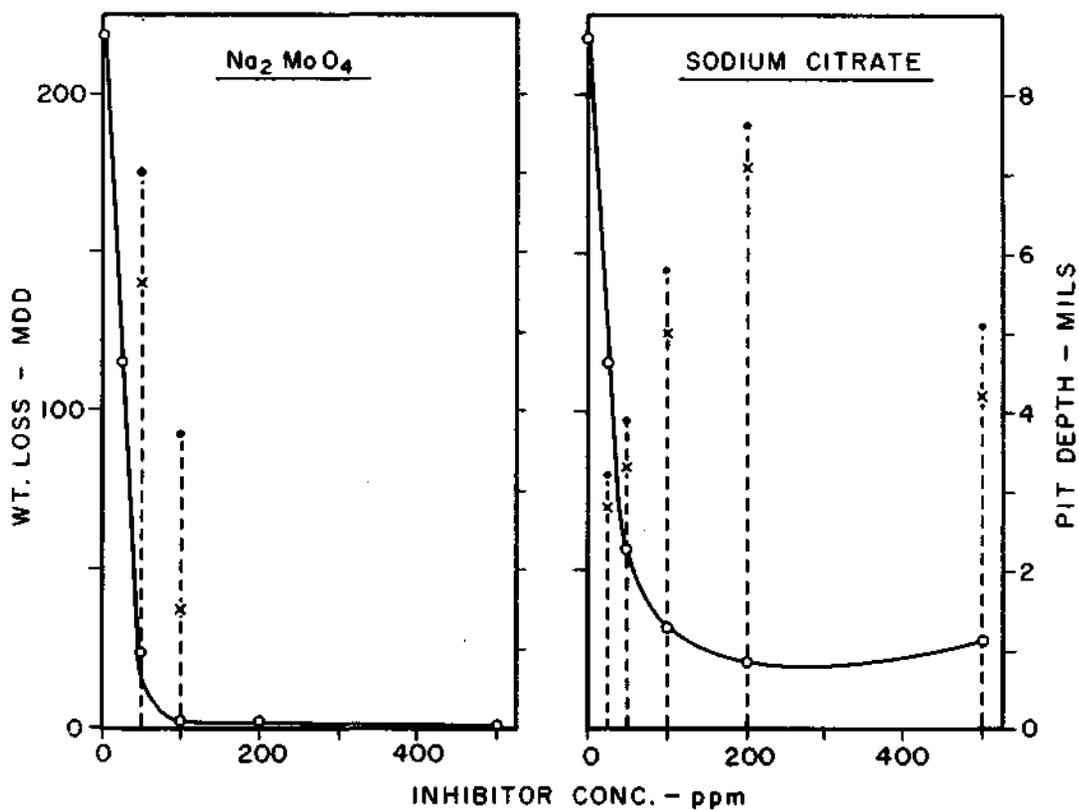


Figure 5. Influence of molybdate (left) and citrate (right) on corrosion of steel

molybdate level of 500 ppm and a pH of 6.5 are shown in figure 6.

A "break" in the anodic arm of the curve occurs before the open-circuit value of the cathode is reached. There is a pronounced increase in the rate of development of anodic polarization. The system appeared quite stable at a measured anode potential of -0.4 volts SCE (saturated calomel electrode), but a subsequent slight elevation of the externally applied emf produced a gradual decrease in the current with an attendant potential slide of roughly 0.12 volts in a passive direction. The progress of this drop was followed by current and potential readings at 5-minute intervals; an essentially steady value was attained after 15 minutes.

The maximum anodic current density is attained just prior to the "break-." The current density is considerably lower than this maximum when the open-circuit potential of the cathode is attained. In fact, it is lower than the short circuit value for the 1:1 cell -- the anodic current density for an infinite cathodic:anodic area ratio is less than for the 1:1 area ratio. Extreme localization of attack in such a situation results in a decrease in the intensity thereof. This tends to retard pit propagation. In short, pit propagation is retarded by the increased rate of development of anodic polarization.

The potential drop through the solution becomes quite appreciable at current densities such as are attained in this molybdate test. A better characterization of the actual anode potential at the "break" is afforded by the broken curves which are corrected for the IR (current times resistance) drops through the solution. (Subsequent figures will include similarly corrected curves whenever the IR drops involved become appreciable.)

Citrate does not show a comparable "break" in the anodic arm of its polarization curve. This is illustrated by the data in figure 7 which show the polarization curves for the differential aeration cell in water treated with 500 ppm sodium citrate at pH 6.5.

The relatively high level of the maximum self-generated anodic current density reflects the pronounced pitting tendency of the citrate inhibitor.

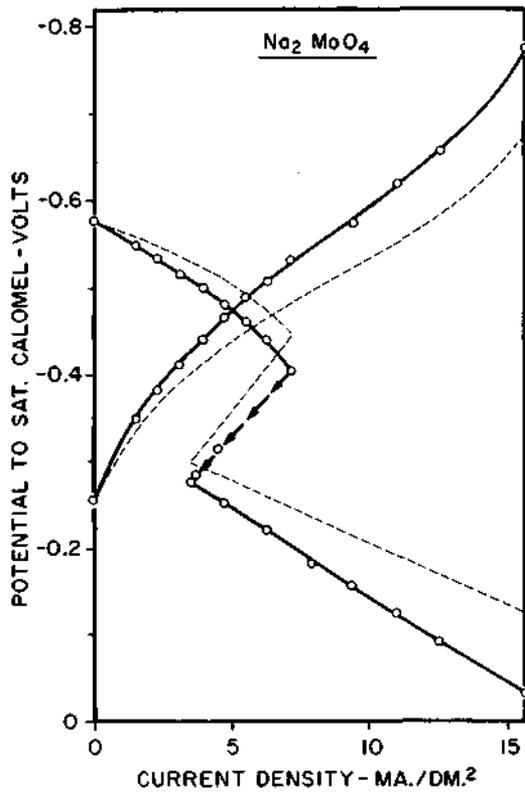


Figure 6. Polarization of differential aeration cell in molybdate treated water

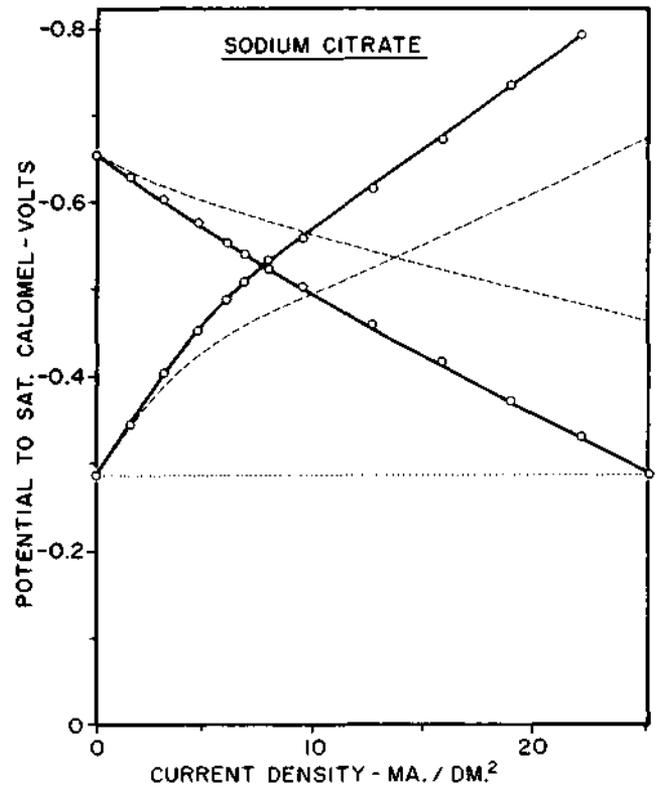


Figure 7. Polarization of differential aeration cell in citrate treated water

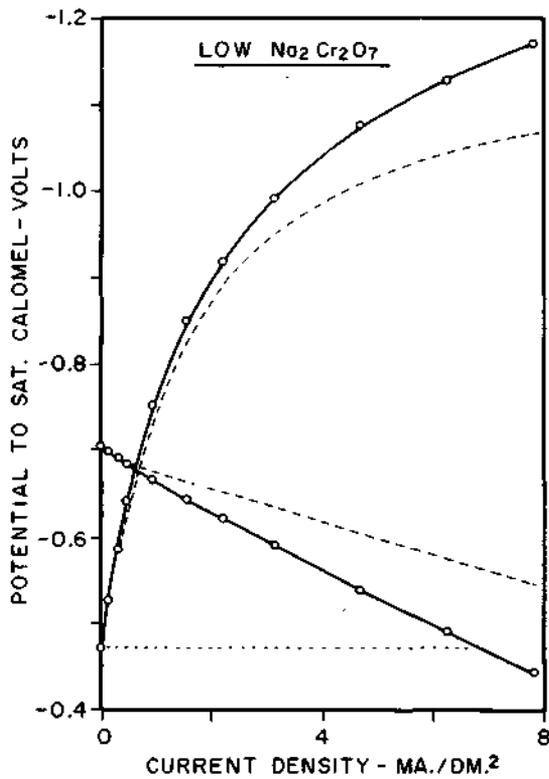


Figure 8. Polarization of differential aeration cell at low dichromate level

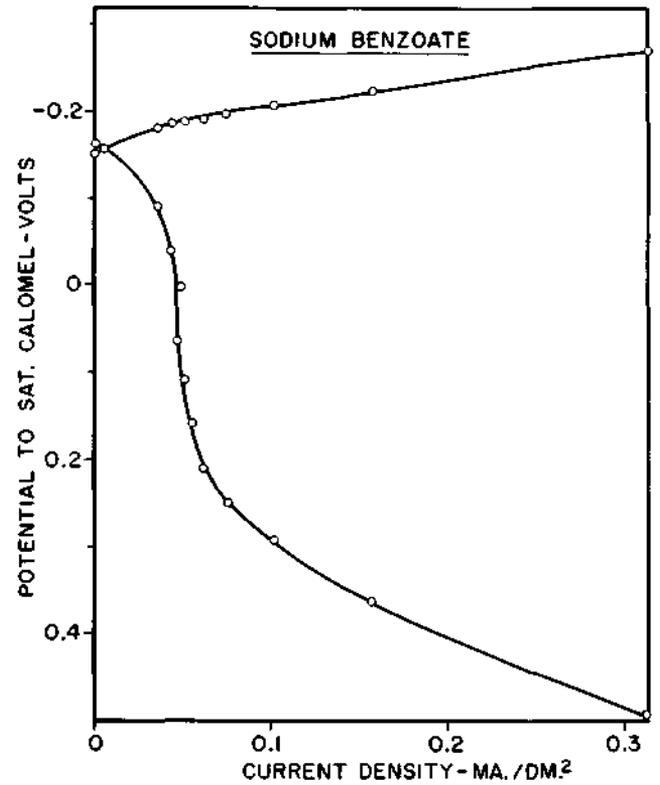


Figure 9. Polarization of differential aeration cell in benzoate treated water

The cause for the potential "break" with the molybdate treated system appears rather obscure. It resembles anodic passivation. However, the potential at which it occurs suggests the involvement of factors other than simple ferric oxide formation.

#### Dichromate

The pitting tendencies of low concentrations of dichromate frequently have been emphasized. The primary function of these low levels of dichromate in waters of appreciable electrolyte content (e.g., most natural waters) is to increase cathodic polarization. This characteristic generally has not been associated with pitting. Consequently, the maximum self-generated anodic current density of such a system is of particular interest.

Polarization data for a differential aeration cell treated with 50 ppm sodium dichromate at pH 6.5 are shown in figure 8. High cathodic polarization is the predominant inhibitive action of the dichromate in this system, but this does not affect the maximum self-generated anodic current density which is high chiefly because the potential difference of the cell is high.

The pitting characteristic of dichromate in this concentration region reflects this high maximum self-generated anodic current density and in turn the relatively high potential difference of the cell.

The high cathodic polarization at this low dichromate level causes the major potential change produced by the external emf to affect the cathode. Such behavior is typical of cathodic polarizers; for example, it is reflected to a pronounced degree by phosphate glasses and by zinc salts.

One result of the increase in cathodic polarization produced by inhibitors of this type is a pronounced decrease in the current density required for attainment of a given cathode potential. This suggests their use in conjunction with cathodic protection.

#### DISCUSSION

Maximum self-generated anodic current density provides a measure of the

pitting potential of an inhibitor. It is proportional to the maximum rate of penetration which may be encountered – that which will be experienced under the most unfavorable area relation (i.e., an infinite cathodic:anodic area).

The actual proximity of approach to such an area ratio will depend largely on the pit density (i.e., the number/unit area), which is primarily a function of the initiative stages of pitting.

Maximum self-generated anodic current density is dependent on three factors: the potential difference of the cell, the anodic polarization rate, and IR drop through the solution. It is not influenced by the cathodic polarization. High potential differences, low rates of development of anodic polarization, and low IR drops enhance pit propagation and vice versa.

IR drops through the solution constitute a significant factor in pit propagation. They also were involved in the determinations of maximum self-generated current densities discussed above, though to a somewhat different extent due to differences in geometric configuration. (The experimental values were based on an infinite cathodic:anodic area ratio with the respective areas 0.5 inch apart.) Consequently, the values obtained are proportional to, but not equivalent to, the maximum rate of pit penetration.

The anodic polarization rate usually fails to increase significantly until the decreased potential difference has brought the attack pretty well under control. Generally, it serves only as an aid during the final development of full protection.

Molybdate provides an exception to the above generalization. The sharp increase in the anodic polarization rate which develops as the current density is raised serves as a major current limiting factor in this system. The increased anodic polarization rate serves to decrease the pitting tendencies of this inhibitor.

Pronounced increases in the rates of development of anodic polarization – somewhat analogous to the "break" observed with molybdate – have been encountered in systems treated with other passivators. In these instances

they have been observed only after the inhibition has become well developed. Further, they have occurred at current densities appreciably greater than the maximum self-generated anodic value.

Benzoate is among the passivators to show such a "break" in its anodic polarization curve. This is shown in figure 9 which contains the polarization data for a differential aeration cell treated with benzoate equivalent to 1% of the sodium salt at pH 6.5. (The inhibitor was added as benzoic acid and was adjusted to pH 6.5 with sodium hydroxide. This was done to avoid introduction of excess foreign electrolyte to which benzoate inhibition is quite sensitive.)

The slope of the anodic arm of this benzoate curve increases to a pronounced degree as the potential drops below about -0.1 volts SCE; this persists to about +0.2 volts SCE. (Equilibrium was attained rather slowly during this stage of the measurements; hence, in this region the externally applied potential was increased by 50 millivolt steps and the cell permitted to stand 5 minutes before current and potential measurements were taken.) This marked increase in the anodic polarization rate occurs at a potential more noble than the open-circuit value of the cathode. Consequently, it does not influence the maximum self-generated anodic current density value.

Nitrite behaves in a fashion quite similar to benzoate. The data considered in figure 3 gave rather ill-defined "breaks" in the anodic polarization curves for the two higher nitrite levels. However, the "break" is more pronounced at pH 6.5, as is shown by the data for 500 ppm sodium nitrite in figure 10.

The slope of the anodic arm increases markedly as the potential drops much below -0.2 volts SCE; this persists to about +0.25 volts (the subsequent decrease in slope is not included in the figure). This pronounced increase in anodic polarization occurs at a potential more noble than the open-circuit value of the cathode, as was the case with benzoate. Again, the "break" does not influence the maximum self-generated anodic current density.

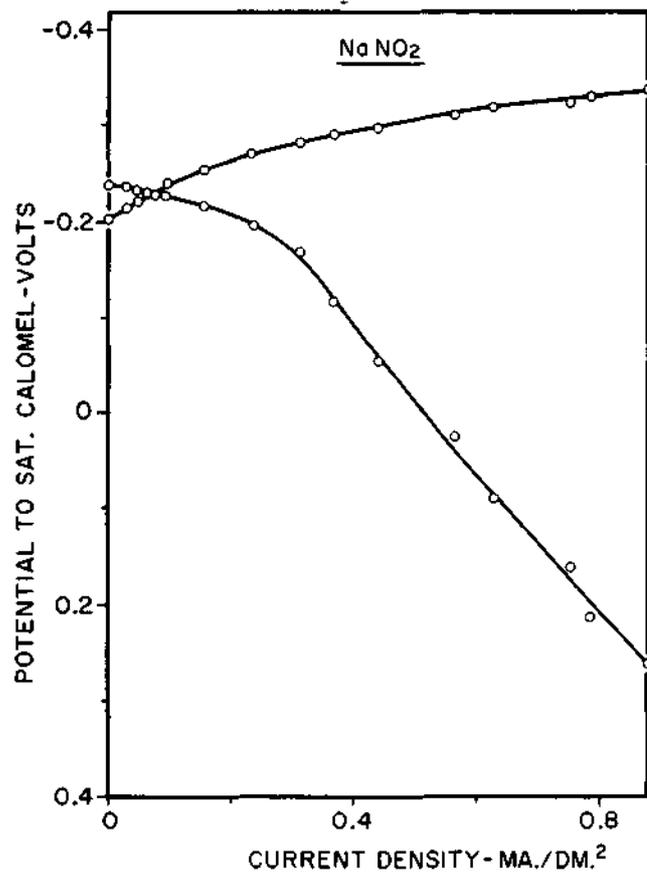


Figure 10. Polarization of differential aeration cell in nitrite treated water

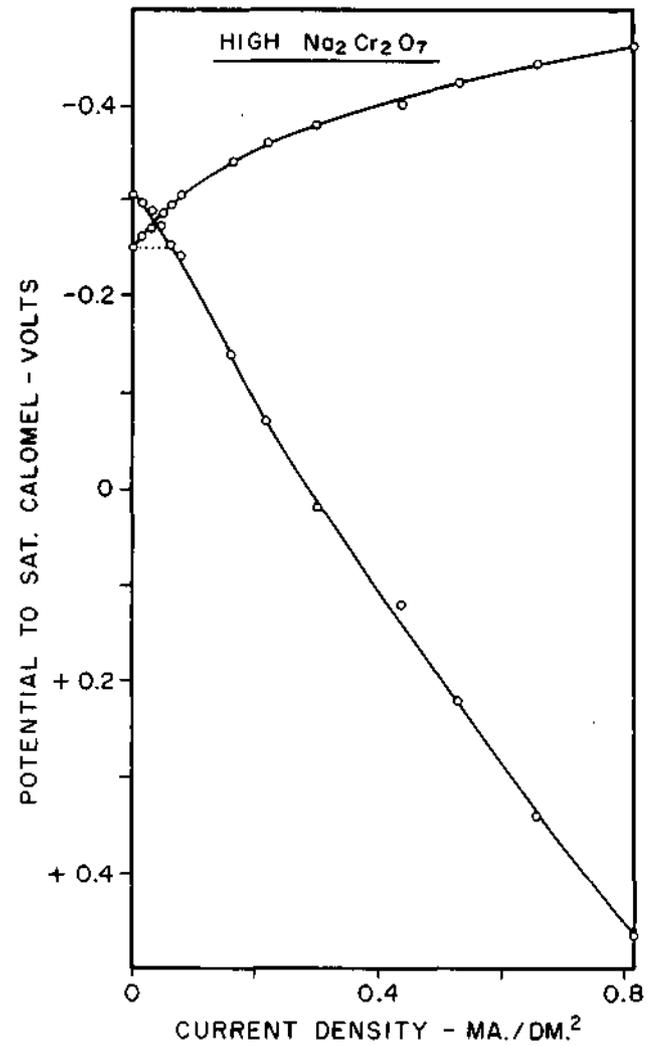


Figure 11. Polarization of differential aeration cell at high dichromate level

The potentials at which the "breaks" in the anodic arms occur with nitrite or benzoate are roughly 0.2 to 0.3 volts more noble than that for the "break" with molybdate. This suggests a difference in the processes involved.

The higher level of the anodic current density at the "break" as compared with the maximum self-generated anodic current density is indicative of better protection with the inhibitor than with the anodically produced passive film. This in turn suggests that the passivators, nitrite and benzoate, provide an added inhibitive function which is not solely involved with maintenance of the oxide film. They also reinforce the protective action of the film, probably as a result of strong adsorption thereon.

