AN ABSTRACT OF THE THESIS OF

<u>Abdullah A. Abu-Al-Saud</u> for the degree of <u>Doctor of</u> <u>Philosophy</u> in <u>Chemical Engineering</u>, presented on <u>August</u> <u>15, 1988.</u>

Title: The Effect of Copolymer and Iron on the Fouling Characteristics of Cooling Tower Water Containing Corrosion Inhibitors.

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Abstract approved:

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Various antifoulant treatment programs and the considerations necessary for the effective use of such programs were examined.

Two different groups of tests, with and without iron contamination, have been carried out on the effectiveness of several of the state-of-the-art copolymers (PA, HEDP, AA/HPA, AA/MA, SS/MA and AA/SA) in the inhibition of the fouling of high hardness cooling tower water containing phosphate corrosion inhibitors (polyphosphates and orthophosphates).

The tests were conducted on metal surfaces (SS, CS, Adm, and Cu/Ni), using simulated cooling water in a specially designed cooling tower system.

For each group of tests at various pH values (6.5, 7.5 and 8.5), the effects of flow velocity (3.0, 5.5, 8.0

ft/sec) and heat transfer surface temperature (130, 145, 160°F) on the fouling characteristics of cooling tower water have been investigated. During the course of each test, the water quality was kept constant.

For the iron tests, the effects of iron presence (2, 3 and 4 ppm Fe) on the fouling characteristics of the cooling tower water have been investigated and discussed for three different situations:

- 1. High hardness cooling tower water and iron.
- High hardness cooling tower water, iron and phosphate corrosion inhibitors.
- 3. High hardness cooling tower water, iron, phosphate corrosion inhibitors and copolymers.

When fouling occurred, measurements were made of the fouling thermal resistance as a function of time. Four different fouling curves were obtained, linear, concave upward, asymptotic and sawtooth curves.

The fouling data obtained were correlated with the Heat Transfer Research, Inc. (HTRI) model and fouling predictive equations and charts were developed.

For the two groups of tests, the effectiveness of each copolymer has been evaluated and the threshold values of surface temperature, flow velocity and pH have been identified. The Effect of Copolymer and Iron on the Fouling Characteristics of Cooling Tower Water Containing Corrosion Inhibitors

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THE EFFECT OF COPOLYMER AND IRON ON THE FOULING CHARACTERISTICS OF COOLING TOWER WATER CONTAINING CORROSION INHIBITORS

I INTRODUCTION

This study is part of an on-going experimental program under way at Oregon State University on the fouling characteristics of cooling-tower water.

Fouling is defined as the formation of deposits on heat exchanger surfaces which impede the transfer of heat and increase the resistance to fluid flow.

Cooling-tower water is utilized as a medium for heat rejection to the surroundings via heat-exchange equipment. Untreated open recirculating cooling-tower water may contain significant concentrations of scale-forming ions, such as Ca^{+2} , Mg^{+2} , CO_3^{-2} , SO_4^{-2} , PO_4^{-3} and SiO_3^{-2} which can form inverse solubility salts at high temperature. These salts may deposit on the hot heat-transfer surface.

Control of pH and the use of scale inhibitors are the common methods by which fouling of cooling tower water can be reduced or, in the best case, prevented. As pH decreases, the solubility of many scale forming salts increases and the deposition rate is significantly reduced. The pH is usually reduced to the range of 6.5 and 7.0 by the addition of sulfuric acid to the cooling water system. Under these conditions, however, the cooling water is slightly corrosive to the material in the

system, therefore corrosion treatment is necessary. Nontoxic phosphate corrosion inhibitors are now being used to meet environmental requirements. However, all of the phosphate-containing treatment programs suffer one major draw back; the phosphate level used must be verv stringently controlled. Too much phosphate causes uncontrolled precipitation of calcium phosphate salts, while too little does not provide the corrosion protection required. To alleviate this problem, corrosion inhibitors are commonly used in conjunction with antifoulants.

The objective of this investigation is to study the effects of state-of-the-art copolymers as antifoulants on the fouling characteristics of cooling-tower water containing phosphate corrosion inhibitors with and without Corrosion inhibitors used in this iron contamination. study are orthophosphate and polyphosphate. Antifoulants polyacrylates, phosphonates (HEDP), used are acrylic acrylate (AA/HPA), acrylic acid/hydroxypropyl acid/sulfuric acid (AA/SA), sulfonated styrene/maleic and acrylic acid/maleic anhydride anhydride (SS/MA) (AA/MA).

The amount of deposit on a heat-transfer surface is measured in terms of the thermal resistance of the deposit. Generally, if the thermal resistance is less than Ø.0001 ft^m hr °F/Btu, the amount of fouling is tolerable, and the heat exchanger operates essentially as a clean heat exchanger.

The most important parameters that effect the fouling process are surface temperature and the surface condition of the heated surface, fluid bulk temperature, flow velocity/shear stress and water quality. A correlation, among the important parameters that affect and control fouling, which will reliably predict fouling resistance or determine conditions under which fouling would not occur would be most useful to the designer and operator of heat exchange equipment.

II GENERAL REVIEW AND LITERATURE SURVEY

Heat Transfer Equations

The effect of fouling in terms of fouling resistance on the design of heat transfer equipment is expressed in the fundamental equation for the overall heat transfer coefficient U_{co} on the outside of the surface as

 $\frac{1}{U_{0}} = \frac{1}{h_{0}} + \frac{A_{0}}{A_{1}} + \frac{1}{H_{ro}} + \frac{A_{0}}{A_{1}} + R_{w} \qquad (2-1)$

and subscript:

0 = outside i = inside w = wall

The convective heat transfer coefficients, h_1 and h_0 , and the thermal resistance of the wall can be determined with reasonable accuracy using well established techniques and correlations.

Accurate general methods for predicting the fouling resistance, which is often a major or even the dominating term in the equation, have not been developed for two reasons. First, fouling varies with time which makes it difficult to justify the assumption of a steady state. Second, the fouling resistance depends on the thermal conductivity of the deposit.

Since the fouling resistance often approaches an equilibrium value, the heat exchanger designer selects the values for fouling resistance from some tabulated values or from experience based on sources which often do not have any relevance to the actual operating conditions. This is unacceptable, as the fouling resistance may be controlling, and can be the most important factor in the sizing of the heat exchange equipment. This can result in the heat exchange equipment operating below normal efficiency or result in the over design of the heat Thus, there is substantial incentive to exchanger. develop correlations which will reliably predict fouling resistances or determine conditions under which fouling would not occur.

Fouling Types

The mechanism of fouling for cooling tower water can vary according to the source and quality (hardness, pH, suspended solid, treatment type, etc...) of the particular water under consideration.

The primary types of fouling occurring in cooling tower water system are precipitation fouling of inverse solubility salts, sedimentation, corrosion of the heat transfer surface and biological growth.

Precipitation Fouling

Precipitation fouling involves the crystallization of dissolved species from solution onto the heat-transfer surface. Precipitation fouling occurs when process to supersaturation of the dissolved conditions lead inorganic salts having inverse solubility with temperature at the heat-transfer surface. Common inverse solubility salts include CaCO₃, CaSO₄, Mg(OH)₂ and Ca₃(PO₄)₂. Normally there is a time interval between the start-up of a clean heat exchanger and the first detection of a decrease in the heat transfer due to fouling. During this time delay or initiation period, negligible fouling observed and conditions that deposition is promote subsequent fouling are established. Among these are establishment of a temperature, concentration or velocity gradient, formation of crystal nucleation sites, or formation of a sticky film on the heat exchanger surface. At a certain point in fouling process, the nucleation sites become so numerous they combine together and the fouling increases rapidly. Precipitation fouling has been reviewed by Hasson (11).

Particulate Fouling

Particulate fouling is defined as the accumulation of

particles such as sand, dust, clay, etc., suspended in the cooling tower water onto heat-transfer surface. It is frequently superimposed on crystallization fouling process. In a few cases, the deposition occurs as a result of gravity, in which case the process is referred to as sedimentation. This type of fouling was reviewed by Gudmundsson (9).

Corrosion Fouling

Corrosion fouling involves an electrochemical reaction of the heat exchanger surface, producing reaction products and roughening of the heat transfer surface. This may both inhibit heat transfer and promote fouling by other mechanisms. This type of fouling was reviewed by Somerscales (30).

Biological Fouling

Warm heat exchanger surfaces can provide suitable environments for bacteria, algae and fungi, which can form layers which significantly decrease the rate of heat transfer. This biofouling is usually prevented in cooling towers by adding chlorine or other biocides. A review of biofouling is by Characklis (3).

Of the above fouling types, precipitation fouling is

the most significant in the fouling of cooling tower water.

Fouling Mechanism

The overall fouling process can be viewed as consisting of five subprocesses:

Initiation

An induction period of a certain time duration is normally present during which conditions that promote subsequent fouling are established. Among these are establishment of a temperature, concentration, or velocity gradient, formation of crystal nucleation sites or formation of a sticky film on the heat exchanger surface. In some cases, an initial enhancement in heat transfer may actually occur because the rough initial deposit may act as a turbulator to break up the viscous sublayer. For more detail see Characklis (2).

Transport To The Surface

The transport mechanisms which are very important for cooling tower water are:

 * Diffusiophoresis: A concentration gradient acts as driving force. (1)
 * Turbulent diffusion: particles become entrained in eddies of turbulent boundary layers and are swept toward the surface.

Attachment

Some of the factors that are thought to contribute to foulant adhesion are van der waals forces, electrostatic forces, the surface tension of the absorbed surface film and external force field. (1)

Transformation

Once the deposit is formed, transformation, i.e. physical or chemical changes, or aging, may occur. (1)

Removal

Removal or re-entrainment of the deposit may begin as soon as an initial layer is deposited. Removal may occur as a result of spallation where material is detached in a large mass or as a result of erosion where material is detached in a particulate form or as a result of dissolution where material is detached in ionic form, Somerscales (30).

Important Parameters

The fouling process of cooling tower water appears to be most affected by flow velocity/shear stress, surface temperature, water quality and the condition of the heated surface, Watkinson (35).

Velocity Effects

Velocity affects the fouling process with respect to both deposition and removal. Velocity influences mass diffusion-controlled deposition processes through convective mass transfer to the surface. The effect of velocity on the removal process is generally correlated in terms of wall shear stress and deposit mechanical strength. (26)

Temperature Effects

In cooling water systems, the temperature of the surface is higher than the bulk fluid temperature. In such cases, the inorganic substances that are inverse solubility salts may deposit on the high temperature surface. The crystallization rate of inverse solubility salts is exponentially related to the inverse of the surface temperature in the form of an Arrhenius type of relationship which is characteristic of a chemical reaction. For constant heat flux operation the temperature at the tube surface-scale interface increases as fouling proceeds and this temperature which increases within the deposit plays a vital role in the aging of the deposit. The aging process produces changes in the crystal structure which effects the strength of the deposit and thereby the removal rate of the deposit. Bulk temperature has an effect on the saturation concentration of the salts in solution and on the rate of crystallization. Thus, the rate of development of fouling resistance generally increases with temperature.

Surface conditions

A rough surface provides numerous nucleation sites which help in initiating the deposition process. Thus, a smooth surface will have correspondingly a longer induction period. In many instances it has been found that once the clean surface is wholly covered by the deposit then the ensuing fouling process is not in any way determined by the tube material or the surface conditions.

Water Quality

In cooling water systems, water quality is a key factor in fouling problems that might occur. Salts with inverse solubility may lead to scaling. Suspended solids may settle out on the heat transfer surface. In general pH and the concentration of different mineral salts components have been used to characterize water chemistry. These quantities can be related to fouling tendencies of water. (27)

Predictive Methods

Recent attempts to mathematically model the fouling processes have been based on the following general material balance.

$$\frac{dR_{r}}{d\theta} = \phi_{d} - \phi_{r} \qquad (2-2)$$

Where:
$$R_{\tau}$$
 = fouling resistance = X_{τ}/k_{τ}
 Θ = time
 p'_{cl} = deposition rate
 p'_{τ} = removal rate
 X_{τ} = instantaneous fouling film thickness
 k_{τ} = thermal conductivity of fouling deposit

The deposition rate function depends upon the mechanism of fouling, the surface temperature, the flow conditions, and the water quality. The removal rate function depends upon the strength of the crystalline structure and the shear stress resulting from the flow of the fluid over the deposit layer. When the removal rate increases with the fouling layer thickness due to the deteriorating stability of the deposit, the deposition and removal rate ultimately become equal resulting in a constant asymptotic fouling resistance value. The basic

problem in fouling research is to determine those parameters which affect deposition and removal rate and to develop predictive correlations to account for these effects. The following authors [Santoso (29), Suitor (22), Story (31), Roy (28), Lahm (19) and Taborek et al (32)] give summaries of the fouling models that exist in the literature as follows:

Kern-Seaton Model (13,14)

This model was the first model to account for simultaneous deposition and removal rates. The model predicts an asymptotic fouling resistance and was derived to obtain curves which could describe fouling data obtained by Katz (14). The deposition rate was assumed to be constant, and the removal rate was assumed to be proportional to the shear stress and to the instantaneous thickness of the deposit layer. Kern and Seaton (15,16) proposed the following model for the material balance Equation:

$$\frac{dXf}{d\theta} = K_1 C^1 W - K_m \tau X_m \qquad (2-3)$$

Where:
$$K_1C^1W$$
 = deposition rate
 $K_m\tau X_r$ = removal rate
 K_1, K_m = constants
 C^1 = concentration of the foulant
 W = flow rate of the liquid
 τ = shear stress
 X_r = instantaneous fouling film thickness

Upon dividing Equation (2-3) by the thermal conductivity of the deposit K_{τ} and integrating, R_{τ} becomes

$$R_{\tau} = R_{\tau}^{*} [1 - exp(-\theta/\theta_{c})] \qquad (2-4)$$

With:
$$R_{\tau}^{*} = \frac{K_{1}C^{1}W}{K_{c}K_{\tau}\tau} \qquad (2-5)$$

and

$$\Theta_{e} = \underline{1}$$
 $K_{e}\tau$
(2-6)

 Θ_{ec} = time constant.

Equation (2-4) shows that R_r will approach R_r^* as time becomes large.

Watkinson-Epstein Model

Watkinson-Epstein (36) postulated that the deposition rate is proportional to the product of the mass flux normal to the surface and the sticking probability. The sticking probability is proportional to the adhesive force and inversely proportional to the hydrodynamic forces at the interface, and the removal rate is similar to Kern-Seaton's model.

$$\phi_{\rm cl} = K^{\rm s} J s$$
 (2-7)

and

$$J = k_m (C_m - C_m)$$
 (2-8)

Where:

K' = proportionality constant s = sticking probabilityJ = mass flux K_m = convective mass transfer coefficient C_m = concentration of foulant at the interface C_b = concentration of foulant in the bulk

Watkinson-Epstein obtained experimental data for sour gas oil and compared the data against the fouling model proposed by Kern and Seaton (15,16). It was found that the asymptotic fouling resistance was inversely proportional to the mass flow rate squared, in contrast to the mass flow rate to the first power in the Kern model Equation (2-4). They also found that the initial fouling rate was inversely proportional to the mass flow rate and dependent exponentially on the initial wall temperature. In the Kern-Seaton model, the initial fouling rate, which is a product of R^*_{τ} and $1/\Theta_{c}$ given in Equations (2-4) and (2-5), is directly proportional to the mass flow rate to the first power and independent of the wall temperature.

HTRI Model

Taborek, et al (33), in a very comprehensive work on cooling tower water, used the Kern-Seaton concept of deposition and removal to postulate a fouling model that also considered water chemistry and its effect on the fouling resistance. The deposition term is a function of the scale surface temperature in an Arrhenius-type crystallization reaction term and water chemistry parameter. Also included is a velocity function for the deposition rate.

$$\phi_{cl} = C_1 F^{\gamma} \Omega^{n} \exp[-E/R_{cl}T_{m}] \qquad (2-9)$$

Where:

C_{1},n	=	constant
F۲	=	deposition velocity functions
Ω	=	water quality term which is a function of LSI
E	=	activation energy of deposit reaction
Re	=	gas constant
T.	=	absolute temperature of the scale surface

The removal term is presented as a function of the wall shear stress, the scale thickness and scale bonding strength of the deposit

$$\phi_{r} = \frac{C_{RT} \chi_{r}}{Y}$$
(2-10)

Where:

 $C_{R} = constant$ Y = scale strength term Combining Equations (2-9) and (2-10) and substituting into Equation (2-2), an expression for the fouling rate is obtained

$$\frac{dR_{+}}{d\Theta} = C_{1}F^{\vee}\Omega^{n} \exp\left[-E/R_{\odot}T_{m}\right] - \frac{C_{e}\tau K_{+}R_{+}}{Y}$$
(2-11)
d Θ

For n=1, integrating Equation (2-9) results in an expression for the fouling resistance as a function of time

$$R_{\tau} = \underline{K_{\Box}} \exp(-E/R_{\Box} T_{w})(1 - \exp(-K_{4}\theta)) \qquad (2-12)$$

$$K_{4}$$

Where:

 $K_{a} = C_{1}F^{\vee}\Omega^{h}$ $K_{4} = C_{a}\mu K_{f}/Y$

After a very large time, the asymptotic fouling resistance, R^* is given by:

$$R_{+}^{*} = \underline{K_{\oplus}} \exp(-E/R_{\oplus} T_{\oplus}) \qquad (2-13)$$

$$K_{+}$$

writing Equation (2-12) in terms of R_{π}^*

$$R_{\tau} = R_{\tau}^{*} [1 - \exp(-\theta/\theta_{c})]$$
 (2-14)

where

$$\Theta_{c} = \underline{1} = \underline{Y}$$
(2-15)
$$K_{4} = C_{e}\tau K_{T}$$

Chemical Treatments

The most commonly used medium for removing heat in industrial processes is water from open recirculating cooling tower systems. Corrosion is one of the most costly problems encountered in cooling towers. It causes two major problems: equipment failure and loss of heat transfer efficiency. The corrosion process can be prevented, or at least, reduced by adding corrosion inhibitors. One of the most successful non-chromate treatments for corrosion inhibition has been phosphate combinations. The problem with phosphate based treatments is the formation of phosphates salts that precipitate on the heat transfer surfaces. Thus cooling tower water is chemically treated to prevent corrosion and or fouling.

Corrosion Inhibitors

Corrosion is an electrochemical process, arising from the existence of areas called anodes, where electrons are lost by metal, and other areas called cathodes, where electrons are accepted. Thus agents that control corrosion have been classified according to the mechanism of their action as anodic or cathodic inhibitors.

The corrosion inhibition process is best summarized as one or more of three general mechanisms (26). In the first, the inhibitor molecule is adsorped on the metal surface by the process of chemisorption, forming a thin protective film either by itself or in conjunction with metallic ions.

In the second, some inhibitors, however, merely cause a metal to form its own protective film of metal oxides.

In the third, the inhibitor reacts with a potentially corrosive substance in the water.

Anodic inhibitors passivate the metal by shifting its oxidation potential at the anode several tenths of a volt in the noble, less positive, direction and slowing the corrosion reaction. A protective, invisible, film is formed along the anode that may eventually cover the entire metal surface and prevent corrosion.

Cathodic inhibitors suppress the reduction of oxygen at the cathode by the electrons of the corrosion current. In contrast to the anodic inhibitors they often form a visible film along the cathode surface, which polarizes the metal by restricting the access of dissolved oxygen to the metal substrate. The film also prevents depolarization by blocking hydrogen evolution sites.

In actual plant operation, usually two or more corrosion inhibitors are blended to utilize the advantages of each and to minimize their respective limitations. Frequently anodic and cathodic inhibitors are combined to give better total metal protection. In this way the plant corrosion control program can be significantly improved.

Orthophosphates

An orthophosphate ion (23,26) behaves as a weak anodic inhibitor by forming a loose film on the surface of the metal. This film is not tenacious and is sensitive to changes in pH. Protection by orthophosphates is meager and uncertain at best. Thus for these reasons and for the danger of calcium phosphate sludge formation, orthorphosphates are rarely used alone for corrosion control.

Polyphosphates

Polyphosphates are cathodic inhibitors. Their inhibition mechanism and their behavior is (23,26) as follows: polyphosphates form a durable polarizing film on the cathodic surface of most metals. The molecule adsorps or bonds with calcium ions to form colloidal particles. These positively charged particles bond tightly to the metal surface and form a protective film.

At high temperatures and low or high pH, polyphosphates revert to orthophosphate. This reversion process is a major problem associated with use of polyphosphates, since orthophosphates are a weak anodic inhibitor which cannot provide the corrosion protection of polyphosphate. Also, orthophosphates can react with other components in the cooling water and form inverse solubility salts which precipitate on heat transfer surfaces. A draw back of polyphosphates is their nutrient potential for algal growth when they revert to orthophosphates.

Dissolved metal ions in the water will have positive and negative effect on the polyphosphate inhibition process. A positive effect of dissolved iron in the water is the strengthening of the protective film through the inclusion of iron. The negative effect is that iron can complex polyphosphate, thereby rendering it useless as an inhibitor. Recent technology has substantially minimized the limitation of polyphosphate by blending with other materials.

Antifoulants

Antifoulants are used alone or in combination in order to properly control fouling. Fouling in an actual cooling tower is an extremely complex phenomenon, thus an understanding of individual foulants and their control is important. Foulants can be calcium compounds, iron oxide, microbiological suspended solids and process contamination. Antifoulants can be polymeric or nonpolymeric (polyphosphate) in Polymeric anti-foulants nature. prevent fouling by two processes. First by acting as scale inhibitors of inverse solubility salts, and second, by dispersing the suspended particles in the cooling

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water. Types and mechanisms of fouling inhibitors are reviewed by (23,26).

Scale Inhibition

Precipitated salts of calcium and magnesium often form dense scales and sludges which are difficult to remove. In addition, they are very effective heat insulators. CaCO₃, CaSO₄, CaSIO₃, MgSIO₃, Ca₃(PO₄)₂ and MgPO₄ particles are ome of the most prevalent scale forming compounds in cooling water systems.

The co-polymers inhibit the scale formation of these compounds by adsorping to the surface of their crystals and disturb their lattice structure and normal growth patterns, thereby preventing them from growing into larger particles. The inclusion of a relatively large irregularly shaped polymer in the scale lattice tends to produce particles that are amorphous in nature and relatively nonadherent thus preventing the deposition of a dense uniformly-structured crystalline mass on the metal surface. In theory these crystals can develop internal stresses which increase as the crystal grows, with the result that the deposit breaks away from the metal surface.

Dispersants

Dispersants are polymers which control particles by increasing the charge on the particle surface by imparting a like charge to them and to the heat transfer surface, thereby keeping the particle repelled and suspended.

There are cationic polymers and anionic polymers, which act as dispersants. Cationic polymers ionize in water to become positively charged. Anionic polymers ionize in water to become negatively charged. For this reason, polymers are oftenly referred to as polyelectrolytes. Because of fouling material, other than the waterborne salts found in cooling water already has a slightly negative surface charge. It is economically sound to add anionic polymers to the water. These increase the negative surface charge and keep particles separated. Dispersants work on water and air-borne foulants such as mud, clay, sand, silt and dirt.

Polyphosphates

Polyphosphates are chelating agents. They alter the crystal structure and produce deformed crystals that prevents the growth of normal calcite crystal that leads to scaling. Chelants are sequestrants that depend upon stoichiometric reactions between themselves and deposit components. A sequestrant is an agent which prevents an ion from exhibiting its normal properties by complexing

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with it below stoichiometric levels. Polyphosphates have been used to control iron and hardness salts for a number of years. Polyphosphates have little effect on the precipitation of calcium sulfate. In recirculating cooling systems, polyphosphates are more often used to control corrosion.

Polyacrylates

Polyacrylates are polymers which have been used as scale control agents and also for the control of suspended matter as a dispersant agent. Polyacrylates adsorp on to the crystal structures of scale forming materials, and thus limits crystal growth and ultimately scale formation. Polyacrylates, like, other polymers act as dispersants by impairing like charges to the surfaces of the particles thus keeping them in suspension.

Phosphonates

Phosphonates do not hydrolyze as easily as polyphosphates. For this reason they are better deposit-controlagents than polyphosphates, whereas polyphosphates are superior corrosion inhibitors. The mechanism of scale inhibition is the same as that of polyphosphates. One phosphonate class is hydroxyetheyidene-1, 1 diphosphonate (HEDP).

Copolymers

Copolymers are being used as dispersants and scale inhibitors in cooling water systems. Copolymers are formed when different monomers are used in the polymerization reaction, thus utilizing the advantages of each monomer and minimizing their respective limitations. Four state-of-the-art copolymers are being investigated in this study.

SS/MA

Sulfonated styrene/maleic anhydride copolymer (SS/MA) prevents the formation and deposition of scale and sludge and in particular calcium phosphate. SS/MA is a highly charged anionic polyelectrolyte that is chemically and thermally stable.

AA/SA

Acrylic acid/sulfuric acid copolymer (AA/SA) is a threshold inhibitor which inhibits crystal growth by introducing an impurity into the lattice of a growing crystal. AA/SA is particularly effective for controlling the precipitation of calcium phosphate. The AA/SA copolymer is a dispersant for suspended materials such as silt and metal oxide.
AA/HPA

Acrylic acid/hydroxypropyl acrylate copolymer (AA/HPA) is an organic scale inhibitor particularly for calcium phosphate. It is also a dispersant agent for particulate matter such as clay and iron oxide.

AA/MA

Acrylic acid/maleic anhydride copolymer (AA/MA), like the above three copolymers, acts as a scale inhibitor and dispersant.

III EXPERIMENTAL EQUIPMENT

The equipment used for this study has evolved over a period of several years. Several earlier studies (4, 9, 21, and 24) and recent studies (19, 28, 29) have described earlier and recent versions of the system. The differences among these studies is the minor paraphrasing of their description of the system. To avoid further paraphrasing in this study, the most recent study of Santoso's (29) description is presented with minor modification as it applies to this study.