Not all of the good passivators show comparable "breaks" in their anodic polarization curves. Sodium dichromate provides such an exception.

Dichromate functions as a very effective passivating inhibitor at relatively high concentration levels. This is illustrated in figure 11 by polarization data for a differential aeration cell in water treated with 2000 ppm sodium dichromate at pH 6.5. The anodic arm of this curve shows no indication of a "break" such as was observed with benzoate or nitrite. However, the degree of anodic polarization suffices to restrain excessive buildup of the current density as the externally applied emf is raised.

Behavior of these systems at anodic current densities in excess of the maximum self-generated values is chiefly of theoretical interest; such conditions rarely are encountered in practice. They require an external emf and cannot be attained with the self-generated current from the cell alone -- regardless of the cathodic:anodic area ratio. They do not "influence" either the maximum self-generated anodic current density values or the pitting tendencies in these systems.

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## GYPSUM SOLUBILITY, A FACTOR IN THE REUSE OF COOLING WATER

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At the present time, cooling water is in short supply in much of our country. With anticipated industrial development such water supplies will be more critical in the future, and the maximum use of available supplies will be necessary. Cooling water often is cooled by partial evaporation and reused. The ultimate goal is to operate at the maximum safe evaporative concentration limit.

For each 10 F cooling, about 1% of water is evaporated, resulting in an equal increase of mineral content. Several common minerals found in cooling water are only sparingly soluble. After sufficient evaporative-cooling cycles, each of these minerals reaches the limit of its solubility and thereafter deposits on heat exchanging surfaces. At times, cooling water concentration limits may be governed by the silica, aluminum, iron, phosphate, or carbonate content. However, in most evaporative-cooling systems, where sulfuric acid is used to reduce carbonate alkalinity, the limit of concentration is controlled by gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). It may be calculated from a knowledge of gypsum solubility in the cooling water.

The limit of evaporative concentration equals the ratio of gypsum content at saturation to the gypsum content of the acidized makeup water. Although various procedures may be used for calculating the above ratio, they all require knowledge of gypsum content at saturation.

### ESTIMATION OF THE LIMITS OF EVAPORATIVE CONCENTRATION

In the past, several methods have been used to estimate the limit of evaporative concentration of a cooling water from its analysis. Probably the oldest is to maintain the products of the  $\text{Ca}^{++}$  and the  $\text{SO}_4^-$ , both

expressed as parts per million, at less than 500,000. Since the values of the products of  $\text{Ca}^{++}$  and the total  $\text{SO}_4^-$  in saturated gypsum solutions have been calculated to be considerably greater than 500,000 and variable, this estimation procedure is of questionable value. Similarly, estimations based on solubility products are in serious error. An accurate method for estimating the limits of evaporative concentration of cooling water has been developed and is described in this paper.

In operating evaporative-cooling systems, cooling water temperatures will range from about 25 C (77 F) to 46 C (115 F) and in some cases to about 90 C (194 F). Cooling waters, and also acidized makeup, will contain gypsum, common-ion salts and noncommon-ion salts. Both the amount and the ratio of these salts will vary greatly. Common-ion salts usually will not exceed 30 equivalents per million (epm), and noncommon-ion salts rarely will exceed 40 epm. Common-ion salts are usually  $\text{Na}_2\text{SO}_4$  and/or  $\text{MgSO}_4$ ; noncommon-ion salts are predominantly NaCl. Because of ionic interaction, each of these variables will influence the solubility of gypsum, and any scheme for predicting gypsum solubility in evaporative cooling waters must consider all of them.

Objectives of the present study were:

To obtain accurate gypsum solubility data under conditions typical of those existing in evaporative cooling systems.

To develop and provide a scheme for calculating gypsum solubility under such conditions.

Using this method, to determine the allowable limit of evaporative concentration for representative acidized cooling waters.

#### GYPSUM SOLUBILITY DETERMINATION

The literature contains very little data regarding the solubility of gypsum, under conditions of salt content and temperature existing in cooling water of evaporative cooling systems. For the purpose of the present study it was necessary to determine the gypsum solubility over a considerable range of conditions. The procedure used is described in the Experimental section. Results are given in tables 1 to 4.

Table 1. Solubility of Saturated Gypsum Solutions

Temp. (°C)	Solubility		Temp. (°C)	Solubility	
	(epm)	(meq/l)		(epm)	(meq/l)
0	25.80	25.84	35	30.92	30.80
5	27.18	27.23	40	30.90	30.72
10	28.30	28.35	50	30.42	30.12
15	29.30	29.33	60	29.44	29.00
18	29.82	29.85	70	28.34	27.77
20	30.14	30.14	80	27.18	26.47
25	30.54	30.52	90	25.66	24.82
30	30.81	30.74	100	24.60 <sup>a</sup>	23.67

All calcium taken to gypsum. Since solution contains about 0.3 epm alkalinity (CaCO<sub>3</sub>), the true solubility at 100 C, is probably 24.3 to 24.4 epm gypsum.

Table 2. Solubility of Gypsum in the Presence of Common-Ion Salts

Temperature (°C)	Common-Ion salts (epm)		Gypsum (epm)	
	<u>Na<sub>2</sub>SO<sub>4</sub></u>	<u>NgSO<sub>4</sub></u>	<u>Exptl.</u>	<u>Calcd.</u>
25	5.0	-	28.87	29.0
25	10.0	-	27.41	27.6
25	15.0	-	26.28	26.4
25	20.0	-	25.33	25.5
25	30.0	-	23.93	23.9
25	40.0	-	22.93	22.9
25	60.0	-	21.68	21.6
25	-	5.04	29.64	29.5
25	-	10.01	28.74 <sup>a</sup>	28.5
25	-	15.00	27.74	27.7
25	-	20.21	27.14 <sup>a</sup>	27.0
25	-	29.96	26.14	26.0
25	-	30.46	26.10 <sup>a</sup>	26.0
25	-	30.60	25.85	26.0
25	-	37.46	25.50	25.5
25	-	44.96	25.16	-
25	-	61.06	24.34	-
25	2.50	2.52	29.29	29.3
25	5.00	5.04	28.13	28.1
25	7.50	7.56	27.18	27.1
25	10.00	10.08	26.30	26.3
25	15.0	15.0	25.12	25.1
45.1	5.00	-	29.32	29.3
45.2	10.00	-	27.94	27.9
45.1	15.00	-	26.84	26.8
45.1	-	5.00	29.94	29.8
45.2	-	10.00	29.15	29.0
45.2	-	15.00	28.33	28.3
45.1	2.50	2.50	29.58	29.5
45.1	5.00	5.00	28.45	28.5
45.2	7.50	7.50	27.35	27.5
75.0	2.50	-	26.96	27.0
90.0	2.50	-	24.83	24.9
100.0	2.50	-	23.6 <sup>b</sup>	-
75.0	5.00	-	26.26	26.3
89.8	5.00	-	24.25	24.2
90.0	5.00	-	24.13	24.2
100.0	5.00	-	22.9 <sup>b</sup>	-
87.8	10.00	-	23.18	23.3
88.7	10.00	-	23.12	23.2
100.0	10.00	-	22.1 <sup>b</sup>	-
50.7	15.00	-	26.40	26.4
51.0	15.05	-	26.49	26.4

Table 2. (continued)

Temperature (°C)	Common-ion salts (epm)		Gypsum (epm)	
	<u>Na<sub>2</sub>SO<sub>4</sub></u>	<u>MgSO<sub>4</sub></u>	<u>Exptl.</u>	<u>Calcd.</u>
60.3	15.00	-	25.55	25.6
74.1	15.00	-	24.06	24.2
88.8	15.00	-	22.21	22.2
100.0	15.00	-	21.0 <sup>b</sup>	-
100.0	20.00	-	20.4 <sup>b</sup>	-
51.5	30.00	-	24.17	24.1
51.0	30.10	-	24.33	24.1
60.0	30.00	-	23.62	23.5
73.5	30.00	-	22.55	22.5
74.4	30.00	-	22.31	22.3
74.8	30.00	-	22.33	22.3
87.3	30.00	-	20.83	20.8
60.0	40.00	-	22.99	22.8
74.2	40.00	-	21.84	21.7
90.0	40.00	-	20.23	20.1
100.0	40.00	-	18.92 <sup>b</sup>	-
89.1	-	5.00	25.11	24.9
61.0	-	15.00	27.01	27.0
73.8	-	15.00	25.88	25.7
87.8	-	15.00	23.86	23.9
60.3	-	30.00	25.55	25.9
75.2	-	30.00	24.39	24.6
85.5	-	30.00	23.14	23.2
60.2	15.00	15.00	24.90	24.9
76.4	15.00	15.00	23.32	23.3
88.1	15.00	15.00	22.16	21.9
	CaCl <sub>2</sub>			
25	5.0	-	28.65	29.0
25	10.0	-	27.17	27.6
25	15.0	-	26.05	26.4
25	20.0	-	25.07	25.5

<sup>a</sup>Harkins 6 Paine<sup>1</sup> (Literature reference 3 of reference 1).

<sup>b</sup>All calcium taken to gypsum. Since solutions are alkaline, calcium is probably in excess.

Table 3. Solubility of Gypsum in the Presence of Noncommon-Ion Salts

Temperature (°C)	Non-common ion salts (epm)		Gypsum (epm)	
	NaCl		Exptl.	Calcd.
25	5.0		31.54	31.6
25	10.0		32.61	32.6
25	15.0		33.55	33.5
25	20.0		34.13	34.4
25	30.2		35.94	36.0
25	31.0		36.20	36.2
25	46.5		38.22	38.5
25	60.6		40.00	40.2
25	80.3		42.32	
25	85.0		42.44	
25	174.4		50.77	
25	330.0		60.99	
25	339.0		61.63	
25	529.0		71.28	
25	667.0		76.55	
25	1300.0		91.52	
81.8	20.0		30.59	30.7
90.1	20.0		29.37	29.4
91.1	20.0		29.25	29.3
82.6	31.0		32.22	32.4
90.3	31.0		31.23	31.3
82.0	85.0		39.16	
82.5	175.2		47.14	
	KCl			
25	5.0		31.70	31.6 <sup>a</sup>
25	10.0		32.68	32.6 <sup>a</sup>
25	15.0		33.65	33.5 <sup>a</sup>
	MgCl <sub>2</sub>			
25	1.0		31.02 <sup>b</sup>	31.0 <sup>a</sup>
25	2.0		31.36 <sup>b</sup>	31.4 <sup>c</sup>
25	4.0		32.05 <sup>b</sup>	32.1 <sup>c</sup>
25	6.0		32.72 <sup>b</sup>	32.8 <sup>c</sup>
25	8.0		33.36 <sup>b</sup>	33.4 <sup>c</sup>
25	10.0		34.00 <sup>b</sup>	34.1 <sup>c</sup>
25	20.0		36.88 <sup>b</sup>	37.0 <sup>c</sup>
25	30.0		39.43 <sup>b</sup>	39.5 <sup>c</sup>
25	40.0		41.62 <sup>b</sup>	41.7 <sup>c</sup>

Calculated as sodium chloride. Extrapolated, Van Veldhuizen (Literature reference 12 of reference 1). <sup>c</sup>Use table X of reference 1. Then calculate as sodium chloride.

Table 4. Solubility of Gypsum in the Presence of Mixtures of Added Common-Ion and Noncommon-Ion Salts

Temperature (°C)	Added Salts (epm)			Gypsum (epm)	
	Na <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub>	NaCl	Exptl.	Calcd.
25	5.0	-	9.9	30.72	30.7
25	5.0	-	99.0	42.53	42.2
25	5.0	-	287.0	57.91	58.6
25	7.5	-	7.76	29.68	29.6
25	15.0	-	15.0	28.50	28.5
25	15.0	-	15.52	28.68	28.6
25	15.0	-	29.70	30.53	30.6
25	15.0	-	30.16	30.68	30.6
25	15.0	-	31.05	30.76	30.8
25	-	15	15.52	30.16	30.1
25	-	15	31.05	32.30	32.4
25	7.5	7.56	22.56	30.38	30.4
25	10.0	10.3	10.0	27.64	27.6
74.2	15.0	-	15.0	26.27	26.3
74.2	15.0	-	30.0	28.83	28.6
74.2	-	15.0	15.0	27.93	27.9
74.2	-	15.0	30.0	30.22	30.1
85.8	-	15.0	15.0	26.53	26.2
85.8	15.0	-	30.0	26.93	26.9
60.7	10.0	10.3	10.0	27.20	27.0
75.0	10.0	10.3	10.0	25.58	25.7
88.0	10.0	10.3	10.0	24.10	23.9

By considering the activity coefficients, an accurate method of calculating gypsum solubility in mixtures of these salts has been developed.<sup>2</sup> The method is described and illustrated later in this paper. Agreement between the experimental values and values calculated in this manner is excellent as can be seen in tables 2 to 4.

## Experimental

Procedure. Distilled water having a maximum conductance of 3 micromhos was used throughout this work. All chemicals used were ACS specification or better in quality. Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), used routinely as the solid phase, was suspended in distilled water (1 pound to 5 gallons) and agitated for one-half hour, followed by settling, filtration on a Bichner funnel, washing with distilled water, and air drying to constant weight in dust-free air at room temperature.

Gypsum Saturation at 25 C. Sealed glass or plastic bottles containing the desired solutions of added salts in distilled water and  $5 \pm 0.1$  grams of gypsum per liter were heated to 40 C, packed in fiberboard containers, and rotated in a  $25 \text{ C} \pm 2$  temperature-controlled room for 24 hours (one saturation cycle). At this time, the solutions were at room temperature. Complete saturation was produced by two saturation cycles. Excess gypsum was removed by filtration (in the temperature-controlled room).

Saturation Above 40 C. This was accomplished by heating a solution, saturated between 25 and 37 C, to the desired higher temperature, with agitation for 30 minutes. Excess gypsum was removed by an internal filter made from alternate layers of paper pulp and glass fiber.

Calcium contents of the filtered, saturated gypsum solutions, at room temperature, were determined by titration using EDTA solution, following ASTM Method D-1126-57,<sup>3</sup> except that 25-ml samples diluted with 50 ml of distilled water were used. Calcium standards, made from primary standard grade calcium carbonate ( $100.0\% \pm 0.1\%$ ), were titrated simultaneously with saturated gypsum solutions. Calcium standards made from water-washed, air-dried gypsum agreed, within experimental error, with those using calcium carbonate.

All data were reported on a weight basis – namely, equivalents per million added salt and/or gypsum. The density of saturated gypsum solutions at 25 C (up to an added salt content of 30 epm) was taken as 1.000 with a maximum error of  $\pm 1$  part per thousand. Above added salt contents of 30 epm, the density of the saturated solution at 25 C was determined. The actual temperature of solutions saturated at a nominal temperature of 25 C ranged from 23 to 27 C. Solubility at the actual temperature was converted to that for 25 C with negligible error, using the solubility-temperature coefficient of gypsum in distilled water, near 25 C. Data obtained at 101 to 102 C were converted to 100 C, similarly.

Results. Accuracy of the calcium determinations with a single analyst are between 1 and 2 parts per thousand, up to 30 epm of magnesium present.

Tables 1 to 4 give results of gypsum solubility obtained by experiments and from the literature. This solubility data for gypsum in water below 80 C agreed within 0.2 epm.

The pH value of the gypsum solutions saturated between 25 C and about 90 C ranged from 6.8 to 7.3. However, the pH of solutions saturated at about 101 C ranged from about 8.0 to 9.4. The methyl orange alkalinities, after 1 to 2 hours boiling, were quite constant, averaging 0.3 epm. The high pH and the methyl orange alkalinity are not caused by sodium alkalinity, since the saturated solutions contained less than 1.4 ppm (0.06 epm) sodium. It is believed that the high pH values were caused by hydrolysis of calcium sulfate, possibly due to formation of an acid sulfate on the surface of the solid phase. Straub<sup>4</sup> encountered similar behavior of calcium sulfate at temperatures between 182 C and 316 C.

Partridge and White<sup>5</sup> have shown that gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), in the presence of water, changes rapidly to hemihydrate ( $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ ) when heated to about 100 C, and that the solubility curves of gypsum and hemihydrate intersect at about 98 C. (Gypsum is less soluble below 98 C.) Hill<sup>6</sup> has shown that high concentrations of NaCl promote hemihydrate formation and that high concentrations of  $\text{K}_2\text{SO}_4$  promote anhydrite formation.

In the present work, calcium sulfate solubilities have been determined,

at 99.8 C  $\pm 0.2$ , after 144 hours refluxing, using conductance methods. In the presence of excess gypsum only, its solubility ranged from 24.0 to 24.4 epm; and in the presence of 32 epm Na<sub>2</sub>SO<sub>4</sub> plus excess gypsum, from 18.6 to 19.2 epm. Solid phase was hemihydrate. These data agree with those in the preceding paragraph and with those in tables 1 and 4 of this paper.

From the foregoing it appears reasonable to assume that, in the present solubility experiments below 90 C, the solid phase is gypsum and that at 100 C it is hemihydrate.

#### CALCULATION OF GYPSUM SOLUBILITY

Solubility of sparingly soluble salts in the presence of common-ion salts is often calculated using the solubility product principle. This was done for gypsum under several conditions of temperature and common-ion salt content. The calculated gypsum solubilities were in poor agreement with experimental values. The errors arise from the fact that concentrations were calculated assuming an activity coefficient of 1. This method does not permit calculation of solubility increases resulting from the presence of noncommon-ion salts.

Stiff and Davis<sup>7</sup> calculated the solubility of gypsum on the basis of empirical factors, but their method is best suited to brines. Lewis and Randall<sup>2</sup> calculated the solubility of gypsum at 25 C, on the basis of the ionic equilibrium existing in saturated solutions. The mean activity of any strong electrolyte is constant in a saturated solution at a fixed temperature, regardless of the added salt content. With binary electrolytes such as gypsum, the relationship between the mean activity coefficient ( $f^{\pm}$ ), the mean activity ( $a^*$ ), and the mean molarity ( $m^{\pm}$ ) is given by equation 1.

$$f^{\pm} = a^*/m^{\pm} \quad (1)$$

Since at saturation  $a^*$  is constant,  $f^{\pm}$  is proportional to the reciprocal of  $m^{\pm}$ , and these variables may be equated by a proportionality constant,  $k$ , for the existing temperature, as in equation 2.

$$kf^{\pm} = 1/m^{\pm} \quad (2)$$

While the value of  $k$  varies only with temperature, the value of  $f^{\pm}$  for saturated gypsum solutions varies with both the amount and kind of added salt present and temperature. When a salt is sparingly soluble,  $k$  may be evaluated by extrapolation of  $1/m^{\pm}$ , as calculated from experimental solubilities, to infinite dilution.<sup>8</sup> Likewise,  $f^{\pm}$  may be evaluated from experimental solubilities when  $k$  is known since  $f^{\pm} = (1/m^{\pm})/k$ . When  $k$  and  $f^{\pm}$  for gypsum are known under existing conditions, solubility may be calculated using the method of approximations.<sup>2</sup> This is done by first assuming a solubility, under existing conditions, and then calculating the value of  $k$ , using known values of  $f^{\pm}$ . This operation is repeated until the calculated value of  $k$  agrees with the known value of  $k$  (table 5).

#### Calculation of $k$ and $f^{\pm}$ for Gypsum Between 25 and 90 C

Plots of  $\log 1/m^{\pm}$  versus the cube root of the ionic strength ( $u^{1/3}$ ), for gypsum, were straight lines up to 15 epm of  $\text{NaSO}_4$  or up to 10 epm of  $\text{MgSO}_4$ , and evaluation of  $k$  was made using equations of the straight lines. Table 5 tabulates  $k$  data for temperatures between 25 and 90 C as calculated from the solubility data of tables 1 and 2. At 25 C, the value of  $k$  is reported as 182 by Lewis and Randall,<sup>9</sup> as 183 by Frear and Johnson,<sup>10</sup> and as 185.6 in the present work.

Data for  $f^{\pm}$ , corresponding to the solubilities tabulated in tables 1 to 4<sup>±</sup> were calculated using known values of  $k$ . Graphical interpolation of the experimental solubility data and of calculated  $f^{\pm}$  data, gives  $f^{\pm}$  in terms of  $u^{1/3}$  for combinations of common-ion salts, noncommon-ion salts, and temperatures existing in evaporative cooling water.

#### Tabulation and Use of $f^{\pm}$ Data

One must know  $f^{\pm}$  in terms of  $u^{1/3}$  for a very large number of combinations in order to meet all conditions existing in evaporative cooling waters. Such data are not reliable if  $u^{1/3}$  appreciably exceeds 0.50. (Figure 1; and reference 1, page 821).

If the type and ratio of added salt mixtures in a series of saturated

Table 5. Value of Proportionality Constant k

Temperature (°C)	k	Temperature (°C)	k
25	185.6	60	214.2
30	188.2	65	219.9
35	191.3	70	225.9
40	194.6	75	231.8
45	198.6	80	237.7
50	203.5	85	245.0
55	208.5	90	252.4

Table 6. Coordinates ( $y^{1/3}$ ,  $\log f^{\pm}$ ) at Intersection Points

Temp. (°C)	$u^{1/3}$	$\log f^{\pm}$	Temp. (°C)	$u^{1/3}$	$\log f^{\pm}$
25	0.3944	0.5459	60	0.3892	0.5008
30	0.3954	0.5364	65	0.3867	0.4976
35	0.3959	0.5278	70	0.3843	0.4945
40	0.3958	0.5205	75	0.3815	0.4923
45	0.3952	0.5137	80	0.3788	0.4908
50	0.3936	0.5084	85	0.3753	0.4898
55	0.3916	0.5041	90	0.3716	0.4896

Characteristics of all logarithms in this table are minus one.

gypsum solutions are kept constant at a fixed temperature, plots of  $\log f^{\pm}$  vs  $y^{1/3}$  are essentially straight lines, providing the total added salt content is not too great. The three curves of figure 1 represent the relation between  $\log f^{\pm}$  and  $u^{1/3}$  for three series of saturated gypsum solutions at 75 C. In the first series, the added salt is increasing amounts of  $\text{Na}_2\text{SO}_4$  (Curve 1); in the second series, increasing amount of  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  on an equal concentration basis (Curve 2); and in the third series, increasing amount of  $\text{NaCl}$  (Curve 3). The three curves intersect when no added salt is present and at all other points are separated in proportion to the fraction in equivalents per million of  $\text{NaCl}$  to total added salt.

The first of the needed points is the intersection point, and its location varies only with temperature. Data for its value is given in table 6. The second of the needed points is arbitrarily selected as that point having an x-coordinate of 0.50. The value of the y-coordinate varies both with the ratio of  $\text{NaCl}$  to total added salt and with temperature. The effect of the ratio of  $\text{NaCl}$  to total added salt on the location of the y-coordinate is shown in

figure 1. For the value of  $y$  at an  $x$  value of 0.50 under various conditions of added salt content and temperature, see table IX of reference 1.

The data for  $\log f^{\pm}$  between 25 and 90 C of the present paper fall on a reasonably smooth curve with  $\log f^{\pm}$  data between 182 and 316 C of Straub.<sup>4</sup>

To illustrate the calculation of gypsum solubility and the use of the various tables, solubility of gypsum at 25 C is calculated when the added salts consist of 7.56 epm of  $MgSO_4$ , 7.50 epm  $Na_2SO_4$ , and 22.56 epm of  $NaCl$ .

As a first approximation, assume that the solubility of gypsum is 30.6 epm. Convert all concentrations from equivalents per million to moles per 1000 grams to give:

<u>Salt</u>	<u>epm</u>	<u>Moles/1000 grams</u>
$CaSO_4$	30.60	0.01530
$MgSO_4$	7.56	0.00378
$Na_2SO_4$	7.50	0.00375
$NaCl$	22.56	0.02256

$Ca^{++} = 0.01530$  moles/1000 g and  $SO_4. = 0.02283$  moles/1000 g

The coordinates of the first point at 25 C are 0.3944 and 0.5459 (table 6).

Fraction of  $NaCl$  to total added salt (as epm) = 0.600. The value of the  $y$ -coordinate of the second point is interpolated as 0.4418 (reference 1, table IX).

The equation of the straight line relating  $\log f^{\pm}$  in terms of  $u^{1/3}$  is calculated as:

$$\log f^{\pm} = -0.9858 u^{1/3} + 0.9347$$

$$\mu = \frac{0.01530 \times 2^2 + 0.00378 \times 2^2 + 0.03006 \times 1^2 + 0.02283 \times 2^2 + 0.02256 \times 1^2}{2} \quad (3)$$

$u = 0.1103$  and  $u^{1/3} = 0.4793$

Using equation 3 and taking antilog,  $f^{\pm} = 0.2899$

$$1/m^{\pm} = 1/(0.01530 \times 0.02283)^{1/2} = 53.50$$

$$k = (1/m^{\pm})/f^{\pm} = 53.50/0.2899 = 184.6$$

The assumed value of gypsum solubility is high since the calculated value of  $k$  is low. Likewise, an assumed value of gypsum solubility at 30.4  $\mu\text{m}$  is also slightly high since  $k$  calculates to 185.3. Finally, an assumed solubility of 30.37 is correct since  $k$  calculates to 185.6. Experimental gypsum solubility under the specified conditions is given in table 4 as 30.38.

#### CALCULATION OF PROPORTIONALITY CONSTANT $k$ FROM THE ELECTRICAL CONDUCTANCE OF SATURATED GYPSUM SOLUTIONS

##### Discussion of Values of $k$ Derived from Solubility Data

As previously mentioned, the data for  $k$  summarized in table 5 were derived from experimentally determined gypsum solubilities in the presence of  $\text{Na}_2\text{SO}_4$  and/or  $\text{MgSO}_4$  over a range of temperatures. Under ideal conditions the value of  $k$  is independent of the type of added salt; under actual conditions it is somewhat higher in the presence of  $\text{Na}_2\text{SO}_4$  than in the presence of  $\text{MgSO}_4$ . During the evaluation of values for  $k$ , it was necessary to avoid the temperature range near maximum gypsum solubility (35 to 40 C) because the change in solubility for even 5 C change in temperature was small. Values of  $k$  through this temperature range were obtained from a smoothed curve of the available data.

Extrapolation to infinite dilution always involves uncertainty, especially when it is necessary to extrapolate a considerable distance, as in the present case. These uncertainties do not extend to calculated gypsum solubilities because any variation of  $k$  from its absolute value is reflected into a similar variation in  $f^\pm$ . The absolute accuracy of the calculated solubilities is of the same degree as the experimental solubilities (see tables 2 to 4).

Because of the uncertainties of extrapolation, it is of interest to have a comparison of data obtained from solubilities with those obtained by other methods.

Calculation of Equilibrium Conditions between  
0 C and 90 C from those at 25 C

When a saturated gypsum solution contains no added salts, solubility and  $m^\pm$  are identical and, if independent determinations of  $f^\pm$  were possible,  $k$  could be immediately calculated using equation 1.

Fossbinder<sup>11</sup> attempted to calculate  $f^\pm$  for a gypsum solution from the electromotive force of a cell containing calcium amalgam electrodes but the reproducibility was so poor that the results had little meaning.

The  $f^\pm$  of  $ZnSO_4$  at 0.01M (molality) and 0 C, as calculated from electromotive force measurements of a cell containing zinc amalgam electrodes, has been reported as 0.400,<sup>12</sup> and the freezing point depressions of  $ZnSO_4$  and  $CaSO_4$  at 0.01M have been reported as 0.0278 C and 0.0270 C respectively<sup>13</sup>: giving an  $f^\pm$  of  $CaSO_4$  at 0.01M and 0 C of 0.389. Extrapolation for the solubility of gypsum at 0 C<sup>14</sup> gives an  $f^\pm$  for saturated gypsum at 0 C of 0.362 and application of equation 2 gives  $k$  for gypsum at 0 C as 214.1.

Of all electrolyte properties, conductance ratio is one of the easiest to measure accurately, and it is unfortunate that this property is not a true measure of  $f^\pm$ . Failure of the conductance ratio to measure dissociation results primarily from the fact that the motion of the ions is retarded by interionic attraction forces.

If the conductance ratio and  $f^\pm$  of a saturated gypsum solution is known at a reference temperature, obviously a ratio or factor exists between the two at the reference temperature. In the present study, conditions at solubility equilibrium were calculated from conductance data on the assumption that this factor is constant over a temperature range and using a reference temperature of 25 C. The necessary data are given in tables 1 and 7 to 10, and the method of calculation is illustrated by a sample calculation at 90 C.

Solubility data for gypsum in water between 0 C and 90 C, expressed as equivalents per million (epm) and milliequivalents per liter (meq/l), are given in table 1. These data are used in all calculations requiring

Table 7. Electrical Resistance of Gypsum Solution at 0 C

<u>Concentration (M)</u> (millimole per Kg H <sub>2</sub> O)	<u>Reciprocal resistance</u> (10 <sup>4</sup> /ohms)
4.08	1.127
5.87	1.522
8.78	2.117
11.76	2.682

Cell constant = 3.651±0.013 ohm<sup>-1</sup> cm<sup>-1</sup>

"Data from Brown and Prue<sup>17</sup>

Table 8. Equivalent Conductance of Gypsum Solutions at Infinite Dilution

<u>Temp.</u> (°C)	<u>Eq. cond. at</u> <u>infinite dilution</u>	<u>Temp.</u> (°C)	<u>Eq. cond. at</u> <u>infinite dilution</u>
0	70.9	35	172.2
5	83.4	40	189.0
10	96.7	50	223.9
15	110.7	60	261.0
20	125.2	70	299.9
25	140.3	80	340.4
30	156.0	90	382.7

Table 9. Equivalent Conductance of Gypsum Solutions and Equations for Calculating Equivalent Conductance in Terms of Temperature

Conc. meq/l at t°C	Equivalent conductance at t°C			Equation" for equivalent conductance in terms of temperature
	18 C	25 C	50 C	
20	68.3	79.2	117.9	y = 1.5500x + 40.4
21	67.7	78.5	116.7	y = 1.5313x + 40.1
22	67.0	77.7	115.5	y = 1.5157x + 39.7
23	66.4	77.0	114.3	y = 1.4979x + 39.5
24	65.8	76.4	113.3	y = 1.4844x + 39.1
25	65.3	75.7	112.2	y = 1.4665x + 38.9
26	64.7	75.0	111.2	y = 1.4531x + 38.5
27	64.2	74.4	110.2	y = 1.4375x + 38.3
28	63.7	73.8	109.3	y = 1.4250x + 38.0
29	63.2	73.2	108.3	y = 1.4094x + 37.8
30	62.7	72.6	107.5	y = 1.4000x + 37.5
31	62.3	72.0	106.6	y = 1.3844x + 37.4
32	61.8	71.4	105.7	y = 1.3719x + 37.1

y is equivalent conductance and x is °C.

Table 10. Measured and Calculated Equivalent Conductance of Saturated Gypsum Solution

Temp. (°C)	Equivalent conductance	
	Measured	Calculated
0	40.74	-
5	46.82	-
10	52.56	-
15	58.85	-
18	62.91	-
20	65.30	-
25	72.3	-
30	78.6	79.1
35	85.5	86.0
40	92.6	93.0
50	107.2	107.4
60	121.0	122.4
70	134.0	138.3
80	146.0	154.1
90	156.6	171.1
100	166.4	-

solubility concentrations. Between 25 C and 70 C several of the solubilities were redetermined during the present study following the procedure of reference 1 and using primary standard calcium carbonate having an average purity of 100.0% in terms of Bureau of Standard's sodium oxalate; five replicates ranging from 99.9% to 100.1% were used. All other solubility data were taken from literature (table 1; references 1 and 15). Densities of saturated gypsum solutions at the several temperatures were obtained from the data of reference 16.

Equivalent conductances of saturated gypsum solutions between 0 C and 100 C are given in table 10. Specific conductance of a saturated gypsum solution at 0 C was obtained by extrapolating the specific conductance of undersaturated gypsum solutions, at 0 C, to the concentration of saturated gypsum solutions at 0 C. Data obtained from Brown and Prue,<sup>17</sup> table 7, gives a specific conductance at 0 C of 1055 micromhos; data obtained in the present study gives a specific conductance at 0 C of 1051 micromhos and at 5 C of 1276 micromhos. Specific conductances of saturated gypsum solutions between 5 C and 20 C were obtained from literature.<sup>18,19</sup> Equivalent conductances of saturated gypsum solutions between 25 C and 100 C were determined, using literature data at 25 C, 50 C, and 100 C<sup>20</sup> for calculating cell constants.

Equivalent conductances of gypsum solutions at 25 C and between 20 and 32 meq/l are given in table 9 and were interpolated from literature data.<sup>20</sup>

Equivalent conductances of gypsum solutions at infinite dilution, between 0 C and 90 C, are given in table 8.<sup>21</sup>

#### Calculation of k from Conductance and Solubility Data

Calculation of k from conductance and solubility data is illustrated by the following sample calculation at a temperature of 90 C.

Gypsum solubility at 90 C is 24.82 meq/l or 25.66 epm (table 1).

The equivalent conductance at 25 C, of a solution having the weight-volume concentration of a saturated gypsum solution at 90 C (24.82 meq/l) is interpolated as 75.8 (table 9), the equivalent conductance at infinite

dilution at 25 C is 140.3 (table 8), and the conductance ratio (CR) of this solution at 25 C is  $75.8/140.3 = 0.5403$ .

A gypsum concentration of 24.82 meq/l at 25 C = 24.84 epm and  $u^{1/3}$  calculates to 0.3676. Since at 25 C,  $\log f_{\pm} = 0.4541$  when  $u^{1/3} = 0.3944$  (table 6) and by definition  $\log f_{\pm} = 0.0000$  when  $u^{1/3} = 0.0000$ , it follows that up to a value of  $u^{1/3} = 0.50$  (page 821, reference 1),  $\log f_{\pm} = -1.151 u^{1/3}$ . Hence when  $u^{1/3} = 0.3676$ ,  $f_{\pm} = 0.3778$ .

Thus a gypsum solution at 25 C, having the same weight-volume concentration as a saturated gypsum solution at 90 C has CR = 0.5403 and  $f_{\pm} = 0.3778$  and the ratio of  $f_{\pm}$  to CR = 0.6992.

In the present calculations it is assumed that multiplying the CR of solutions at equal concentration but at temperature above or below 25 C, by 0.6992 will give  $f_{\pm}$  for that solution.

At 90 C, CR of saturated gypsum is  $156.6/382.7 = 0.4092$  and  $f_{\pm} = 0.4092 \times 0.6992 = 0.2861$ . Then  $k = (l/m_{\pm})/f_{\pm}$  (equation 2) =  $77.94/0.2861 = 272.4$

Similar calculations were made for other temperatures and the data are tabulated in column b of table 11.

Column a of table 11 contains k data between 25 C and 90 C obtained originally from solubility measurements (table 5). Reasonably good agreement exists between the data of columns a and b up to 60 C, but not thereafter.

When equivalent conductances for a given concentration of gypsum are plotted against temperature, the resulting curve is almost a straight line to 60 C and thereafter drops off. In order to project the straight line curve to 90 C, data for equivalent conductance between concentrations of 20 to 32 meq/l and at 18 C and 50 C were obtained by a combination of interpolating data from literature<sup>20</sup> and data obtained experimentally, followed by calculation of linear equations. Literature data for equivalent conductance<sup>20</sup> were used to calculate cell constants. The data so obtained are tabulated in table 9.

Table 11. Values of Proportionality Constant k for Gypsum

Temperature (°C)	Value of k at temperature °C and under conditions a to c		
	a	b	c
0	-	193.6	-
5	-	189.4	-
10	-	188.8	-
15	-	187.1	-
20	-	185.8	-
25	185.6	185.9	185.8
30	188.2	188.2	187.0
35	191.3	190.6	189.5
40	194.6	193.3	192.0
50	203.5	200.4	199.9
60	214.2	213.1	210.6
70	225.9	228.6	221.9
80	237.7	247.0	234.2
90	252.4	272.4	249.4

Column a - Data taken from table 5.

Column b - Data calculated using a value of k at 25 C of 185.6 and equivalent conductance of saturated gypsum as measured (table 10).

Column c - Data calculated as in column b except that equivalent conductance of saturated gypsum is from linear equations (table 9).

Application of the equations of table 9 to the solubility concentrations of table 1 permits the estimation of equivalent conductance of a saturated solution at the desired temperature. A comparison of measured and calculated values for equivalent conductance of saturated gypsum solutions is given in table 10.

Values of  $k$  for gypsum were then calculated as in the previous calculation except that calculated values of equivalent conductance were used in place of measured values. The data for  $k$  so obtained are tabulated in column c of table 11. It is noted that the data of column c is in agreement with corresponding data obtained from solubilities (column a) up to 90 C.

#### Discussion

In table 5 the values of  $k$  for gypsum rise smoothly with increasing temperature between 25 C to 90 C, no minimum occurring at the temperature of maximum solubility. The same increase occurs in the present study. However, the value for  $k$  of gypsum at 0 C obtained in the present study (table 11) does not agree well with the value calculated from  $f_{\pm}$  of  $ZnSO_4$  at 0 C.

The lack of agreement between the measured and calculated equivalent conductances of table 10 is not unusual. Since very soluble electrolytes ( $MgSO_4$  etc.) and undersaturated gypsum solutions behave similarly, reaction between solid phase (gypsum or hemihydrate) and complex ions (bisulfate), as discussed on page 820 of reference 1 is ruled out. Interionic attraction phenomena (asymmetry effect, electrophoretic effect, and ion association) are likely causes. The influence of these phenomena on solubility equilibrium should be minimal in the absence of a potential gradient.

Despite these irregularities it must be agreed that confidence should be placed on the reported calcium sulfate solubilities because of the good agreement obtained between  $k$  values derived by solubilities and by conductance and with experimental solubility values.

## PRACTICAL ESTIMATION OF GYPSUM SOLUBILITY

While the agreement between experimental and calculated gypsum solubilities is very good (see tables 2 to 4), these calculations are tedious. For practical use, a relatively easy empirical procedure has been devised for estimating gypsum solubility in cooling water containing up to 30 epm of common-ion salt and up to 40 epm of noncommon-ion salt.

This method uses a direct reading table (table 12) to give the gypsum solubility at 40 C in the presence of  $\text{MgSO}_4$  and/or  $\text{NaCl}$ , a chart (figure 2) to correct for decreased solubility in the presence of  $\text{Na}_2\text{SO}_4$ , and a second chart (figure 3) to correct for decreased solubility when the temperature is above 40 C. If the temperature is below 40 C, correction is made using the difference in solubility of gypsum between 40 C and the given temperature (table 1).

Practical estimation of gypsum solubility is illustrated using a saturated gypsum solution at 25 C containing 7.5 epm of  $\text{Na}_2\text{SO}_4$ , 7.56 epm of  $\text{MgSO}_4$ , and 22.56 epm of  $\text{NaCl}$ . Assuming the common-ion content to be entirely  $\text{MgSO}_4$ , gypsum solubility is interpolated from table 12 as 31.3 epm at 40 C. A correction of -0.8 epm is obtained from figure 2 for decreased gypsum solubility arising from 7.50 epm  $\text{Na}_2\text{SO}_4$ .

Finally, a correction of -0.3 epm, for decreased gypsum solubility arising from the difference in solubility between 40 C and 25 C, is obtained from table 1. Gypsum solubility = 30.2 epm.

The above procedure permits estimation of gypsum solubility to a maximum temperature of about 90 C. While it is less accurate than the approximation method, a combination of the two permits accurate calculations with moderate effort.