The equipment was designed to simulate the operating conditions of a commercial cooling tower system. A schematic flow sheet of the complete system is shown in Figure III-1. It consists of three main parts: the heat exchanger system, test sections and the cooling tower system. To eliminate the effect of corrosion on the fouling characteristics as much as possible, non-corrosive materials are used throughout the cooling tower system. Piping was primarily of polyvinylchloride (PVC) or chlorinated polyvinylchloride (CPVC), stainless steel and glass.



Figure III-1: Schematic Flow Diagram of Experimental Equipment

Heat Exchanger System

In order to maintain a constant bulk temperature of the water being tested a heat exchanger system was employed. The heat exchanger system is a closed loop circulating system. City water, heated to 120 - 130°F in a 40 gallon domestic electric water heater is pumped to the shell side of countercurrent shell and tube heat exchanger. The cooling water to be tested is heated in the tube side of the heat exhanger. The heat exchanger has 19 stainless steel tubes with 1/2 in OD, 16 BWG wall, and a length of 7 feet. A temperature controller regulates the heated water flow rate to the heat exchanger to maintain a constant water bulk temperature in the test system.

Test Sections

After the cooling water is heated in the heat exchanger, it flows through the test sections. A test section of annular geometry is shown in Figure III-2. The heater rod has an outside diameter of .42 inches and is heated electrically over a length of 4 inches. Four chromel-constantan thermocouples are embedded in the heater wall to record the wall temperature as deposit accumulates on the rod surface. They are located on the



Figure III-2: Annular Geometry of Test Section

same cross-sectional plane 90° apart from each other. The outer glass tube has an inside diameter of .75 inches and the overall length of the test section is 16 inches. The test sections are mounted in Portable Fouling Research Units (PRFU) provided by Heat Transfer Research, Inc., (HTRI).

The test fluid flows through the annular section between the heater rod and the glass tube. Fouling occurs on the outside of the heated portion of the inner tube.

Conditions such as flow rate and surface temperature of the heated section can be set easily to the desired level by making appropriate adjustments in the flow rate of the water to be tested and the power input to the heater.

TABLE III-1

ID NUMBER	MATERIAL	OUTSIDE DIAMETER (in)	HEATED SECTION LENGTH (in)	A	k/x (E (THERM B	Itu∕hr ft 10COUPLES C	°F) 5) D
24Ø	SS	Ø.42	3.95	6,531	3,876	7,156	11,996
120	CuNi	Ø.4215	3.90	48,543	22,882	9,348	11,930
115	Adm	Ø.4225	3.9	37,881	34,961	70,095	32,499
238	SS	Ø.422	3.90		52,730	14,836	
239	SS	Ø.421	3.80	25,369	8,229	8,164	10,148

HTRI Heater Rod Specifications

Note:

k = Thermal resistance of rod.

x = Distance of thermocouple below surface of the rod.

- SS = Stainless steel (316L).
- Adm = Admiralty.

CuNi = Copper-Nickel (90/10)

Heater rods and specifications such as dimensions and thermal resistances of the tube wall are provided by HTRI. These values of each rod used in the investigation are summarized in Table III-1.

Cooling Tower System

The cooling tower system consists of three major parts: the spray cooling tower, the cooling tower sump and the blowdown unit. The total volume of cooling tower water in the system is about 260 liters. Cooling water is circulated through the system, absorbing heat in the heat exchanger and in the test sections and then is cooled in the spray cooling tower.

Spray Cooling Tower

The spray cooling tower is a cylindrical empty column 2 feet in diameter, 20 feet high. It is mounted concentrical above the cooling tower sump. After water flows through the test sections, it flows to the top of the cooling tower where it is sprayed through spray nozzles and falls through the tower. An induction fan at the top of the cooling tower draws air up through the tower and out the top.

Cooling Tower Sump

The cooling tower sump is a reinforced plastic cylindrical tank 4 feet high, 34 inches in diameter, with 1/8 inches thick wall. Water from the cooling tower spray is returned to the cooling tower sump to be recirculated.

Fortified city water was supplied to the cooling tower sump from the make-up tank through a level control valve to make up for evaporation and discharge losses. Other additives to the system were added directly to the cooling tower sump by means of metering pumps. Sulfuric acid (.05N) flows by gravity through a solenoid valve which was activated by pH controller.

Blow Down Unit

As the cooling tower water evaporates, the concentration of the mineral constituents increases due to the input of fortified city water and other additives being fed continuously to make up for the evaporative losses. In order to maintain a constant cooling tower water quality (mineral content), blowdown was withdrawn from the bottom of the cooling tower sump. A metering pump was used to control the rate of blowdown from the system, and the discharge was collected in the calibrated blowdown storage tank.

Data Acquisition System

Two data acquisition systems were utilized. The first system was a Digitec 1000 Datalogger. This equipment was capable of scanning the system sensors (temperature, flow, power, pH, conductivity and corrosion rate) at desired intervals (one minute to five hours) and print out the results in millivolts on a paper tape.

The second system was a Hewlett-Packard HP85 microcomputer for data acquisition. With this combination, it was possible to scan the system at any desired time during a test. Flows, temperatures, heat fluxes, fouling resistances, pH, conductivity and corrosivity could be printed out after each scan. At the end of a test all data were tabulated and plots of velocity, surface temperature, fouling resistance, pH, conductivity and corrosion rate as a function of time were produced by the computer.

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IV EXPERIMENTAL PROCEDURES

Experimental Program

The purpose of this study is to determine the effectiveness of state-of-the-art copolymers as fouling inhibitors with, and without iron contamination and using phosphates as corrosion inhibitors. Several parameters which significantly affect fouling will be investigated. Three different velocities (3, 5.5 and 8 ft/sec) and surface temperatures (130, 145 and 160°F) will be covered. The three major water chemistry parameters are pH, corrosion inhibitor additives and fouling inhibitors additives. The effect of the material of the heated surface will be studied.

The main constituents of the city water and additives free system water are shown in Table IV-1. Runs 302 to 407 are without iron addition.

These will be referred to as non-iron tests. Beginning with run 408, iron will be added to the system through a metering pump. These will be referred to as iron tests. The addition of the iron will be accomplished by adding the required amount of ferrous sulfate heptahydrate (Fe SO₄.7 H $_{\cong}$ O) to the system.

For the duration of the investigation, phosphate corrosion inhibitors as orthophosphates and polyphosphates will be used. Table IV-2 shows the additives that will be used in each group of tests.

Table	IV-1.	Cons	stituents	of	the	City	Water
		and	Additive-	-Fre	e Sy	/stem	Water

Constituent	City Water	System Water Average Values
Specific conductance, micrombo	100	1700
Sulfate, ppm SO ₄	1Ø	8ØØ
Chloride, ppm Cl	1Ø	4Ø
Total hardness, ppm CaCO ₃		1000
Calcium hardness, ppm CaCO ₃	27	66Ø
Magnesium hardness, ppm CaCO ₃		34Ø
Copper, ppm Cu		Ø.1
Iron, ppm Fe		Ø.1
Sodium, ppm Na		60
Zinc, ppm Zn		Ø.9
Chromate, ppm CrO4		1.Ø
Total phosphate, ppm PO ₄		Ø.2
Silica, ppm SiO _m	20	35
Suspended Solids, mg/l		1Ø

	Additives									
Run Nos.	None	HEDP	PA	PP	OP	AA/HPA	AA/MA	SS/MA	AA/SA	Fe
302-307		2-4	2-4	4-5	5-6					
308-313				4-5	5-6					
314-323				4-5	5-6	1Ø				
324-332					1Ø	1Ø				
333-335					1Ø					
336-338				4-5	5-6					
339-341				4-5	5-6		10			
342-344				4-5	5-6			1Ø		
345-347				4-5	5-6				10	
348-365				4-5	5-6	10				
366-371				4-5	5-6		10			
372-374				4-5	5-6					
375-380				4-5	5-6			1Ø		
381-383				4-5	5-6					
384-395				4-5	5-6				1Ø	
396-401				4-5	5-6		1Ø			
402-407				4-5	5-6			1Ø		
408-413				4-5	5-6					2
414-419				4-5	5-6					4
420-429		2-4		4-5	5-6					4
430-435				4-5	5-6		10			4
436-438										
437-450			<u> </u>							З
451-461				4-5	5-6					з
462-469		1Ø		4-5	5-6					З

acid

Table IV-2. Additives Used in Each Group of Tests.

numbers represent ppm

HEDP	-	1-Hydroxyethylidene-1, 1-diphosphonic (Monsanto 2010)
PA	-	Polyacrylate (Goodrich K732)
PP	-	Polyphosphate added as $Na_zP_zO_7$
0P	-	Orthophosphate added as Na₃PO₄
AA/HPA	-	Acrylic acid/hydroxypropyl acrylate
AA/MA	-	Acrylic acid/maleic anhydride
SS/MA	-	Sulfonated styrene/maleic anhydride
AA/SA	-	Acrylic acid/sulfonic acid
Fe ·	-	Iron added as FeSO₄ 7·H₂O

Procedure

SYSTEM TO OBTAIN DESIRED WATER QUALITY

The system to obtain desired water quality was described by previous studies. The following description is adapted from the following studies (17, 29) with minor modification as it applies to this study.

The local city water contains about 20 ppm of calcium hardness and about an equal amount of silica. It is therefore, necessary to fortify the city water with calcium and magnesium to obtain the compositions shown in Table IV-1.

The complete water conditioning system is shown in Figure IV-1. City water (float controlled) and saturated calcium and magnesium sulfate solution (provided by a metering pump) flow into the well agitated make-up tank. The saturated calcium sulfate solution (fortifying solution) is prepared by mixing city water with powdered native calcium sulfate from Fisher Scientific. The required amount of magnesium sulfate is also added into the fortifying solution.

The mixture from the make-up tank flows through a float controlled valve to the cooling tower sump. The water to be tested was pumped through the cooling tower system by the circulation pump. The bulk water temperature was adjusted to the desired set point. The circula-



Figure IV-1: Water Conditioning System

tion of water was continued until the hardness and silica concentrations increased to the desired level, after which the blowdown was withdrawn from the cooling tower sump by a metering pump to maintain the desired water quality.

Other materials were added directly to the cooling tower sump. Phosphate corrosion inhibitor of appropriate composition was added at a constant rate to the sump through a metering pump. Antifoulant additives (whenever used) were added directly to the cooling tower sump by means of a metering pump. Iron as ferrous sulfate heptahydrate Fe SO₄.7H_EØ was also added directly to the sump through a metering pump.

The pH was controlled at the desired level by the addition of sulfuric acid (.05N) or sodium hydroxide, as needed, which flowed by gravity through a solenoid control valve which was activated by a pH controller.

RUN INITIATION

After the desired water quality for a particular run was obtained, the heater rods were fitted into the test sections. Then flow rate and surface temperature were set to the desired values by making appropriate adjustments in the flow rate and the power input to the heaters.

The Hewlett Packard 3540 data logger and the Digitec 1000 data logger were activated. The Digitec 1000 data logger was set to record every two hours throughout run

duration. The Hewlett Packard 3540 data logger was set to record ten readings at two minute intervals for calibration purposes, then it was set to record at six hour intervals for the remainder of the test.

PROCESS MONITORING

The system water was analyzed everyday for hardness, silica, sulfate, chloride and level of additives. Samples were taken at the beginning and at the end of each set of runs and were sent to Betz laboratories for complete analysis.

Corrosion, conductivity and pH were measured by online instruments and recorded by the data logger.

The amount of flow from blowdown, fortifying solution, city water and additives were recorded daily. Evaporation rates were calculated from daily flow-rate measurements. Typical flow rates and volumes are given in Table IV-3.

The blowdown rate is adjusted so that the Holding Time Index (HTI) in the system is about 24 hours. The HTI is the time required for the concentration of a constituent in the system to be reduced by 50% without addition of that constituent to the system. Variation in environmental conditions in the laboratory brought about fluctuation in the evaporation and city water rate. The fluctuation was not serious because the mineral content of

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the city water is small compared to the amount of minerals in the cooling tower water. The flowrate of the fortifying solution could be adjusted manually to maintain a constant water composition.

Table IV-3 Typical volumes and flowrates.

Volume in the system	260	1
Evaporation	100 - 200	l/day
City water	200 - 300	l/day
Blow down	175	l/day
Saturated CaSO ₄ solution	50 - 90	l/day
Inhibitor solution	2 ~ 3	l/day

Flow rates and power levels were monitored daily and adjusted manually whenever they were found to deviate from their original set values.

A volume of 20 ml commercial chlorine bleach was added daily directly into the cooling tower sump and 70 ml was added to the make-up water tank for control of biological growth.

RUN TERMINATION

Generally runs were terminated when the fouling resistance reached a constant value or when essentially no fouling was observed (i.e. the measured fouling resistance was less than .0002 hr ft^{ee} °F/Btu after about 150 hour duration). In many instances, runs were terminated while the fouling resistance was still increasing. Usually, in

these runs, sufficient data were obtained, so that the correlational methods used were applicable and it was apparent that the ultimate asymptotic fouling resistance would not be acceptable in an operating heat exchanger. When runs were terminated, the heater power and water flow in the test sections were turned off, the heater rods were removed from the test sections and the deposit, if any, was scraped off from the rod. After it was thoroughly dry, the sample was sent to the DuPont Company for chemical analysis, and then the heater rods were cleaned using a standard procedure and reused.

V CALCULATION PROCEDURES

Calculation of Fouling Resistance

The method of calculation of the fouling resistance is presented in the experimental procedure and the data acquisition system manuals. All previous fouling studies that used the cooling tower system used in this study, included the method of calculation of the fouling resistance (19, 29, 31). To avoid repetition and paraphrasing, the following was adapted from Santoso (29).

The method of calculation of the fouling resistance is based on the quantities defined in Figure V-1. During a test, flow rate in the test section, bulk temperature and heater power remained essentially constant. Under these conditions the temperature at the liquid/solid interface (Ts) is assumed to remain constant.

The wall temperature, Tw, was calculated from the wall thermocouple temperature, Tc, and the thermal conductance k/x between thermocouple and the heater wall by the Equation:

$$Tw = Tc - \frac{Q/AH}{k/x}$$
(5-1)

where

 $Q/AH = heat flux, Btu/hr ft^2$



Figure V-1: Cross Section of Clean and Fouled Test Section

At constant heat flux and constant velocity, the difference between the surface temperature, Ts and the bulk temperature, Tb is constant. The surface temperature is determined as follows.

$$Ts - Tb = \frac{Q/AH}{h}$$
(5-2)

where

The local bulk water temperature is calculated with the Equation:

$$Tb = \frac{Q}{B.020B(f)(C_{p})(W_{r})} + Tin \qquad (5-3)$$

where

8.0208 is the multiplication factor to convert gpm to ft³/hr.

Clean Condition (beginning of the run)

$$Ts_{c} = Tw = Tc - \frac{Q/AH}{k/x}$$
(5-4)

where

subscript = denotes the clean condition

Thus the heat transfer coefficient for a clean rod,

 h_{e} , is calculated from Equation (5-2) using Ts_e found in Equation (5-4):

$$h_{e} = \underline{Q/AH}$$
(5-5)
Ts_e - Tb

It is related to the flow velocity by Equation:

$$h_{e} = K V_{e}^{m}$$
(5-6)

where

K = proportionality constant m = .7 if V>4 ft/sec or .93 otherwise = clean condition

When a run is started, 10 scans of the data sensors are made at 2 minute intervals, from which an average value of K is calculated.

$$Kavg = \left(\sum_{k=1}^{149} h_{k} / V_{k}^{m}\right) / 10$$
 (5-7)

The value of Kavg computed above remains constant provided the assumption of constant bulk temperature holds.

Fouled Condition:

For a given velocity, h = Kavg V‴

(5-8)

The surface temperature for the fouled condition Ts, can now be determined from Equation (5-2):

$$Ts = \frac{Q/AH}{h} + Tb$$
 (5-9)

and finally, the fouling resistance Rf can be calculated by Equation:

$$Rf = (T_{C} - T_{S}) - 1 \qquad (5-10)$$

$$Q/AH \qquad k/x$$

The calculations were carried out by a Hewlett Packard 85 computer in conjunction with an HP 3054 Datalogger.

Error Estimation:

This is an estimate of the possible error in the measured value of the fouling resistance.

The relative error in the heat flux can be calculated from Equation:

$$\frac{d(Q/AH)}{(Q/AH)} = \frac{dQ}{Q} \pm \frac{dDROD}{DROD} \pm \frac{dL}{L}$$
(5-11)

where

Q = heater power consumption
DROD = outside diameter of clean heater rod
L = heated length section

and

$$\frac{dQ}{Q} = \frac{dQmv}{Qmv}$$
(5-12)

The heat flux and bulk temperature are relatively constant during a run.

Using Equation (5-2), the relative error of Tc and Tin can be calculated by the following equation:

$$\frac{dT}{T} = \begin{bmatrix} \frac{.949}{(Tmv + 5.02)} & dTmv, Tmv < -1.0 \\ \frac{.8765}{(Tmv + 4.72)} & dTmv, Tmv \ge -1.0 \end{bmatrix} (5-13)$$

The relative error of the bulk temperature is calculated from Equation (5-3):

$$\frac{dTb}{Tb} = Z_1 \frac{dQ}{dQ} \pm Z_1 \frac{dWF}{dWF} \pm Z_1 \frac{Z_P}{Z_P} \frac{WFTin}{dTin} \frac{dTin}{dTin}$$
(5-14)

where

$$Z_1 = \frac{Q}{Q + Z_{aa}}$$
(5-15)
Q + Z_{aa} Tin WF

$$Z_{a} = 8.0208 (f) (C_{p})$$
 (5-16)

and from Equation (5-3):

$$\frac{dWF}{WF} = \frac{dWmv}{(Wmv - 4)}$$
(5-17)

Clean Condition

From Equation (5-4):

 $\frac{(k/x)T_{c}}{Z_{3}} \frac{dT_{c}}{T_{c}} \stackrel{\pm}{=} \frac{(Q/AH)}{Z_{3}} \frac{d(Q/AH)}{Q/AH} \stackrel{\pm}{=} \frac{(Q/AH)}{Z_{3}8} \frac{d(k/x)}{(k/x)}$ (5-18)

where

$$Z_{\oplus} = (k/x) T_{C} - Q/AH \qquad (5-19)$$

and from Equation (5-15):

$$\frac{dhc}{hc} = \frac{d(Q/AH)}{Q/AH} \pm \frac{Ts_{c}}{Ts_{c}} \pm \frac{dTs_{c}}{Ts_{c}} \pm \frac{Tb}{Ts_{c}} \frac{dTb}{Ts_{c}}$$
(5-20)

Fouled Condition:

The relative error in surface temperature is obtained by differentiating Equation (5-9).

$$\frac{dTs}{Ts} = \frac{(Q/AH)}{Z_4} \frac{d(Q/AH)}{d(Q/AH)} \pm \frac{Q/AH}{Z_4} \frac{dh}{dh} \pm \frac{hTb}{dTb} \qquad (5-21)$$

where

$$Z_{4} = Q/AH + hTb$$
(5-22)

Since the flow velocity also remains essentially constant throughout the run:

$$\frac{dh}{h} = \frac{dhc}{hc}$$
(5-23)

Finally, from Equation $(5-1\emptyset)$ the relative error of the fouling resistance is:

$$\frac{dRf}{Z_{s}} = \frac{(k/x)}{Z_{s}} T_{c} \frac{dT_{c}}{Z_{s}} \pm \frac{(k/x)}{Z_{s}} T_{c} \frac{dT_{s}}{Z_{s}} \pm \frac{(k/x)(T_{c}-T_{s})}{T_{s}} T_{s} Z_{s}$$

$$\frac{d(Q/AH)}{Q/AH} \pm \frac{Q/AH}{Z_{s}} \frac{d(k/x)}{k/x} \qquad (5-24)$$

where

$$Z_{s} = (k/x)(T_{c}-T_{s}) - Q/AH \qquad (5-25)$$

Setting appropriate errors to each measured variable:

dTm∨	=	±	.005 millivolts
dD2	=	±	.0005 millivolts
dQ	=	±	.ØØ5 milli∨olts
dL	=	±	.005 millivolts
d(k/x)	=	±	50 millivolts
d(Wm∨)	=	±	.005 millivolts

the numerical values of the maximum relative error of the surface temperature and fouling resistance can be calculated from Equations (5-21) and (5-24).

The maximum experimental error in absolute value of the measured fouling assistance is ±15%. Within a run, the precision is much less than this as indicated by fouling resistance time plot in Appendix F. Several earlier studies (19, 29, 31) present a sample of calculation for fouling resistance and error estimation.

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<u>Calculation of the Inner Wall Shear Stress for Flowing</u> <u>Water</u>

Properties of water $(50 \le T \le 200^{\circ}F)$ $\mu = viscosity, lbm/ft sec$ $= \frac{(242/3600)}{(\Gamma = + 8078.4] \cdot = + \beta} 2.1482 - 120$ (5-26)

where

 $\Gamma = \frac{(T+459.72)}{1.8} - 281.615$ (5-27) $T = \text{temperature, }^{\circ}F$ $\int = \text{density, } \frac{16m}{ft^{\odot}}$ = 63.45 - .0156T $= \text{kinematic viscosity, } \frac{ft^{2}}{sec}$ $= \frac{\mu}{f}$

Flow rate/velocity

GPM = flowrate, gallon/minute
V = velocity, ft/sec

The fluid properties are evaluated at the bulk temperature of the fouling fluids.

Smooth Annular Ducts

 d_{ee} = I.D. of outer tube, inches d_1 = O.D. of inner tube, inches V = velocity, ft/sec = (.4085) GPM / ($d_{ee}^2 - d_1^2$) Re = Reynolds number

$$= \frac{(4 r_{H}) V}{(12)(\alpha)}$$
(5-28)

where

$$4 r_{H} = \frac{d_{P}^2 - d_{max^2}}{d_{e}}$$
, inches (5-29)

$$dmax^{2} = \left(\frac{de^{2} - d_{1}^{2}}{\ln(d_{e^{e^{e}}}/d_{1}^{e^{e}}} \right)$$
 (5-30)

 τ_{a} = shear stress on outer wall, lbf/ft^a

$$= \frac{f}{2g_{e}} \int \frac{\sqrt{2}}{2g_{e}}$$
(5-32)

 τ_1 = shear stress on inner wall, lbf/ft²

$$= \tau_{a} \left(\frac{d_{a}}{d_{1}} \right) \frac{d_{a} 2 - d_{1} 2}{d_{a}^{2} - d_{a} x^{2}}$$
(5-33)

d = ID of tube, inches V** = water velocity, ft/sec Re = Reynolds number = $(d/12) \vee \int / \mu$ f = friction factor = $.079 (Re^{-...m})*$ (Re > 5000) r = wall shear stress, lbf/ft^2 = $f \int V^2 / 2 g_m$ $g_m = 32.17 \ lbm ft/lbf sec^2$

combining all relationships

$$\begin{aligned} \mathbf{\tau} &= .0395 \ \underline{\mu} - \underline{\mathbf{z}} - \underline{\mathbf{z}} - \underline{\mathbf{z}} - \underline{\mathbf{z}} \\ \mathbf{g}_{e} &(\mathbf{d}/12) - \underline{\mathbf{z}} \\ \end{aligned} \tag{5-35}$$

* If the tube wall has a known roughness, a friction factor equation that also includes roughness should be used.

** If water flow in tube is known in terms of gallons per minute (GPM), then the velocity (ft/sec) is V = 4(GPM) / $[(60)(7.48)(\pi)(d/12)^2]$

Fitting The Fouling Curves

From the model developed by Heat Transfer Research, Inc. (HTRI), it was expected that the most of fouling resistance vs time curves could be represented by Equation:

$$Rf = RF (1 - exp (-\theta / \theta_c))$$
 (5-35)

The above equation assumes that fouling begins as soon as the test begins. However, on many of the runs in this study, an induction period or dead time of a certain duration was observed during which negligible fouling deposition occurred. Therefore, it was necessary to modify the above equation to include the induction period as follows

$$R_{\tau} = R^{*}_{\tau} \left[1 - \exp\left(-(\theta - \theta_{d})/\theta_{c}\right)\right]$$
 (5-36)

where $\theta_{\rm cl}$ is the induction period or dead time.

In order to solve for the constant R^* , and θ_c , it was necessary to use a nonlinear regression since Equation (5-35) cannot be linearized. A summary of the method of nonlinear regression analysis is given in Appendix I.

VI. RESULTS AND DISCUSSION

In order to understand the fouling process and how to control it, the fouling must be related to time, water quality, liquid flow rates, heat transfer surface temperature and the condition of the heat transfer surface.

Relations of this type could be used to design heat transfer equipment subject to fouling, and to formulate operating and cleaning schedules for heat transfer equipment.

It is clear from the literature on fouling that it is a broad and expanding subject. Thus the researcher on fouling must be content to work toward narrow and well defined objectives if progress is to be made toward finding better means of dealing with fouling problems.

In order to properly control fouling, an understanding of individual foulants and their control is required. For cooling tower water containing phosphate corrosion inhibitors several state of the art copolymer are currently manufactured to mitigate calcium phosphate deposition. The task of the fouling researcher is then to test their effectiveness in preventing fouling under various conditions of water quality, flow rates and heat transfer surface temperature and how they will affect the fouling characteristics of the cooling tower water fouling.

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Hopkins (13), who studied how ferric oxide fouls heat transfer surface in a 304 stainless steel tube, recommended his use of crevice corrosion to explain his fouling data.

Taborek (32), believes that the progress in fouling research requires the systematic collection of data on a wide variety of fouling systems and the subjection of such data to the various predictive fouling models in the literature.

In an attempt to shed light, or if possible, to answer some of these questions in the area of cooling tower water fouling, it was decided to examine the fouling behavior of high hardness cooling tower water with and without iron as a contaminant.