## ESTIMATION OF EVAPORATIVE CONCENTRATION

Figure 4 presents a graphical estimation of gypsum deposition and a procedure for estimating the limit of evaporative concentration. In figure

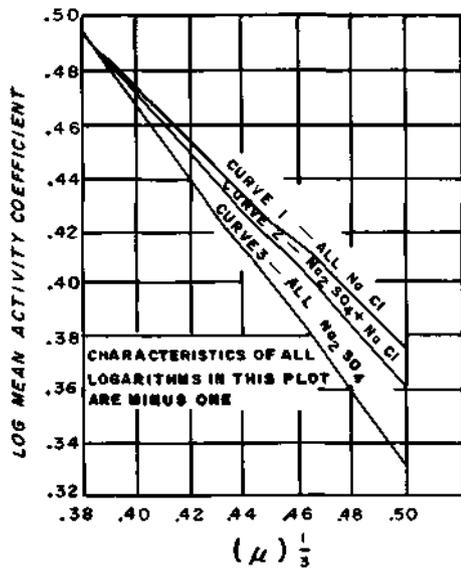


Figure 1. Log mean activity coefficient versus  $(\mu)^{1/3}$  for gypsum at 75 C in the presence of  $\text{Na}_2\text{SO}_4$  and or  $\text{NaCl}$

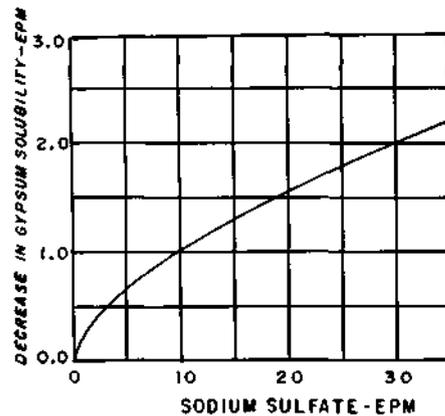


Figure 2. Decrease of gypsum solubility by sodium sulfate in common-ion salts

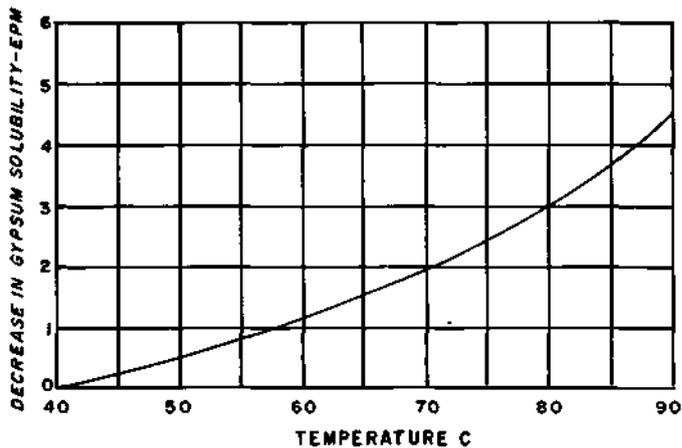


Figure 3. Decrease in gypsum solubility at temperatures above 40 C

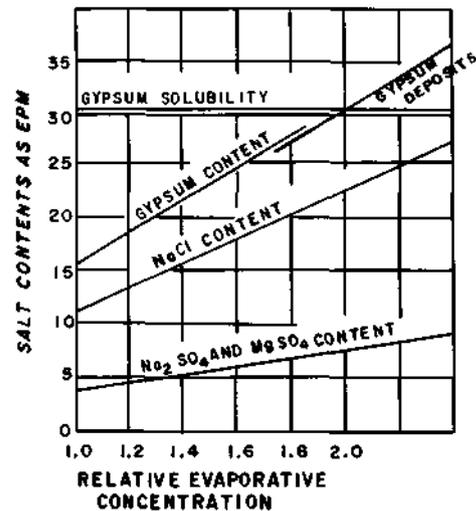


Figure 4. Graphical estimation of gypsum deposition

Table 12. Epm CaSO<sub>4</sub> at 40 C in Presence of MgSO<sub>4</sub> and NaCl

NaCl, (epm)	MgSO <sub>4</sub> (epm)																	
	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>12</u>	<u>14</u>	<u>16</u>	<u>18</u>	<u>20</u>	<u>25</u>	<u>30</u>
0	31.1	30.8	30.5	30.3	30.1	29.8	29.6	29.4	29.2	29.0	28.8	28.4	28.1	27.8	27.5	27.3	26.8	26.4
1	31.3	31.0	30.7	30.5	30.3	30.0	29.8	29.6	29.4	29.2	29.0	28.6	28.3	28.0	27.7	27.4	26.9	26.5
2	31.5	31.2	30.9	30.7	30.4	30.2	29.9	29.7	29.5	29.3	29.1	28.8	28.4	28.1	27.8	27.6	27.0	26.6
3	31.6	31.3	31.0	30.8	30.6	30.3	30.1	29.9	29.7	29.5	29.3	28.9	28.6	28.3	28.0	27.7	27.2	26.8
4	31.8	31.5	31.2	31.0	30.7	30.5	30.2	30.0	29.8	29.6	29.4	29.1	28.7	28.4	28.1	27.9	27.3	26.9
5	32.0	31.7	31.4	31.2	30.9	30.7	30.4	30.2	30.0	29.8	29.6	29.3	28.9	28.6	28.3	28.0	27.4	27.0
6	32.2	31.9	31.6	31.4	31.1	30.9	30.6	30.4	30.2	30.0	29.8	29.4	29.1	28.7	28.4	28.1	27.5	27.1
7	32.4	32.1	31.8	31.5	31.3	31.0	30.8	30.5	30.3	30.1	29.9	29.6	29.2	28.9	28.6	28.3	27.7	27.2
8	32.5	32.2	31.9	31.7	31.5	31.2	30.9	30.7	30.5	30.3	30.1	29.7	29.4	29.0	28.7	28.4	27.8	27.4
9	32.7	32.4	32.1	31.8	31.6	31.3	31.1	30.8	30.6	30.4	30.2	29.9	29.5	29.2	28.9	28.6	28.0	27.5
10	32.9	32.6	32.3	32.0	31.8	31.5	31.3	31.0	30.8	30.6	30.4	30.0	29.7	29.3	29.0	28.7	28.1	27.6
12	33.3	33.0	32.7	32.4	32.1	31.8	31.6	31.3	31.1	30.9	30.7	30.3	30.0	29.6	29.3	29.0	28.3	27.8
14	33.7	33.3	33.0	32.7	32.4	32.1	31.9	31.6	31.4	31.2	31.0	30.6	30.3	29.9	29.6	29.3	28.6	28.1
16	34.1	33.7	33.4	33.1	32.8	32.5	32.2	32.0	31.8	31.5	31.3	30.9	30.5	30.2	29.8	29.5	28.8	28.3
18	34.4	34.0	33.7	33.4	33.1	32.8	32.5	32.3	32.1	31.8	31.6	31.2	30.8	30.5	30.1	29.8	29.1	28.6
20	34.7	34.3	34.0	33.7	33.4	33.1	32.8	32.6	32.4	32.1	31.9	31.5	31.1	30.8	30.4	30.1	29.4	28.8
25	35.6	35.2	34.9	34.5	34.2	33.9	33.6	33.4	33.1	32.9	32.7	32.2	31.8	31.5	31.1	30.8	30.1	29.4
30	36.4	36.1	35.8	35.5	35.2	34.9	34.6	34.4	34.1	33.9	33.6	33.2	32.7	32.3	31.9	31.6	30.7	30.0
35	37.1	36.8	36.5	36.2	36.0	35.7	35.4	35.2	34.9	34.7	34.4	33.0	33.5	33.1	32.6	32.2	31.4	30.6
40	37.9	37.6	37.3	37.0	36.7	36.4	36.1	35.8	35.6	35.3	35.1	34.6	34.1	33.7	33.3	32.9	32.0	31.2

4 a relative evaporative concentration of 1 represents the concentration of the starting makeup water, and the intersection of the gypsum content - gypsum solubility curves at two relative evaporative concentrations indicates that gypsum deposits at two concentrations. The mineral content of some waters is too low to plot accurately (say only 1/10 of the example of figure 4). In such cases a preliminary concentration of 10 may be assumed and the appropriate factor of 10 applied to the limit of evaporative concentration of the original makeup water.

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## ALGAE AND THEIR CONTROL IN COOLING WATER SYSTEMS

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The algae are universally distributed in nature. Their normal habitat is wherever physio-chemical conditions exist for their growth and development such as in ponds, streams, and in industrial and municipal water systems. Although the majority of the algae are truly aquatic and are found submerged in water, there are also those types which are terrestrial.

One of the most interesting characteristics of the algae is that they are found in practically all parts of the world. Some species are generally considered as cosmopolitan, whereas others are only indigenous to specific areas. The universality of most species of algae and the localisms of others are governed by their physiological response to their environment and upon the method by which they are distributed in nature. The algae are transported from one locality to another principally by streams, rivers, birds, and the wind. The birds are probably one of the most important means of transporting algae from one place to another. The algae can be carried by birds in the partially dried mud which adheres to their claws and by lodging in their feathers. The migratory aquatic birds can carry these algae great distances. The distance, of course, will vary with the migratory and feeding habits of the birds. The wind can also play an important role in the dissemination of algae. It has been demonstrated that the prevailing winds and other wind currents play an important role in the dissemination of plant pathogens.

The algae are members of the lower class of plants. They differ from other microscopic plants in that they possess the green pigment chlorophyll. The green color of the chlorophyll is often masked by the presence of other colored substances. Hence, all algae are not green in color. The algae, like the higher plants, can manufacture their own food with the process

known as photosynthesis. This process of manufacturing food is absent in fungi, yeasts, bacteria, protozoa, crustaceans, and many other forms of microscopic life.

Although light is essential for photosynthesis, the algae like other chlorophyll-bearing plants differ in their response and in their tolerance to light intensity. Some species of algae grow equally well in shaded areas and under high illumination. On the other hand, some of the aerial algae will grow only in shaded areas. The algae growing on the surface of ponds, in shallow streams, and in the distribution troughs of open-deck cooling towers are considered as growing in direct sunlight. Those species of algae which normally grow deeply submerged in lakes or ponds are not so fully illuminated and would probably cease to exist in direct sunlight or under high light intensity. There are also those species which can grow in the dark. Some of the species of algae which have been found growing in dark portions of fresh and industrial cooling water systems are species of Euglena, Chlorococcum and Anacystis.

Temperature, like sunlight, has a limiting effect upon the growth of any single species of algae. These organisms can grow over a broad temperature range. They can be found growing in ice water as well as in hot springs. However, the majority of the algae prefer to grow in a cool to moderate temperature range. Those species commonly found in cooling water systems appear to have an optimum range between 15 and 25 degrees centigrade. In general, the algae which are native to the tropics or which grow in warmer environments will not usually survive the winters in a temperate climate. The low temperature algae are often present in such numbers that they will color snow red, yellow, green, or brown.

The elements essential for the growth of algae are in general the same as those required for the growth of the higher plants. Silicon is required by the diatoms. Calcium and magnesium may be the limiting elements for many species. There are usually a greater number of algae in hard water than in soft water primarily because of the utilization of dissolved bicarbonates. However, the total mineral content of a given water does not appear to have too great an effect upon the growth and development of algae in nature.

Under laboratory conditions the mineral content of a nutrient medium may have a very definite effect, and in many cases is the limiting factor for their continued growth and development.

The algae are truly ubiquitous. They can be found living in fresh water, sea water, or in relatively high brine. Although most species of algae are considered as aquatic, there are those species which are considered terrestrial or aerial. The terrestrial algae obtain water from air and are able to endure long periods of drought. These algae are found on the bark and leaves of trees, on rocks, stone cliffs, and upon the exposed portions of cooling towers, particularly in those areas which are only occasionally wetted due to spillage of water or to an occasional spray.

The size and shape of algae vary greatly. If normal fresh water algae grew as large as normal plants, they would be cultivated as ornamentals because of their beauty and geometric design. The algae vary in size from several microns in diameter to several hundred feet in length. The large species are the marine types and are of no great significance in industrial water systems even in those systems which use sea or brackish water on a once-through basis.

One of the principal reasons why algae are important is their ability to produce large numbers in different water systems. For example, it has been estimated that in Wisconsin more than 130 tons of algae per day flow into the Fox River from Lake Winnebago.<sup>2</sup> Later studies reported by Wisniewski showed the distribution and populations of different algae in the Fox River. Algal counts in excess of 100,000 per milliliter had been reported for the White River in Indiana.

In both municipal and industrial water systems the algae are responsible for significant losses due to operational problems. They produce objectionable odors and taste and in general adversely affect the quality of the finished product. In water treating plants the algae clog filters, color the water, and produce objectionable odors and taste. In addition, algae may change the chemical characteristics of water such as pH, total alkalinity, general mineral content, and turbidity.

During the period when the algae are exposed to light they consume carbon dioxide and release oxygen. During the periods of darkness the algae consume oxygen and release carbon dioxide. Thus, this reversal in process results in daily variation in pH and in the carbonate content of the water. This phenomenon has also resulted in many industrial problems as well as being directly responsible for fish kills in those lakes and rivers which are heavily seeded or support the prolific growth of algae. The algae can also become major problems in many industries such as the pulp and paper, and the electronics industry.

An interesting industrial problem occurred in a paper mill. In this case the presence of algae caused no particular problem during the general manufacture of the paper; however, the result produced in the finished paper was disastrous. In this particular case the algae became a component of the paper and as a result became a part of the finished sheet. During the drying operation the algae in the paper were killed, but the small amount of fat present in each of the cells resulted in an area which refused to absorb the developing chemical. This refusal to absorb the chemical resulted in a product which was wholly and completely unsatisfactory as a blueprint grade of paper. The growth of algae in the piping and other equipment in the water systems in an electronic plant has also resulted in serious losses in production time and in the final rejection of a large number of television and other similar tubes. The presence of algae causes poor adherence of chemicals on the surface of the glass as well as producing voids in the essential coating.

Although slime deposits are commonly considered to be the result of the growth and development of bacteria and fungi, there are slime formations which are caused by slime forming algae. These deposits can be found in reservoirs, water lines, in cooling condensers, and so forth. Rarely, however, will the deposit be composed only of algae. Usually the deposits will be a combination of bacteria and algae. Although light is necessary for the growth of algae there are those species which can grow in the dark. Although a large variety of algae can be associated with slime, it is the blue-green algae which are the most common. This group of algae contain

those species which produce heavy mucilaginous capsules or sheaths.

The algae growing either as localized patches or as heavy slime accretions can produce metabolic products which set up cell action, which in turn can corrode concrete and metal pipes. Corrosion can also be attributed to or accelerated by the production of oxygen and carbon dioxide. In addition to their effect upon industrial and municipal water systems the algae have caused an unestimable amount of damage to recreational areas and to farm animals. Perhaps the most dramatic and publicized effect of algae upon aquatic life is the condition known as red tide. This condition is produced only in the ocean and occurs periodically along the Southeastern Gulf Coast of the United States. The red tide is caused by a very large number of flagellates, which gives the sea water its characteristic red color. During the period of the red tide many fishes are killed.

There are also reports on the toxic effect of fresh water algae to man and animals. Symptoms of dermatitis and hay fever have been reported also. In addition, the algae have been implicated in some gastrointestinal upsets. There are many records on the toxic effect of different species of algae to domestic and wild animals. In all cases the blue-green algae are the causative organisms. The animals most commonly affected are cattle, horses, sheep, pigs, rabbits, and in general those animals which drink from lakes, ponds, and streams. Anacystis, a blue-green algae, is most commonly involved with the death of these animals.

To determine the role that algae may play in different industrial problems it is necessary to know the types and number of algae present. There are several different procedures that can be used to enumerate algae in different waters. Obviously, some species of algae are more readily enumerated than others. In some cases, where the species and the nutrient requirements are known, it is possible to count the algae with standard bacteriological count procedures. A more direct and rapid procedure, which has been found to be very helpful in evaluating the role of algae in slime formation and in industrial fouling, is the direct microscopic count. This procedure consists simply of counting the number of algae in a known volume of water. This is accomplished readily with the use of Palmer's Nanno-

plankton Counting Cell. In general, cooling water systems usually contain a large number of diatoms. These organisms appear to grow very readily in most systems but their significance has not been demonstrated. However, the presence of a large number of diatoms in water will undoubtedly have an adverse effect upon filters and other water treating equipment. The diatoms, however, have been associated with and implicated in such specific problems as in-plant water purity in those plants which produce television tubes and the sort.

It is axiomatic that the growth and development of algae must be controlled in water systems. It may, however, not always be desirable or practical to completely eliminate the algae from a water system. In order to control the growth and accretion of algae in water systems to a point where they do not contribute to corrosion, fouling of filters, effect upon heat transfer, and so forth, it is necessary to understand their sensitivity to different chemical agents.

The method of evaluating an algaecide that has been found to be practical in the laboratory is a modification of the procedure suggested by Palmer and Maloney. Briefly the procedure consists of growing the test algae in a suitable culture media. This culture media is prepared, sterilized, and dispensed into Erlenmeyer flasks. The proper aliquot of the algaecide under test is then added to each of the culture flasks. This medium is thoroughly mixed and inoculated with the desired test organism. The inoculated flasks are then placed under illumination and allowed to incubate at 72 F. After 21 days of incubation observations are made for the amount of algal growth in each flask. The concentration at which no visible growth occurs in the culture media is considered as the inhibiting concentration.

The type of test organisms will vary with the problem at hand. For example, if a particular species of algae is extremely troublesome in a given system the relative toxicity of several different materials can be determined either for the pure species of the algae or for the composite as it is found in that particular system. The test substrate may be a

medium prepared in the laboratory or it may be the water from the system in which the organism was obtained or isolated. We have found that several species of algae are excellent test organisms; however, the species most commonly used in our studies are Chlorella pyrenoidosa, Euglena gracilllis, and Scenedesmus obliquus. The inhibiting concentrations for several different chemical compounds as evaluated under laboratory conditions are given in table 1. Several formulations are included also in table 1 primarily to demonstrate the relative merits of specifically formulated products over straight chemical compounds. This difference is more pronounced when comparisons are made between several different test organisms and under practicable field conditions.

Although most of this discussion has concerned algae, many of the principles involved in the control of algae in industrial plants apply to the control of other species of troublesome microorganisms. These other species of microorganisms would include the bacteria, the fungi, and certain species of the animal kingdom. The marine species of the animal kingdom are also involved in industrial fouling, principally species of mollusk. A recent introduction of an Asiatic species of a serpulid worm resulted in a serious industrial problem. This marine animal produces a calcareous scale which fouls and restricts the flow of water in flumes and pipes. This has become a very serious problem in certain brackish or salt waters. The organism will grow rapidly and reduce the diameter of a pipe an inch every two to three months.

Although there is a similarity in the application of algaecides and other biocides to industrial water systems, the selection of the proper biocide is extremely important. Usually the biocide that will adequately control bacterial and fungal slime accretions will also control algae and the fouling due to the lower species of the animal kingdom. However, where fouling is caused principally by either the algae or the animal kingdom, the selection of the biocide should be made on the basis of controlling these specific species. The algaecides in general are fed at lower concentrations than the biocides employed for either bacterial or fungal slime control because they are generally less effective and con-

Table 1. Relative Toxicity of Different Chemicals to Three Different Species of Algae

<u>Chemical</u>	Test organisms		
	<u>Chlorella</u> <u>pyrenoidosa</u>	<u>Euglena</u> <u>gracillis</u>	<u>Scenedesmus</u> <u>obliquus</u>
	(Inhibiting concentration in ppm)		
8-hydroxyquinoline	5	150	5
Lauryl pyridinium chloride	3	100	0.5
Copper sulfate	400	1000	50
Copper naphthenate (8%)	200	200	50
2,3,dichloro-1,4 naphthoquinone (50%)	0.5	1	50
phenylmercuric acetate	1	0.5	1
Rosin amine D acetate (50%)	3	500	100
3-(3,4-dichlorophenyl)1,1-dimethylurea (80%)	6	200	1
Copper dichloroisocyanurate	3	100	100
Alkyl (C <sub>12</sub> -C <sub>16</sub> )dimethylbenzylammonium chloride (50%)	2	40	10
3,5 dimethyltetrahydro 1,3,5 2H thiadiazine-2-thione	8	10	15
Terramycin (45)	25	100	25
Acrolein (technical)	0.5	3	8
Combination of sodium pentachlorophenate, sodium dimethyldithiocarbamate, and alkyl (C <sub>12</sub> -C <sub>16</sub> ) dimethylbenzylammonium chloride	10	10	6
Combination of alkyl (C <sub>12</sub> -C <sub>16</sub> ) dimethylbenzylammonium chloride and tributyl tin oxide	2	5	8
Combination of methyldodecylbenzyl trimethyl ammonium chloride, methyldodecylxylene vis (trimethyl ammonium chloride), and tributyl tin oxide	3	80	15

sequently would be ineffective against the slime forming organisms. Therefore, wherever an algae problem predominates it is, of course, most economical to treat the system to control this particular species.

Thus in selecting the proper algaecide for a given water system, it is best to first determine the types of organisms present and to determine their resistance to specific biocides. The relative toxicity of different biocides can usually be determined in the laboratory; if it is not practicable to develop this information immediately for a specific system, previously published data may serve as an adequate guide. However, in any event, it is best to determine the nature of the biological complex in the slime accretion and to determine the causative organism(s). This can often be accomplished by a thorough microscopic examination of the slime deposit and a study of the variables which may affect plant operating conditions, chemical composition of the water, and any other conditions which are germane to the entire operation.

After the biocide has been selected, it is necessary to determine which method of application will give the most satisfactory and economical results. It is best to determine the point and method of application for each specific system. In some cases the choice can be made on the basis of sound scientific data, and then on the other hand, there are those systems where the choice must be based upon a combination of scientific principles and sound practical experience. The method of applying the selected biocide can be continuous, intermittent (shock), or a combination of continuous and shock. Formulas have been developed to determine the maximum contact time permitted for a biocide in a given system when the material is fed on a continuous basis. This formula can be expressed as follows:

$$\text{Contact time, days} = V/BD$$

V = volume of water contained in the system, gallons

BD = blowdown and windage losses, gallons per day

A formula<sup>3</sup> has also been found to be practicable in the application of a shock treatment when the concentration of the biocide has been depleted

to 25% of the original. This formula can be presented in its simplified form as follows:

$$T = 1.385 (V/BD)$$

T = retention time, days

V = system capacity, gallons

BD = blowdown and windage loss, gallons per day

These formula are useful only when the biocide employed is not readily depleted from the recirculating, by aeration, or by detoxification by the product produced or other contamination of the water.

In some severe slime problems, it may be necessary to first treat the recirculating water at a relatively high dosage rate. A satisfactory procedure is to reduce the volume of the water in the sump to the lowest permissible operating level. The blowdown is shut off. The biocide is then added at the previously determined dosage rate. This concentration is maintained at this level for at least three days. During this period of time, makeup water is added to maintain the proper cycles of concentration. Additional biocide is added daily in an amount to treat the makeup water at a level and to maintain the original dosage level in the system. After the third day, the blowdown valve is opened and the system restored to its proper water level and operation.

After the system has been cleaned of slime deposits, a regular treatment regime should be followed. This treatment regime should take into consideration the rapidity of action of different biocide(s), the types or organisms responsible for the problem, compatibility of the biocide with relation to the other treatments employed in the water system, and local conditions governing the discharge of plant effluents into receiving streams. Thus, the evaluation of any biocide for any given water system requires the consideration and the evaluation of a large number of factors.

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## COOLING WATER CONTROLS

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Cooling water systems are designed to provide adequate cooling of process fluids or gases. The design engineer puts his best knowledge and experience into each system. His purpose is to provide trouble-free operation, long life of equipment, and maximum design efficiency to the user of this equipment. Assuming proper engineering design, the system will provide adequate cooling as long as the original design characteristics are unchanged. However, a number of factors involved in system operation influence design characteristics and can cause unsatisfactory cooling system performance.

The majority of the problems that cause unsatisfactory operation come from the water used in the cooling system. The water itself can and does cause interferences; however, the greatest cause is the contaminants carried by the water. These contaminants can cause severe loss in heat transfer efficiency and rapid deterioration of metal and nonmetallic components. Water, the universal solvent, can rapidly dissolve metallic components. Proper control of the water and its contaminants will provide satisfactory cooling system operation. The problems caused by the water and its contaminants are categorized as scale, corrosion, fouling, and/or microbiological activity. The controls maintained on recirculating cooling water are all designed to eliminate or minimize these four problems.

### Water and Its Contaminants

The water added to recirculating systems replaces water lost generally by two ways: 1) evaporation as a vapor, and 2) bleed-off or unintentional losses as a liquid. The makeup water can come from many different types of sources such as rivers or wells and in any type of condition – clean or dirty, pure or contaminated. This water can be the greatest source of

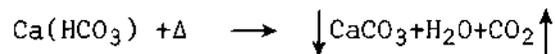
contaminants or it may be the least source. Though water is important to consider in the control of the common problems, it is not the most important; the contaminants present in the system are the main causes of problems. Controls should be designed for the system water and its contaminants.

Let's consider the why, what, and when of cooling water controls.

Why Control?

Without any of the important controls, the common problems that cause inefficient cooling operations are easily and quickly observed. These problems result from the characteristics of system operation. The water temperature is raised. The water is aerated. Dissolved and suspended solids are concentrated as a result of water evaporation. New dissolved solids are added. Suspended solids and microorganisms are scrubbed from the air. Examples of each important type of problem are:

Scale. Normally soluble constituents such as calcium, magnesium, and silica will overconcentrate and will precipitate as a hard scale on heat transfer surfaces. This scale will significantly reduce heat transfer rate in the system. For example:



Corrosion. The oxygen saturated water will be aggressive to system metals and will cause corrosion. The accumulation of corrosion products will reduce the heat transfer rate.

Fouling. The suspended solids from the raw water supply, from air scrubbing, clarifier carryover, or corrosion, will settle from the flowing cooling water stream on heat transfer surfaces. This will not only reduce heat transfer efficiency but will also start corrosion due to differential oxygen cells established beneath deposits.

Microbiological Growth. Microorganisms from the raw water or scrubbed from the air find a favorable environment in the higher temperature, more nutritive cooling water stream. These organisms will multiply to form visible deposits. These deposits will then reduce heat transfer efficiency

and promote corrosion in much the same way as will inorganic suspended solids. In addition, certain microorganisms, such as *Desulfovibrio* and *Clastridia*, can, by the generation of corrosive gases, directly result in system metal deterioration.

All or only one uncontrolled problem can cause reduction in operative efficiency of the cooling system. Often the lack of control on one problem such as microorganism control can cause all other controlled problems to be adversely affected or even fail completely. Complete system control is the only effective control.

What Controls?

Only those whose purpose is preventing operating problems should be employed. It is also important to realize that overcontrol can be a problem -- establishing too many control limits can pointlessly increase the total complexity and cost of system operation. The proper controls to be established must be selected on the basis of the potential problems in the particular system and, more important, on the limits of the treatment program. The guiding principle should be -- "Maintain the minimum control that will provide acceptable system efficiency with your treatment program."

Scale Control. Scale control is primarily dependent on the solubility constants of many different compounds. Calcium salts offer the greatest scale potential. In an untreated system calcium carbonate is usually the first compound to form scale. In a system with chemical treatment, several different compounds may be the primary component of scale: calcium sulfate, calcium phosphate, and silica. Maximum solubility levels of each potential scale compound that can be tolerated in the system water depend upon the type of treatment used in the water. Important factors to consider for a treated water are shown in table 1.

A useful tool in determining control limits to avoid calcium carbonate scale formation is the Ryznar Stability Index (Stability Index =  $2pH_s - pH$ ). The interrelationships involved in calculating the Stability Index are easily reduced to mechanical computing devices. However, it should be

Table 1. Factors Involved in Scale Formation

pH	Phosphate
Alkalinity-	Temperature
Calcium	Dissolved solids
Magnesium	Silica
Sulfate	

Table 2. Typical Control Limits for Commonly Used Treatments

<u>Treatment</u>	<u>Common controls to prevent scale</u>
Polyphosphate type	Calcium (as CaCO <sub>3</sub> ) - 400 ppm max pH - 6.0-6.5 Silica (as SiO <sub>2</sub> ) - 150 ppm
Organic-phosphate type	Calcium (as CaCO <sub>3</sub> ) - 800 ppm max pH - 6-7 Silica (as SiO <sub>2</sub> ) - 175 ppm
Chromate type (no phosphate)	Calcium (as CaCO <sub>3</sub> ) - 1000 ppm max pH - 6-7 Silica (as SiO <sub>2</sub> ) - 150 ppm
Organic-chromate type	Calcium (as CaCO <sub>3</sub> ) - 1200 ppm max pH - 6-8 Silica (as SiO <sub>2</sub> ) - 175 ppm
Organic-based	Calcium (as CaCO <sub>3</sub> ) - 1000 ppm pH - 7-8 Silica (as SiO <sub>2</sub> ) - 225 ppm

remembered that this calculation measures only the tendency toward calcium carbonate precipitation and gives no indication of the tendency towards the formation of scales of other materials.

The tendency toward other pure scales (such as tri-calcium phosphate) can also be reduced to chart calculation. However, it is extremely difficult to accurately predict the specific composition of a scale that will form from the heterogeneous composition of the average recirculating cooling water. Therefore, each system water must be considered and appropriate separate controls selected in order to avoid the most likely types of scale formation from that water.

Typical controls and limits used with commonly used treatments are given in table 2. These control limits require consideration of system flow, temperature, and other nonscaling contaminants.

Corrosion Control. The general approach for corrosion prevention has been the establishment and maintenance of protective films by chemicals such as chromate, phosphate, zinc, cadmium, ferrocyanide, or certain proprietary organic formulations in the tower water. Water is used to carry the chemicals to the metal surfaces to be protected. The controls involved in corrosion inhibition, then, are those controls necessary to assure the formation and maintenance of these protective films. The most effective chemicals are proprietary formulations. Phosphate, chromate, or other tests are generally used to control levels of treatment. With new organic, nonphosphate, nonchromate, corrosion inhibitors, control is by color or special tests.

Control levels for the various corrosion inhibitors are provided by the suppliers of these formulations. Attention must be paid to their recommendations, since their familiarity with specific treatments makes them aware of controls for best results.

Average control levels of chemical treatment to provide corrosion inhibition without dangers of producing scale or foulants from the treatment are shown in table 3.

To provide maximum corrosion protection, the best control is to maintain proper inhibitor levels. This does not always mean that if some is good, more is better; higher than recommended dosages may worsen results depending upon the treatment program.

Other important considerations that should be made as controls are the reactions of inhibitors with: minerals in the water, contaminants from the air or process, organics in the water, system construction chemicals, and any foreign substances continuously or periodically added intentionally or accidentally into the system water. Often these adversely affect the inhibitor or contribute to fouling that prevents the inhibitor from performing properly.

Fouling Control. Fouling is differentiated from scale by the physical characteristics of the deposit. Fouling is generally softer, more voluminous, and more subject to physical factors such as velocity and flow patterns. The controls that are established to prevent fouling deal with limits on these physical factors and on chemical factors that can influence the amount or condition of suspended solids and the type of treatment used to control fouling. Such factors can include any or all of the factors as shown in table 4.

The control limits set must depend on the conditions existing in the particular system; all these factors are related and must be considered individually and collectively for each system.

The control levels to prevent fouling will depend greatly on the chemical treatment being added to the system. Processed organic formulations designed for the specific task of fouling prevention have been available for some years. If such a treatment is being used, higher limits of most fouling constituents can be effectively controlled and more adverse temperature and flow conditions can be tolerated. Combinations of these factors can be accepted where treatments without antifoulants would fail.

Microbiological Control. The raw water introduced to the recirculating cooling system will generally contain living microorganisms -- bacteria, algae, fungi. Organisms will also be scrubbed from the air into

Table 3. Typical Control Levels  
for Corrosion Inhibition

<u>Treatment type</u>	<u>Dosage (ppm)</u>	
	<u>Initial</u>	<u>Maintainence</u>
Polyphosphate-based (PO <sub>4</sub> )	40-60	20-40
Organic-polyphosphate-based (PO <sub>4</sub> )	40-60	10-20
Chromate-phosphate (CrO <sub>4</sub> )	40-60	15-30
Chromate-based (CrO <sub>4</sub> )	40-60	15-20
Organic-chromate (CrO <sub>4</sub> )	40-60	5-15
Organic-based (total treatment)	200-300	50

Table 4. Factors Influencing Fouling

Makeup water contamination	Process contamination
Holding time	Type of corrosion inhibitor
Suspended solids	Velocity
Iron	Temperature
Manganese (Mn)	pH
Alumina (Al <sub>2</sub> O <sub>3</sub> )	

the water. When these organisms multiply to form visible deposits, a fouling and/or corrosion problem exists. Therefore, it is desirable to keep the concentration of microorganisms below the level at which visible deposits appear.

The generally accepted technique of microbial control involves the continuous or periodic addition of a toxic material to the recirculating water. This provides a regular reduction of microbiological concentration so that organisms never reach the level of deposit formation. Obviously, one control limit on microbial activity is the absence of deposits. However, this is a "go - no go" type of control which is unsatisfactory in that its application permits the deposit which the control is intended to avoid. A more rational control involves periodic analysis of system water for microorganism concentration. Empirical data gathered over a number of years from operating systems indicates that if organism counts per milliliter in the recirculating water are kept below certain levels, it is extremely unlikely that microbiological deposits will form. These levels vary with the type of organism involved (see table 5).

As with other control limits, the figures in table 5 cannot be applied to every system without a thorough consideration of system operating and contamination characteristics.

#### When Control?

Whenever a set of control limits is selected for a particular cooling water system, it is clear that these limits should be maintained to prevent scale, corrosion, fouling, and microbiological growth. In this sense, cooling water controls should be maintained on a continuous basis. This is not to say that each of the water characteristics selected for control purposes should be monitored continuously (although some may be) but rather to indicate that the control testing program, once the test frequency is decided on, must be considered as providing continuous protection to the system.

The physical and environmental characteristics of the individual system play an important part in determining the frequency with which any

Table 5. Tolerable Levels of Various Troublesome Organisms

<u>Organism type</u>	<u>Organisms/ml</u>
Bacteria	
Non-sporeforming	50,000
Sporeforming	100
Corrosive	0
Iron-depositing	0
Fungi	100
Algae	Few
Total bacterial count	500,000

Table 6. Minimum Daily Analyses Cooling Tower Systems

<u>Test</u>	<u>Frequency</u>
pH and/or alkalinity	Once/shift
Inhibitor level (PO <sub>4</sub> , CrO <sub>4</sub> , organic)	Once/day
Cycles of concentration (NaCl, dissolved solids, calcium)	Once/day

single control test will be performed. The general principle in determining control frequency should be - the more serious, more likely, or more rapid a variation in water characteristic, the more frequent should be the control test for that characteristic.

Concentrated sulfuric acid is used in most moderate or large recirculating cooling water systems for pH and alkalinity control. Relatively slight variations in acid feed can very rapidly cause wide fluctuations in system pH and alkalinity. Such a variation can cause an extremely severe corrosive or scaling condition. For this reason, a frequent measure of system water pH or alkalinity is more desirable.

Many systems have recirculating water pH monitored continuously and plotted on a pH cell-recorder device. Systems also have controlling devices so that variations from pre-set limits will increase or reduce acid feed from chemical equipment. The use of a pH recorder-controller is the ultimate today in pH control. However, these instruments require maintenance for optimum performance.

Generally speaking, other water characteristics are not measured on a continuous basis. This is due to the lack of analytical equipment capable of reliable continuous monitoring. Devices have been marketed recently however which can continuously measure water characteristics such as hardness, silica, phosphate, and residual chlorine.

The technique which has been most widely accepted is based on a minimum of chemical analyses selected to measure system acidity or alkalinity, level of dissolved and/or suspended solids, and the concentration of chemical inhibitor present (see table 6).

Other water characteristics, such as concentration of iron, alumina, chlorine, sulfate, hardness, and contaminants may be of particular importance to an individual system and, because of this, tests for these characteristics may also be included in the regular testing schedule.

Because of system characteristics it may be necessary to perform routine tests more frequently. Examples are wide fluctuation of water requirements, effect of contaminants on pH or treatments, and use of

different water supplies.

Control testing for microbiological conditions is generally performed on a much less frequent basis than is testing for inorganic water constituents. The reason for this is twofold. First, the development of microorganisms to the point of visible deposits in the average system is a slower process than the development of problems due to variations in inorganic water characteristics. Secondly, these control tests are more difficult in regard to equipment and experience necessary for proper interpretation. For these reasons, microbiological control tests are generally run on a once or twice per month basis as a part of the service provided by water treatment chemical suppliers.

Who Controls?

The principal responsibility for the control program should be held by system operators since test results may dictate immediate corrective measures. Fortunately, most control tests are easily understood and can be run quickly.

In some large plants, the responsibility for chemical control testing has been assigned to laboratory personnel. This sometimes results in a higher degree of accuracy in test results; however, this procedure has a danger. . Lack of communication between laboratory and operating personnel can delay a need for corrective action long enough to permit severe deposition or corrosion to occur. If laboratory control testing appears to be desirable in a particular plant, very definite policies should be established so that recirculating cooling water system operators are immediately advised of any variations from recommended control limits discovered by laboratory personnel.

System Characteristics Versus Controls

Although the physical characteristics of a particular recirculating cooling system play a vital role in the entire question of system controls, the effects of such characteristics are all too frequently overlooked.

To assure optimum results, consideration must be made of both system physical characteristics and water quality in establishing an effective control program.

The system capacity, metallurgy, operating characteristics, and equipment types are the basic design factors influencing control.

The system holding capacity, its turnover (holding capacity in gallons divided by recirculation rate) and the cycles of concentration carried provide a measure of water retention time. This often is referred to as the holding time index (HTI) or half-life of the system. Long HTI of 48 hours or more will tend to moderate or slow swings in recirculating water quality that might be caused by variations in treatment. For example, a spill of acid into a system with a long holding time index would be expected to provide a less rapid change in pH than a similar spill into a system with a relatively short HTI. Therefore, testing for pH in a large system could, conceivably, be performed on a less frequent basis. Conversely when systems have a long HTI it takes much longer to correct adverse conditions of pH, contamination, or low inhibitor levels. For this reason, certain control tests, such as chromate concentration, may have to be performed more frequently on larger systems.

Similarly, system metallurgy can influence the control program. Physically joined dissimilar metals in a system can lead to corrosion problems which, in turn, can lead to problems of scale and/or fouling. Widely different types of metals in a system, such as the presence of copper alloys and aluminum or mild steel, can influence metal loss due to plating. Though corrosion control in a system may be effective for mild steel, sufficient copper can plate on aluminum to cause failure within a few months. Often the chemical treatment and its associated control program will be controlled by the various types of metal in the system.

Operating characteristics can also influence the control program. A particular heat exchanger may operate under particularly high temperature conditions and, because of this, special controls may be required on the entire system or, at least, special control attention may have to be paid

to this particular exchanger to avoid problems of corrosion, scale, or fouling.. The system may operate 8 out of 24 hours, or the heat load may vary greatly, or steam condensate may be added occasionally, or the wind may cause acidic or alkaline gases to be picked up by the tower. These operating characteristics influence not only the control program but the treatment considerations as well. It is important to be aware of the usual and the unusual operation of the system to effectively control against a program failure.

Equipment types in the system can also influence the control program. Low water velocity equipment (such as compressor jackets or shell-side cooling water) provide a more severe potential for scale and fouling. Other types of equipment that can cause an effect on a control program are: refrigeration machines in air conditioning; barometric condensers; reaction vessel jackets (alternately heating and cooling); flash heaters; multi-pass heat exchangers; elevated overhead condensers; and compressor jackets and carrying lines. Any control program should be so designed as to pay particular attention to the types of equipment used in the entire system.

The makeup water, added to the recirculating system is as influential on the final control program decided on as is the chemical corrosion inhibiting or antifouling treatment being used.

For example, a makeup water which is high in iron will dictate a more frequent analysis of total and soluble iron in the recirculating cooling water. A makeup water suspected of being high in microbiological organisms (such as sewage effluent) will dictate more stringent microbiological control testing. A makeup water drawn from a clarifier will require relatively frequent testing for alumina or iron in the recirculating cooling water.

Therefore, the characteristics of the recirculating system and of the makeup water, although relatively inflexible, must also be considered in determining the most effective control program.