<u>General Data</u>

The experimental data for all the tests conducted in this study are available at the Department of Chemical Engineering, Oregon State University, (Contact: J.G. Knudsen). These data (for each run) are daily cooling tower water chemical analysis and flow rates. Tables of fouling resistance as a function of time, pH, surface temperature, flow velocity, corrosivity, heat flux and ambient temperature along with summary statistics of these values are also available at the Department of Chemical Engineering, Oregon State University. However, tables showing average and standard deviation values of cooling tower water analysis and flow rates are given in Appendices J and K, respectively. In an earlier study, Herbig (12) solubility data were compiled and saturation curves were constructed for the cooling tower water. These data along with solubility data for iron systems are given and discussed in Appendix M.

Results Presentation and Data Treatment

A summary of all runs are presented in a format shown in Table E-1 in Appendix E. This table shows run number, run duration, run condition (velocity, surface temperature, pH), additives, the asymptotic or final fouling resistance value and heater rod surface material.

Time plots of fouling resistance along with time plots of velocity, temperature and water quality (pH, conductivity and corrosivity) is another way of presenting the data, (See Appendix F). For each run, these plots allow one to determine if variations of any of these parameters during the run has an effect on the fouling resistance.

The final fouling resistance at run termination is presented in Appendix E, in a series of three dimensional figures, Figures E-1 through E-16. These figures are

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pictorial representations of all runs grouped according to the cooling water with same additives. For a given constant water quality, the three major parameters of interest are water velocity in the test section, surface temperature of the heated section and the pH of the water in the system, these parameters are shown on the figure. The cell of this matrix shows the final fouling resistance, the heater rod material type and the run number. The results displayed in these figures show (in a qualitative manner) the effect of velocity, surface temperature and pH on the fouling characteristics of a given water.

The threshold values for each fouling inhibitor under which fouling would not occur ($R^*_{\pi} < \emptyset.0001$ hr ft[@] °F Btu) are presented in Table VI-6.

Composite plots were constructed to show qualitatively the affect of various parameters on the fouling. These figures are given in Appendix G.

Throughout the subsequent sections where data are discussed and analyzed, a reference is made to the appendices and figures mentioned in this section.

Tests Without Iron:

The objectives of the proposed research without iron contamination were as follows:

1. To determine the effect of various state of the art antifoulants in reducing or eliminating calcium phosphate fouling of cooling tower water containing phosphate corrosion inhibitors under various conditions of pH, flow velocity and surface temperatures.

2. It was suspected that some antifoulants are a source of or increase fouling tendency. Thus one objective of this investigation was to determine and identify those antifoulants and the conditions at which they increase the fouling tendency.

3. In addition to information this study provides about the characteristics of the cooling tower water fouling, the data, when correlated, will allow prediction of fouling behavior under similar conditions.

A total of 107 tests were conducted to investigate the three objectives listed above. The following sections discuss and describe these tests.

Run Description and Discussion

1. No additive (runs 436-438)

The results of this additive combination are shown in Figure E-1.

These runs were essentially blank runs in which no additive whatsoever was added to the high hardness water (Table IV-1) used in this study.
The effect of velocity on the fouling resistance for runs 436 (5.5 ft/sec), 437 (8 ft/sec) and 438 (3 ft/sec) is shown in Figure G-1. The effect of velocity shown in Figure G-1 is consistent in that higher velocity produces less fouling.

These runs were at 160°F and pH of 7.5. While the rate of fouling for the additive-free water was not high, there is no indication in Figure G-1 that an asymptotic fouling resistance has been attained. After a long time unacceptable levels of fouling would probably occur particularly at the two lower levels of velocity (5.5 and 3.0 ft/sec).

2. Additive: 4-5 ppm PP, 5-6 ppm OP, 2-4 ppm HEDP, 2-4 ppm PA (runs 302 through 307).

The results of this additive combination are shown in Figure E-2.

All runs for this water were at 3 ft/sec and a pH value of 7.Ø. Runs 302 through 304 were at 145°F and comparison of these runs is given in Figure G-2. Runs 305-307 were at 160°F and comparison of these runs is given in Figure G-3. Considerable fouling occurred with this additive. Therefore, the use of HEDP in combination with polyacrylate do not appear to be effective in deposition tendency of reducing the water containing polyphosphate and orthophosphate corrosion inhibitors. The material of the heater used in these runs has little

effect, carbon steel shows somewhat higher scaling than stainless steel and copper/nickel at 145°F but somewhat lower at 160°F.

3. Additives: 4-5 ppm PP, 5-6 ppm OP (runs 308-313, 336-338, 372-374 and 381-383).

The results of this additive combination are shown in Figure E-3.

With this additive, runs 372-374 at 160°F and 6.5 pH, was being flushed from the system. copolymer AA/MA Composite plots comparing runs 311, 313 both at 160°F and 6.5 pH (Figure G-4) and runs 336-338 at 160°F and 7.5 pH(Figure G-5) show the effect of velocity and in general agree with the fact that a higher velocity produces less The composite plot comparing (Figure G-6), run foulina. 309 and 310 both at 145°F shows the effect of increasing pH from 7.0 to 7.5. Figure G-7 compares runs 313 with stainless steel heater rod and run 372 with Admiralty heater rod both at identical conditions. The results are comparable and agree within the experimental error of the At 6.5 pH and 130°F, insignificant fouling measurement. occurred for this additive.

4. Additive: 10 ppm OP (runs 333-335).

The results of this additive combination are shown in Figure E-4.

With this additive, minimal fouling was observed at velocities higher than 3 ft/sec. As expected, higher fouling occurred at 3 ft/sec and was increasing quite rapidly. The effect of velocity for this additive is shown in Figure G-8. Runs were at 6.5 pH and 160°F.

5. Additive: 10 ppm OP, 10 ppm AA/HPA (runs 324-332).

The results of this additive combination are shown in Figure E-5.

With this additive, all runs were at 160°F. Runs 324-326, runs 327-329 and runs 330-331 were at pH 6.5, 7.5 and 8.2 respectively. For all tests, it appears that negligible fouling would occur at the three pH levels investigated. The values of fouling resistance at pH 7.5 and 8.2 would seem to indicate that this additive combination is effective in reducing the tendency of fouling. Figure E-5 shows the fouling resistance values for the runs of this additive.

6. Additive: 4-5 ppm PP, 5-6 ppm OP, 10 ppm AA/HPA (runs 314-324 and 348-365).

The results of this additive combination are shown in Figure E-6.

Four levels of pH; 8.1, 8.5, 7.5 and 6.5, were investigated for this additive combination. At these pH levels, the copolymer AA/HPA was effective in reducing the fouling tendency of the phosphate. At a pH level of 7.5,

very little fouling was observed. Higher but insignificant fouling resistance at 160°F occurred for pH levels of 6.5 and 8.5 compared to those at pH of 7.5. This could be due to the higher phosphate level for the runs in which the pH levels were 6.5 (24 PP, 80 OP) and 8.5. The effect of pH for this additive is shown in Figure G-9. Figure G-9 shows that the trend with respect to pH is consistent in the sense that lower pH produces less fouling. Figure G-10 shows the effect of pH at 8.5 and velocity for runs 348-350. The pH dropped for runs 348-350 at 200 hours and significant fouling occurred. This could be due to the pH decrease, since much of the suspended calcium phosphate dissolved. Hence, as pH was brought to the desired value, rapid fouling occurred. Low fouling occurred at pH 7.5 at 160°F for runs 351-353. Figure G-11 shows the effect of velocity for these runs. This figure also shows that with 5.5 ft/sec higher fouling occurred for no explainable reason compared to the runs at 8 and 3 ft/sec which unexplainably differ little from each other. Very little fouling occurred at pH 7.5 and 130°F for runs 316 and 317. Figure G-12 shows the effect of velocity for runs 316 and 317. The effect of velocity for runs 354-356 is shown in Figure G-13. The curve for 3 ft/sec in this figure agrees guite well with that obtained for run 314 shown in Figure G-14. Figure G-15 also shows consistent behavior with respect to velocity for runs

357-359. A sudden increase in fouling resistance started to occur at about 125 hours. See Figure G-15 and time plots for these runs in Appendix F. This sudden increase in fouling resistance is not apparent except that at this time pH started increasing slowly reaching a value close to 9.0 at the end of the runs. Conductivity decreased slowly during this period of increasing pH. Had the sudden increase in the fouling resistance not occurred, it appears that the asymptotic fouling resistance would be in the range 0.0001 to 0.0003 hr ft °F/Btu. The fouling resistance for runs 363-365, pH of 6.5 and 160°F,was increasing slowly at run termination. The runs were terminated because of the abnormally high phosphate levels, (24 ppm PP, 80 ppm OP). The effect of velocity for these runs is shown in Figure G-16.

Figure G-17 shows the effect of surface temperature for runs 320 and 321. Figures G-18 and G-19 show consistent behavior with respect to surface temperature for runs 356-359 and 353 and 362 respectively. In general less fouling was observed at lower surface temperature (130°F); the amount of fouling was very small. Figure G-72 shows the effect of pH and surface temperature for runs 317 and 323.

7. Additive: 4-5 ppm PP, 5-6 ppm OP, 10 ppm AA/MA (runs 339-341, 366-371, 396-401).

The results of this additive combination are shown in Figure E-7.

With this additive, three pH levels were investigated; 6.5, 7.5 and 8.5. Composite plots in Figure G-20 for runs 339-341 at 160°F and pH is 7.5, Figure G-21 for runs 366-368 at 160°F and pH is 6.5 and Figure G-22 for runs 368-371 at 130°F and pH of 6.5 show the effect of velocity and temperature. For all three conditions, significant fouling occurred although at a lower rate of the higher velocity as would be expected. Consistent behavior with respect to surface temperature is shown in Figure G-22 for runs 368 at pH 6.5 and 160°F and run 371 at pH 6.5 and 130°F. Runs 368 and 371 both were at 3 ft/sec.

Significant fouling was obtained for this additive at a pH of 6.5 at phosphate levels about two times those employed at a pH level of 7.5. In all cases of different combinations of surface temperatures and flow velocities at pH's of 6.5 and 7.5, fouling was increasing rapidly, showing little tendency to approach an asymptote.

For this additive, runs 396-398 at 160°F and 399-401 at 130°F were at a pH of 8.5. The effect of velocity for runs 396-398 and runs 399-401 are shown in Figures G-23 and G-24 respectively. This effect is consistent with the results obtained at pH's of 6.5 and 7.5. The irregulari-

ties shown in Figure G-24 were caused by a power failure at about 300 hours. While the equipment was idle, the pH decreased and much of the suspended calcium phosphate dissolved. Hence, when the equipment was restarted, rapid fouling occurred with subsequent sloughing of the deposit as pH was brought to 8.5. The effect of surface temperature at pH of 8.5 is shown in Figure G-25. This figure shows that at 8 ft/sec the effect of surface temperature is consistent with the results obtained for pH's of 6.5 and 7.5 for 8 ft/sec. However, in Figure G-26 (runs 398-401) and for 3 ft/sec, surface temperature appears to have little effect. This is probably due to the presence of considerable suspended solids of calcium phosphate in the bulk stream at a pH of 8.5. Also, the higher average phosphate content for run 401 at 130°F could have caused the fouling resistance to be higher than expected.

For all tests, acrylic acid/maleic anhydride (AA/MA) copolymer was not effective in mitigating the precipitation of calcium phosphate.

8. Additive: 4-5 ppm PP, 5-6 ppm OP, 10 ppm SS/MA (runs 342-344, 375-380, 402-407).

The results of this additive combination are shown in Figure E-8.

For different combinations of surface temperatures and flow velocities, three pH levels; 8.5, 7.5 and 6.5

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were investigated. For pH of 6.5, Figures G-27 and G-28 show the effect of velocity and surface temperature respectively. Values of fouling resistance at pH's of 6.5 and 7.5 show in Figure E-8 show that this additive fouled somewhat more at pH of 6.5 than that at pH of 7.5. This is probably due to higher phosphate levels at pH of 6.5 (50% higher) than that at pH of 7.5.

Figure G-27 (runs 375-377) shows that the curves of 5.5 ft/sec and 8.0 ft/sec are nearly coincident. This is probably due to higher phosphate levels experienced at pH of 6.5. Figure G-28 also shows the effect of surface temperature for runs 377 and 380 both at 3.0 ft/sec and a pH of 6.5. There was virtually no deposition at a surface temperature of 130° F.

For a pH of 8.5, runs 402-407, the effect of velocity at 160°F is shown in Figure G-29. For runs 402-407, although the asymptotic fouling resistance for both 3.0 ft/sec and 5.5 ft/sec appear to ultimately approach each other, the results are consistent with preview results of the velocity effect. The effect of velocity for runs 405-407 and at 130°F is given in Figure G-30. Figure G-30 inexplicably shows the fouling resistance at 5.5 ft/sec to be greater than that at 3.0 ft/sec.

The effect of surface temperature is shown in Figure G-31 (8 ft/sec) and Figure G-32 (3 ft/sec).

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At the conditions investigated for this additive, the amount of fouling was very small over the range of velocities covered, indicating that sulfonated styrene/ maleic anhydride (SS/MA) is an effective copolymer in reducing the fouling tendency of polyphosphate/orthophosphate inhibitors.

9. Additives: 4-5 ppm PP, 5-6 ppm OP, 10 ppm AA/SA (runs 345-347, 384-389, 390-395).

The results of this additive combination are shown in Figure E-9.

With this additive, three pH levels 6.5, 7.5 and 8.5 were investigated. Figure E-9 shows the results for all the runs with 10 ppm active acrylic acid/sulfuric acid (AA/SA) copolymer. Virtually no fouling was observed at the conditions of the tests. This copolymer appeared to be very effective in preventing fouling by the polyphosphate/orthophosphate corrosion inhibitor. The effect of velocity and temperature and pH is shown in Figures G-33 to G-37, respectively.

This additive showed somewhat higher fouling at the high surface temperature $(160\,^{\circ}\text{F})$ at both pH at 6.5 and 8.5 than that at pH of 7.5. At the pH levels of 6.5 and 8.5, the orthophosphate (OP) level was 50 to 75% greater than at 7.5. Figure G-33 for runs 384-386 at pH of 6.5 shows that the fouling to be increasing at a constant rate but

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does show some tendency to level off at a value in the Ø.ØØØ5 hr ft °F/Btu range.

For no explainable reason, there is insignificant velocity effect shown in Figure G-33. In Figure G-34 for runs 390-392, pH of 8.5, the fouling appeared to level out at about Ø.ØØØ1 hr ft °F/Btu at about 40 hours. However, during this period pH was very erratic dropping to below 7.0 and then increasing before stabilizing at about 60hours. At 40 hours a sudden increase in fouling occurred probably due to the behavior of the pH. The asymptotic fouling resistance, even after the sudden increase, is still not exceedingly high, Ø.ØØØ2 to Ø.ØØØ6 hr ft °F/Btu. For no apparent reason, the asymptotic fouling resistance for 5.5 ft/sec is significantly lower than that for 3.0 ft/sec, a result that is not consistent with previous results.

A consistent behavior with respect to surface temperature is shown in Figures G-35 and G-36 for runs 386, 389 and runs 392, 395, respectively. Virtually no fouling was observed at the surface temperature at 130°F. The effect of pH is shown in Figure G-37 for runs 386 (pH of 6.5) and 392 (pH of 8.5). It appears that lower fouling occurs at pH of 6.5 but results are inconclusive because of the effect of erratic pH values during run 392.

Effectiveness of Copolymers in Reducing the Fouling Tendency of Phosphate Corrosion Inhibitors

For ρН of 8.5, four different copolymers were compared in figures G-38 (8.0 ft/sec, 160°F), G-39 ft/sec, 160°F), G-40 (8.0 ft/sec, 130°F) and G-41 (3.0(3.ft/sec, 130°F). In all cases, AA/MA was not an effective copolymer in reducing calcium phosphate deposition. AA/HPA and AA/SA were both very effective at a surface temperature of 160°F. At 130°F surface temperature AA/SA was very effective and slightly more effective than AA/HPA. AA/SA and AA/HPA are compared in figure G-68. AA/SA appeared as if it would be effective if variation in the pH during Run 392 (Appendix F) had not occurred. AA/HPA (Run 356) is reasonably effective showing a probable asymptotic fouling resistance of 0.0004 hr.ft2di°F/Btu. Generally, SS/MA is only moderately effective, except at 8.0 ft/sec and 130°F it is about as ineffective as AA/MA.

For pH of 7.5, Figures G-66 for runs 314, 338, 344 and 347, all at 3 ft/sec, and G-67 for runs 315. 340. 343 and 348, all at 8.0 ft/sec, compare the effectiveness of various copolymers in reducing calciumphosphate deposition. In the case of the copolymer AA/HPA, SS/MA and AA/SA fouling was effectively reduced by their presence in all cases acceptable fouling experienced. and The copolymer, AA/MA had no effectiveness reducing fouling tendency. In fact, a greater fouling rate and ultimately higher final fouling resistance was experienced with this

copolymer presence than when it was absent (Runs 337,338).

For pH of 6.5, the effectiveness of the copolymers in reducing the calcium phosphate deposit is shown in G-65, for runs 311, 365, 368, 377 and 386. For this and at the extreme conditions of 3.0 ft/sec velocity 160°F surface temperature, AA/HPA and AA/SA were very effective. SS/MA was reasonably effective giving asymptotic fouling resistance about 70% of those when no copolymer was used. Copolymer AA/MA was ineffective.

Iron Tests:

The objectives of the proposed research with iron as a contaminant were as follows:

1. To determine the effects of total iron concentration, the type of iron (ferric or ferrous, particle or colloidal) on the fouling characteristics of cooling tower water.

2. To determine how well various antifoulants will reduce or eliminate iron fouling for various flow velocities and surface temperatures.

3. To determine how well the fouling data from such a system fits predictive models.

A total of 62 tests were conducted to test the effects of the presence of iron. These can be divided into several categories.

1. Runs on high hardness cooling tower water to determine the influence of iron concentration on the amount of fouling. Also to determine the influence of flow velocity and surface temperature on the fouling characteristics of the cooling tower water when iron is present.

2. Runs to determine the influence of iron on the characteristics of the cooling tower water containing phosphate corrosion inhibitors.

3. Runs to determine the effectiveness of antifoulants in reducing or eliminating the deposition of iron.

4. Runs to test the validity of some of the various hypothesis made concerning the iron fouling.

Table E-1 and Figures E-1 through E-16 show the operating and water quality condition for all runs. For runs for which fouling occurred, the fouling data was fitted to Equation (5-35). Results are given in Table VI-1.

Run Description and Discussion

1. Additive: 4-5 ppm PP, 5-6 ppm OP, 2 ppm Fe (runs 408-413).

Six runs with this additive are shown in Figure E-10. These runs were the beginning of an extensive investigation of the effect of the presence of iron in the cooling tower water. The runs with iron consisted of the addition of soluble iron (FeSO₄·7H $_{m}$ O) directly to the cooling tower sump at a rate to maintain a given total iron content in the water.

For the six runs shown in Figure E-10, total iron content was maintained at a nominal 2 ppm in the cooling tower water. For these runs, the solution in the iron supply vessel showed some precipitation of brownish iron oxide.

The pH of the cooling tower water was maintained at 7.5. The effect of velocity is shown in Figure G-42 (160°F). For these conditions, the effect of velocity is consistent with previous observations. Considerable fouling occurred at all velocities and sloughing of the deposit occurred at all velocities. The effect of velocity shown in Figure G-43 (130°F) indicates an inconsistency. Run 412 (8.0 ft/sec, Cu/Ni) shows more fouling than either of the other runs, run 413(3.0 ft/sec, SS) and run 411 (5.5 ft/sec, SS). A possible explanation to this inconsistency is the following: For this additive combination (Run 412, 8.0 ft/sec, Cu/Ni), the Cu/Ni rod surface corroded and the corrosion products on the rod surface served to immobilize the deposit materials at the wall and thus reduced the removal effect of velocity.

2. Additive: 4-5 ppm PP, 5-6 ppm OP, 4 ppm Fe (runs 414-419).

With this additive, three runs (runs 414-416) at 160°F and three runs (417-419) at 130°F are shown in Figure E-11. The level of total iron in the system was maintained at a nominal 4 ppm. The effect of velocity for runs 414-416 at 160°F is shown in Figure G-44 and the results are consistent with previous observations with respect to the effect of velocity, although initially velocity appeared to have little effect. For these runs in this section and subsequent sections, a small amount of sulfuric acid was added to the vessel containing the ferrous sulfate solution in order to clarify it and dissolve the precipitate that was present during runs 408-413 (2 ppm total iron).

The nominal level of phosphate corrosion inhibitor was 4-5 ppm polyphosphate and 5-6 ppm orthophosphate. While it was attempted to maintain these levels for runs 417-419, some deviations occurred. Generally the total phosphate ranged between 10 and 14 ppm.

Negligible fouling was observed for this additive at the low surface temperature of 130°F. Figure G-45 shows

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the effect of velocity and the results are consistent with previous observations.

Figure G-46 compares runs 415 and 418 at 8 ft/sec and Figure G-47 compares runs 416 and 419 at 3 ft/sec, showing the effect of surface temperature, despite the somewhat higher level of iron in runs 415 and 416 (3.7% versus 3.0%, in runs 418 and 419). The effect of surface temperature appears to be consistent with the results of previous observations. For run 415, the rapid increase in fouling is due to a decrease in pH due to adding the iron solution at a high rate to increase iron content. As the pH was brought back to the desired level of 7.5, a more reasonable fouling resistance was obtained.

3. Additive: 4-5 ppm PP, 5-6 ppm OP, 4 ppm Fe, 2-4 ppm HEDP (runs 420-429).

This was a series of tests to determine the effectiveness of low levels of HEDP in reducing fouling by iron and phosphate corrosion inhibitors. The results are shown in Figure E-12.

In Figure G-48 for runs 420 (5.5 ft/sec), 421 (8.0 ft/sec) and 422 (3.0 ft/sec), the effect of velocity is shown at pH of 7.0 and surface temperature of 160°F. The effect of velocity is consistent with previous results. That is, very low fouling occurs at 8.0 ft/sec and considerable fouling occurs at 3.0 ft/sec.

A number of duplicate runs were made with this

additive and the results are shown in Figure G-49. For runs 422-426 (at pH of 7.5, velocity of 3.0 ft/sec and surface temperature T_m of 130° F), fair agreement is obtained between the various runs if the sloughing of deposits for runs 424, 425 and 426 is neglected. This sloughing occurred early in the course of the runs. Sloughing is not predictable and is highly dependent on the nature of the deposit and the nature of the heater surface.

Some of the differences observed between runs may be due to the variation of phosphate content during the runs. For runs 422, 423 and 424 (which agree well with each other neglecting the early sloughing of the deposit of runs 424), the total phosphate content of the water was 11-13 ppm with a standard deviation of about 4.6. However, for runs 425 and 426 the total phosphate was about the same but the standard deviation was only about 2.2.

The conclusion is that only fair reproducibility of results is obtained among the series of runs shown in Figure G-49. But this may be due to the fluctuation of the phosphate content of the water during the runs.

Figure G-50 shows the effect of surface temperature for this additive in which run 422 (160°F) is compared with run 429 (130°F). Virtually no fouling is observed at

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the low surface temperature while significant fouling is observed at the high surface temperature.

4. Additive: 4-5 ppm PP, 5-6 ppm OP, 4 ppm Fe, 10 ppm AA/MA (runs 430-435).

Results for this additive are shown in Figure E-13. This was a series of runs to determine the effectiveness of the copolymer AA/MA (acrylic acid/maleic anhydride) in minimizing the fouling of water containing phosphate corrosion inhibitors and iron. In agreement with previous results with AA/MA without iron discussed previously, it is seen that AA/MA is not effective at minimizing fouling and in fact appears to enhance fouling.

The effect of velocity is shown in Figure G-51 in which runs 430 (5.5 ft/sec), 431 (8.0 ft/sec) and 432 (3.0 ft/sec) are compared at surface temperature of 160°F. The effect of velocity is consistent with previous results if the sloughing of the deposit for all the runs is neglected. Considerable sloughing occurred at each velocity.

The effect of surface temperature is virtually negligible for this additive, as indicated by Figure E-13 and Figure G-52 in which run 431 (160°F) are compared at 8.0 ft/sec. However, if the sloughing of the deposit for run 431 is neglected, the resulting fouling would have been somewhat greater for the higher surface temperature run. The effectiveness of HEDP and AA/MA is shown in Figure G-53, in which run 414 (no additive), run 420 (2-4 ppm HEDP), and run 430 (10 ppm AA/MA) are compared. The ineffectiveness of AA/MA is evident. HEDP may have some slight effect in reducing fouling since run 414 (no additive) contained an average of 3.7 ppm total iron while run 420 (2-4 ppm HEDP) contained 2.8 ppm of iron and yet the fouling for both runs is nearly the same.

5. Additive: 3 ppm Fe (runs 439-450).

Results for this additive, which consisted of 3.0 ppm Fe, is shown in Figure E-14.

The effect of velocity, shown in Figure G-54 for runs 439 (5.5 ft/sec), 440 (8.0 ft/sec) and 441 (3.0 ft/sec) is consistent with previous results. Comparing Figure G-54 with Figure G-1 shows the dramatic effect of the presence of iron in water. For example, at 3.0 ft/sec, the fouling resistance for run 438 (no Fe) was about 2.0E-4 hr ft≈ °F/Btu at 280 hours while at the same run duration for run 441, the fouling resistance was about 8.0E-4 hr ft^æ °F/Btu. Figure G-55 compares three identical runs at 5.5 ft/sec at T_{m} of 160°F in which the water contained 3.0 ppm of total iron. Good agreement is shown between runs 439 and 448. Run 445 shows a significantly higher fouling resistance after about 80 hours. At this time, a power failure occurred. When the equipment was idle the pH

dropped lower than 7.5. When the system was restarted, the fouling rate was much higher than for runs 439 and 448. Similarly, Figure G-56 compares three identical runs at 3.0 ft/sec and T_m of 160° F. These runs compare very well with each other. However, the effect of the power failure at 80 hours for run 447 is evident. As the equipment was restarted considerable sloughing occurred. Had this sloughing not occurred, the resulting fouling for run 447 would have been greater than for runs 441 and 450 in agreement with the results shown in Figure G-55 for runs 439, 445 and 448.