## Conclusions

In conclusion, it may be said that every recirculating cooling water

system must have an effective control program to enable the treatment to provide long life and trouble-free operation and indicate when changes in system operation must be made. The absence of important controls can cause rapid metal penetration by corrosion or system plugging by scale, fouling, or microbiological growth. There is no question that an ineffective control program will demand system shutdown and cleanup. It can cause excessive, additional manpower costs, loss of product sales, loss of a desirable environment in both temperature and temper, and certainly equipment replacement costs. It is much more reasonable to institute a control program that will not only eliminate these extreme measures but which will be designed to assure optimum system operation. An effective control program can be established by:

- 1) Identifying and ranking the potential problems in the particular system.
- 2) Selecting the particular factors to be controlled on the basis of relative importance, and
- 3) Determining the frequency of control testing by coordinating the relative importance of the various factors to be controlled with the availability of control personnel and facilities.

An adequate control program means adequate control of the operating and replacement costs of the equipment. It will pay for itself many times over in economy and efficient system operation.

PREVENTION OF HEALTH HAZARDS  
IN DESIGN OF COOLING WATER SYSTEMS

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The U. S. Public Health Service Drinking Water Standards point out that drinking water supplies should be obtained from the most desirable source which is feasible and efforts should be made to prevent or control pollution of this source. Over a billion dollars a year is being spent to clean up pollution and to maintain a high quality of water in our streams and underground reservoirs. Even with this protection of the sources of our water supplies, large sums are also required to build, maintain, and operate water purification works to produce drinking water safe for human consumption as well as suitable for many other community uses.

Protection of this processed water throughout its course from the treatment plant to the ultimate consumer is also required, or one of the major objectives, viz., protection of life, may be jeopardized. One of the common failures in protection in the distribution system is the existence of cross-connections which are pipes between potable water and nonpotable water or fluid. It would appear unnecessary that we recall the 1933 Chicago epidemic of amoebic dysentery, which took 98 lives, as dynamic evidence of the need to control cross-connections but, because of either the ignorance or carelessness of some, cross-connections continue to exist in our water supply systems and threaten our health and even our lives.

#### Potable Water Contamination Through Cross-Connections

A survey was made in 1961 for cross-connections in Federal buildings in Washington, D. C. Direct connections of potable water lines to cooling water systems were the most commonly observed plumbing hazard. This kind of connection was observed in 53% of the buildings surveyed.<sup>1</sup>

There have been several incidents of contaminated drinking water from cooling water systems, a dramatic example of which took place in a large city library. In 1958 an employee using a drinking water fountain in this city library noticed that the water stream issuing from the spout was yellowish, and the matter was called to the attention of the building engineer. Upon investigation, it was found that the chilled water pipe system supplying the fountains, was directly connected to another chilled water system in which heavy dosages of chromates were used for corrosion control. Someone forgot to close the valve! Fortunately, color called attention to this toxic material so that it could be removed from the drinking water supply lines.

Another example of the problem of unapproved connections to potable water systems was a situation which developed in a small town shortly after World War II. A builder of rental housing being unable to obtain an extension of the town water supply to serve a half dozen houses just beyond the town limits made an unapproved connection to the city's system by piping these houses to a single yard faucet with a small galvanized iron pipe. A businessman located outside the town limits and near these houses, who decided that his water supply problem could be solved by extending the unauthorized water line to his business, made the connection and promptly learned that the pressure was inadequate to serve his needs. He then installed a small hydropneumatic system to raise the pressure. One Monday morning he observed cloudy water coming from the drinking fountain and immediately proceeded to investigate the source of contamination. It did not take long to learn, however, that one of the housewives was filling her wash tubs with the garden hose when his pump started, and the vacuum drawn from the side of the pump syphoned water from the washing tub. This was a temporary cross-connection, and the reduced pressure resulted from inadequate carrying capacity of the water pipe and improper pump connections. Fortunately, in this case the contamination was visible and detected in time to prevent harm. Hundreds of other cross-connection cases have been documented.

## Characteristics of Cooling Systems

A cooling water system, whether it be for industrial or personnel use, contains or may contain all the elements conducive to the occurrence of cross-connections. These are: 1) a liquid system which contains or may contain a fluid of quality inferior to that of potable water; 2) a direct pipe connection to the potable water system; 3) higher pressure in the cooling water system than in the potable water system.

A typical example of an industrial-commercial type cooling water system design is shown by figure 1. Some systems are operated without the outdoor cooling tower, but the basic elements are similar.

On figure 1, the cross-connection is at the point where the potable water line joins the cooling system. The health hazards are at the connection to the drain, at the open tray of the cooling tower, and from the introduction into the cooling water system of chemicals used for the control of corrosion or growths of organisms. Frequently chromates are used for corrosion control, and these chemicals contain toxic hexavalent chromium. At the drain connection, it is possible for waste water to be pulled back into the cooling water system, thus endangering the potable water system.

Figure 2 illustrates one of the most dangerous cross-connections ever discovered by Public Health Service engineers. The design and installation caused the direct connection of the city water to the sanitary sewer system with a head of 15 feet of sewage above the condenser. The valves to and from the condenser were normally kept open.

A more complex chilled water system is shown by figure 3. Here the public health is endangered at three points, 1) the connection of the city water to the chilled water loop, 2) the direct connection of the condenser water line to the drain, and 3) the direct connection of the potable water to the condenser water.

It is emphasized that a cooling water system hazard often overlooked is the use in such systems of heavy concentrations of chemicals such as the chromates.

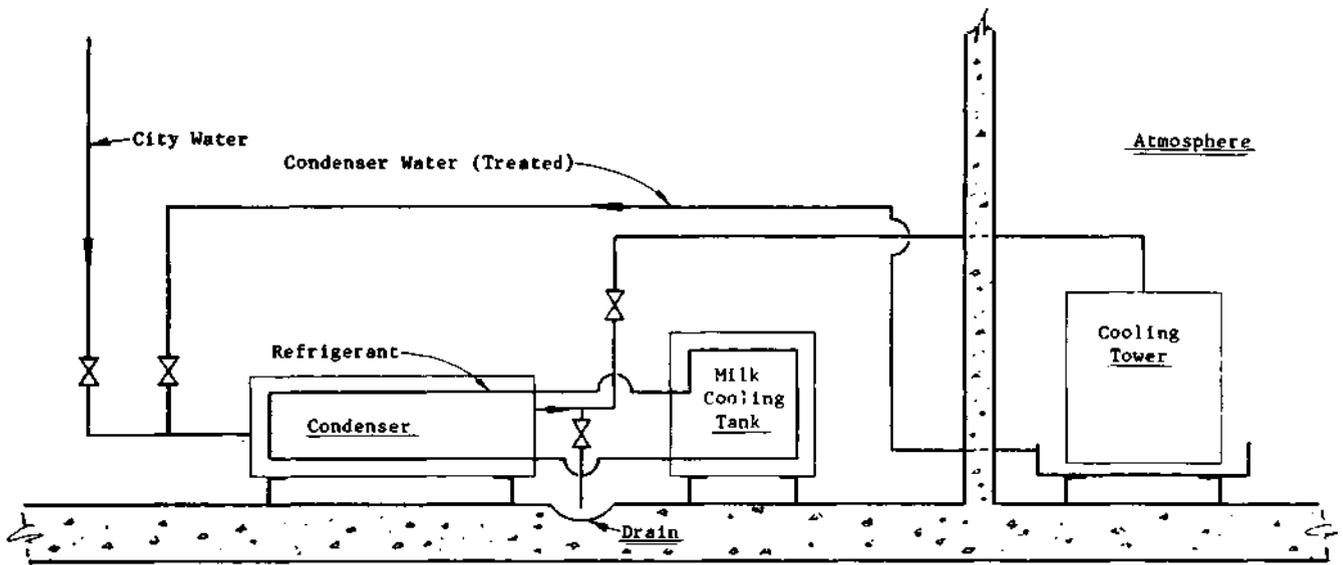


Figure 1. Simple cooling water system with cross connection

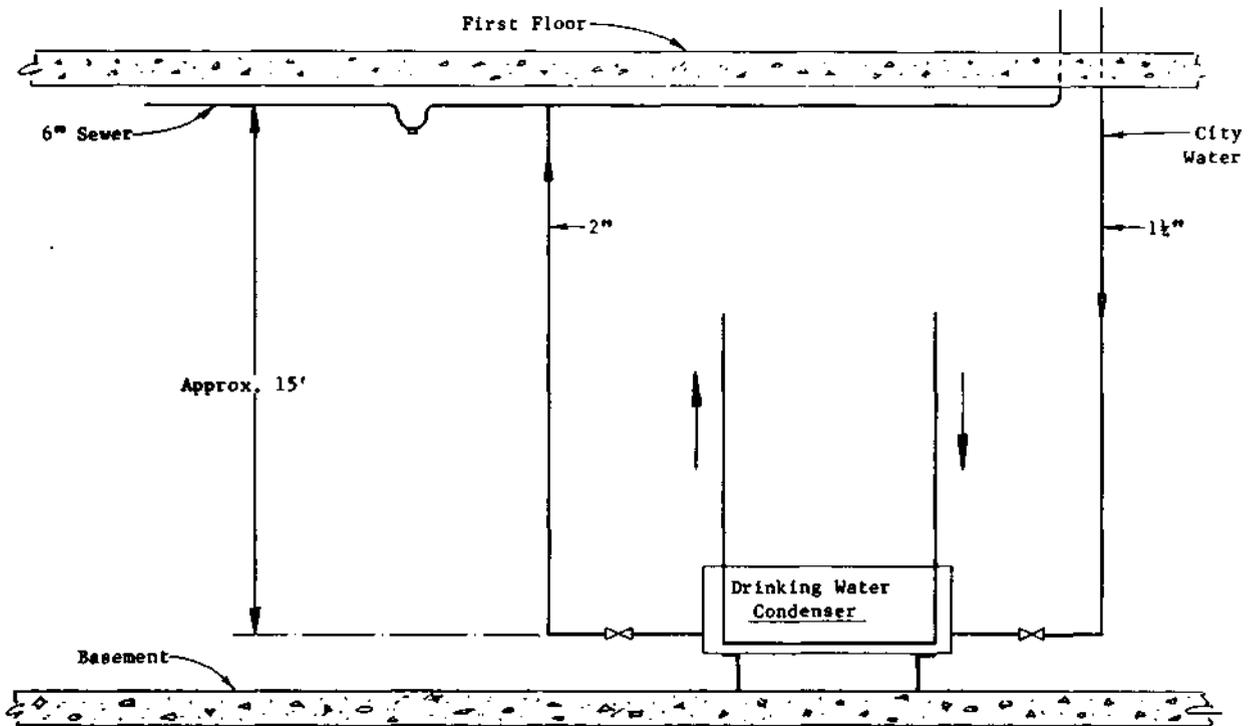


Figure 2. Dangerous cross connection through cooling water system

## Public Health Significance and Control

Controlling potable water quality encompasses three principal activities, viz., protecting the source of supply, treatment to improve the quality of water as required, and protection of the water during its distribution to the ultimate consumer. Responsibility for water quality in these activities is divided. Although the water company has principal responsibility up to the connection to consumers plumbing, additional responsibility for pollution control is held by Federal, State, and other agencies. Protection of the water beyond the consumers connection is the responsibility of the consumer and health and plumbing agencies. Usually it is in the consumers water system or plumbing that cross-connections produce a problem. It is most likely here that cooling water systems could produce problems.

Water quality control includes concern for the quality of the product and the system which produces and delivers it. The quality of the product is evaluated against a water quality standard, and the system is evaluated against a system or operating standard. The water quality standard is concerned with impurities which might be present in the source waters and not removed by treatment and substances which might be added by treatment and remain in the product. It is also concerned with impurities which might be introduced into the water from the system conveying it or equipment in which it is used. The quality standard cannot, however, include chemical or physical limits for all impurities which might be introduced from extraneous sources. The control of such contamination is included in a system or operating standard.

The Public Health Service Drinking Water Standards<sup>2</sup> cover this control by the following sections:

"2.2 - Frequent sanitary surveys shall be made of the water supply system to locate and identify health hazards which might exist in the system. The manner and frequency of making these surveys, and the rate at which discovered health hazards are to be removed, shall be in accordance with a program approved by the Reporting Agency and the Certifying Authority.

**A.** Cross-connection between city water and the chilled water system, installed for the purpose of filling the chilled water system.

**B.** Cross-connection between city water and condenser water, used for filling the system and for supplying city water for condenser operation when tower is not used.

**C.** Solid connection between condenser and sewer, installed in this manner because the sewer is subjected to occasional back pressure.

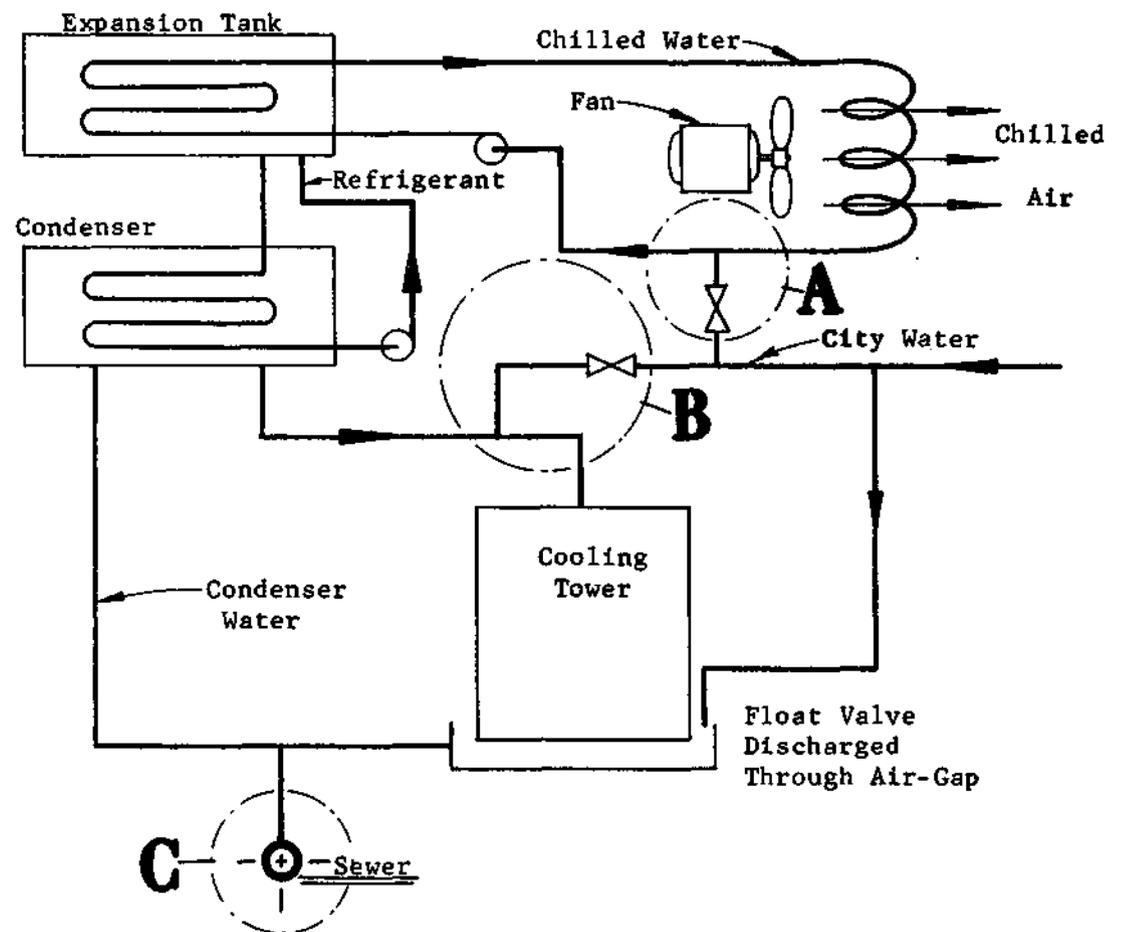


Figure 3. Complex cooling water system showing cross connections

"2.3 - Approval of water supplies shall be dependent in part upon: (a) Enforcement of rules and regulations to prevent development of health hazards; (b) Adequate protection of water quality throughout all parts of the system, as demonstrated by frequent surveys; (c) Proper operation of the water supply system under the responsible charge of personnel whose qualifications are acceptable to the Reporting Agency and the Certifying Authority; (d) Adequate capacity to meet peak demands without development of low pressures or other health hazards; and (e) Record of laboratory examinations showing consistent compliance with the water quality requirements of these Standards."

Health hazards are defined as "conditions, devices or practices in the water supply system and its operation which create or may create a danger to the health and well-being of the water consumer. An example of a health hazard is a structural defect in the water supply system whether of location design, or construction, which may regularly or occasionally prevent satisfactory purification of the water supply or cause it to be polluted from extraneous sources."

A connection to a potable water system of a water system which is not considered potable, or is not controlled for potability, in a way which could cause a flow of water from the latter to the former is a health hazard according to this definition. Although the nonpotable system might not have been designed to contain substances which would endanger health, the fact that it is not controlled as a potable water system constitutes a potential danger because of possible changes which might make it unsafe. Such changes as modification of the solutions in the nonpotable system or connections to other systems, might cause the system to be a real danger to the potable system.

A cooling water system is a good example of such a nonpotable system. The functions of this system differ from those of a potable water system, and modifications of operation might be required which would preclude maintenance of a potable supply of water in the cooling system. Control of corrosion, lime scaling, and biological growths usually require the addition of special materials. Some of the materials might not damage the quality of potable water, but assurance that new materials in the future will be as safe cannot be made without controlling the system on a potability

basis. Such a restriction would be an unnecessary obstacle to operating the system to accomplish its primary objective.

If the concept of physical separation of the two systems is acceptable, it should not be necessary to discuss specific chemicals used in cooling systems with respect to their toxicity to humans. Although there are many which could be tolerated in drinking water, the fact that those in current use are not limited to these is sufficient to make the cooling system potentially dangerous. The chromium compounds are quite popular and the literature points out new materials succeeding in cooling water control. Some of these new materials are toxic and some are of unknown toxicity. In view of the trend toward more use of complex organic molecules, it appears likely that materials of unknown toxicity will be tried. In view of this and the fact that already some potentially dangerous chemicals are being used, it is necessary to prevent cross-connections of cooling systems with potable water systems.

Recapitulating, cooling water systems frequently afford conditions conducive to a cross-connection with a drinking water distribution system. The question will be asked what can be done to eliminate these hazards. The safest solution is an air-gap wherever potable water is to be fed into the chilled water system. An air-gap should also be used wherever a chilled water system drain is discharged to a sewer system.

A recommended method for providing protection is through the use of an expansion tank such as shown by figure 4. Here the potable water is indirectly connected to a tank which takes or yields, as may be required, water from and to the chilled water system.