6. Additive: 4-5 ppm PP, 5-6 ppm OP, 3 ppm Fe (runs 451-461).

Results for this additive are shown in Figure E-15. Figure 39 shows the effect of velocity in which runs 451 (5.5 ft/sec), 452 (8.0 ft/sec) and 453 (3.0 ft/sec) are compared at Ts of 160°F. At the end of the runs the effect of velocity is consistent with previous results. All runs showed a rapid increase in fouling resistance early in the runs. Inspection of the water analyses showed that, initially, the water contained about 12 ppm of total iron. As the runs proceeded, the iron content of the water was gradually reduced to about 3.0 ppm. The average iron level for the runs is 4.9 ppm with a standard deviation of 3.2. It is interesting to note that as the iron content is reduced the deposits are sloughed off and the fouling resistance attains an apparent constant value considerably below the maximum value which was attained early in the runs.

Figure G-58 compares 3 identical runs at 3.0 ft/sec and Ts of 160°F. All runs appear to converge to approximately the same fouling resistance (even run 453, in which the water initially had a very high iron content and very high fouling was observed early in the run).

Figure G-1 (no additive), G-54 (3 Fe), and G-57 (4-5 PP, 5-6 OP, 3 Fe) can be compared to show the effect of additives. For example, at a velocity of 3 ft/sec and Ts of 160°F and at a run duration of 180 hours, the fouling resistance for run 438 (no additive) (Figure G-1) is 1.0 E-4 hr ft⁼ °F/Btu, for run 441 (3.0 Fe) (Figure G-54) is 3.0 E-4 hr ft⁼ °F/Btu, and for run 453 (4-5 PP, 5-6 OP, 3 Fe) (Figure G-1) is 11.0 E-4 hr ft⁼ °F/Btu. Increased fouling occurs when iron is present in the water and even more fouling occurs when iron is present along with phosphate corrosion inhibitors. The fouling effects of the iron and the phosphates appear to be additive as discussed below.

These three runs complete the investigation of the effect of the presence of iron along with the phosphate inhibitor at a surface temperature of 130°F. The results are shown in Figure E-15R and plotted in Figure G-59 which shows the effect of velocity. Very low fouling is observed for this combination of additives under these conditions. Figure G-59 shows that the effect of velocity is consistent with previous results with fouling increasing as the velocity decreases. The average orthophosphate level was somewhat greater than 10 ppm and average iron level was 4 ppm. Even under these conditions the fouling appears to be insignificant at the three velocities investigated.

7. Additive: 4-5 ppm PP, 5-6 ppm OP, 3 ppm Fe, 10 ppm HEDP (runs 462-469).

This series of runs was designed to investigate the effect of the presence of HEDP along with the iron and the phosphate corrosion inhibitor. The results are shown in Figure E-16 and the effect of velocity is shown in Figures G-60 (160° F), G-61 (130° F) and G-62 (160° F). Runs 464SS and 469SS are duplicates as are runs 462SS and 468SS.

Significant fouling is observed in Figures G-60 through G-62 even at the low surface temperature of 130°F Figure G-61. The results indicate that HEDP is not effective in inhibiting calcium phosphate and iron deposition and it even appears to enhance the fouling.

The effect of velocity shown in Figures G-61 through G-62 is consistent with previous results with fouling increasing as velocity decreases. The effect of velocity is not as significant as would be expected from previous results indicating that the deposit is probably quite hard and quite adherent to the heater surface so that the removal rate is lower than would be expected with a soft deposit. At 130°F surface temperature (Figure G-61) the effect of velocity is almost negligible in the range 3.0 to 5.5 ft/sec.

The effect of surface temperature for this additive combination is shown in Figure G-63 (8.0 ft/sec) and Figure G-64 (3.0 ft/sec). The effect of surface temperature is consistent with previous results with fouling increasing as surface temperature increases. At 8.0 ft/sec, however, the effect of surface temperature is not large but at 3 ft/sec the surface temperature has a large effect with the fouling at 130°F being about one half of that at 160°F.

The average concentration of additives for these sets of runs is fairly uniform although the average iron level is somewhat low; 1 ppm for runs 462 through 467 and 2 ppm for runs 468 and 469. Average orthophosphate level ranged from 6.7 to 8.4 ppm and polyphosphate ranged from 3.1 to 4.4 ppm.

Effect of Iron in the Presence of Phosphate Corrosion Inhibitors at a pH of 7.5

The effect of the presence of iron in the cooling tower water containing corrosion inhibitors is shown in Figures G-69 (8.0 ft/sec), G-70 (5.5 ft/sec) and G-71 (3.0 ft/sec). In all runs which are compared in these figures, the phosphate level was nearly the same and the major difference was the iron content.

In Figure G-69, for runs 337 (no iron), 409 (1.9 ppm Fe) and 415 (3.7 ppm Fe), slightly higher fouling is observed for run 409 compared to run 337. However, run 415 shows very little fouling even though the water contained 3.7 ppm Fe. One reason for this low fouling may have been due to the nature of the deposit which at the high velocity of 8.0 ft/sec was more easily removed than the deposits from runs 337 and 409.

In Figure G-70 for runs 336 (no iron), 408 (1.9 ppm Fe), 414 (3.7 ppm Fe), 454 (3.5 ppm Fe) and 457 (3.9 ppm Fe) slightly higher fouling is observed for runs (except for run 414) containing 3.5 to 3.9 ppm Fe compared to run 336 for which no iron was present. Runs 454 and 457 (3.5 to 3.9 ppm Fe) compare guite well with each other. It appears, on the average, that asymptotic fouling resistance for these runs would be 15 to 25 percent greater than when no iron is present. In this set of comparisons, Run 408 (1.9 ppm Fe) showed higher fouling than Run 336 (no iron). This is consistent with the result obtained at 8.0 ft/sec. The fouling for Run 414 (3.7 ppm Fe) is considerably lower than that for runs 454 and 457 which contain the same amount of iron. This was also true for Run 415 (compared to Run 337). Again, this may be due to the type of deposit formed in runs 414 and 415.

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The comparison at 3.0 ft/sec is shown in Figure G-71. Again, the water containing 1.9 ppm Fe (Run 410) shows the highest fouling. The fouling for water containing 3.5 to 3.9 ppm Fe (runs 416, 456, 458) is lower than the fouling for Run 410 but somewhat higher than the fouling for water containing no iron (Run 338).

Figure G-59 shows the effect of velocity at 130°F. Although average orthophosphate level was somewhat greater than 10 ppm and average iron level was 4 ppm, the fouling appeared to be insignificant at the three velocities investigated because of the low surface temperature of the heater.

In summary, it appears that the presence of iron (3.5 to 3.9 ppm Fe) causes somewhat higher fouling (15 to 25 percent above that for water containing no iron). Water containing 3.5 to 3.9 ppm Fe showed lower fouling than water containing 1.9 ppm Fe, possibly due to the nature of the deposits formed with the higher iron content water. The high fouling for the low levels of iron (1.0 ppm Fe) could also have been due to the presence of precipitate in the iron solution supply tank. From the above discussion it was concluded that the fouling effects of the iron and the phosphates appear to additive.

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Effectiveness of HEDP Copolymer in Reducing the Deposition of Iron

Water containing phosphate corrosion inhibitors and iron was investigated with 10 ppm HEDP additive. The effectiveness of this additive in inhibiting deposition is shown in Figure G-74 (3.0 ft/sec, 160°F) and Figure G-76 (5.5 ft/sec, 160°F). In all cases, the presence of HEDP appears to enhance the fouling rather than inhibit it.

Effect of Iron on the Distribution of Deposit on the Heater Rod Surface

In the Run Description section (Iron test section, additive no. 5), the effect of operational parameters of flow velocity and surface temperature was discussed. The discussion showed that the effect of flow velocity and surface temperature is consistent with previous results obtained for high hardness cooling tower water with and without phosphate corrosion inhibitors, i.e. higher velocities tend to reduce the fouling, and lower surface temperatures tends to reduce the fouling.

In this section the nature of the deposit (its composition and distribution over the heater rod) is discussed. A total of 11 runs, starting with runs 439, were conducted during the course of this investigation containing only high hardness water and 3 ppm iron. Iron was maintained in solution by the addition of sulfuric acid to the iron solution tank.

For Runs 439 (5.5 ft/sec, 160°F) and 441 (3 ft/sec, (both with stainless steel heater rods), 160°F) the deposit was a gelatinous film of ferric hydroxide which had a tan color. The gelatinous deposit was over the heated area only. Since Runs 436-438 showed that high hardness cooling tower water without phosphate corrosion inhibitor at a pH of 7.5 is not in scaling condition, it is speculated that fouling was only due to the iron presence. There was no deposit on the non-heated areas of the heater rod. This led to the speculation that heat transfer plays a major role in the formation and bonding of the iron film to heater rod surfaces. To explain this, it was postulated that if the mass transfer alone caused the formation and the bonding of the deposit film, then there would be a fouling film all over the heater rod surface, heated and nonheated areas.

To verify this postulation, Runs 439 and 441 were repeated (Runs 445 and 447). The results supported the postulate in that a gelatinous tan colored film of ferric hydroxide was obtained again only on the heated area of the heater rod. To further support the postulate, Runs 439 and 441 were again repeated (Runs 442 and 444), but this time the surface temperature was different (Ts of 130°F) while Runs 439, 441, 445 and 447 have Ts of 160°F. The results of Runs 442 and 444 showed no deposit on the heater rod. This indicates again that mass transfer alone

cannot form a deposit of iron film and that heat transfer at a surface temperature of 130°F does not cause iron particulate to bond to the heater rod surface. This suggests that a threshold energy level was needed before This behavior film could form. is this gelatinous explained later in this chapter through the help of Some properties of Fe(OH)_a are coagulation theory. help explain the formation of the presented here to gelatinous film on the heated area. When hydrated ferric hydroxide coalesces, it forms a gelatinous material. This material has the power of absorbing large quantities of water when heated in solution. This explains the presence of the gelatinous film only on the heated area of the The hot surface helps Fe(OH)₃ to heater rod surface. absorb large quantities of water and thus coagulation large flecks of red-brown gelatinous takes place and $Fe(OH)_{\Im}$ form and deposit on the hot surface. The hot surface causes Fe(OH)₃ to grow by helping the colloidal particles to aggregate and thus the deposit forms.

Runs 440, 443 and 446 (CuNi heater rod, 8 ft/sec and 160°F) showed a very interesting behavior of iron deposition process. In Run 440 the deposit was particulate in nature, depositing only on the non-heated area of the heater rod in contrast to Runs 439 and 441 (which were run for the same run duration and same water quality simultaneously with Run 440) with stainless steel rods where

deposits of gelatinous film of ferric hydroxide formed only on the heated area of the heater rod. The color of the deposit was mainly brown, suspected to be the color of a mixture of particles of iron oxide and ferric hydroxide, with some particles having a pale bluish color (olive green color) suspected to be copper corrosion. Table H-1 shows appreciable amount of copper present in the deposit along with iron, silica and aluminum. The presence of an appreciable amount of copper and the presence of manganese for the first time in the deposit was found only for those runs where iron was present in the cooling tower water. The visual observation and the constant presence of copper and manganese in the deposit collected from the surface of the copper/nickel rod support the conclusion that copper corrosion is taking place in the copper/nickel rod since there is no other source of copper and manganese except from copper oxide forming on the surface of the heater further investigate the particle deposition rod. То process on the Cu\Ni heater rod, Run 440 was repeated (Run The same behavior was observed in this repeat run 443). (Run 443). In this run, no deposit was observed on the heated area and only a deposit of particles was present on the non-heated region. From these two runs, 440 and 443, it was possible to postulate:

a. The copper/nickel surface corrosion by playing the role as a substrate has the ability in absence of heat to bond physically with iron particles with a force enough to resist the shear forces.

b. The rough surface of copper/nickel rod (which had been in use for a very long time) played a role in trapping the particles and then by agglomeration, the particles grew in size.

c. On the heated area of the heater rod, the heat exerted a retarding force for the particles, and the speculation here is that a thermophoresis process is occurring.

To investigate postulates a, b and c, a third test under the same conditions as Runs 440 and 443 was conducted (Run 446). A new copper/nickel rod was used in this run. The result of this run was consistent with runs 440 and 443 which suggests that the roughness of the surface probably did not play a major role and that the surface corrosion was the major factor in forming the particle deposit.

With respects to part c above, it is speculated that heat transfer acted as a retarding force which forced the particles away from the heated surface, or by weakening the bonding force and thus shear forces were able to remove the particles as they reached or formed on the surface or by the thermophoresis process (i.e. material migrates from the hot surface back to the liquid bulk which is cooler than the surface). Where there was no

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heat transfer, the mass transfer process was able to transport the particulate material to the surface and the particles bonded to the surface. This indicates that a shear force of 8 ft/sec alone is not strong enough to prevent deposit at the non-heated area.

Hopkins (13), in his work on the fouling of a stainless steel tube by $Fe_{a}O_{a}$, used the crevice corrosion phenomenon to explain the fouling mechanism of $Fe_{=}O_{=}$ on the stainless steel tube. Hopkins, in his conclusion of his work, recommends that his use of crevice corrosion to explain his data be tested by more work on iron fouling. Since the fouled surface of the copper/nickel rod in this investigation was found to be in a corroded condition, it is of interest to use Hopkins postulate in explaining the deposition mechanism on copper/nickel rods. The fundamentals of crevice corrosion are described by Fontana and Greene (7). Briefly, the principle requirements for crevice corrosion of material in aqueous media are a metal surface partially shrouded by a non-conductor (i.e. a spotty $Fe_{a}O_{a}$ deposit), creating a stagnant crevice which acts as anode:

M M^{m++} + ne⁻⁻ (M = Fe, Cu, Cr, and Ni)

a relatively large cathodic area (i.e. the unfouled portions of the tube) at which:

and trace amounts of an aggressive ion such as the chloride ion (as used in this study to prevent biofouling), which serves to transport and precipitate the metallic ion as a corrosion product (rather than allowing it to form a protective oxide film);

 $M^{n+} \cdot ncl^{-} + nH_{a}O = M(OH)_{n} + nH^{+}Cl^{-}$

with the H+Cl⁻⁻ promoting further attack.

Hopkins (13), stated that corrosion products on the surface serve to bind the red hematite deposits more firmly to the wall and using crevice corrosion phenomenon he postulated that the initial spotty fouling triggers further fouling by the crevice corrosion process. The stabilization of the initially loose deposit structure by the corrosion products serves to suppress the release mechanism. From the discussion above, and from the discussion earlier about the nature of the deposit and the corrosion of the copper/nickel rod, it appears that the behavior of the iron particles deposition process on copper/nickel surface is in agreement with Hopkins' use of crevice corrosion process and postulation. However, to further investigate this assumption, more tests designed specifically for this purpose is needed, since the above

discussion was based only on visual observation of the presence of particles. The possibility of the presence of very small particles on the copper/nickel heated surface need also be checked by closer examination of the surface.

Deposit Distribution on the Heater Rod Surface in the Presence of Iron and Phosphate Corrosion Inhibitors at pH of 7.5

of iron when phosphate corrosion in-The effect hibitors were present was discussed earlier (Effect of Iron in the Presence of Phosphate Corrosion Inhibitors at in terms of the thermal fouling a pH of 7.5 Section) it was found on the average that resistance values, asymptotic fouling would be 15 to 25 percent greater than present. The results for copper/nickel when no iron was Runs 452 and 455 for this additive obtained in rod consistent with the previous results combination were obtained for high hardness and iron water. Thus the postulates and explanations given in the previous section is further supported by the observation of the deposit nature and distribution in these runs. Although phosphate corrosion inhibitors are present in these runs, a layer of copper corrosion was observed in both Runs 452 and 455 on Two layers were observed on the the nonheated area. nonheated area; the first layer was bluish-green in color and on top of it a second layer of a large number of brown colored particles. With this additive, all runs, includ-

ing runs with copper/nickel rods, had a tan, wet layer of a powdery-like deposit on the heated area of the heater The composition of the deposit of Runs 452 and 455 rod. When the runs were terminated and is given in Table H-1. the heater rods were removed from test sections for deposit collection, and after the tan cleaning and colored, wet-powdery deposit was dried, the deposit became very loose and started to fall off the surface of the heater rod and a second layer which was of a white color suspected to be mainly of calcium phosphate appeared. This second layer had to be removed mechanically from the heater surface. The tightness and compactness of this second layer is consistent with all previous results and observation of the nature of calcium phosphate deposit. The above observations permit the following speculations:

1. In the case of copper/nickel rod, the phosphate corrosion inhibitors were not able to prevent copper corrosion from occurring when iron was present. This is perhaps due to either the behavior of the corrosion inhibitor in this condition or due to the concentration of the inhibitors used. Thus further experimentation is required.

2. In the case of the heated area, deposition occurred for all runs, the above discussion (Effect of Iron in the Presence of Phosphate Corrosion Inhibitors at a pH of 7.5 Section and additive number 6 in Run Description and Discussion Section) showed the effect of the presence of iron on the fouling characteristics of the cooling tower water is additive, i.e. layer of inverse solubility salts with a particulate layer of iron product of ferric hydroxide on top of it.

Deposit Distribution on the Heater Rod Surface in the Presence of AA/MA, HEDP, Iron and Phosphate Corrosion Inhibitor

Effectiveness of HEDP copolymer with this additive combination in reducing iron deposition was discussed in an earlier section of this chapter. With this copolymer, a heavy precipitation of deposition material was experi~ enced for all flow velocities, surface temperatures, surface materials and HEDP levels. The deposit heater covered the rods on heated and non-heated areas with an apparent thicker layer of deposit on the heated area. The deposit also covered all the glass tubes that house the heater rods and the flow meters to a point it was impossible to permit visual observation of the deposit. The deposit in this case was also powdery in nature with a faint tan color indicating formation and deposition of particulate ferric hydroxide. The deposit was easily removed from the surface of the heater rod. It was very difficult, almost impossible to maintain 3 ppm iron in the cooling water when HEDP was present.

Towards the end of Runs 468 and 469, the addition of HEDP copolymer was terminated and the iron concentration went up to the desired level of 3 ppm. This indicates that HEDP acts as an agglomerating agent instead of acting as an inhibitor in this case.

Runs 430-435 were conducted to test the effectiveness of AA/MA in preventing iron deposition. Runs 430-432 were at 160°F and 433-435 were at 130°F. At both temperatures the deposit was a gelatinous film of ferric hydroxide covering the heated area of all rods stainless steel and copper/nickel alike. For the copper/nickel rod (Run 434) only a brown color and greenish particles were found to cover the non-heated area. Deposit collected from the surface of copper/nickel rod (Run 434, Table H-1) showed a significant amount of copper which indicated copper/nickel rod surface corrosion.

Effect of the Material of the Heater Surface

The results presented herein generally support the conclusion that the material of the heater surface has little effect on the fouling. Figure G-2 for runs 302 (SS), 303 (CS) and 304 (CuNi) indicate that before the deposit sloughed off the heater, carbon steel showed somewhat higher fouling with stainless steel and copper/nickel about equal. After the deposit sloughed off, all three surfaces fouled at the same rate. Figure G-3
for runs 305 (SS), 306 (CS) and 307 (CuNi) shows good agreement with little difference between stainless steel and copper/nickel and erratic behavior on the carbon steel. For carbon steel, if sloughing had not occurred at about 75 hours, it would also not have been very different from the other two surfaces. Figure G-7 for runs 313 (SS) and 372 (Adm) shows good agreement between the two materials.

Reproducibility of Results

Several duplicate runs were made. The comparison between duplicate runs is shown in Figures G-73 through G-74. Figures G-73 and G-75 compare runs in which the additives are only phosphate and iron. In Figure G-73 (8.0 ft/sec, 130°F) there is relatively good agreement between the runs (Runs 418 and 460) and generally the fouling is very low. The somewhat higher fouling shown by Run 460 could be due to a slightly higher phosphate content of the water (14.9 versus 12.1 ppm) and slightly higher iron content (4.0 versus 3.0 ppm). The same observations apply to Figure G-75 (3.0 ft/sec, 130°F) but in each case the fouling is very low.

Figure G-76 (5.5 ft/sec, 160°F) compares Runs 462 and 468. For these runs the water contained 10 ppm HEDP in addition to the phosphate and the iron. Both phosphate

and iron levels are comparable and good agreement is observed between the two runs.

Figure G-74 (3.0 ft/sec, 160°F) compares Runs 464 and 469 in which the water contained 10 ppm HEDP in addition to the phosphate and the iron. Good agreement is observed between the two runs up to about 100 hours. The fluctuation of pH for Run 469 and the slightly high iron content of the water (2.0 versus 1.0 ppm) may explain the deviation between the two runs beyond 100 hours.

Deposit Composition

For additive combinations for which deposit occurred, the deposit was collected and analyzed. With the exception of the presence of very minor constituents, the deposit was mainly calcium phosphate. When iron was added to the cooling tower water, iron was also present in the deposit as a major constituent along with calcium phosphate components.

Chemical analysis of the deposits is shown in Appendix H, Table H-1. This table shows the run number, the condition of water quality for which the deposit occurred and the percentage of the constituent of the deposit. Table H-1 (Deposit Composition Table) and Table VI-1 (lists run number and R^*_{τ}) can be used to match the deposit and its thermal resistance.

Types of Fouling Resistance - Time Curves Obtained

The fouling curves could be assigned to four distinct categories; asymptotic, linear, concave upward and (occasionally) a sawtoothed curve. A sawtooth curve was obtained when the deposit gradually built up, suddenly sloughed off the heater rod surface and then built up to the same, or higher, level before it sloughed off again. Linear and concave upward curves were observed only for a few runs with linear curves occurring more frequently.

In Table VI-1, runs which have such curves are identified and the fouling-time curve for each run is given in Appendix F. In Figure VI-1A, the types of the fouling resistance-time curves obtained in this study are shown. Curve A represents a linear fouling behavior; Curve B represents a concave upward fouling behavior; Curve C represents an asymptotic fouling behavior and Curve D represents a sawtooth fouling behavior.

It was observed during the course of the investigation that runs for which a linear fouling behavior was obtained, the deposit was hard and difficult to remove from the surface of the heater rod, indicating strong adhesion to the heater surface. Linear fouling curves result when deposition rate is constant and there is no removal or the difference between the deposition rate and removal rate is constant. Runs which exhibited concave

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Figure VI-1A: Fouling Resistance Time-Curves

upward curve behavior suggests that the deposition rate increases or the removal rate decreases with time. Taborek et al (32), reported that this case was not experimentally observed and it is most undesirable. The deposit for the concave upward fouling behavior was also hard and difficult to remove from the heater rod surface, suggesting strong bonding of the deposit to the heater surface wall and between the deposit constituent. Curve C shows an asymptotic curve which is a common characteristic of cooling tower water fouling. Curve C was the most frequent type of fouling curve obtained in this study. It illustrates fouling behavior as described by Kern and Seaton (15) and thus it can be fitted to Equation (5-36):

$$R_{+} = R_{+}^{*}[1 - e_{xp}(-(\Theta - \Theta_{e})/\Theta_{e})]$$
 (5-36)

The deposit showing the asymptotic fouling behavior was a soft deposit that was easy to remove from the heater rod surface. Frequently the deposit falls off the heater surface upon drying. In this case of asymptotic fouling, the assumption is that the removal rate increases with the thickness of the deposit layer, indicating that shear strength of the deposit is decreasing or other mechanisms deteriorating the stability of the deposit layer is taking place. In this case, deposition rate and removal rate ultimately become equal resulting in an asymptotic form of the fouling resistance-time curve. It is also possible that asymptotic behavior may result from the deposition rate decreasing with increasing deposit thickness to the point where essentially no deposition occurs.

Figure VI-1A also shows a delay time, $t_{\rm D}$. This delay or dead time was reported frequently in the literature of fouling. Table VI-1 list the dead time that was obtained for various runs in this study. It was observed during this period that an enhancement of heat transfer occurred due to increases roughness of the surface as nucleus formation proceeds.

Analysis of the Fouling Data

A nonlinear regression analysis was used to fit the data of the runs shown in Table VI-1 to Equation (5-36). The regression analysis was performed to obtain θ_{e} , θ_{e} and R*, of Equation (5-36). In some cases it was necessary to fix the dead time θ_{e} so negative values of R, would not result from the regression.

For the runs which had a negative fouling resistance value at the beginning of the run, the abscissa was shifted before performing the regression analysis.

For runs in which the deposit sloughed off, only a portion of the fouling curve was fitted to Equation



Figure VI-1 Normalized -ln ø_e vs Velocity

(5-36). In some of these runs the fouling value before and after sloughing was about the same.

In some cases the fouling resistance-time curves had an increasing deposition rate and data for these runs was not fitted to Equation (5-36). Since this equation is good only for constant deposition rate. The fouling resistance-time curve in this case is concave upward.

No regression analysis was performed for most runs that had a fouling resistance value of $R^{*}_{\tau} \leq \emptyset. \emptyset \emptyset \emptyset 1$ ft²hr°F/Btu. Runs that were analyzed are shown in Table VI-1.

For some of the runs, the fouling resistance-time curves were very close to linear. These runs were fitted using simple linear regression to obtain the slope of the line which represent the deposition rate. Hence only ϕ_{cl} is reported.

In Table VI-1 values of θ_{cl} , θ_{cl} , R^*_{τ} , deposition rate $(p_{cl} = R^*_{\tau}/\theta_{cl})$ and R^2 (The coefficient determination) are given for each run. Table VI-1 also show, for each run, foot notes about the conditions under which regression was or was not performed.