#### Summary

Because of inherent characteristics, cooling water systems constitute a potential danger to potable water systems supplying them. It is not enough to simply avoid the use of dangerous chemicals in chilled water systems for they may become contaminated in other ways. Also use of chemicals is often necessary to the proper functioning of the cooling water

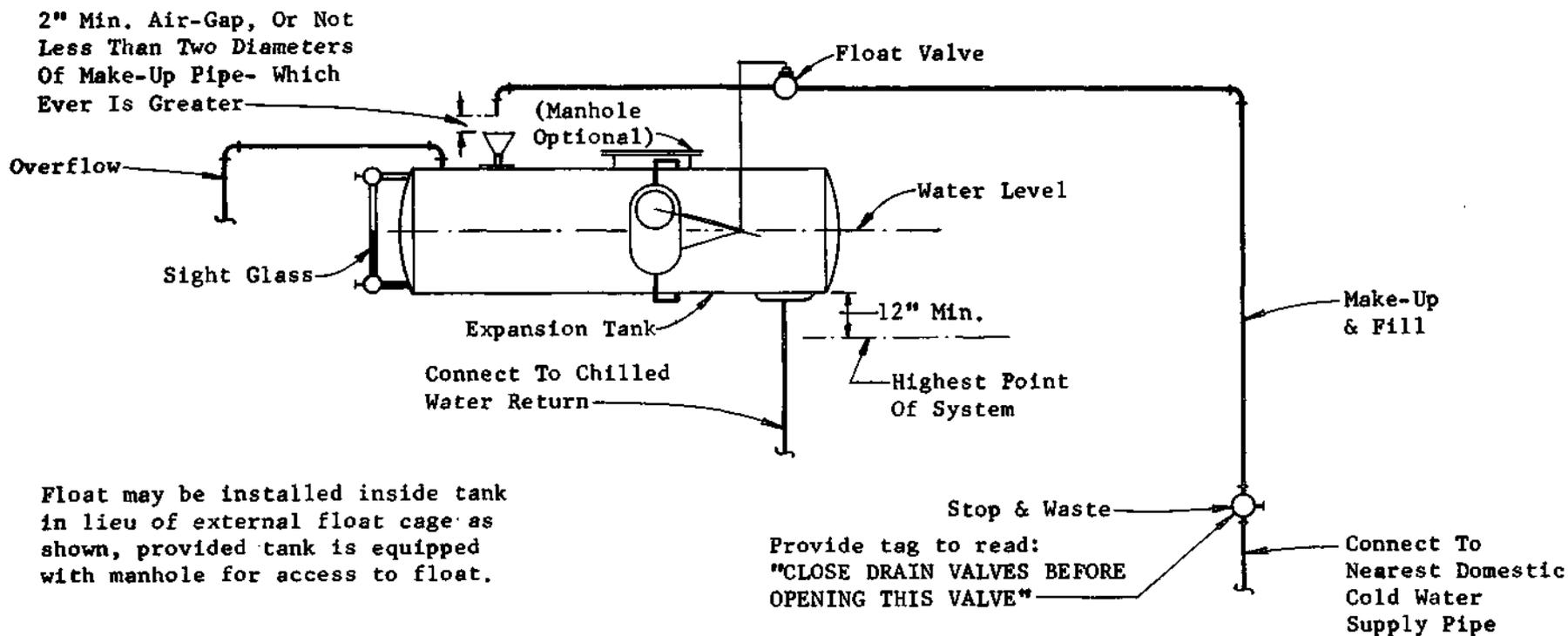


Figure 4. Method for separating cooling and potable water systems  
(Courtesy General Services Administration)

system. The best prevention of health hazard is in the physical separation of the two systems.

Those responsible for design, installation, and maintenance of cooling systems should be cognizant of the hazards to the public health these systems present and the contributions which they can make toward insuring the protection of potable water supplies.

A document useful to the understanding and correction of cross-connections is Public Health Service Publication No.957, Water Supply and Plumbing Cross-Connections.<sup>3</sup>

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OPERATING EXPERIENCES WITH ION EXCHANGE  
CHROMATE RECOVERY SYSTEM

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Chromate bearing corrosion inhibitors are today widely applied in open cooling water recirculating systems. Compounds of sodium chromate ( $\text{Na}_2\text{CrO}_4$ ) are employed in a large variety of formulations either alone or in combination with other recognized inhibitors such as polyphosphates and zinc salts.

Hexavalent chrome concentrations in the 20-50 ppm range are common, with levels of 300-500 ppm being employed in smaller systems where economics permit or when the corrosive service warrants.

These corrosion inhibitors are continuously being lost because of windage and blowdown from the cooling tower. Such losses of chromate inhibitor are undesirable for two primary reasons:

- 1) Economic loss of valuable inhibitor which must be replaced.
- 2) Pollution and contamination of water courses due to hexavalent chrome discharge.

Most states in the United States have adopted regulations which limit the discharge of toxic hexavalent chrome into water bodies. The cooling tower operator is therefore faced with a multifaceted problem in utilizing chromate bearing inhibitors. He must often limit the concentration to an undesirable extent to avoid polluting, be forced to install expensive waste treatment facilities to destroy the hexavalent chrome, or use more expensive non-chromate inhibitor treatments.

In an effort to overcome these restrictions Cochrane Division initiated laboratory work in 1963 to determine whether an ion exchange process could be developed to handle cooling tower blowdown, extract hexavalent chromate

from it, and recover the chromate for reuse as corrosion inhibitor makeup to the cooling tower.

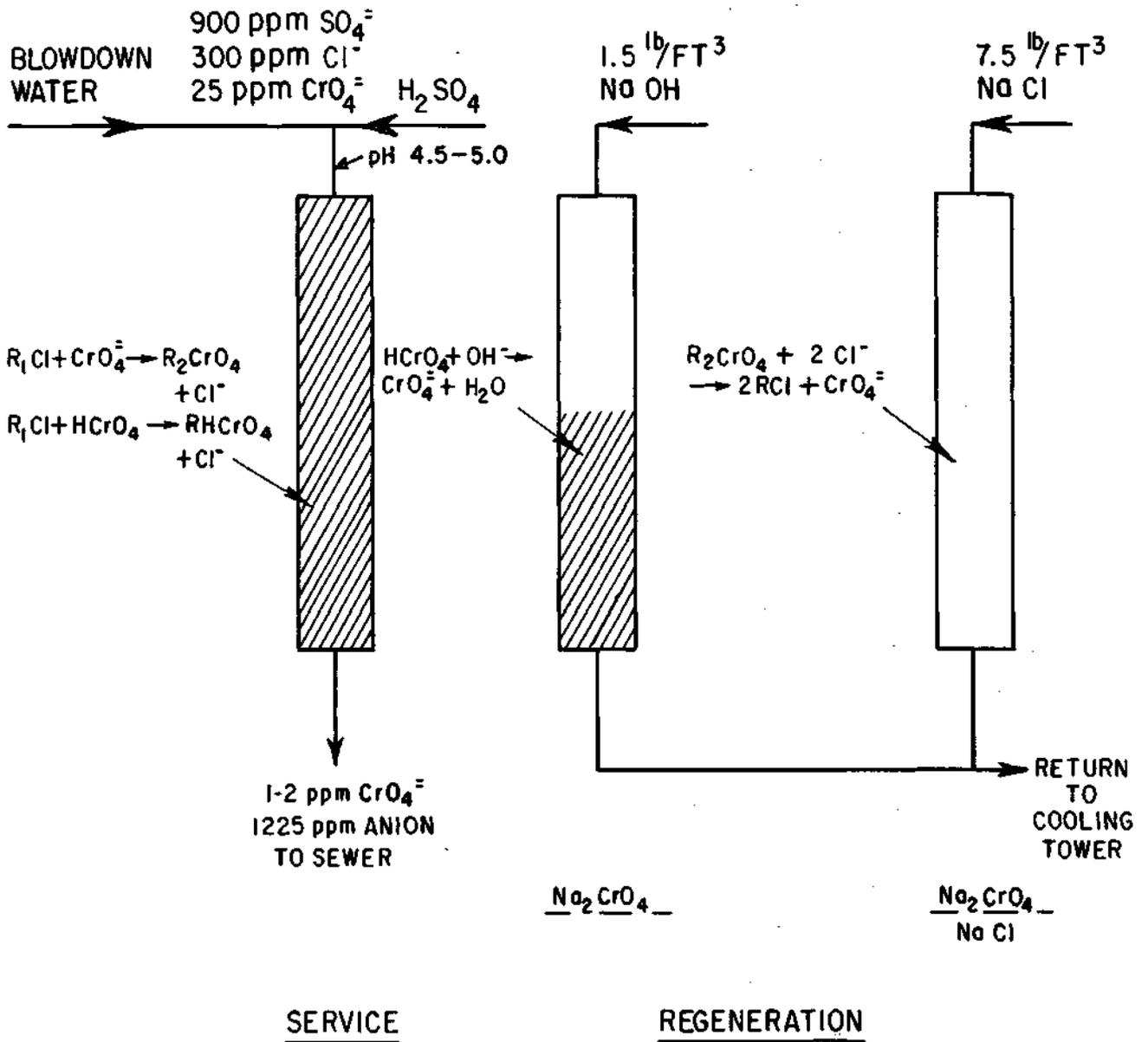
After many months of effort, a successful method of recovering the chromate from synthesized cooling tower blowdown water was developed using a strong base anion exchange resin such as Nalcite SBR or Rohm and Hass IRA-400.

The process employs a single strong base anion exchange unit operating on the salt or chloride cycle. In service the pH of the incoming tower blowdown water (normally 6-7) is adjusted to 4.5-4.8 by direct acid feed prior to introduction into the ion exchange unit. This pH range has been found to be optimum to enhance the selectivity of the resin for chromate over the competing sulfate, bicarbonate, and other anions. In this pH range some chromate is converted to bichromate ion which is quite selectively adsorbed by the resin producing very high capacity and low leakage even with chromate concentration in the feed of 20-50 ppm in a total of 1000-1200 ppm anion. In regeneration following a conventional resin backwash the bichromate ion held by the resin is stripped by an alkaline neutralization using stoichiometric quantities of sodium hydroxide mixed with a salt regenerant. The quantity of alkali required, related to the pH of the feed during loading and the capacity, varies from 1.5 to 2.0 lb/ft<sup>3</sup> at a feed pH of 4.5-4.8.

The effluent of the alkali-salt regeneration contains the chromate stripped from the resin column and may be returned to the cooling system or held in a storage tank for reuse. The system is illustrated on figure 1.

#### Pilot Plant

After successful laboratory work, a pilot unit was installed at a municipal utility outside Philadelphia, Pennsylvania, in September 1963 and operated for about 9 months on actual cooling tower blowdown. Pilot studies were conducted at rates up to 15 gpm on a 12-inch diameter recovery unit treating blowdown water with chromate levels in the 20-40 ppm range. The test program was designed to answer five basic questions:



R = RESIN MATRIX

Figure 1. Ion exchange chromate recovery system

- 1) Could high operating capacities be obtained in actual field installations?
- 2) Would the chemical regeneration technique accomplish a high degree of recovery?
- 3) Could chromate recovered along with other anions be reused in the cooling tower?
- 4) What would happen to the ion exchange resin when exposed to the effects of biocides, suspended solids, lignin, etc.?
- 5) What unforeseen operating and control problems would be found in the field which were not experienced in tightly controlled laboratory studies?

Results of the pilot system operation were reported in an earlier paper. (L. Sloan, "An Ion Exchange Method of Recovery and Reuse of Chromate Inhibitor From Cooling Tower Blowdown Water," presented at Cooling Tower Institute Summer Meeting, New York, 1964.) This work confirmed that hexavalent chrome in the concentration range of 20-50 ppm found in cooling tower blowdown water could be selectively extracted, and eluted from an anion exchange chromate recovery system. Chromate recoveries in the 90-95% range were consistently obtained with average leakage of chrome at the 1-2 ppm level.

After 8 months of operation the resin total capacity had dropped 15%, but no loss in operating capacity was experienced.

Recovered chrome was returned to the cooling tower cold well, and with periodic fortification with the corrosion inhibitor (a zinc-chromate mixture) proved as effective in corrosion control as found in previous operation.

Early work was carried out on an unfiltered feed. High suspended solids in the blowdown water contributed to hydraulic problems causing high pressure loss. A conventional pressure filter installed upstream of the chromate recovery unit eliminated this problem.

#### Operating Systems

In August and October 1964 two chromate recovery systems were installed which serve as a good cross section for gaining operating experience.

The first of these systems was a manually operated unit treating blowdown water containing more than 300 ppm hexavalent chrome; the second was an automatic system operating on a 25-30 ppm chromate system. The remainder of this paper will be devoted to the description of the operation of these units.

#### High Chromate System

In August 1964 a chromate recovery system was installed in a pharmaceutical plant located just outside Philadelphia. Prior to the installation of the system, the cooling tower operator had been using a nitrite-fluoride proprietary inhibitor because of strict pollution regulations regarding the discharge of toxic hexavalent chrome to the creek. With the availability of the chromate recovery, the operator switched to a high chromate (300 ppm) treatment and now purchases makeup chemical in the sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ) form.

The cooling tower served by the chromate recovery unit is a 2000-ton capacity unit of the two-cell induced draft design. Water from the tower is used to cool two 750-ton chillers. There are three recirculating pumps each rated at 2480 gpm versus a 95-foot discharge head. During the winter only one pump is used; in the summer two, with one as a spare. Temperature drop across the tower is 10-12 F in winter and as high as 30 F in summer. Blowdown for the tower is manually set on the basis of solids concentration and conductivity.

Tower pH is maintained in the range of 6.5-7.0 by periodic addition of sulfuric acid. Bacterial growth is controlled by periodic shock feeding 20% hypochlorite solution. No further chemical treatment other than the hexavalent chromate inhibitor is utilized.

The chromate recovery system includes a 30-inch diameter by 7-foot straight side vessel charged with 22 ft of strong base anion exchange resin Nalcite SBR. All internals, vessel lining, piping, and valving are polyvinyl chloride construction.

Regeneration is effected by a small centrifugal pump connected by

common piping to two polyethylene-lined steel regenerant drums, one each for salt and caustic.

A positive displacement type metering pump fed from a 66 Be sulfuric acid carboy is used to reduce the pH of the incoming blowdown water to 4.5-5.0 prior to passage through the exchange unit. The acid feed pump operates throughout the service or loading cycle.

Service runs are terminated on the basis of volumetric throughput based on an inlet totalizing meter. Runs are arbitrarily held to a 4 lb chromate ( $\text{CrO}_4$  )/ft<sup>3</sup> resin loading. Tower blowdown rate varies seasonally but averages between 8 and 20 gpm depending on load.

Regeneration of the chromate recovery column is carried out in two steps. First, approximately 2 lb caustic soda ( $\text{NaOH}$ )/ft<sup>3</sup> resin is passed downflow through the unit. This alkali neutralizes the chromate adsorbed as dichromate and strips off approximately one half of the chromate. Alkali is followed by a sodium chloride regeneration at 7.5 lb/ft<sup>3</sup> dosage which elutes the remaining chromate. The elute of the two regeneration steps is collected in the recovery tank along with a short rinse.

Chromate eluted from the exchanger is collected in a 1000-gallon surge tank. Since under normal conditions the chromate recovery unit runs for 24-48 hours between regenerations, the recovered chromate is returned to the cooling tower by means of a small centrifugal pump on a continuous basis at a rate of 0.5-1.0 gpm.

Typical makeup and blowdown water analyses are illustrated in table 1. The disproportionate build up of chloride and sulfate in the blowdown water reflects the non-chromate anion returned to the cooling tower with the recovered chromate. Analyses of the recovery chromate in the recovery tank show a ratio of chromate to chloride of 1:1 and chromate to sulfate to 1:0.35. The recovery tank contains 88 lb chromate ( $\text{CrO}_4$  ), 97 lb chloride ( $\text{Cl}^-$  ), and about 31 lb sulfate ( $\text{SO}_4^{=}$  ) in approximately 1000 gallons.

Table 1. Analyses of Cooling Tower Water

<u>Ion</u>	<u>Makeup Conc.</u>	<u>(ppm)</u>	<u>Ion</u>	<u>Blowdown Conc., (ppm)</u>
Calcium (as CaCO <sub>3</sub> )		210	Calcium (as CaCO <sub>3</sub> )	395
Magnesium (as CaCO <sub>3</sub> )		50	Magnesium (as CaCO <sub>3</sub> )	100
Bicarbonate alkalinity (HCO <sub>3</sub> <sup>-</sup> )		189	Sulfate (SO <sub>4</sub> <sup>=</sup> )	250
Sulfate (SO <sub>4</sub> <sup>=</sup> )		80	Chloride (Cl <sup>-</sup> )	390
Chloride (Cl <sup>-</sup> )		34	Chromate (CrO <sub>4</sub> <sup>-</sup> )	280
			Turbidity	20-40
Conductivity, in micromhos		480	pH	6.9
pH		7.1		

#### Leakage

One of the critical factors in the operation of the chromate recovery system is the requirement that hexavalent chromate leakage be held to under 2 ppm. Earlier in this paper it was stated that tight pollution regulations had previously prevented the tower operator from using a chromate based inhibitor. Although some variations occur in the effluent, leakage normally averages between 0.5 and 1.5 ppm chromate. Leakage during an exhaustion is somewhat sensitive to solids content and inlet pH. Figure 2 illustrates a representative cycle with inlet pH adjusted to 4.5-5.0 and chromate leakage under 1.0 ppm. Some variations in pH levels are experienced because the acid feed system is a blind feeder and pH will be sensitive to both composition and flow rate changes. Operation of the system has been shown to be sensitive to composition and pH changes in that occasionally higher leakage levels are experienced when good house-keeping is not maintained.

#### Resin Life

A second important factor to be considered in the chromate recovery installation is the effect on the ion exchange resin of operating the

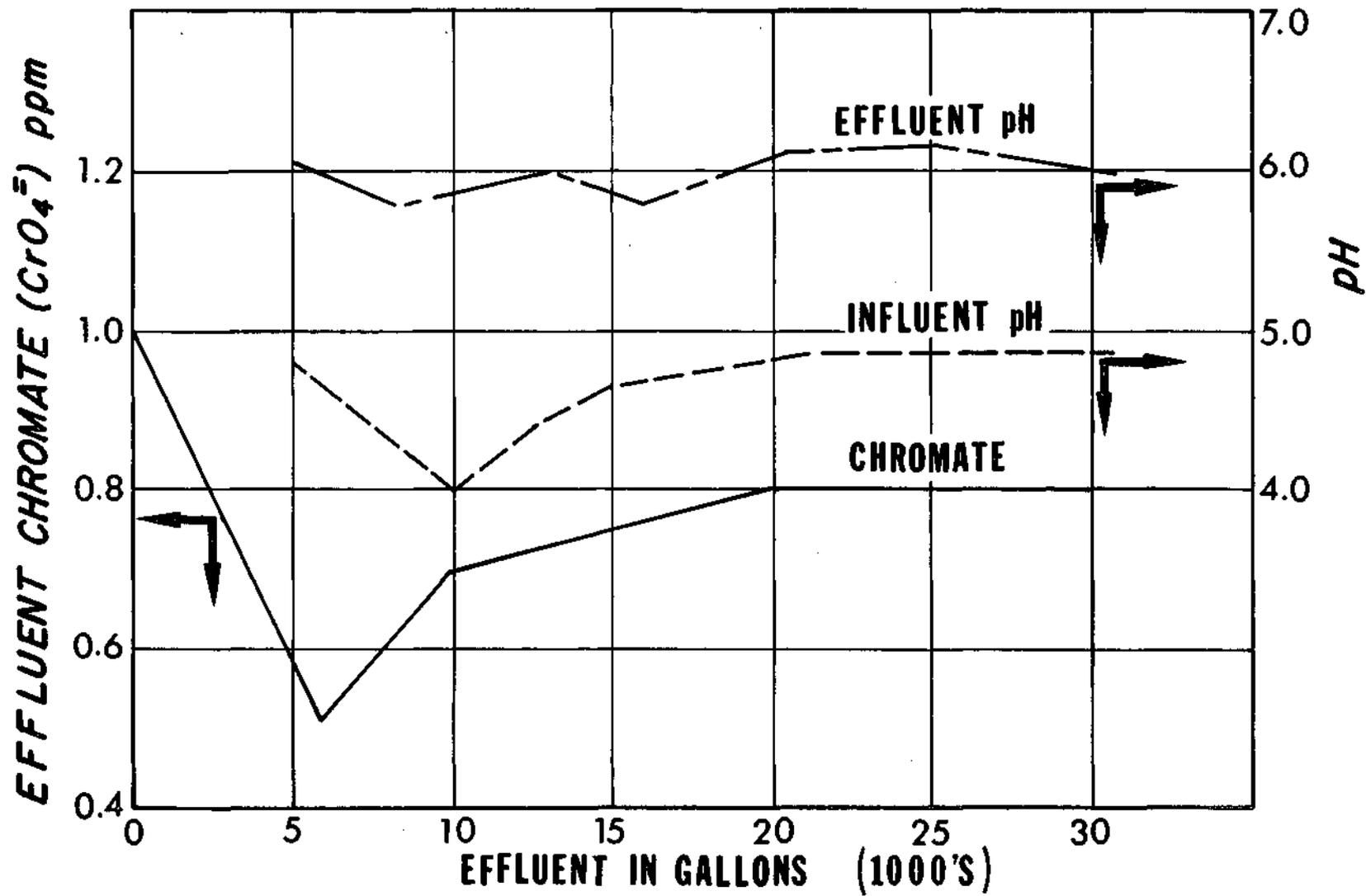


Figure 2. Chromate recovery system - 300 ppm CrO<sub>4</sub><sup>2-</sup> feed

system in a high chromate environment under acidic pH conditions. In pilot plant studies which were carried out with chromate levels in the 20-50 ppm range approximately 15% of the total capacity of the resin was lost after 8 months of operation. No loss in operating capacity was experienced, however, at any time during the test program.