Values of Θ_{cd} , Θ_{cd} , R_{r}^* and p_{cd} were then used to correlate the data of the HTRI model. Appendix I contains a summary of the method of non-linear regression used in this study.

RUN	DEAD TIME	TIME CONSTANT	ASYMPTOTIC FOULING	DEPOSITION RATE	COEFFICIEN OF	T
NUMBER	HOUR	HOUR	D#1 <i>0</i> 4	_	DETERMINATIO	
	Pa	νe	RAXID	р _а	K=	
			r —			
302	40.33	81.62	6.63	8.13E-6	.92	
303	ø.ø	50.06	8.11	1.62E-5	.85	1
3Ø4	ø.ø	31.09	7.14	2.30E-5	.51	
305	3.27	128.80	11.10	8.62E-6	1.00	
306	43.66	410.78	9.03	2.2ØE-6	.93	
307	ø.ø	116.06	11.94	1.Ø3E-5	1.00	
308	*	*	*	*	*	(7)
309	ø.ø	6.Ø1	2.08	3.45E-5	.59	
31Ø	ø.ø	195.10	23.12	1.19E-5	.97	
311	ø.ø	158.82	16.19	1.02E-5	.97	
312	6Ø.Ø	21.72	.26	1.22E-6	.64	
313	ø.ø	108.30	6.19	5.72E-6	.95	
314	10.0	77.82	4.57	5.87E-6	.98	
315	14.Ø3	126.28	2.07	1.64E-6	1.00	
316	*	*	Ø.38	*	*	(4)
317	*	*	Ø.Ø5	*	*	(4)
318	*	*	*	*	*	(5)
319	*	*	*	*	*	(5)
32Ø	5.39	43.23	Ø.81	1.88E-6	.96	
321	*	*	Ø.23	*	*	(4)
322	ø.ø	839.23	14.11	1.68E-6	.70	
323	ø.ø	4.35E1Ø	4.32E8	9.92E-7	.98	
324	*	*	Ø.71	*	*	(4)
325	ø.ø	1.37E7	4.68E4	3.41E-7	.89	
326	ø.ø	383.74	5.43	1.42E-6	.99	
327	50.86	12.44	1.7Ø	1.36E-5	.95	
328	50.69	10.99	1.02	9.25E-6	.94	
329	33.75	26.84	1.88	7.ØØE-6	.90	
33Ø	5.0	65.32	1.23	1.89E-6	.93	
331	ø.ø	26.50	1.14	4.29E-6	.96	
332	5.83	27.91	.73	2.61E-6	.95	
333	40.09	217.65	1.15	5.30E-7	.83	
334	4.28	140.58	.80	5.67E-7	.96	
335	ø.ø	170.53	1.84	1.08E-6	.91	
1	1	1	;	1		

TABLE VI-1 Regression Analysis

TABLE VI-1 (cont.) Regression Analysis

	DEÁD TIME HOUR	TIME CONSTANT HOUR	ASYMPTOTIC FOULING	DEPOSITION RATE	COEFFICIE OF DETERMINAT	NT ION
	0 _d	θ_	R∓x10*	۶a]
224	aa	40 11	6 58	1-64E-5	. 95	
330	0.0 0 0	29 99	5.37	1.79E-5	.91	
338	0.0 0 0	31.61	7.11	2.25E-5	.93	l
339	0.0	156.49	15.81	1.Ø1E-5	1.00	
340	Ø.Ø	213.09	15.36	7.21E-6	1.00	
341	ø.ø	77.89	16.1Ø	2.07E-5	.99	
342	84.Ø	47.44	.36	7.57E-7	.69	
343	7.0	55.24	. 44	8.ØØE-7	.91	ļ
344	ø.ø	36.72	1.48	4.02E-6	.95	
345	*	*	*	*	*	(6)
346	*	*	*	*	*	(6)
347	*	*	×	*	*	(6)
348	18.36	63.67	5.64	8.86E-6	.98	•
349	1.14	91.21	4.47	4.9ØE-6	.97	
35Ø	ø.ø	54.35	4.78	8.79E-6	.96	
351	1.66	33.8Ø	3.03	8.97E-6	.98	
352	1.66	22.33	1.94	8.7ØE-6	.98	
353	1.66	25.92	1.84	7.11E-6	.93	
354	ø.ø	21.38	3.71	1.74E-5	.99	
355	ø.ø	14.42	1.58	1.10E-5	.94	
356	ø.ø	11.45	3.96	3.35E-5	.98	
357	24.68	36.47	2.14	5.88E-6	.97	
358	2.68	260.71	3.46	1.33E-6	.94	
359	11.65	100.59	4.03	4.01E-6	.78	11.5
360	*	*	0.10	*	*	(4)
361	*	* 	0.14	1 505-4	· · · ·	(4)
362	2.44	46.30	. /0	1.505-6	.71	
363	14.75	210.07	3.41	1.582-6	.75	
304		140.14	2.44	3 145-4	.75	
303	0.0	22 07	12 22	5 12E-5	. 92	
300	0.0		10.73	8.05E-5	.96	
369	8 8	20 02	14.16	7.07E-5	.94	
369	<i>a</i> . <i>a</i>	75.28	2.61	3.47E-6	.96	
370	15.2	22.09	3.53	1.60E-5	.98	
371	16.33	23.95	4.58	1.91E-5	.98	
- · •		1	1			

TABLE VI-1 (cont.) Regression Analysis

RUN NUMBER	DEAD TIME HOUR	TIME CONSTANT HOUR	ASYMPTOTIC FOULING	DEPOSITION RATE	COEFFICIE OF DETERMINAT	ION
	0 4	θ_	R\$×1Ø≁	, ¢a	RE	
·		· · · · · · · · · · · · · · · · · · ·				
372	ø.ø	54.7Ø	3.00	5.48E-6	.98	
373	.93	8.52	1.36	1.59E-5	.81	
374	.93	27.14	6.63	2.44E-5	.97	
375	11.93	106.05	4.95	4.66E-6	1.00	
376	3.92	73.46	3.77	5.14E-6	1.00	
377	2.91	85.47	8.22	9.62E-6	.99	
378	*	*	Ø.24	*	*	(4)
379	*	*	ø.ø2	*	*	(4)
38Ø	*	*	ø.2ø	*	*	(4)
381	*	*	.25	*	*	(4)
382	*	*	.15	*	*	(4)
383	*	*	.57	*	*	(4)
384	*	*	3.61	1.92E-6	*	(4)
385	10.66	392.94	8.3Ø	2.11E-6	. 94	
386	*	*	3.1Ø	1.68E-6	*	(1)
387	2.6	58.47	.66	1.13E-6	.72	
388	ø.ø	264.70	1.3Ø	4.9ØE-7	.79	
389	9.Ø	413.5Ø	2.06	4.98E-7	.78	
390	11.43	11.17	.85	7.61E-6	.8ø	
391	6.4	13.66	1.Ø	7.32E-6	.90	
392	1.4	36.45	2.29	6.3ØE-6	.93	
393	*	*	.23	*	*	(4)
394	*	*	.19	*	*	(4)
395	*	*	.12	*	*	(4)
396	2.45	412.05	32.55	7.9ØE-6	1.00	
397	2.45	398.23	25.71	6.46E-6	1.00	
398	1.42	99.04	17.61	1.79E-5	1.00	
399	6.21	450.34	23.12	5.14E-6	.99	
400	6.21	427.20	10.85	2.54E-6	.98	
4Ø1	1.21	276.15	31.27	1.13E-5	1.00	
402	4.68	53.86	10.92	2.Ø3E-5	.98	
4Ø3	8.68	92.06	7.64	8.3ØE-6	.99	
4Ø4	.68	27.97	9.79	3.5ØE-5	.99	

TABLE VI-1 (cont.) Regression Analysis

RUN NUMBER	DEAD TIME HOUR	TIME CONSTANT HOUR	ASYMPTOTIC FOULING	DEPOSITION RATE	COEFFI OF DETERMI	CIENT
	0 ₄	θε	R‡x1Ø⁴	¢a	Rª	
4Ø5	16.38	157.7Ø	14.4Ø	9.13E-6	.96	
406	9.11	1113.69	32.57	2.92E-6	.95	
4Ø7	11.11	84.94	12.95	1.53E-5	.98	
4Ø8	ø.ø	415.44	39.Ø3	9.39E-6	.89	
409	ø.ø	92.06	12.72	1.38E-5	.77	
41Ø	1.4	170.55	26.59	1.56E-5	.86	1
411	4Ø.87	165.44	8.06	4.87E-6	.94	
412	42.87	215.69	24.86	1.15E-5	.98	
413	46.87	317.98	26.57	8.36E-6	.98	
414	1.23	26.12	4.32	1.65E-5	.97	
415	1.23	9.75	1.37	1.40E-5	.83	
416	4.23	31.00	10.17	3.28E-5	.99	
417	Ø.Ø	21.62	.59	2.73E-6	.55	
418	ø.ø	18.57	.32	1.73E-6	.42	
419	*	*	.27	*	*	(4)
42Ø	.96	6Ø.41	5.71	2.45E-6	.95	
421	Ø.Ø	57.78	3.72	1.44E-6	.92	
422	Ø.Ø	85.98	8.99	1.05E-5	.98	
423	2.31	76.54	16.62	2.16E-5	.94	(
424	15.31	70.91	23.87	3.37E-5	.97	
425	.62	80.43	21.72	2.7ØE-5	.84	
426	*	*	2.16	*	*	(7)
427	1.23	1.65	.63	3.83E-5	.87	
428	*	*	. 44	*	*	(1,4)
429	*	*	17	*	*	(4)
430	4.33	11.94	3.20	2.68E-5	.93	(8,3)
431	4.33	239.66	20.01	8.35E-6	.99	(8,3)
432	1.33	31.17	6.87	2.21E-5	.99	(8,3)
433	1.1	64.98	6.18	9.52E-6	.99	
434	1.1	190.05	9.69	5.1ØE-6	.99	
435	×	*	10.14	6.73E-6	97.88	(2,10)
436	*	*	.89	*	41.47	(1,4)
437	*	*	.33	*	88.14	(1,4)

TABLE VI-1 (cont.) Regression Analysis

RUN NUMBER	DEAD TIME HOUR	TIME CONSTANT HOUR 0-	ASYMPTOTIC FOULING	DEPOSITION RATE	COEFFIC OF DETERMIN R [#]	CIENT
	~ a	~~		, ,		
438	ø.ø	4.92	.45	9.17E-6	.77	
439	*	*	2.44	*	*	(2,10)
44Ø	ø.ø	250.47	.77	3.Ø8E-7	.84	
441	78.12	189.22	12.15	6.42E-6	.96	
442	*	*	.74	*	*	(1,4)
443	ø.ø	60.65	.49	8.05E-7	.76	
444	ø.ø	799.59	4.75	5.94E-7	.82	
445	89.17	1231.76	34.63	2.81E-6	1.00	
446	1.95	80.52	3.02	3.76E-6	.98	
447	45.85	52.10	6.69	1.29E-5	.95	
448	160.24	589.06	16.7Ø	2.84E-6	.98	(8)
449	21.41	54.54	11.97	2.20E-5	.97	(3,8)
451	.81	32.27	18.70	5.80E-5	1.00	(3)
452	.8	19.26	18.26	9.48E-5	.97	(3)
453	.76	24.27	22.56	9.30E-5	1.00	(3)
454	5.50	94.97	10.06	1.06E-5	.97	
455	20.63	25.05	7.89	3.15E-5	1.00	
456	6.73	89.47	12.27	1.37E-5	.97	
457	3Ø.8	153.45	17.23	1.12E-5	.96	
458	64.0	88.63	16.67	1.89E-5	.98	
459	ø.ø	177.99	2.09	1.17E-6	.84	
46Ø	ø.ø	56.77	.73	1.29E-6	.85	
461	1.46	3248.28	39.07	1.20E-6	.95	
462	1.49	210.43	16.62	7.9ØE-6	1.00	
463	*	*	7.3	.Ø3	.99	(1)
464	1.46	119.97	15.08	1.26E-5	1.00	
465	2.67	1755.76	56.44	3.21E-6	1.00	
466	.67	1200.16	29.68	2.47E-6	1.00	
467	ø.ø	353.44	15.32	4.33E-6	.99	
468	.82	216.82	17.69	8.16E-6	.99	
469	.82	254.53	27.19	1.07E-5	1.00	
1			1	1		

Note: (1) Fouling increased linearly with time.

(2) Fouling curve concave upward.

(3) Fouling sloughed off during run.

(4) Insignificant fouling R⁺₊ ≤ Ø.ØØØ1 ft² hr F°/Btu.

(5) Computer problem.

(6) Fouling value less than zero.

(7) Rod Problem.

(8) Power failure.

(10) Final fouling value.

Data Reduction and Discussion

HTRI Model

The HTRI model is used to correlate the fouling data obtained in this study. This model was discussed in Chapter II and a summary is given here.

The HTRI model is a semi-theoretical model whereby the fouling resistance-time curves can be predicted in the form of an initial fouling rate and an asymptotic fouling resistance. Taborek, et al.(32) discuss this model in length.

This model is based on the fundamental material balance Equation:

$$\frac{\mathrm{d}R_{*}}{\mathrm{d}\theta} = \phi_{\mathrm{cl}} - \phi_{\mathrm{r}} \qquad (2-2)$$

where

 $R_r = fouling resistance$ $\Theta = time$ $\phi_{cl} = deposition rate$ $\phi_{r} = removal rate$

The deposition and removal rates are represented by the following relationships:

$$\phi_{ci} = C_{1}F_{\gamma}\Omega^{n}exp[-E/R_{ci}T_{m}]$$
(2-9)

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Determination of HTRI Model Correlation Constant from Data

Determination of the constants and functions of the model equations was discussed in great detail by Taborek, et al (32). In the present study, the method of determination is adapted for the use of modern computers. From the data, experimental sets were selected in such groupnings as to isolate single effects and to allow determination of the functions required for solution of Equations (2-9) and (2-10).

Deposition Rate

The initial rate, ϕ_{cl} , of deposition can be obtained by differentiating and evaluating the derivative of the equation of fouling (5-35) at $\theta = \theta_{cl}$.

$$R_{\tau} = R_{\tau}^{*} [1 - \exp(\theta - \theta_{c})/\theta_{c}] \qquad (5-35)$$

$$\phi_{cl} = \frac{dR}{d\theta} \begin{vmatrix} e = \frac{R^{*}}{\theta_{cl}} \end{vmatrix} = \frac{R^{*}}{\theta_{cl}}$$
(6-1)

 R^*_{τ} , Θ_{e} and Θ_{el} and thus ϕ_{el} can be determined from fitting the experimental data to Equation (5-35). Values of R^*_{τ} , Θ_{el} , Θ_{el} and ϕ_{el} are given in Table VI-1.

By maintaining a constant water quality, Ω^n becomes constant and Equation (2-9) reduces to the form of Equation (6-2):

$$\phi_{d} = C_{B} F_{v} \exp(-E/R_{d}T_{m}) \qquad (6-2)$$

where:

 C_{\odot} = constant which includes Ω^n F_{\sim} = velocity function E = activation energy of reaction R_{\odot} = gas constant T_{\odot} = absolute surface temperature

The experimentally obtained value of p_{c} along with the operational parameters of velocity and surface temperature can now be used to determine the velocity function, the constant C_{a} and the activation energy E of Equation (6-2).

The Velocity Function, F.

Sets of data with the same water quality and surface temperature and their corresponding deposition rate ϕ_{ci} were selected for correlation. ϕ_{ci} was plotted against velocity to fit Equation:

$$\ln \phi_{\rm d} = \ln C_{\phi} - V/C_{\tau} \tag{6-3}$$

These plots are shown in Appendix L. Normalizing these plots by plotting $\ln(\phi_{cd}/C_{cb})$ against velocity (Figure VI-1), the average slope of Ø.2704 is obtained with average standard deviation of Ø.03.

Thus the velocity function
$$F_{\nu}$$
 is of the form of:
 $F_{\nu} = \exp(-\emptyset.2704V)$ (6-4)

Equation (6-4) shows that F_{ν} is a decreasing function of velocity. Since ϕ_{d} is directly proportional to F_{ν} in Equation (6-2), increasing velocity will have the effect of decreasing ϕ_{d} . Taborek et al (32) reported the following velocity function for cooling tower water:

 $F_{\sim} = \exp(-1/3 V)$

Santoso (29) obtained the following velocity function for the cooling tower water:

$$F_{\sim} = exp(-.352V)$$

The velocity functions obtained in this study and those reported by Santoso and Taborek et al are in reasonable agreement.

The Activation Energy Constant, E.

Rewriting Equation (6-2) with the F_{\sim} as determined previously:

$$\ln(\phi_{\rm e}/F_{\rm v}) = \ln C_{\rm e} - E/R_{\rm e}T_{\rm m}$$
(6-5)

where:

 T_{w} = absolute temperature

and selecting sets of data each with the same water quality, $\ln(\phi_{d}/F_{\nu})$ is plotted versus $(1/T_{m})$ to determine the constant C_{\oplus} and the constant E for each of the fifteen water qualities considered. These plots are shown in Appendix L. The values of C_{\oplus} and E are tabulated in Table VI-2. Values of C_{\oplus} and E show that C_{\oplus} and E depend on water quality. These values also show a great dependency of C_{\oplus} on water quality compared to that of E. The results also indicate that the value of E has an affect on the value of C_{\oplus} . Higher or lower value of E will result in higher or lower C_{\oplus} , respectively. This effect of E on C_{\oplus}

No general pattern was observed between pH and E. Waters with iron contamination have lower E when additive(s) such as HEDP is present. This was expected since these additive(s) provide more heterogeneous nucleation. A considerable variation of the activation energy E was

TABLE VI-2

Constants to be used in equations (6-5), (6-12), (6-13)

 $(Rg = 1.987 \text{ Btu/lbmole *R}) \\ 130 \leq Ts \leq 160*F \\ .08 \leq \tau \leq .43 \text{ lbf/ft}^2 \\ a = (\alpha + 1) 1.75 \qquad \alpha = (a/1.75) - 1$

WATER	ADDITIVES	pН	C,	E	C.	•	α j	ъ
	(FEN)		ft2*F/Btu	Btu/lbmol	hr			
1	4-5 PP 5-6 OP 2-4 PA 2-4 HEDP	7.0	7.976E-3	7.3062E3	1.341E-19	-11.66	-7.66	5.645
5	4-5 PP 5-6 OP	7.5	2.53468	3.511E4	4. 640E -63	1.838	. 85	29.016
3	4-5 PP 5-6 OP 19 AA/HPA	8.1	4.323E7	3.539E4	7.816E-7	0.315	82Ø	3.244
4	4-5 PP 5-6 OP 18 AA/HPA	8.5	2.542610	4.109E4	2.207E7	. 698	681	-2.9 6 7
5	4-5 OP 5-6 PP 18 AA/MA	7.5	2.28 5 E13	4.944E4	1.75162	9.068	961	-3.396
6	4-5 OP 5-6 PP 18 AA/MA	8.5	3.834E-1	1.138E4	3.474E2	2.128	.216	. Ø89
7	4-5 PP 5-6 OP 10 SS/MA	8.5	3.238E3	2.158E4	1.186E11	2.625	.5	-4.0
8	4-5 PP 5-6 OP 10 SA/MA	6.5	4.098E3	2.416E4	3.579E-2	2.471	.412	1.903
9	4-5 PP 5-6 OP 2 Fe	7.5	1.118E1	1.551E4	1.958	6.726	585	.732
10	4-5 PP 5-6 OP 4 Fe	7.5	5 4.394E17	6.1 56 E4	3.941E-3	1.483	152	6.628

TABLE VI-2 CONTINUED

Constants to be used in equations (6-6), (6-11), (6-13)

(Rg = 1.987 Btu/lbmole *R) 130 ≤ Ts ≤ 160*F .08 ≤ τ ≤ .43 lbf/ft² a = (α + 1) 1.75 α = (a/1.75) - 1

WATER	ADDITIVES (PPM)	рН	Cs ft²•F/Btu	E Btu∕lbmol	C₄ hr	a	α	Ъ
11	4-5 PP 5-6 OP 4 Fe 2-4 HEDP	7.5	1.265E18	6.331E4	1.223E-3	1.349	229	2.064
12	4-5 PP 5-6 OP 4 Fe 10 AA/MA	7.5	3.121E2	1.852E4	2.541E-4	Ø.233	867	1.867
13	3 Fe	7.5	4.303E15	5.778E4	6.433E-13	1.972	.127	6.628
14	4-5 PP 5-6 OP 3 Fe	7.5	4.859E31	9.975E4	4.168E25	123	-1.07	-11.298
15	4-5 PP 5-6 OP 3 Fe 10 HEDP	7.5	2.296E3	2.237E4	5. 0 81E4	1.461	165	-1.581

found among the fifteen waters considered in this study. E values ranged from 9.975E4 to 7.306E3.

As was found by Santoso (29), no particular pattern was observed in this study with respect to pH or the type of additive used. It therefore appears, at least for present, the individual values of C_{\Im} and E should be used with the specific additive combination for which they were obtained.

With the functions of Equation (6-2) determined above, it can now be used to calculate the deposition rate ϕ_{cl} with measured values of velocity and surface temperature for each water quality considered in this study.

The deposition rate values obtained from the model Equation (6-2) are plotted against the experimentally obtained deposition rate values Figure VI-2, while some scattering of data can be expected from the inherent complexity of fouling, the correlation between deposition rate values predicted by Equation (6-2) and those obtained experimentally appear quite sound. The average standard deviation of the ratio (experimental values over model values) is 58%.

Removal Rate

In chapter II, Equations (2-10) and (2-15) show that the removal rate and the time constant are inversely proportional to each other:



Figure VI-2 Error Plot of Øet

ød : ft² hr ⁰F/Btu

$$R_{\#} = R_{\#}^{*}(1 - \exp(-\Theta/\Theta_{m}))$$
 (2-14)

$$\phi_{\tau} = \underbrace{\underline{C}}_{\mathbb{P}} \underbrace{\Upsilon X}_{\Psi} \tag{2-10}$$

$$\Theta_{e} = \frac{\gamma}{C_{e}\tau K_{r}}$$
(2-15)

Equation (2-15) shows that the removal rate is a function of the time constant Θ_{e} . Equation (2-14) has a slope of 1 at $\Theta=\emptyset$:

$$\frac{d[R_{+}(\Theta)/R_{+}]}{d(\Theta/\Theta_{c})} = (e^{-\Theta/\Theta_{c}})_{\Theta=\emptyset} = 1 \qquad (6-6)$$

Equation (2-14) also shows that with presence of removal rate the value of R_r reaches 63.2% of its final value R^*_r when the time elapsed is equal to one time constant, Θ_c . Consequently, we have:

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<u>Time</u>	elap	se	ed _					<u> </u>	<u> </u>	4 0
R+(⊖)	as	%	of	its	asymptotic	value	R*+	86.5	75	78

Thus, after four time constants, Θ_{c} , the R_{r} value has essentially reached its asymptotic value.

With the removal rate function determined from fitting the experimental fouling time data to Equation (5-35) by non-linear regression as described in Appendix I, the experimentally obtained value of Θ_{ee} can now be used to determine a functional relationship as given in Equation (2-15):

$$\Theta_{e} = \underline{Y}$$
(2-15)

Based on the argument given by Taborek et al (32), the characterizing function of the deposit structure Y is assumed to be a primary and increasing function with flow velocity. Thus:

Knudsen suggests(17, No.1), that shear stress and not velocity is the more fundamental parameter in removal rate. Also correlating the removal rate data with shear stress will allow the results to be used for other geometries by matching their corresponding shear stresses. For HTRI test sections with water flowing at bulk temperature of 115°F, the fluid shear stress is given by the following equations:

$$(1b_{\tau}/ft^{e}) = 1.1159 \times 10^{-e} V^{1-75}$$
 (6-7)

where:

V = ft/sec.

A description of the method of calculation of shear stress for the HTRI test section is given in Appendix D.

Although the effect of temperature on the strength of the deposit and thus the removal process is known, the way in which the temperature effect takes place is not known. However, several postulations are found in the literature. Santoso (29), stated that fouling studies to date, including HTRI model, have not quantified the effect of temperature on the removal process. As temperature of the deposit increases, the strength of the deposit should be affected and thereby also the removal rate. Thus in this study the Santoso (29) method of including temperature term in the removal equation is adapted. It is assumed that the deposit structure Y is a function of both surface temperature and velocity:

 $Y \propto V^{a_1} T_{a_1}^{b_2}$ (6-8)

where

To make the surface temperature a correlated variable, it is expressed as an exponential function with power b.

The removal rate function (2-14) can now be expressed as:

$$\Theta_{m} = C_{4} \tau^{\alpha} T_{m1}^{b}$$
 with $\alpha = (a/1.75) - 1$ (6-9)

Coefficient C₄ includes the proportionality constant of Equation (6-8) and the quantities $C_{\mathbb{Z}}K_{\tau}$ of Equation (2-14). $C_{\mathbb{Z}}K_{\tau}$ is assumed constant for each water quality. With experimental values of $\Theta_{\mathbb{Z}}$, velocity and surface temperature, the quantities of C_4 , α and b were determined using multiple linear regression analysis. This was done for each of the fifteen waters considered. The values of C_4 , α and b appear to be dependent on the water quality, their values do not show a specific pattern or correlation with pH.

In Figure VI-3 the experimentally obtained values of Θ_{cc} are plotted against the values of Θ_{cc} obtained by the model Equation (6-9). The average standard deviation of the ratio (experimental values over the model values) is 67%.



 θ_{e} : hours

Discussion of Model Constants E, a and b

Activation Energy, E

The activation energy E values tabulated in Table VI-2 are discussed in this section. At a pH of 8.5, water 4, 6 and 7 show that the smallest activation energy value is obtained for water 6. This result is consistent with the findings discussed in earlier sections about the ineffectiveness of AA/MA copolymer in inhibiting fouling. Since smaller activation energy implies that deposit materials would not have difficulty to form. This leads to the speculation that AA/MA copolymer helps promote heterogeneous nucleation and thus less energy is needed for crystallization of fouling constituents.