The high chromate recovery system was sampled after about 6 months of service. Total capacity of the exposed resin declined 12% during this period; however, no decline in operating performance has yet been experienced.

#### Recovery Costs

An arbitrary loading of 4 lb/ft<sup>3</sup> chromate (CrO<sub>4</sub><sup>-</sup>) or 5.6 lb/ft<sup>3</sup> sodium chromate (Na<sub>2</sub>CrO<sub>4</sub>) is applied in the recovery unit or a total of 88 lb CrO<sub>4</sub> is collected. Regenerant chemicals required are as follows:

18 lb sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )	@ \$ .02/lb	= \$ .36
40 lb caustic soda (NaOH)	@ \$ .05/lb	= 2.00
154 lb sodium chloride (NaCl)	@ \$ .01/lb	= <u>1.54</u>
		. \$ 3.90
<u>\$3.90</u>	=	4.4¢/lb chromate (CrO <sub>4</sub> <sup>=</sup> ) removed
88 lb chromate (CrO <sub>4</sub> <sup>=</sup> )		

Recovery efficiencies can be further improved by increasing the loading of chromate in the system to as high as 5 to 5.5 lb chromate (CrO<sub>4</sub><sup>=</sup>)/ft<sup>3</sup>.

#### Low Chromate System

A second chromate recovery system placed in service in October 1964 on the East Coast was designed to handle up to 80 gpm cooling tower blowdown water containing 20-25 ppm chromate.

An automatic 30-inch diameter by 7-foot straight side unit charged with 20 ft<sup>3</sup> strong base anion exchange resin treats up to 80 gpm blowdown water. Service runs are terminated by means of a volumetric totalizing meter with reset head in the service influent. When a preset volume of

water has been treated, regeneration is automatically initiated and carried through. Recovered chromate is sent to a 500-gallon holding tank from which it is repumped at a continuous rate back to the cooling tower.

The tower is being operated on a proprietary zinc chromate inhibitor which is still being added periodically to replace inhibitor lost in carryover.

In normal operation, a service cycle lasts about 4 days because of the relatively low chromate level and high capacity. The pH of the influent is adjusted to 4.5-5.0 and regeneration is effected by a net usage of 7 lb/ft<sup>3</sup> sodium chloride (NaCl) and 1.5 lb/ft caustic soda (NaOH).

Because of the low winter cooling load, the chromate recovery unit is being operated at a reduced throughput rate with regenerations occurring every two weeks. Thus far not enough cycles have been impressed on the system to report as significant; however, to date the system has been recovering in excess of 90% of the hexavalent chrome being handled by it. More frequent cycling will be experienced with the coming of summer.

#### Other Pilot Plant Activity

Because of the many factors which must be considered before the installation of a chromate recovery system can be recommended, at least six tower operators are at present running small pilot scale chromate recovery units. Economics of the recovery system will naturally vary from plant to plant depending on cost of present inhibitor treatment, piping modifications, need for prefiltration, pollution regulations, and many other factors.

Chromate recovery systems will generally be attractive to cooling systems using higher chromate levels, greater blowdown rates, or to those facing stringent pollution regulations.

#### Conclusions

Systems such as those described in this paper demonstrate that chromate recovery can be successfully and economically practiced. Recovered chromate can be reused in cooling towers without harmful effect if proper provision

is made for chromate reuse. Chromate recovery systems such as those described in this paper demonstrate the twofold advantage of chemical recovery and pollution abatement.

## USE OF SEWAGE PLANT EFFLUENT AS COOLING TOWER MAKEUP

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The construction of a steam-electric power generating station in Amarillo, Texas, created a requirement for a source of water of about 3000 gpm for cooling tower makeup. The source was required to be from a supply which would be dependable from day to day throughout the expected 40-year useful life of the plant. Further specifications require cooling water to be non-scale forming at the 80-120 F skin temperature of the heat exchange surface. Corrosion rates of iron and admiralty brass should be less than .006 inches per year, and the water must not cause unusual deterioration of redwood cooling towers.

Sewage plant effluent was chosen for this source, and after three years of experience reasonable and economical solutions have been found for the problems encountered. This paper is a discussion of the nature of the sewage plant effluent employed by us, the problems encountered, and the results obtained. We believe that this case may be typical enough to be of general interest.

In common with many areas in the Southwest, Amarillo has no lakes nor rivers of sufficient size to supply water in the amount which we needed. The most common source of water is from wells which are drilled some 300 to 400 feet into the Ogallala sand formation. The production from this ancient strata for domestic and agricultural use is currently greater than the rate of replenishment. Since the basic reason for the increased pumpage of underground water is population growth, this source of water will obviously become less accessible for industrial use as time passes, and the general economy of the region will benefit from any successful effort to conserve this valuable natural resource.

Necessity, therefore, called our attention to sewage as a dependable supply of usable water which, in spite of certain unfavorable characteristics, has been successfully employed by several industries. Various steel companies have found use of this water for many years as reported by Keefer and Wolman.<sup>2</sup> Electric power companies have been successfully using this water in New Mexico,<sup>3</sup> Nevada,<sup>4</sup> and in Denison, Texas. Dozens of other industries have also found good use, or shall we say "reuse," for this often overlooked supply. Necessity, as in our own case, might have caused the initial trial, but its continued use by industry is simply good engineering practice.

When we had determined that sewage plant effluent was available and considered the history of its use as mentioned earlier, we began an investigation into the quality and characteristics of the local supply and studied various systems of treatment which would produce suitable cooling tower makeup.

We were advised from the literature on the subject and from users that in addition to the usual water treating problems, we must deal with scaling concentrations of orthophosphates, foaming due to detergents, and extreme biofouling due to nitrogenous materials in the water.

Further education came from Mr. C. H. Scherer, Superintendent of Water Reclamation and Sewage Treatment for the city of Amarillo.<sup>5</sup> Mr. Scherer listed three characteristics typical of sewage plant effluent as it affects industry:

- 1) The average nonfilterable solids added to the potable water which carries waste from our homes and industry amounts to 2 or 3 pounds per thousand gallons. This additional 250 to 350 ppm total solids will be in the sewage plant effluent.
- 2) Sewage disposal plants clean and purify the incoming water to various degrees depending upon the design and operation of the plant. The quality of the effluent is affected by retention time, temperature, and the presence or absence of materials toxic to the bacterial life used to degrade the organic material present in the sewage.
- 3) The chemical and biological nature of the effluent from a sewage plant will vary from hour to hour, from day to day, and from season to season.

Guided by these three important points, a study was undertaken to determine the analysis of this water and its reaction to various treatments. Grab samples and daily composite samples were analyzed over a long period of time. Records obtainable from the sewage plant were used to determine seasonal variations. In some sections industrial wastes from canneries, dye plants, tanneries, etc., can cause wide seasonal variations in the sewage plant effluent. The analysis shown in table 1 is typical.

Table 1. Analyses of Typical Samples (ppm)

	A		B	C
	City water	Sewage effluent	Cold lime treatment	Cooling water system
Calcium (as CaCO <sub>3</sub> )	110	140	140	350
Magnesium (as CaCO <sub>3</sub> )	130	160	80	200
Sodium (as CaCO <sub>3</sub> )	30	300	300	750
Bicarbonates (as CaCO <sub>3</sub> )	230	300	0	40
Carbonates (as CaCO <sub>3</sub> )	0	0	250	0
Hydroxides (as CaCO <sub>3</sub> )	0	0	70	0
Sulfates (as CaCO <sub>3</sub> )	20	30	30	500
Chlorides (as CaCO <sub>3</sub> )	20	300	300	750
Nitrates (as CaCO <sub>3</sub> )	0	2	2	5
Phosphates (as CaCO <sub>3</sub> )	0	40	1	2
SiO <sub>2</sub>	65	65	40	100
Ammonia	0	20	20	20
pH	7.9	7.9	10.5	7.8

At this point the orthophosphate content predicted a problem since tricalcium phosphate is an insoluble scale former at low temperatures.<sup>6</sup>

A series of jar tests were undertaken to determine the applicability of cold lime treatment for the reduction of phosphate and calcium. Sewage disposal plant water treated with 2 1/2 pounds of lime per thousand gallons and coagulated with 1/4 pound of alum resulted in phosphate reduction to 1 ppm and lower, but the calcium was completely sequestered and showed no reduction. The analysis shown under B in table 1 is of interest.

Calcium reduction did not occur even at a pH of 10.5. A very desirable side benefit is noted due to the precipitation of magnesium and the attendant reduction of silica from 45 to 25 ppm as the hydroxide of magnesium absorbed the ionized silica in the classical 3 to 1 ratio. (Incidentally, there is no colloidal silica in the Amarillo city water nor in the sewage disposal plant effluent. This is of little interest to cooling water users but might be most pertinent to industries investigating this source for boiler makeup.) Underground water in the Southwest is commonly high in ionized silica. It is usual to encounter 50 to 70 ppm silica, as  $\text{SiO}_2$  in raw well water. Cooling water systems with more than 150 ppm  $\text{SiO}_2$  will deposit a fairly pure silica scale on hot surfaces starting at about 140 F skin temperatures. Such being the case, silica concentration in a cooling system is quite often the index to blowdown control. Southwestern Public Service Company operates plants in eleven different locations in the Southwest and at nine of these, the cycles of concentration in the cooling systems are limited by silica concentrations.

Subsequent to these studies, cold lime treatment was selected for the pretreatment of the cooling tower makeup for our steam electric power plant in Amarillo. Pebble quick lime and granulated alum seemed to offer the best form of chemicals from the storage, handling, and feeding standpoint.

The equipment and flow cycle of the cold lime reactors now installed and operating satisfactorily is fairly typical. A high and variable rate of sludge recirculation is very desirable and the lower rising rates of .8 to 1.0 gallons per minute per square foot are prudent design factors for this type of water because of the difficulties encountered in coagulation during poor or borderline operation of the sewage disposal plant.

If industry is to make optimum and satisfactory use of sewage disposal plant effluent, it must receive treatment from a well designed, well operated plant because incomplete organic decomposition produces effluent which will become septic and nonsettlable in cold process softeners regardless of chlorine residual. We do not feel qualified to explain the reasons why nondecomposed organics conflict with coagulation of cold process

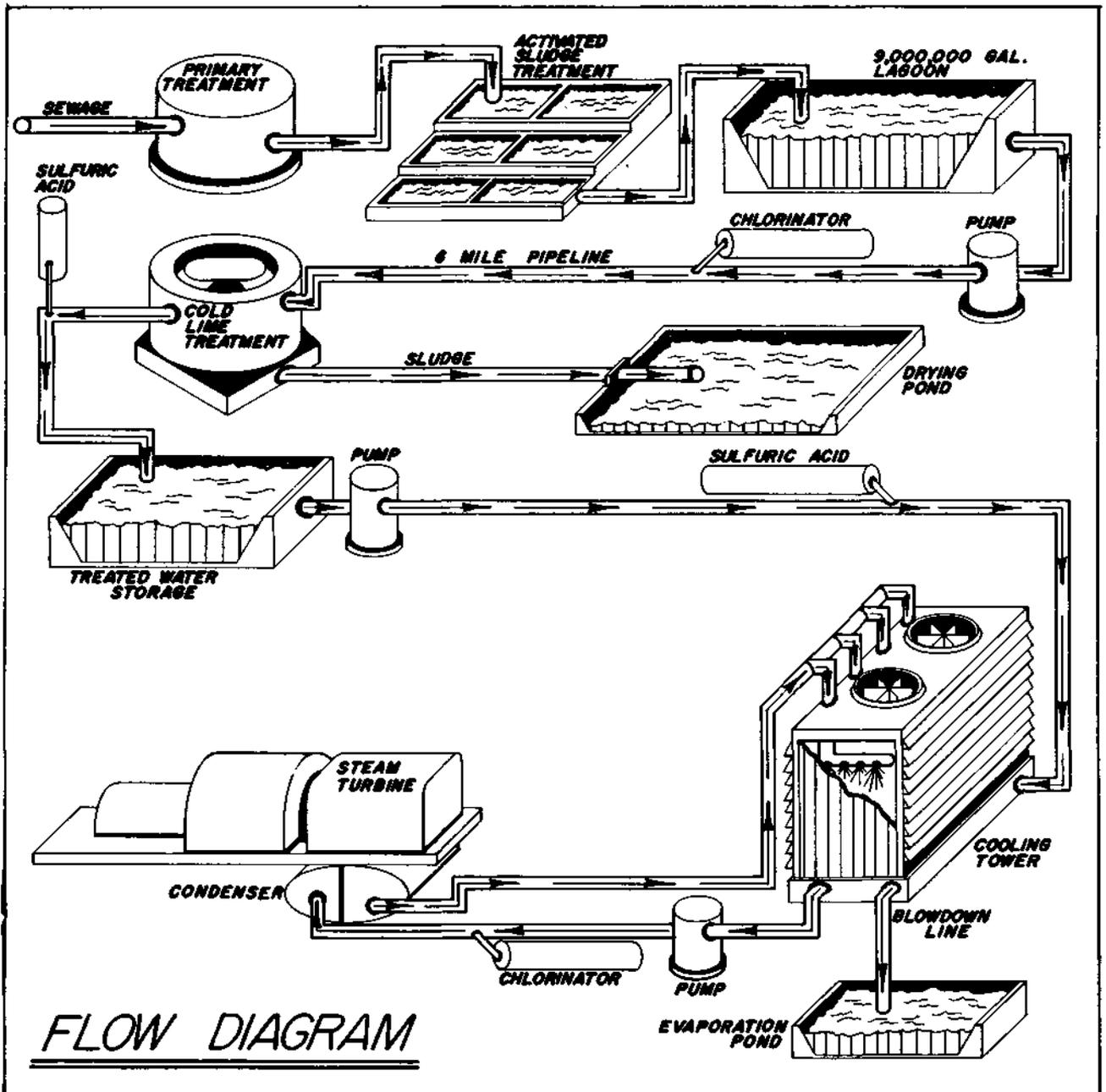
treated water; however, this is the universal observation of sewage plant effluent water users. Anytime that the bacteria used to degrade and oxidize organics at the disposal plant are ineffective, water from the process is difficult, if not impossible, to coagulate. Bacteria are variously sensitive to low concentrations of many materials, such as zinc and chromium. High organic content or very low organic content sewage may smother or starve their life processes. Amarillo has a well designed disposal plant using the activated sludge principle, and it is well supervised. Mr. C. H. Scherer has promoted reasonable and necessary sewer-use ordinances which make it possible to produce a highly usable reclaimed water from the Amarillo sewage disposal plants.

If you do not find a sewage disposal system that is designed and operated expertly and protected from violent bacterial toxins by adequate city ordinances, there are many well documented reasons to believe that you have no dependable, treatable, economical source of industrial water. Preliminary scouting of design, supervision, and ordinance control should go hand in hand with chemical analysis in the early study of sewage plant effluent quality.

Be alert to the possibility of an excellent disposal plant operation which may subsequently become overloaded. This is a risk in most situations, of course, but the local political and economical atmosphere might allow abuses which would prove disastrous to the quality of "reclaimed" or "industrial water." These possibilities should be considered when the time comes to prepare the terms of the contract between industry and city.

A flow diagram of our completed system is shown on the next page.

The remaining characteristics of sewage disposal plant water which concerned us was the variable nature of this source. The city of Amarillo lagoons about 24-hour volume. This is ordinarily designed to assure quantity in case of process difficulties. This is not adequate to "flywheel" the quality of the water so that the constituents are constant enough to allow chemical treatment to be varied at the rate to consistently produce accurately treated water. Our continued policy is to overtreat with lime



and coagulants by about 20% to insure adequate reduction of phosphates. Alum is the most successful coagulant we have found, but polyelectrolites are used to supplement the alum during difficult periods.

There have been no problems with foam in our system. Detergents are present in the makeup to the extent of 4 to 15 ppm as ABS. Foam does occur but never in quantities which affect cooling tower operation or spill from the basin. With the new biodegradable detergents now coming into use it is to be expected that problems from this source will diminish.

This pretreatment produces makeup water which when concentrated would tend to increase in pH and deposit calcium carbonate scale in the condensers. The calcium does not stay sequestered after leaving the cold process reactor. Oddly enough the collection system at the top of the reactor tanks and the makeup piping which carries the cold process effluent to storage basins and hence to the cooling tower is scaled with calcium carbonate scale. , This after-precipitation and scaling characteristic in the cooling water system is eliminated by the addition of sulfuric acid at two points. Acid is injected immediately following the cold lime reactor to lower the pH from about 10.5 to 9.5 which eliminates the after-precipitation. Just before the makeup enters the cooling tower, acid proportioning pumps inject sulphuric acid in quantities necessary to accurately maintain the pH of the circulating water at 7.8 and control the scaling in the cooling system. Acid injection at the two separate points is necessary because of the presence in the makeup cycle of the 2 million gallon storage lagoon which would complicate accurate pH control in the cooling system if acid injection was attempted only at the cold lime reactor outlet. The analysis of an average sample of circulating water is shown under C in table 1.

Heavy dosages of chlorine gas are fed to the circulating pump suction to control biofouling of the heat exchange surfaces in the condenser. We are using an average of 68 pounds of chlorine per million gallons of makeup in the plant being operated on sewage disposal plant water, compared with 10 to 15 pounds of chlorine in plants using well water,

Sewage disposal plant effluent is chlorinated as it leaves the sewage plant to control biofouling of the water lines. This water arrives at our cold process treatment plant with from 1 to 5 ppm free chlorine residual. However, the water contains both ammonia and nitrate nitrogen and is highly nutrient to a variety of slime forming organisms. The circulating system therefore incubates a vast quantity of slime formers and the chlorine demand is such that a chlorine feed rate of 2 ppm at the pump suction produces only 0.2 ppm at the condenser discharge. The retention time is less than 2 minutes. The figures vary considerably but these given are typical after chlorinating for from 4 to 6 hours. When the chlorinators are shut down, the free chlorine residual falls to zero in a very few minutes.

One such chlorination period every other day is the present standard and maintains the heat exchanger in a fairly clean condition indefinitely. The definition of "fairly clean" in this case is a change in steam temperature minus water-out temperature (terminal difference) of three degrees, from 6.0 to 9.0 F. A light deposit of 50% silica, 40% copper, and 10% organic is formed on the tube surface. At this time, this deposit is thought to be the unremoved residue of chlorinated organisms, along with materials held by the colonies and corrosion products from the admiralty brass condenser tubes which are observed to be microscopically pitted. Corrosion of the admiralty tubes is thought to be due to biological reactions of this water.<sup>7</sup> It appears to be a dezincification with the copper remaining or being redeposited. The admiralty tubes are inhibited with phosphorus. Investigations now underway are expected to throw more light on the mechanism of this corrosion process.

For the time being, the deposit is of more economical interest than the corrosion since the corrosion rate of the admiralty has been repeatedly measured at .002 to .004 ipy and the rate of iron at .004 to .007. The scale has been successfully removed from one condenser with inhibited hydrochloric acid, at a cost of \$3,500.

Detailed inspections of the cooling towers in this system indicate that the redwood is not deteriorating at any measurable rate. The redwood

is Erdalith-treated to standard penetration and retention schedules as outlined by the Cooling Tower Institute. The hardware is silicon bronze and shows no corrosion. Silicon bronze banding material cracks in one to two years. It is thought that improper technique was used in clinching the band back on the buckles. This unnecessary stressing may have caused corrosion cracking in the high chloride water.

The cooling towers in this system have poly-styrene grid type fill. No failure nor unusual changes in shape or dimensions have been noted in this material in the three-year period of operation.

In concluding this report, I note that it seems to recommend the use of sewage plant effluent as cooling tower makeup. Let us hasten to correct this to the extent of stating that it was our intent only to reassure and comfort those contemplating its use. Our problems have been many; however, we prefer to consider them as opportunities, and as time passes we hope to find better methods and smoother operation.

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