Water 5 at a pH of 7.5 has a higher E value than water 6 at pH of 8.5 (both waters have the same additive combination). This is also consistent in that higher pH values leads to lower solubility, and thus particulates and colloids will settle on the heat transfer surface providing secondary nucleation sites which promote a heterogeneous nucleation and thus less energy is required for crystallization. Water 5 and 12 have the same pH of 7.5 and the same additive combination with the exception of the presence of 4 ppm Fe in water 12. These two waters show clearly that the presence of iron in the water reduced the activation energy drastically from 4.94E4 to

1.85E4. This is also consistent in that the presence of solid and contaminant material in the water will help and promote heterogeneous nucleation.

By comparing water 9, 10 and 14 all at pH of 7.5, the following is observed: although water 9 has less iron than water 10 and 14 it has a very small E value compared to that of water 10 and 14. This result is contradictory in that more contaminant promotes more heterogeneous nucleation and thus less energy is needed for crystalliza-To explain this contradiction, the conditions at tion. which tests of each water were conducted were examined. It was found that for water 9 no acid was added to the iron solution tank and that the iron tank contained a brown colored solution with a layer of ferrous hydroxide precipitate on the bottom. Thus for water 9, a mixture of Ferrous hydroxide solution and particles was added to the This addition of particles and ferrous hydroxide svstem. promoted more heterogeneous nucleation resulting in a lower energy of activation. For water 10 and 14 sulfuric acid was added to the iron solution tank to maintain the iron in solution as it was added to the system. In this case no iron particles were present in the iron tank and no particles were added to the cooling water from the iron solution tank. Thus colloidal ferric hydroxide formed in the system. Hence, waters 10 and 14 did not have as much iron particles as water 9 and this resulted in a higher

value of E.

Iron has more than one oxidation state and the most stable is oxidation state +3. This suggests that Fe(II) can be oxidized to Fe(III) without great difficulty. In acidic solution with the presence of oxygen at 1 atm pressure, Fe(II) compounds are readily oxidized to Fe(III).

 $4Fe^{a+}(mq) + Oa(q) + 4H^+(mq) + 4Fe^{a+}(mq) + 2HeO$ But even at lower partial pressures of oxygen, as in the atmosphere, and less acidic media, the above reaction may still be spontaneous.

In aqueous solution, Fe(II) is pale green and Fe(III) is colorless. Fe(III) ion hydrolyzed to Fe(OH)_a in solution. Further evidence for the hydrolysis reaction comes from the fact that aqueous solutions of Fe(III) are acidic.

Comparison of waters 2, 10 and 14 all at a pH of 7.5 shows that higher activation energy is obtained when iron is added to the phosphate containing water (water 9 is not included in the comparison for the reasons discussed in the previous paragraph). This is in contradiction with the fact that the presence of contaminant reduces the activation energy values. Thus more experimentation is needed in order to check the reproducibility of the E values. It is also evident from comparing waters 12 and

15, both at a pH of 7.5, that when antifoulant copolymers at 10 ppm concentration were added (to phosphate water with iron contamination i.e. water 10 and 14), E values were reduced significantly. A possible explanation is that, first, iron deposit on the heater rod surface provides secondary nucleation sites thus promoting heterogeneous nucleation which requires less energy and thus smaller activation energy. Secondly, HEDP and AA/MA, by adsorping on to the crystal structures, play the role of being impurities and inhibit the growth of a homogeneous crystals by homogeneous crystallization. Thus the heterogeneous crystallization dominates, which requires a smaller activation energy than homogeneous crystallization.

Activation energy of water 13 represents the energy required for Fe(OH)₃ colloids to agglomerate. This process is explained through the help of the coagulation theory.

When two colloids come in close proximity there are two forces acting on them. The electrostatic potential created by a "halo" of counter ions surrounding each colloidal particle reacts to repel the other particles, thus preventing contact. The second force, an attraction force (van der waals force), supports contact. This force decreases more rapidly with distance than the electrostatic potential, but is stronger at close distance. The net force of these two forces as they relate to one colloid is repulsive at greater distances and becomes attractive only after passing through a maximum net repulsive force, called the energy barrier, at some distance between colloids. Once the force becomes attractive, an agglomeration of the particles takes place.

A means of overcoming the energy barrier must be available before agglomeration of particles can occur. Brownian movement, the random movement of smaller colloids because of molecular bombardment which results from the energy provided by heat transfer, may produce enough momentum for particles to overcome the energy barrier and thus collide.

In this study then, E in its arrhenius-type expression represents the energy that colloids must possess before agglomeration can take place and thus the forming of larger colloidal particulates which bond to the heat transfer surface. Parkins (25) who studied the formation of surface films in pressurized reactors systems, included E in an Arrhenius-type expression in his deposition rate expression. In Parkins' work E was defined as the energy required for chemical linkage.

Since water qualities and additives used in this study are different from those used by Santoso (29) a one to one comparison of activation energy is not possible. However, comparing E ranges may shed light on the extent

of the range of E value for cooling tower water fouling for the purpose of generalization. The range of E values obtained in this study is 9.98E4 (water 14) to 7.31E3 The values obtained by Santoso (29) ranged (water 1). from 2.09E5 (20 ppm CrO₄, 4 ppm Zn, 3 ppm HEDP and pH of 8.0) to 1.44E4 (20 ppm CrO₄, 4 ppm Zn, 200 ppm suspended solids and a pH of 7.5). It appears that activation energy ranges are comparable. In Santoso's study, the highest activation energy value is about twice as much as the value obtained in this study. Likewise, the lowest activation energy values is about twice as much as the value obtained in this study. If water number 1 is excluded, then a much more comparable range would be obtained between the two studies. This range would be 9.98E4 (water 14) to 1.14E4 (water 6) compared to the same range of Santoso's which is discussed above.

Constants a and b

The positive values of parameter a (with exception of water 1) tabulated in Table VI-2 indicate that the scale strength factor is an increasing function of velocity. This result supports the concept on which HTRI Model was based i.e. the strength of the deposit structure is directly proportional to the flow velocity.

With respect to the parameter b, a discussion of the effect of surface temperature on the scale strength is

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necessary. The postulation is that some deposits (which were observed in this study also) appear to break down at higher temperatures. That is, as the temperature within the deposit (which is represented by the surface temperature in this study) increases, a structural change takes place within the deposit and the deposit may easily slough off after it reaches a certain thickness. The scale strength of this type of deposit is a decreasing function of surface temperature and the value of b is negative. The growth of deposits with negative values of b, could be much easier controlled by fluid shear stress. Even low shear stress will probably be effective in removal of deposit, (Santoso (29)).

Positive values of b suggest that a solid encrustation may result as temperature within the deposit in-Surface temperature is used here as pseudo creases. temperature to characterize the temperature changes within the layer of the deposit. Values of the b parameter tabulated in table VI-2 show that the presence of the copolymer additives such as AA/HPA, AA/MA etc. have a very strong effect on the b values. This is indicated by considering water no. 2 with no copolymer additive. Water no. 2 has b value of 29.016 which indicates that a higher surface temperature will result in a stronger deposit structure, while all other waters have either a negative b value or smaller positive values of b ranging from Ø.089

to 6.268. As postulated above, negative values of b will result in a weaker deposit structure with higher surface temperature.

During the discussion of E for water 13, it was indicated that heat transfer was acting as a source of energy required for the occurrence of agglomeration, thus the effect of the surface temperature is one of promoting agglomeration. This effect of temperature is also indicated by the positive value of b for water 13. A positive value of b indicates that higher surface temperature will produce more adhesive and coherent deposit film.

<u>Scale Strength</u>

On the assumption of constant thermal conductivity of the deposit layer K_r, Equation (2-15) shows that the time constant Θ_{ee} is directly proportional to the ratio of the deposit structural strength function Y to the fluid shear stress, τ as:

$$\Theta_{\rm m} = \underline{Y} \tag{2-15}$$

also

$$\Theta_{cc} \propto Y/\tau$$

since

 $Y \propto V^{ax} T_{ax1}^{b}$ (6-8)

then

$$\Theta_{ee} \tau \propto V^{**} T_{**1}^{**}$$
 (6-11)

Thus, $\Theta_{et} \tau$ or equivalently Y is an indicator of the sensitivity of the deposit to velocity and surface The effect of flow velocity and deposit temperature. surface temperature was discussed earlier. Plots of $\theta_{e}\tau$ versus surface temperature and velocity for each water quality are given in Appendix L. These figures indicate that strength of deposit Y is an increasing function of flow velocity which indicates that for the same deposit, higher velocity tends to produce a deposit of higher strength by making the deposit more compact and tight. Velocity also has a removal function through shear stress forces. It was found that deposits of similar composition could have different shear strength depending on the water quality for which deposits took place.

Fouling as a Function of Time and Asymptotic Fouling Resistance, R^{*}-

With all functional relationships determined from experimental data as shown in the previous sections in this chapter, Equations (6-2) and (6-12) can now be used to predict the deposition rate φ_{ct} and the removal rate φ_{rr} .

$$\phi_{cl} = C_{B}F_{v} \exp^{-(E/R_{g}T_{m})}$$
(6-2)
$$\phi_{r} = \frac{R}{C_{4} \tau^{\alpha} T_{w1}^{k}}$$
(6-12)

By substituting Equations (6-2) and (6-12) into Equation (2-2) and integrating, fouling resistance, R_r as a function of time is obtained

$$R_{\tau} = C_{\Theta}C_{4}F_{\tau} = T_{w1} = \exp(-E/R_{G}T_{w})[1 - \exp(-\theta/C_{4}T = T_{w1})] \qquad (6-13)$$

where

 T_m = absolute surface temperature $T_{m,1}$ = surface temperature in °F

or in terms of the time constant $\boldsymbol{\theta}_{\mathrm{m}}$

$$R_{\pi} = C_{\Theta} F_{\vee} \Theta_{\omega} e \times p \left(-E/R_{\Theta} T_{m}\right) \left[1 - e \times p \left(-\theta/\Theta_{\omega}\right)\right]$$
(6-14)

To obtain the asymptotic fouling value R_{τ}^* , Equation (6-14) after a long time becomes:

$$R_{\pi}^{*} = C_{\oplus} F_{\vee} \theta_{\oplus} \exp(-E/R_{\oplus}T_{\oplus})$$
 (6-15)

with

$$\Theta_{cc} = C_4 \tau \propto T_{m1}$$
 (6-9)

and

$$F_{\vee} = \exp(-\emptyset.2704_{\vee})$$
 (6-4)

or, in terms of shear stress:

$$Fv = exp(-3.522 \tau^{-37})$$
 (6-16)

Equation (6-15) is now a predictive model equation the asymptotic fouling resistance for each water for quality considered in this study. As found by Santoso (29), it has not been possible in this study to develop a correlation, so that a single set of parameters could apply to all water gualities considered in this study. Thus the values of the parameters $C_{\ensuremath{\varpi}}$, C4, $\alpha,$ b and E which are tabulated in Table VI-2, have to be used with their corresponding water qualities. The use of these parameters are also limited to a wall shear stress of $\emptyset.\emptyset B \leq \tau$ \leq Ø.43 lb+/ft² and surface temperature of 130°F \leq Tm \leq 160°F. In Figure VI-4, the experimentally obtained asymptotic fouling resistance is plotted against the values predicted by the model Equation (6-15). The average deviation of the ratio (experimental values over those of the model Equation (6-15)) is 48%.

A comparison of the experimental values and those values obtained from the model equations for deposition rate p_{cl} , time constant Θ_{cl} and asymptotic fouling resistance R*r is given in Table VI-3.



R_r**+ :** ft² hr ⁰F/Btu

Water No.	Run No.	đ. Exp.	€. Predict. Eq. 6-2	Ratio	θ _e Exp.	θ _e Predict. Eq. 6-9	Ratio	(R,)E+4 Exp.	(R.)E+4 Predict. Eq. 6-15	Ratio
	302	8.128E-06	8.128E-05	1.000	81.620	81.810	0.998	6.634	6.650	0.998
	303	1.620E-05	8.128E-06	1.993	50.060	49.950	1.002	8.109	4.050	1.997
1	304	2.296E-05	8.128E-06	2.825	31.090	77.530	0.401	7.138	6.302	1.133
-	305	8.620E-06	9.416E-06	0.915	128.790	124.170	1.037	11.102	11.692	0.950
	305	2.199E-06	9.416E-06	0.234	410.780	135.140	3.040	9.031	12.725	0.710
	307	1.029E-05	9.416E-06	1.093	116.060	120.380	0.964	11.936	11.335	1.053
	338	2.250E-05	4.722E-05	0.476	31.610	31.610	1.000	7.112	14.927	0.476
2	336	1.640E-05	2.402E-05	0.683	40.110	40.110	1.000	6.576	9.635	0.683
_	337	1.790E-05	1.222E-05	1.465	29.990	29.990	1.000	5.370	3.664	1.466
	353	7.110E-06	6.428E-06	1.105	80.920	91.205	0.887	5.754	5.862	0.982
	314	5.870E-06	6.428E-06	0.913	77.810	91.205	0.853	4.565	5.862	0.779
3	351	8.970E-06	3.270E-06	2.743	33.800	38.230	0.884	3.033	1.250	2.426
	320	1.880E-06	3.270E-06	0.575	43.230	38.230	1.131	0.811	1.240	0.654
	362	1.500E-06	1.492E-06	1.005	46.500	46.550	0.999	0.697	0.694	1.004
	354	1.740E-05	1.877E-05	0.927	21.380	21.380	1.000	3.712	4.013	0.925
	355	1.100E-05	9.550E-06	1.152	14.420	14.420	1.000	1.582	1.377	1.149
	359	4.010E-06	6.769E-06	0.592	100.590	73.940	1.360	4.032	5.005	0.806
4	350	8.790E-06	6.769E-06	1.299	54.350	73.940	0.735	4.775	5.005	0.954
	357	5.880E-06	3.443E-06	1.708	36.470	39.100	0.933	2.143	1.346	1.592
	348	8.860E-06	3.443E-06	2.573	30.670	39.100	0.784	2.716	1.346	2.018
	349	4.900E-06	1.751E-06	2.798	91.210	122.130	0.747	4.472	2.139	2.091
	366	5.120E-05	4.320E-05	1.185	23.870	24.530	0.973	12.219	10.500	1.153
5	371	1.910E-05	1.150E-05	1.661	23.950	37.568	0.638	4.578	4.320	1.060
	369	3.470E-06	5.850E-06	0.593	75.280	49.650	1.516	2.613	2.904	0.900
	396	7.900E-06	8.541E-06	0.925	412.050	394.320	1.045	32.546	33.324	0.977
. :	397	6.460E-06	4.299E-06	1.503	398.230	454.400	0.876	25.714	19.534	1.316
6	401	1.130E-05	1.039E-05	1.088	276.150	307.720	0.897	31.169	31.965	0.975
	399	5.130E-06	5.283E-06	0.971	450.340	387.070	1.163	23.123	20.452	1.131
-	400	2.540E-06	2.688E-06	0.945	427.200	445.040	0.958	10.846	11.989	0.905
	404	3.500E-05	3.555E-05	0.985	27.970	42.836	0.653	9.792	15.228	0.643
	402	2.030E-05	1.808E-05	1.123	53.860	61.224	0.880	10.924	11.072	0.987
7	403	8.300E-06	9.199E-06	0.902	92.060	92.030	1.000	7.638	8.466	0.902
	407	1.520E-05	1.459E-05	1.042	84.940	84.923	1.000	12.952	12.390	1.045
	405	9.130E-06	7.421E-06	1.230	157.700	157.737	1.000	14.399	11.706	1.230

Table VI-3 Comparisons of Experimental Values vs Model Equations for ø_d, θ_c, and R_r

Table VI-3 (cont.) Comparisons of Experimental Values vs Model Equations for p_{σ} , θ_{c} , and R_{τ}

Water No.	Run No.	€. Exp.	9 ₀ Predict. Eq. 6-2	Ratio	θ _e Exp.	θ _e Predict. Eq. 6-9	Ratio	(R+)E+4 Exp.	(R,)E+4 Predict. Eq. 6-15	Ratio
	385	2.110E-06	1.430E-06	1.476	392.940	392.941	1.000	8.299	5.620	1.477
8	389	4.980E-07	2.039E-06	0.244	413.500	264.700	1.562	2.058	5.397	0.381
-	387	1.130E-06	i.037E-06	1.090	58.470	58.470	1.000	0.658	0.606	1.086
	388	4.900E-07	5.276E-07	0.929	264.700	264.700	1.000	1.296	1.397	0.928
	410	1.560E-05	1.697E-05	0.919	170.550	194.440	0.877	26.593	32.991	0.806
	408	9.3902-06	8.632E-06	1.088	415.440	363.100	1.144	39.028	31.342	1.245
9	409	1.380E-05	4.391E-06	3.143	92.060	132.930	0.693	12.720	5.837	2.179
-	413	8.3602-06	8.947E-06	0.934	317.980	311.900	1.019	26.572	27.906	0.952
	411	4.870E-06	4.455E-06	1.093	165.440	167.610	0.987	8.063	7.629	1.057
}	415	3.280E-05	3.889E-05	0.843	31.000	30.850	1.005	10.171	11.999	0.848
10	414	1.650E-05	1.978E-05	0.834	26.120	26.850	0.973	4.319	5.193	0.832
	415	1.400E-05	1.006E-05	1.392	9.750	23.750	0.411	1.370	2.390	0.573
	417	2.730E-06	1.560E-06	1.750	21.620	21.720	0.995	0.591	0.339	1.743
	462	7.900E-06	2.708E-05	0.292	210.430	76.310	2.758	16.618	20.667	0.804
}	425	2.700E-05	2.708E-05	0.997	80.430	79.500	1.012	21.721	21.531	1.009
	424	3.370E-05	2.708E-05	1.244	70.910	76.230	0.930	23.867	20.645	1.156
1 11	423	2.160E-05	2.708E-05	0.798	76.540	76.720	0.998	16.617	20.778	0.800
	422	1.050E-05	2.708E-05	0.388	85.980	81.180	1.059	8.992	21.986	0.409
	420	2.450E-06	1.378E-05	0.178	60.410	61.460	0.983	5.707	8.467	0.674
	421	1.440E-06	7.007E-06	0.206	57.780	52.570	1.099	3.719	3.684	1.010
	432	2.200E-05	4.121E-05	0.534	31.170	30.731	1.014	6.872	12.663	0.543
}	430	2.680E-05	2.096E-05	1.279	11.940	12.255	0.974	3.197	2.570	1.244
12	431	8.350E-06	1.066E-05	0.783	239.66	239.600	1.000	20.000	25.555	0.783
}	433	9.520E-06	9.726E-06	0.979	64.98	64.980	1.000	6.184	6.344	0.975
	434	5.100E-06	4.966E-06	1.027	190.05) 190.050	1.000	9.685	9.348	1.036
	449	2.190E-05	8.160E-06	2.684	54.54) 198.830	0.274	11.972	16.224	0.738
1	447	1.280E-05	8.160E-06	1.569	52.10	0 181.110	0.288	6.693	14.778	0.453
13	441	6.420E-06	8.160E-06	0.787	189.22	189.220	1.000	12.150	15.440	0.787
	445	3.7502-06	2.111E-06	1.776	120.52	0 224.130	0.538	4.520	4.732	0.955
	440	3.080E-06	2.111E-06	1.459	250.57	0 250.570	1.000	7.714	5.288	1.459

Water No.	Run No.	€. Exp.	¶∎ Predict. Eq. 6-2	Ratio	θ _e Exp.	θ _e Predict. Eq. 6-9	Ratio	(R,)E+4 Exp.	(R _f)E+4 Predict. Eq. 6-15	Ratio
	457	1.120E-05	7.531E-05	0.149	153.450	26.520	5.786	17.232	19.973	0.863
	454	1.060E-05	7.531E-05	0.141	94.960	26.520	3.581	10.058	19.973	0.504
	451	5.790E-05	7.531E-05	0.769	32.270	26.520	1.217	18.699	19.973	0.936
14	455	3.150E-05	3.831E-05	0.822	25.050	13.110	1.911	7.886	5.023	1.570
	452	9.480E-05	3.831E-05	2,475	19.270	13.110	1.470	18.259	5.023	3.635
1	459	1.170E-06	1.227E-06	0.954	177.990	275.940	0.643	2.087	3.398	0.614
}	460	1.290E-06	6.242E-07	2.067	56.770	136.900	0.415	0.733	0.854	0.858
	469	1.070E-05	1.705E-05	0.628	254.530	254.530	1.000	27.200	44.550	0.511
15	468	8.160E-06	8.672E-06	0.941	216.820	213.600	1.015	17.688	18.523	0.955
	462	7.900E-06	8.672E-06	0.911	210.430	213.600	0.985	16.620	18.523	0.897
	467	4.330E-06	6.770E-06	0.640	353.440	353.440	1.000	15.320	23.929	0.540
STD (n)			0.661			0.739			0.504
Average				1.139			1.105			1,055
% Deviation				58.000			66.800			47.800

Table VI-3 (cont.) Comparisons of Experimental Values vs Model Equations for ϕ_{c} , θ_{c} , and R_{τ}

Conditions Showing Insignificant Fouling

Threshold values of pH, flow velocity, shear stress and surface temperature for various additive combinations are shown in Table VI-4. Under these conditions the asymptotic fouling resistance is expected to be less than or equal to Ø.ØØØ1 ft² hr °F/Btu. R*_# ≤Ø.ØØØ1 ft² hr °F/Btu is the threshold value for fouling resistance used in this study. Other basis for establishing a threshold The threshold values shown in Table VI-4 mav be used. were inferred from the matrix Figures E-1 to E-16 in Appendix E and from Table VI-1 where many runs for various additive combinations show fouling resistance value less than or equal to 0.0001 hr ft² °F/Btu. The shear stress in Table VI-4 was calculated from Equation (6~7) for the HTRI test section with water flowing at bulk temperature of 115 °F.

TABLE VI-4

	THRESHOLD VALUE FOR FOULING										
ADDITIVES	рН	VELOCITY ft/sec	SHEAR STRESS lbf/ft ² Eq. (6-7)	SURFACE TEMPERATURE •F							
NON IRON TEST											
1. NO ADDITIVE	≤ 7.5	2 3.0	2.076	≤ 16Ø							
2. 4-5 ppm PP, 5-6 ppm OP, 2-4 ppm HEDP, 2-4 ppm PA	*	*	*	Ŧ							
3. 4-5 ррм РР, 5-6 ррм ОР	≤ 6.5	2 3.0	≥.076	≤ 1 30							
4. 10 ppm OP	≤ 6.5	> 5.5	> .22ø	≤ 16Ø							
5. 10 ррм ОР, 10 ррм АА/НРА	≤ 7.5 ≤ 6.5 ≤ 8.2	> 5.5 > 3.ø ≥ 8.ø	> .22Ø > .076 ≥ .425	≤ 160 ≤ 160 ≤ 160							
6. 4-5 ppm PP, 5-6 ppm OP 10 ppm AA/HPA	≤ 7.5 ≤ 6.5	≥ 3.Ø ≥ 3.Ø	≥ .076 ≥ .076	≤ 145 ≤ 16Ø							
7. 4-5 ppm PP, 5-6 ppm OP	*	*	*	+							
8. 4~5 ppm PP, 5-6 ppm OP 10 ppm SS/MA	≤ 7.5 ≤ 6.5	≥ 5.5 ≥ 3.0	≥.22Ø ≥.076	≤ 160 ≤ 130							
9. 4-5 ppm PP, 5-6 ppm OP 10 ppm AA/SA	≤ 7.5 ≤ 6.5 ≤ 8.5	2 3.Ø 2 5.5 2 5.5	2.076 2.220 2.220	≤ 160 ≤ 130 ≤ 160							

Threshold Values For Various Additives

* Not found in ranges investigated (asymptotic fouling resistance was always greater than .0001 hr ft² °F/Btu).

			THRESHOLD VALUE FOR FOULING											
ADDITIVES				рН		VELOCITY ft/sec		SHEAR STRESS 1bf/ft ² Eq. (6-7)			SURFACE TEMPERATURE °F			
	IRON TEST				T									
1.	4-5 ppm PP, 5-6 ppm OP 2 ppm Fæ		4	ł			Ħ			*			¥	
2.	4-5 ppm PP, 5-6 ppm OP 4 ppm Fe	< <	17	7.5	5	> 2	8. 3.	Ø	>	.42 .Ø7	6 6	< \$	160 130	
з.	4-5 ppm PP, 5-6 ppm OP 4 ppm Fe, 2-4 ppm HEDP	٤	7	7.5		2	э.	Ø	2	.07	6	٤	130	
4.	4-5 ppm PP, 5-6 ppm OP 4 ppm Fe, 10 ppm AA/MA		•	ł			*			*			*	
5.	3 ppm Fe	1	7	7.5	5	2	5.	5	2	. 22	Ø	<u>۲</u>	130	
6.	4-5 ppm PP, 5-6 ppm OP 3 ppm Fe	≤	7	7.5	5	2	8.	Ø	2	.42	5	٤	130	
7.	4-5 ppm PP, 5-6 ppm OP 3 ppm Fe, 10 ppm HEDP		4	ł			¥			*			*	

Threshold Values For Various Additives

* Not found in ranges investigated (asymptotic fouling resistance was always greater than .0001 hr ft² *F/Btu).

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VII. APPLICATION OF RESULTS

Model Correlational Equations

The model equations developed in Chapter VI. may be used in several ways. Apparent uses of the relations would be:

1. The prediction of Θ_{e} thus knowing the time, the fouling value, R_{r} , would need to reach 98% of R_{r}^{*} .

2. The prediction of the effect of shear stress forces, and thus, the flow velocity effect, and the prediction of the effect of the surface temperature.

3. The fouling resistance as a function of time.

4. The prediction of the asymptotic fouling resistance, R_{r}^{*} .

5. The prediction of the deposition rate, ϕ_{cr} , and removal rate, ϕ_{rr} .

In summary, the model equations are:

a. The time constants, θ_{cc} $\theta_{cc} = C_4 \tau_{cc} T_{wl}^{tc}$ (7-1)

b. The flow velocity function, F_{\sim} $F_{\sim} = \exp(-3.522 \tau^{\varnothing-\Xi7})$ (7-2)

c. The Asymptotic Fouling Resistance,
$$R_{\pi}^{*}$$

 $R_{\pi}^{*} = C_{\oplus} \mathcal{F}_{\nabla} \Theta_{\oplus} [exp (-E/R_{g}T_{m})]$ (7-3)

d. The fouling resistance as a function of time, R_{τ} $R_{\tau} = C_{\odot}F_{\vee}\Theta_{c}[exp(-E/R_{\odot}T_{\bullet})][1-exp(-\Theta/\Theta_{c})]$ (7-4)

or in terms of
$$R_{+}^*$$
 and Θ_{ee}
 $R_{+}^*(\Theta) = R_{+}^* [1 - \exp(-\Theta/\Theta_{ee})]$ (7-5)

where

θ_e = time constant, hours
r = shear stress, lb_f/ft²
T_m = heater absolute surface temperature, °R
T_{m1} = heater surface temperature, °F
C₃ = ft² °F/Btu
C₄ = hours
E = deposit activated energy, Btu/lbmol
Rg = gas constant, 1.987 Btu/lbmol °R
Rf = fouling resistance, ft² hr °F/Btu
R*_f = asymptotic fouling resistance, ft² hr °F/Btu

As was stated in Chapter VI., values of C_{\oplus} , C_{+} , α , b and E which are tabulated in Table VI-2 are unique for each additive combination, flow velocity (shear stress of $\emptyset. 08 \le \tau \le 0.43 \ lb_{\tau}/ft^2$) and surface temperature (130 $\le T_{\pm}$ $\le 160^{\circ}F$) for which they were derived.

Threshold Curves

For a given water quality, equations (7-1), (7-2) and (7-3) could be used to construct contours of the asymptotic fouling resistance, R^*_r , as a function of flow velocity and heater surface temperature. Figures VI-5 (a-o) are threshold curves for the 15 water quality modeled in this study. The threshold values of R^*_r shown in these Figures are $\emptyset.\emptyset\emptyset\emptyset1$, $\emptyset.\emptyset\emptyset\emptyset2$ and $\emptyset.\emptyset\emptyset\emptyset3$ ft² hr $^\circ$ F/Btu. Other threshold values of R^*_r could be used as basis of the threshold curves. For a given additive, these curves permit the determination of the operational parameters (flow velocity/shear stress and heat transfer surface temperature) under which a certain asymptotic fouling resistance, R^*_r , would be maintained.

Charts to Predict R*+

With surface temperature (or velocity) held constant at various values, Equations (7-1), (7-2) and (7-3), may be used to construct plots of R^*r as a function of velocity (or surface temperature). Figures VI-6a through VI-60 are plots of R^*r as a function of velocity at three levels of surface temperature (130°F, 145°F and 160°F) for the 15 water quality studied. These plots permit the determination of the condition of velocity for each level of surface temperature at which a particular R^*r value will occur.













Surface Temperature (°F) Figure VI-5; Contour of Asyptotic Fouling vs Velocity and Surface Temperature



Velocity (ft/sec)









vs Asymptotic Fouling Resistance and Velocity









vs Asymptotic Fouling Resistance and Velocity



vs Asymptotic Fouling Resistance and Velocity



Velocity(ft/sec) Figure VI-6n Curves of Constant Surface Temperature vs Asymptotic Fouling Resistance and Velocity



Figure VI-60 Curves of Constant Surface Temperature vs Asymptotic Fouling Resistance and Velocity

Fouling Resistance-Time Curves

Once the time constant Θ_{c} and the asymptotic fouling resistance R*_# are determined from Equations (7-1) and (7-3) respectively, Equation (7-5) may be used to develop fouling resistance-time curves. These plots will help in plant-shutdown scheduling.

Threshold Values

Table VI-4 may be used to select additive combinations along with threshold values of flow velocity (shear stress), heater surface temperature and pH at which the asymptotic fouling resistance. $R_{+\tau}^*$ is not expected to exceed a threshold value of $\emptyset.\emptyset\emptyset\emptyset1$ ft² hr °F/Btu.

Application to Other Geometries

In order to use the results of this study for flow of a given water in other geometries (annular flow was used in this study), the wall shear stress of the flow in other geometries would be matched to those of this study. For example, to obtain a velocity in smooth tube that results in comparable shear stress to those used in this study, Equation (5-34) should be used.

Consider water flowing in 1 in I.D. smooth tube at a bulk temperature of 100°F then

 $\int = 61.9 \text{ lbm/ft}^{\oplus}$ $\mu = 4.6 \times 10^{-4} \text{ lbm/ft sec}$

Thus, to determine flow velocity in the smooth tube required to give wall shear stress of $\emptyset.425 \ lb_{+}/ft^2$ ($\emptyset.425 \ lb_{+}/ft^2$ corresponds to flow velocity of 8 ft/sec in HTRI annular test section used in this study), Equation (5-34) is used

 $\emptyset.425 = (\emptyset.0395) \frac{[(4.6)(10^{-4})]^{0-25}}{(32.17)(1/12)^{-25}}$

from which

V = 10.13 ft/sec

thus, flow velocity of 10.13 ft/sec in a smooth tube will give a shear stress of 0.425 lb_{τ}/ft^2 .

Several numerical examples showing some of the application of such results and equations obtained in this study in the design and operation of heat transfer equipment are given in an earlier study by Santoso (29).

VIII. CONCLUSIONS

In the previous chapters, the fouling data for a variety of additives were presented and discussed. Data was also correlated according to the HTRI model. The following are conclusions:

1. The tests showed that it is possible to minimize the effect of fouling that result from adding phosphate corrosion inhibitors by maintaining appropriate levels of certain controlling parameters of copolymer additives, heater surface temperature, flow velocity and pH.

2. The operational parameters of pH, flow velocity and surface temperature were found to significantly influence the fouling characteristic of all additive combinations considered in this study. However, it was always the case that high flow velocity (8 ft/sec), low surface temperature (130°F) and low pH (6.0 to 7.5) are conditions at which virtually no deposition occurred for all additive combination considered in this study with exception of those additive combinations that had AA/MA copolymer.

3. Various copolymers were tested in this study with respect to their effectiveness in reducing the fouling

tendency of phosphate corrosion inhibitors. Some were found to be considerably more effective than others.

For pH of 8.5, AA/MA copolymer was not an effective copolymer in reducing calcium phosphate deposition. AA/HPA and AA/SA copolymers were both very effective at surface temperature of 160°F. At surface temperature of 130°F AA/SA was very effective and slightly more effective than AA/HPA. SS/MA copolymer was only moderately effective except at 8.0 ft/sec and 130°F where it was effective. Otherwise SS/MA was about as ineffective as AA/MA.

For pH of 7.5, copolymers AA/HPA, SS/MA, and AA/SA were effective in reducing the fouling of phosphate corrosion inhibitors . In all cases fouling was reduced by their presence and acceptable fouling was experienced. The copolymer AA/MA had no effectiveness in reducing fouling tendency; in fact, a greater fouling rate and ultimately higher final fouling resistance was experienced with this copolymer presence than when it was absent.

For pH of 6.5, the effectiveness of the copolymers in reducing the calcium phosphate deposition was very good. At the extreme conditions of 3.0 ft/sec flow velocity and 160°F surface temperature, AA/HPA and AA/SA copolymers were effective; SS/MA was reasonably effective giving an asymptotic fouling resistance about 70% of that when no copolymer was used. Copolymer AA/MA was ineffective.

4. The effect of iron in the presence of phosphate corrosion inhibitors was studied with respect to its effect on the fouling characteristic of the cooling tower water. It appears that the presence of iron (3.5 to 3.9 ppm Fe) causes somewhat higher fouling (15 to 25 percent above that for water containing no iron). Water containing 3.5 to 3.9 ppm Fe showed lower fouling than water containing 1.9 ppm Fe, possibly due to the nature of the deposits formed with higher iron content water. With respect to the fouling characteristic of the cooling tower water containing iron and phosphate corrosion inhibitors, the effect of iron and phosphate appears to be additive and the fouling-time curve, for when no iron is present, is not altered in any way.

5. The effectiveness of HEDP copolymer in reducing the deposition of iron was investigated in this study. In all cases, the presence of HEDP copolymer appears to enhance the fouling.

6. Fouling of cooling tower water containing phosphate corrosion inhibitors with and without iron present was investigated on four different heater surface materials, stainless steel (SS), carbon steel (CS), admiralty brass and 90/10 copper nickel. Virtually no difference was observed in either the fouling rate or fouling resistance of the deposit formed on these sur-

7. Several duplicate runs were made and good reducibility of the data can be obtained when identical conditions are maintained between the duplicate runs. Fluctuations in pH and differences in phosphate and iron content of the water can cause disagreement between duplicate runs.

8. For the phosphate inhibitors, the major constituent of the deposit was calcium phosphate. When iron was present in the water, it was also present in the deposit.

9. Various additive combinations and conditions showed insignificant fouling. For these additive combinations and conditions, threshold values and conditions of water quality, surface temperature and flow velocity (shear stress) were established.

10. Fouling values, when fouling occurred, were obtained under very well defined condition of water quality, heat transfer surface temperature, flow velocity (shear stress). These values can be used by heat exchange equipment designers and operators, Tables VI-1, VI-3.

The fouling data for a variety of additive 11. combinations were correlated according to the HTRI model. The resulting correlation has provided parameters which specific for each water considered in Table VI-2. are Threshold curves for the asymptotic fouling resistance were produced using HTRI model correlations. These curves, along with HTRI equations, can be used by the designers and operators of the heat exchange equipment. The designers can use them to predict the fouling values that they can use in their designs; the operators can use them to follow the progression of the fouling. It will also help plant shut-down scheduling. Given the heat transfer surface temperature, flow velocity (shear stress should be used in all relations developed in this study), fouling resistance as a function of time, the asymptotic fouling resistance and the time constant can be calculated for each of the fifteen water considered or similar Also for a specific water, condition of flow waters. velocity, surface temperature can be calculated for a specific additive combination.

12. Correlating the removal rate function with the heat transfer surface temperature gave a good agreement with HTRI model and gave support to Santoso (29) qualitative assumption of the effect of temperature on removal rate.

13. The presence of additives in the water affects the deposit strength dependency on surface temperature. Adding copolymer to the cooling tower water reduced the value of the exponent b to which the surface temperature is raised. The b value reduced from 29 for no additive to a value in the range of 0.08 to 6 or negative value with additives.

14. It was possible to use HTRI model to correlate the data for the additive combination which contained only iron and no phosphate corrosion inhibitor. In fact the fouling characteristic of the cooling tower water was in no way different from water having no iron present. The deposit in this case was a gelatinous film of ferric hydroxide. Due to the presence of water in this gelatinous film, a high fouling resistance was experienced.

15. The presence of various antifoulants did not alter in any way the fouling characteristics of the cooling tower water. The fouling resistance time-curve still follows an asymptotic fouling curve of constant deposition rate. The presence of these antifoulants made the strength of the deposit structure weaker, thus it was easily sloughed off by the shear forces. Also it was possible, because of the weak deposit, to operate at relatively high
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APPENDICES

APPENDIX A

NOMENCLATURE

A	Surface area, ft ²
AA	Area of flow in an annulus, ft²
АН	Area of heated cross-section, ft²
Ъ	Exponent in Equation (6-11)
C1 - C-7	Constants
C 1	Foulant concentration, lbmole/ft ^a
Ср	Heat capacity of water, Btu/lbm °F
d	Tube diameter, in
dı	Outside diameter of an annuli, in
dæ	Inner diameter of an annuli, in
DIGLAS	Inside diameter of glass tube, in
DROD	Outside diameter of heater rod, in
E	Energy of deposition, Btu/blmol
f	Local friction coefficient, lbf/ft²
F∨	Velocity dependent
9 c	32.17 lbm ft/lbf sec²
h	Convective heat transfer coefficient
K,K@K4	Proportionality constants
k	Thermal conductivity of rod material, Btu/hr ft °F
Kı	Fouling deposition rate, ft ² °F/Btu
K₂	Constant in fouling removal rate term, hr -1
kf	Thermal conductivity fouling deposit, Btu/hr ft°F
L	Length of heated section of rod, in
Μ	Mass flow rate, lbm/hr

m	Empirical constant
n	Exponent on water quality function
Q	Rate of power supply, Btu/hr
Qm∨	Power transducer reading, millivolts
r 2	Correlation coefficient
R	Heat transfer resistance, ft² hr ºF/Btu
Re	Reynolds number
Rf	Fouling resistance, ft² hr °F/Btu
Rfi	Fouling resistance of ith point, ft² hr ºF/Btu
(Rf) _#	Final fouling resistance, ft² hr ºF/Btu
R*	Asymptotic fouling resistance, ft² hr ºF/Btu
Rg	Universal gas constant, Btu/lbmol °R
SS	Sum of squares deviations
т	Temperature, °F
ть	Local bulk water temperature, °F
Тс	Wall thermocouple temperature, °F
Tin	Inlet bulk water temperature, °F
Tm∨	Temperature, millivolts
Ts	Temperature of fouling deposit surface, °F
Τw	Temperature of wall, °F
U	Overall heat transfer coefficient, Btu/hr ft²
v	Fluid velocity, ft/sec
W	Mass flow rate, lbm/hr
WF	Volumetric flowrate, gpm
Wm∨	Flow transducer, millivolts
×f	Instantaneous fouling deposit thickness, in

x/k Thermal resistance of tube wall, ft² hr ^oF/Btu

 $Z_1...Z_{23}$ Variables defined in section V

SUBSCRIPTS

a∨g	Average value
с	Clean condition
f	Fouled condition
i	Inside of tube
0	Outside of tube
m∨	Millivolts reading

GREEK LETTER

α	Exponent in Equation (6-11)
θ	Time, hr
өс	Time constant, hr
θd	Time at beginning of test when the fouling rate is essentially zero, hr
θi	Time at ith point, hr
ч	Viscosity, lbm/ft sec
ſ	Density,lbm/ft®
τ	Fluid shear stress at wall, lbg/ft²
ød	Deposition rate, ft² °F/Btu
ør	Removal rate, ft² °F/Btu
Y	Deposit strength factor
Ω	Water quality function

APPENDIX B

CALIBRATION EQUATIONS

WATTMETER TRANSDUCER

$$Q = 341.3 \times Qm \vee \tag{B-1}$$

where

Q = heater power consumption, Btu/hr

Qmv = wattmeter transducer reading, miilivolts

THERMOCOUPLES: CHROMEL - CONSTANTANT (TYPE E)

T = 32.583 (Tc_{mv} + 5.02) -949 $Tc_{mv} < -1.0$ (B-2) T = 38.529 (Tc_{mv} + 4.72) -9765 $Tc_{mv} \ge -1.0$

where

T = temperature, °F Tc_{mv} = thermocouple output, millivolt

ROTAMETERS

$$WF = Flowcal (Wmv-4) (B-3)$$

where

WF = volumetricl flowrate, gpm
Flowcal = constant, characteristics of flow transducer
Wmv = millivolt reading of flow transducer

CHEMICAL ANALYSIS PROCEDURES

A sample of the cooling tower water was analyzed daily for total hardness, calcium hardness, magnesium hardness, magnesium hardness, sulfate (SO₄), chloride (Cl), silica (Si), orthophosphate (OP), polyphosphate (PP) and iron when iron was present.

The procedure, chemical reagents, equipment and daily analysis values for the chemical analysis of the cooling tower are available at chemical engineering department, Oregon State University, Corvallis Oregon. The daily analysis of these constituents for each run is given in Appendix J.

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APPENDIX D

SAMPLE CALCULATIONS

In Chapter V., the method of calculation of fouling resistance for clean and fouled condition and the method of error estimation of fouling resistance for fouled and clean conditions were given. These methods are a part of the data acquisition and estimation software used to monitor and read the various system parameters in this study. Several earlier studies present a sample of calculation for fouling resistance and error estimation. Some of these studies are (19, 28, 29).

SHEAR STRESS CALCULATION

dæ	=	D	I	GL	AS
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- = .75Ø in
- d₁ = DROD
 - = .420 in
- f = 61.66 lbm/ft[™]

from Equation (5-30):

 $dmax^{2} = \frac{(.75\%^{2} - .42\%^{2})}{\ln (.75\%^{2} - .42\%^{2})} = .383 \text{ in}$

from Equation (5-29):

 $4r_{H} = (.750^2 - .333^2) / .750 = .306$ in

$$Re = \frac{(.306) (V) (61.66)}{(12) (1.42 / 3600)} = (3.987) (10^{3}) V$$

$$f = (.076) [(3.987) (10^{3}) V]^{-.25}$$

$$= (9.564) (10^{-3}) V^{-.25}$$

from equation (5-32)

 $\tau_{a} = \frac{(9.564) (10^{-3}) \vee (-23) (61.66) (\vee 2)}{(2) (32.2)}$ $= (9.157) (10^{-3}) \vee (-25)$

and equation (5-33)

 $\begin{aligned} \Upsilon_{1} &= (9.157) \ (10^{-3}) \ V^{1-75} \ (.750 \ / \ .420) \ \underline{(.333-.4022)} \\ &= (1.116) \ (10^{-2}) \ V^{1-75} \end{aligned}$ $\begin{aligned} \Upsilon_{1} & (1bf/ft^{2}) = (1.116) \ (10^{-2}) \ V^{1-75} \ , \qquad V = ft/sec \end{aligned}$

APPENDIX E

SUMMARY OF TEST RESULTS

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A summary of runs 302 through 469 is given in Table E-1 and Figure E-1 through E-16.

Table E-1 shows run numbers, run duration, heater surface material, final or asymptotic fouling values and run condition (pH, velocity, heater surface temperature and additives).

Figure E-1 through E-16 are matrix figures which show run numbers, heater surface material, final or asymptotic fouling resistance and the additive combination used. These parameters are given as a function of surface temperature, flow velocity and pH. The symbols, CS, Ad, CuNi and SS refer to carbon steel, admiralty, 90\10 copper/nickel and stainless steel.

SUMMARY OF RUNS

RUN	DURATION (hours)	VELOCITY (ft/sec)	T S (F)	RfxE4 (*)	AVERAGE CALCIUM HARDNESS (ppm)	рН	ADDITIVES (**)
302(5.5	.) 335 6	3 0	145				• • • •
303(C.S	335.6	3.0	145	9.0	1 0/11	7.0	1,2,0,
304 (Cu-	N1) 335.6	3.0	145	2.8	1041	2.0	1 2 8
305(S.S	.) 262.7	3.0	160	9.7	1051.7	7.0	1 2 8
306(C.S	.) 262.7	3.0	1.60	3.6	1051.7	20	1 2 8
<u>307 (Cu-</u>	<u>Ni) 262.7</u>	3.0	160	10.6	_1051.7	7.0	1.2.8
308(S.S	.)	5.5	145	(Rod P	roblem)	7.0	1.2
1 <u>309(C.S</u>	<u>.) 167</u>	5.5	145	2,8	962	7.0	1.2
310(C.S	.) 506.3	5.5	145	20.4	927.7	7.5	1.2
311(Adm	.) 188	3.0	160	10.6	676.2	6.5	1.2
<u>312(Adm</u>	<u>.) 146</u>	5.5	160	(Rod P	roblem)	6.5	1.2
<u>313(Adm</u>	<u>.) 194</u>	5.5	160	5,8	682.1	6.5	1,2
1314(Adm	.) 167	3.0	160	4.1	671.2	7.5	1.2.3
<u>115(Cu-)</u>	<u>Ni) 167</u>	<u> </u>	<u>160</u>	1.4	671.2	2.5	1.2.3
316(Adm.) 164	3.0	130	0.9	645.9	7.5	1,2,3
<u>317(Cu-)</u>	<u>vi) 164 –</u>	<u> </u>	130	0	645.9	7.5	1.2.3
GIN(Adm.	,)	(C	mnuter	Problem	۱		
<u>919(Cu-l</u>	<u>1)</u>			1700100	, 		
()20(Adm,) 162	5.5	1.60	0.9	650	7.5	1.2,3
<u>121(Cu-!</u>	$\frac{1}{162}$	<u></u>	145		550	7.5	1,2,3
)44 (AGM, 222 (AGM,		3.0	160	3.0	619.6	8.1	1,2,3
$\frac{22}{22}$	$\frac{1}{210}$	5.0	160	1.9	619.6	8.1	1.2.3
324(3.3)	107	2.2	160	0.8	592.5	6.5	3,4
023(04-1	1 167	n.u	100	0.0	592.5	6.5	3.4
020($\frac{107}{147}$		100	<u> </u>	592.5	6.5	
328(Cv-X	5) 187 H) 167	2.2	160	1.0	634.2	7.5	3,4
320(1 m	1 167	3.0	1.60	1.1	634.2	7.5	3,4
R30/5 5	167	<u> </u>	140	$-\frac{1.9}{1.3}$		7.5	
831 (01-1	(10)	7•2	160	1.5	000	8.2	3,4
9.71(00-0 832(1,4m	1 167	3.0	1.60	1.2	660	0.2	3,4
877(S S	$\frac{107}{165}$	5.5	160	<u> </u>		8.2	
834(Cn_N	(10)	3 3 0	1.60	0.6	670.4	0.5	. 4
935(&d=.	1 165	3.0	1.60	1.2	670.4	0.2	4
A36(5.5	163	5 5	160	$\frac{1.2}{7.1}$	670.4	<u></u>	
37(Cu-N	14) 163	3.5	1.60	6 1	626.3	(+)	1,2
838(Adm.) 163	3 0	1.60	2 8	626 2	1.7	1,2
39(S.S.	165	5.5	1.60	10.7	622 1	<u>-(+)</u>	<u> </u>
840(Cu-N	11) 165	8.0	1.60	8.4	622 4	7 5	4,4,7
841 (Adm.) 165	3.0	160	14.3	622 4	7 5	1 2 5
						<u> </u>	<u> </u>

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4 : OP 10 ppm 5 : AA/MA 10 ppm 9 : PA 2-4 ppm TABLE E-1 CONTINUED

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				SUMMA	ry of ru	SK		ر ر ۲ •	
1	RUN	DURATI (hout:	(ON VELO) (ft	CITY TS /sec) (7	RfxE) (*)	4 AVERAGE Calcium Hardnes (ppm)	55	ADDITIVES (**)	1111
	342(S 343(Cu 344(Ad	S.) -16 1-Ni) 16 1m.) 16	7 5 7 8 7 3	5 160 0 160 0 160	0.4	609.8 609.8 609.8	7.5 7.5 7.5	1,2,6 1,2,6 1,2,6	-1 1 1
	345(S. 346(Cu 347(Ad	S.) 16 1-N1) 16 hm.) 16	58 5 58 8 58 3	.5 160 .0 160 .0 160	0 0.1 0 0.18 0 0.19	5 612.6 8 612.6 9 612.6	7.5 7.5 7.5	1,2,7 1,2,7 1,2,7	
								•	1 1 1
								•	
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	! !								1 1
	! ! !								1
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(*) : (ft ** '2) * hr * F / btu (**) 1 : PP 4-5 ppm 6 : S 2 : OP 5-6 ppm 7 : S 3 : AA/HPA 10 ppm 8 : H 4 : OP 10 ppm 9 : P 5 : AA/MA 10 ppm · 6 : SS/MA 1C ppm 7 : SA/AA 10 ppm 8 : HEDF 2-4 ppm 9 : PA 10 ppm

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I 1 TABLE E-1 CONTINUED

SUMMARY OF RUNS (348 - 395)

-			******	******	*****	******	****	*****
1						AVERAGE		:
:	RUN	DURATION	VELOCITY	TS	RfxE4	CALCIUM	ρH	ADDITIVES!
	#	(hours)	(ft/sec)	(F)	(*)	HARDNESS		(**)
						(ppm)		t
-				100.04				
	348	379	5.80	129.94	13.89	651.9	8.5	1,2,3
	349	379	8.40	131.17	1.8/	651.9	8.5	1,2,3
	350	379	3.00	129.86	10.85	651.9	8.3	1,2,3
	351	426	5.50	160.52	3.18	756.4	7.5	1,2,3
	352	426	7.90	162.07	2.03	756.4	7.5	1,2,3
	353	426	3.00	160.37	1.98	736.4	7.5	1,2,3
	354	147	5.44	158.79	3.67	588.0	8.5	1,2,3
	355	147	7.98	160.55	1.72	588.0	8.5	1,2,3
	336	147	3.00	159.55	4.21	588.0	8.3	1,2,3
	357	323	5.43	129.02	7.31	528.8	8.5	1,2,3
	338	323	7.90	129.23	4.04	528.8	8.5	1,2,3
	339	323	3.00	129.12	6.99	528.8	8.5	1,2,3
	360	141	5.48	130.81	0.10	529.8	1.3	1,2,3
	361	141	8.09	130.74	0.14	529.8	1.5	1,2,3
	362	141	3.00	130.50	0.62	529.8	1.5	1,2,3
	363	131	5.53	159.73	1.59	946.9	5.5	1,2,3
	364	131	8.06	160.78	1.59	946.9	6.5	1,2,3
	365	131	3.00	160.13	2.01	946.9	6.5	1,2,3
	366	169	5.52	163.30	14.20	464.6	6.5	1,2,4
	367	· . E .		165.53	11.80	464.6	6.5	1,2,4
	368	169	3.00	163.25	16.54	464.6	6.5	1,2,4
	369	167	5.59	130.30	2.38	472.9	6.5	1,2,4
	370	167	7.97	132.72	3.73	472.9	6.5	1,2,4
1	371	167	3.00	131.36	5.03	472.9	6.5	1,2,4
;	372	• 94	5.47	161.31	2.42	558.0	6.5	1,2,7
;	373	94	8.05	162.37	1.59	558.0	6.5	1,2,7
;	374	94	3.00	161.78	6.40	558.0	6.5	1,2,7
;	375	214	5.52	162.12	4.04	672.5	6.5	1,2,5
;	376	214	8.11	161.77	3.58	672.5	6.5	1,2,5
1	377	214	3.00	162.85	6.96	672.5	6.5	1,2,5 ;
1	378	162	5.47	131.44	0.24	765.0	6.5	1,2,5
:	379	162	7.95	131.70	(0.02)	765.0	6.5	1,2,5 ;
;	380	162	3.00	131.41	(0.20)	765.0	6.5	1,2,5 ;
1	381	48	5.52	131.78	0.25	800.0	6.5	1,2,7 ¦
;	382	48	8.03	131.52	0.15	800.0	6.5	1,2,7 1
;	383	48	3.00	131.31	0.57	800.0	6.3	1,2,7 ¦
;	384	199	5.47	160.35	3.61	835.7	6.3	1,2,6 1
;	385	199	8.09	161.00	3.16	835.7	6.5	1,2,6 :
;	386	199	3.00	159.56	3.10	835.7	6.5	1,2,6
;	387	133	5.51	129.32	0.68	768.0	6.5	1,2,6
;	388	133	8.03	129.16	0.51	768.0	6.5	1,2,6
;	389	133	3.00	129.53	0.62	768.0	6.5	1,2,6
;	390,	238	5.47	160.37	5.68	729.4	8.5	1,2,6
;	391	238	8.02	160.34	2.32	729.4	8.5	1,2,6
;	392	238	3.00	159.43	4.28	729.4	8.5	1,2,6
;	393	. 141	5.42	128.60	0.23	768.8	8.5	1,2,6
;	394	141	8.02	128.06	0.19	768.8	8.5	1,2,6
;	395	141	3.00	129.10	0.12	768.8	8.5	1,2,6 ;;
			·····································			: 2 월 왕 송 송 전 위 약 목 :	****	뽁≈≈≈≈≈¤\$\$\$\$\$\$\$
	(*)	: (ft **	2) * hr	* 7 / 1	stu			
(:	**)	1:4-5	ppm poly-	-phospha	te	4 : 10 A	A/MA	
	:	2: 5-6	ppm orth	o-phosph.	ate	5 : 10 S	5/MA	
	:	3:10	AA/HPA			6:10 A	4/5 R	
						7 : CO-PO	_YMER	IS BEING F

TABLE E-1 CONTINUED

SUMMARY OF RUNS (395 - 416)

RUN \$	DURATION (hours)	VELOCITY (ft/sec)	.TS (F)	Rf×E4 (+)	AVERAGE CALCIUM HARDNESS {ppm}	рH	ADDITIVES (++)	
395 397 398 399 400 401 402 403 404 405 405 405 405 405 405 409 410 411	532.43 532.43 532.43 532.43 378.21 378.21 114.69 114.69 114.68 114.68 220.11 220.11 220.11 252.4 252.4 252.4 252.4	5.50 8.00 3.00 5.53 3.07 3.00 5.50 8.01 3.00 5.49 8.01 3.00 5.50 8.01 3.00 5.50	159.85 160.16 159.85 130.91 132.64 131.74 158.60 160.66 159.20 128.53 127.15 128.54 158.58 161.50 160.26 128.92	15.18 19.50 21.11 13.39 6.33 24.51 8.63 4.85 8.97 9.86 5.56 11.36 5.60 5.14 14.62 5.84	827.3 927.3 927.3 677.3 677.3 677.3 831.0 831.0 831.0 840.0 840.0 840.0 840.0 840.0 840.0 840.0	83838888888888888888888888888888888888	1,5,5,5,5,5,5,5,5,5,5,5,5,5,5,5,5,5,5,5	
412 413 414 415 415	228.87 226.87 112.2 112.2 112.2	8.01 3.00 5,50 8.00 3.00	128.32 159.04 160.16 158.63	14.00 11.60 4.01 1.45 10.05	840.0 640.0 639.0 639.0 639.0	7.5 7.5 7.5 7.5 7.5	2,5,7 2,5,7 2,5,8 2,5,8 2,5,8	

(*) : (ft ** 2) * hr * F / btu (**) 1 : 10 ppm AA/HA 2 : 4 - 5 ppm Poly-phosphate 3 : 10 ppm SS/MA 4 : 4 - 5 ppm Ortho-phosphate 5 : 5 - 6 ppm Ortho-phosphate 6 : 2 - 4 HEDP 7 : 2 ppm Iron 8 : 4 ppm Iron TABLE E-1 CONTINUED

5UMMARY OF RUN5 (417 - 458)

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	RUN	DURATION	VELOCITY		RfxE4	AVERAGE CALCIUM	ن عد عد Hq	ADDITIVES
	*	(hours)	(ft/sec)	(F)	(*) 	(ppm)		(**)
	417	168 168	5.50	132.50	0.71 0.31	754.0 754.0	7.6 7.6	2,3,5
ii	419	168	3.00	130.20	0.27	754.0	7.6	2,3,5
	420	232	5.50	159.40	4.20	645.0 645.0	7.5	2,3,4,5
	421	232	3.00	161.40	11.00	645.0	7.5	2,3,4,5
İ	423	167	3.00	158.80	11.50	538.0	7.4	2,3,4,5
	424	167	3.00	158.50	5.60	622.0	7.6	2,3,4,5
ii	426	166	3.00	162.50	2.20	622.0	7.6	2,3,4,5
	427	164	5.50	130.10	0.70	-623.0	7.6	2,3,4,5
	420	164	3.00	132.10	0.20	623.0	7.6	2,3,4,5
1	430	257	5.50	160.30	5.50	603.0	7.4	1,2,3,5
	431	257	8.00	159.70	5.20	603.0	7.4	1,2,3,5
ii	433	161	5.50	127.10	3.70	600.0	7.4	1,2,3,5
1	434	161	8.00	129.20	4.70	600.0	7.4	
	435	263	5.50	159.80	0.90	745.0	7.5	NONE
i	437	263	8.00	159.60	1.80	745.0	7.5	NONE 1
	438	263	3.00	158.10	2.10	745.0	7.5	
1	440	301	8.00	162.60	0.60	. 710.0	7.5	6
İ	441	301	3.00	161.20	8.00	710.0	7.5	6
	442	192 192	5.50	130.30	0.40	666.0	7.5	6 1
ii	444	192	3.00	130.40	0.70	666.0	7.5	6
1	445	. 305	5.50	159.10	5.50	703.0	7.6	6
	445	305	3.00	160.50	6.90	703.0	7.6	6 1
ii	448	303	5.50	158.10	3.50	736.0	7.6	6
	449	303	3.00	160.10	9.20	736.0	7.6	6 1
	451	177	5.50	160.30	6.20	657.0	7.6	2,3,6
11	452	177	8.00	160.30	4.10	657.0	7.6	2,3,6
	453	1// 257	5.50	160.40	9.60	720.0	7.6	2,3,6 11
ij	455	NOTE:		HEATER	FAILED	720.0	7.6	2,3,6 1
	456	. 257	3.00	160.50	12.00	720.0 712.0	7.6	2,3,6
	458	205	3.00	129.53	13.00	712.0	.7.6	2,3,6 11
				_	_			
	(*) (**)	: (ft ** 1 : 10	2) Thr	: * F/ 1a	btu	4 : 2 - 4	maa	HEDP
	v " <i>j</i>	2:4-5	ppm poly	phosphat	e	5 : 4 ppm	Fe	
		3: 5-6	ppm orth	ophospha	te	6 : 3 ppm	Fe	



FOULING RESISTANCE STILL INCREASING AT END OF RUN * DEPOSIT PERIODICALLY REMOVED DURING RUN

FIGURE E-1 RESULTS WITH WATER CONTAINING NO ADDITIVES 197





RESULTS FOR PHOSPHATE CORROSION INHIBITOR WITH NO COPOLYMER ADDED

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RESULTS FOR PHOSPHATE CORROSION INHIBITOR WITH 10 PPM AA/HPA COPOLYMER ADDED





RESULTS FOR PHOSPHATE CORROSION INHIBITOR WITH 10 PPM SS/MA COPOLYMER ADDED

FIGURE E-8
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TEMPERATURE - F

FOULING RESISTANCE STILL INCREASING AT END OF RUN * DEPOSIT PERIODICALLY REMOVED DURING RUN

FIGURE E-9

RESULTS FOR PHOSPHATE CORROSION INHIBITOR WITH 10 PPM AA/SA COPOLYMER ADDED



FOULING RESISTANCE STILL INCREASING AT END OF RUN * DEPOSIT PERIODICALLY REMOVED DURING RUN

> FIGURE E-10 RESULTS WITH 2 PPM TOTAL IRON







FIGURE E-12 RESULTS WITH PHOSPHATE, IRON AND HEDP



FOULING RESISTANCE STILL INCREASING AT END OF RUN * DEPOSIT PERIODICALLY REMOVED DURING RUN

FIGURE E-13 RESULTS WITH PHOSPHATE, IRON AND AA/MA .



FIGURE E-14 RESULTS WITH 3PPM IRON AS THE ONLY ADDITIVE



* DEPOSIT PERIODICALLY REMOVED DURING RUN

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FIGURE E-15 RESULTS WITH PHOSPHATE AND 3PPM IRON



FOULING RESISTANCE STILL INCREASING AT END OF RUN * DEPOSIT PERIODICALLY REMOVED DURING RUN

FIGURE E-16

RESULTS WITH 4-5 PPM POLYPHOSPHATE, 5-6 PPM ORTHOPHOSPHATE, 3 PPM TOTAL IRON, 10 PPM HEDP FOULING RESISTANCE - TIME CURVES

These plots are in sequence for Run 302 through 469. These plots include fouling resistance-time curves along with plots of pH, conductivity, corrosivity, surface temperature and velocity as a function of time. These plots allow one to see if variation of any of these parameters affect the fouling resistance.





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APPENDIX G

COMPOSITE PLOTS OF SELECTED RUNS





COMPOSITE PLOT RUN # 302,303,304









COMPOSITE PLOT RUN # 333,334,335







COMPOSITE PLOT RUN # 354-356





COMPOSITE PLOT RUN # 314,315















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COMPOSITE PLOT RUN # 366-368





COMPOSITE PLOT RUN # 399,400,401







COMPOSITE PLOT RUN # 397,400







COMPOSITE PLOT RUN # 375-377





COMPOSITE PLOT RUN # 402,403,404







COMPOSITE PLOT RUN # 403,406



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COMPOSITE PLOT RUN # 404,407







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COMPOSITE PLOT RUN # 356,392,398,404



COMPOSITE PLOT RUN # 358,394,400,406











COMPOSITE PLOT RUN # 411-413



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COMPOSITE PLOT RUN # 415,418







COMPOSITE PLOT RUN # 420,421,422





COMPOSITE PLOT # RUN 422,429







COMPOSITE PLOT # RUN 431,434







COMPOSITE PLOT # RUN 414,420,430











COMPOSITE PLOT # RUN 441,447,450

FIGURE G-Se Comparison of Identical Tests.





FIGURE G-SE

Comparison of Identical Tests.



COMPOSITE PLOT RUN # 459,460,461







COMPOSITE PLOT RUN # 468,469



COMPOSITE PLOT RUN # 465,466,467



COMPOSITE PLOT RUN # 464,467






COMPOSITE PLOT RUN # 337,409,415











COMPOSITE PLOT RUN # 418,460 Run 41800 7.5 pH 8.0 It/suc 130 F 4-5 PP 5-6 OP 3 Fe 0.8 0.7 FOULING RESISTANCE (FT-2+Hr-F/Btu) Run 450000 7.5 pH 8.0 ft/840 130 F 4-5 Pp 5-6 op 3 Fe 0.8 ٩ vo.? 4⁹ . 0.5 "°o 0.4 0.3 A 0.2 м 2.3 PP, 9.8 OP, 3.0 Fe 19. 618 0.1 0 0 20 40 60 80 100 120 140 160 180 TIME(hours) п 418 ÷ 460 FIGURE G-73 COMPARISON OF IDENTICAL RUNS





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TIME(hours)

461 + 419 FIGURE G-75 COMPARISON OF IDENTICAL RUNS





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APPENDIX H

DEPOSIT COMPOSITION

RUN #	P	Ca	Si	Mg	Na/Zn	Zn	Fe	Al	S	C1	K	Na	Cu
338	1	1.01	. 169	.120	.063	.030	.244	.100	.115	.080	.074		
341	1	1.14	.105	.121	.036	.026		.061	.073				
348	1	1.08	.125	.143	.059	.024		.079	.076				1
349	1	1.08	.124	.123	.071	.029		.076	.081	.062			[
350	1	1.03	.138	.148	.069	.026		.089	.092	.067			
351	1	1.08	.182	.122	.087	.047	.042	.104					
352	1	1.20	.148	.102	.070	.063	.047	.079	.079	.069			[
353	1	1.11	.22 7	.128	.090	.046	.051	.118	.087	.087	.079		
354	1	1.18	.127	.134	.045	.025		.074		.066			
355	1	1.11	.120	.133	.062	.026		.081					
356	1	1.13	.137	.145	.045	.021	_	.085	.085	.075			
357	1	. 98	.175	.134	.050	.020	.034	.110	.069	.065			}
358	1	1.03	.164	.150	.054	.023	.034	.104		.080			
359	1	1.11	.204	.135	.053	.023	.042	.129	.078	.067			
366	1	. 29	. 203	.074	.061	.026	.191	.478					.054
367	1	.32	.164	.069	.061	.037	.210	. 448					.075
368	1	.30	.230	.081	.058	.035	.218	.489			.075		.0/9
375	1	.46	.313	.100	.069	.033	.309	.356	.127	.093	.094		.045
376	1	.44	.242	.094	.075	.035	.279	.327	.115	.088	.082		.05/
377	1	.45	.299	.102	.086	.030	.206	.383	.111	.087	.088		.041
390	1	.99	.163	.152		.047	.047	.105	.100	.081		.080	.0306
391	1	.93	.159	.150		.055	.042	.113	.103	.089		.102	.0307
392	1	.95	. 185	.182		.056	.061	.123	.121	.09/		+10Z	.0433
396	1	1.39	.386	.292		.032	.046	.134	.139	.102		.081	
397	1	1.60	.379	.270		.034		.125	.14/	.092		.023	0220
398	1	1.35	.390	.262		.048	.022	.133	.133	.033		.109	.0320
399		1.13	.12/	.190				.081	.0//	.003		140	
400		. 3/	.134	.138				104	470. NGV	.003		.043	
401		1.11	134	.133			050	142	175	101		.031	
402		1.15	170	.102			.010	109	147	0.84		. 050	
403		1.10	1/2 247	.1/1			051	149	197	098		1000	
404		1.33	171	142				.114	.132	.077			
405		1 12	1/1	125				.090	.125	.073			
400		1.13	210	150			035	.130	.134	.072		.050	
407		1 55	•210	.100		.045	.091	1100	.173				
400		1 44		091		041	. 089	. 101	.157	,			
410		1 55	155	086		.047	. 105		.178				
411		1 08	192	.104		.053	. 205	.100					
412		. 91	.185	.130		.047	.231	.111	.113				
413		.95	.174	.122)	.045	.188	.099					
419		- 63	.349		•	.077	476	.228	.227	,			.315
420		.86	.211	. 121		.052	.337	.128					
421	1	_74	.227	.103	3	.049	.470	.127	.111				.128
422		1.11	. 223	.116		.078	. 490	.104	.114	ł			
1 722	1	****			-								

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TABLE: H-1 CHEMICAL ANALYSIS OF DEPOSIT COMPOSITIONS (values ratioed to P)

RUN #	P	Ca	Si	Ng	Na/Zn	Zn	Fe	Al	S	C1	K	Na	Cu
423	1	1.08	.265	.128		.059	.367	.132	.113		.106		
424	1	1.07	.234	.116		.063	.366	.118	.108				
428	1	.56	.290	.129		.072	.447	.189		.160			.383
433	1	.91	.314	.169		.068	1.005	.199	.282	.220	.162		
434	1	.82	.252	.135		.062	.678	.179	.369	.228	.139		.206
435	1	. 82	.266	.173		.053	.566	.171	.286	.161		.095	
*440C	1	.58	1.294			.183	1.591	.527	.402	.325	.318		.638
441	1	1.72	1.461	.329		.365	1.604	.502	.642	.401	.366	.418	
446	1	.91	5.129	.639		.779	1.841	1.456	.870				.930
*446 C	1	.63	2.228			.237	1.969	.693	.625		.469		1.195
¥447	1	1.53	3.507	.608		.584	3.987	1.013	1.432	.861	.859	.689	. 389
451	1	1.21	.197	.144		.049	.142	.122	.137			.089	
452	1	1.32	.210	.124		.052	.205	.117	.154	.091		.079	
452C	1	.67	.352	.123		.073	.636	.186	.147	.129			.169
453	1	1.45	.226	.108		.060	.238	.124	.168			.075	
454	1	.93	.199	.132		.104	.213		.116			.120	.034
455	1	. 91	.215	.138		.099	.243	.123				.128	.059
455C	1	.60	.313	.127		.075	.529	.190	.151	.137			.215
456	1	.89	.202	.142		.085	.200		.120	.095		.134	
457	1	. 97	.201	.146		.104	.278						
458	1	.86	.219	.132		.095	.293	.131	.123				
462	1	.73	.192	.121		.055	.323	.123					
462	1	.61	. 228	.128		.037	.360	.143	.132				
463	1	.70	.205	.113		.057	.392						
463C	1	.67	.218	.119		.039	.401	.137	.117				
464	1	.76	.211	.129		.062	.349						
464C	1	.70	.231	.112		.043	.532	.138					
465	1	.58	.193	.095		.048	.675	.121					
465C	1	.54	.200	.107		.038	.555	.127	.112				
466	1	.51	.210	.107		.036	.542	.128					
466C	1	.51	.212	.101			.541	.131					
467	1	.56	.204	.102		.042	.607						
467C	1	.59	.207	.102		.043	.653	.131					
468	1	1.07	.216	.104		.040	.445	.130	.139		.108		
469	1	1.19	.192	.098		.038	.463	.126	.164				

TABLE: H-1 CONTINUED CHEMICAL ANALYSIS OF DEPOSIT COMPOSITIONS (values ratioed to P)

C: non-heated area of heater rod surface.

*440C: Mn = 0.254 *446C: Mn = 0.375 *447 : Cr = 0.948

APPENDIX I

NONLINEAR REGRESSION

The nonlinear regression procedure obtains least squares estimates of the parameters in a nonlinear regression model. Since analytical solution is not available in this case, the procedure uses a search algorithm in an attempt to determine the estimates which minimyze the residual sum of squares.

The following nonlinear relation was used to fit the experimental data.

$$R_{\pi}(\Theta) = R \star f \left[1 - \exp(-(\Theta - \Theta_{el}) / \Theta_{el} \right]$$
 (5-35)

In fitting the runs data θ_{cl} was treated as variable to be found along with R*f and θ_{cl} . However, when the result of the regression produced a negative fouling resistance value, θ_{cl} was fixed at a value that gives the best coefficient of determination.

In this appendix plot of the result of the regression is shown for runs 302 through 469 in sequence. Examination of these plots should be done with conjunction of Table VI-1.

The algorithm used for the nonlinear regression was developed by Marquardt (1963), and is a compromise between using a straight linearization method and the method of steepest descent.

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AVERAGE COOLING TOWER WATER QUALITY

TABLE J-1

- AVERAGE COOLING TOWER WATER DUALITY

Run B Average Std. Dev	Total Hard. as CaCO3 ppm	Ca Hard. as CaCO3 ⁻ ppm	Hg Hard. as CaCO3 gpm	Sulfate as SO4 ppm	Poly Phospt as PO4 ppm	Ortho Phospt as FO4 ppm	Silica AS SiO2 ppe	PH		
302-4 Average IStd. Dev.	1567.5 54.6	1041 20.1	526.5 51.8	.1450 50	6.12 0.72	5.81 . 0.81	33.8 1.89	7.0		
305-7 Averaçe Std. Dev.	1552 69.8	1051.7 75.0	470.4 67.1	1460 44.7	3.91 0.89	5.07 0.75	33.9 2.30	7.0 0.02		
: 308-9 Average Std. Dev.	1386.6 145.7	962 124.6	424.4	1273.3 87.3	5.96 1.76	4.73 0.61	34.5 0.71	6.96 0.09		
310 Average Std. Dev.	1439.5 227.8	927.7 155.0	511.8 111.9	1500	4.57 1.56	3.49 1.29	37.3 2.34	7.51 0.04		
311-2 Average Std. Dev.	1071.2 32.9	676.2 24.1	394.8 14.9	1066.7 57.7	6.29 2.0	- 6.21 0.80	36 1.4	6.52 0.04		
., 31,7 :Average :Std. Dev.	1101.9 45.9	682.1 23.8	419.7 29.3	1025 28.9	5.8 0.47	5.22 0.38	36 1	6.54 0.05		
:: 314-5 ::Average ::Std. Dev.	: 1085.1 : 54.0	671.2 22.1	413.9 49.1	1042.5 105.3	6.49 1.41	5.01 0.66	31 2.3	7.50		
:: 316-7 ::Average ::Std. Dev.	1044.6 14.4	645.9 10.8	398.7 9.9	9 66.7 28.9	5.99 0.84	5.3 1.30	29.5 0.70	7.50		
:: 320-1 ::Average :Std. Dev.	1043.8 15.3	650 13.1	393.8 9.2	930 24.5	6.24 0.50	5.43 0.30	34.3 4.04	7.47 0.08		
:: 322-3 ::Average ::Std. Dev.	998.6 22.3	619.6 18.7	378.9 25.4	880 10	4.10 1.23	4.58 0.79	35.7 1.15	8.09 0.09		

.

TABLE J-1 CONTINUED

AVERAGE COOLING TOWER WATER QUALITY

•	R u n B Average Std. Dev	Total Hard. as CaCO3 ppa	Ca Hard. Ias CaCC3 Ippa	Ng Hard. as CaCO3 ppa	Sulfate as SO4 ppa	Poly Phospt as PO4 ppa	Ortho Phospt as PO4 ppa	Silica as SiO2 ppa	РН
	324-6 Average Std. Dev.	94 3.8 27.8	592.5 15.7	. 351.3 16.7	897.5 33.0	· • • • •	9.45 1.1	36.5 2.12	6.45 0.05
	327-9 Average Std. Dev.	100 2.5 71.3	634.2 45.3	367.5 31.1	952 114.1		9.24 1.25	37.5 0.70	7.50 C.1
	330-2 Average Std. Dev.	1051.4 25.0	660 19.1	393 20.3	982.5 53.8	: 	8.1	37	8.18 0.05
	333-5 Average Std. Dev.	1110.2 15.5	670.b 6.77	435 18.4	1096.7 1 [°] 95	 	9.4	36.5 0.71	6.52 0.04
	336-8" Average Std. Dev.	1031.8 . 43.9	626.3 26.7	405.6 20.9	900 	4.3 1.3	- 4.66 0.71	36 1.41	7.5
. 1	339-11 Average Std. Dev.	1007.8 11.3	622.4 13.0	385.4 23.4	890 58.9	5.76 0.32	6.1 0.34	34.3. 2.52	7.48 0.04
	342-4 Average Std. Dev.	101 3. 2 42 . 2	609.8 34.2	403.3 24.6	830 14.1	5.76 1.24	: 6,1 1 0,75	: 30.7 4.16	7.52
	345-7 Average Std. Dev.	1014.6 57.9	612.6 41.0	: 1 402 1 20.6	868 39.6	: 1. 5.28 11.42	: 6.8 : 1.4		7.40
TABLE J-1 CONTINUED AVERAGE COOLING TOWER WATER QUALITY

و الماري الذي الذي الذي الم الم الم	و الد الله بين الدي ال الله ال	براد کا کامل کا تراسط		د خا اد بردی خ جدود			ب المشاهد بله بلد بي ا	
	1 Total	Ca	i Ma	Sulfate	Poly :	Ortho :	Silical	1
	Hard.	Hard.	Hard.	. 25	Phoset	Phosat		РН
		an CaCO	an CaCO	504	Las PO4			1
Average								
Std. Dev			. ppm .	:			ppan i	
348-349-330								
Average	1,055.58	631.92	399.23		8.07	10.4/	26.67	8.05
Std. Dev.	63.01	41.75	28.24	1 39.27	9.49	10.27	1.50	0.36
	! ————		1					
351-352-353	1	1	1 ·		1	1	1 1	1
Averade	11,146.92	756.35	1383.65	:936.15	1 5.93	: 9.96	128.50	17.53
Std. Dev.	221.05	158.06	1 77.32	213.52	5.85	1.66	3.07	0.02
354-355-356			1			•	1 1	1
	894.00	588.00	306.00	732.00	4.69	6.28	26.40	8.39
Averaye Cha Davi		42 99	1 47 05	34.29	1.40	1.51	0 49	0.42
3t0. J v v.					!			
						•		
357-358-359								-
Average	909.53	1328.75	329.55	1710.91	3.20		2/.32	
Std. D e v.	125.91	1166.30	: 51.45	106.81	0.54	0.51	1.54	0.04
	!					I	 	
360-361-362	1	1	:		1	1	1	
Average	: 902.50	529.83	255.83	716.67	5.90	13.80	130.33	17.50
Std. Dev.	68.28	214.50	1 31.28	62.36	4.40	4.83	1.25	0.08
						!		
262-364-368	1	. –	1		1	t	1	
	11 202 12	-	1356 35		23.78	80.32	33.17	6.58
Average	11,303.13	770.00				1 16 00		
Std. Dev.	57.21	67.48	104.66	00.02		. 10.77	0.43	10.23
366-367-368	1	1	1	¥	1			
Average ·	816.50	464.55	:451.95	:514.50	110.60	13.95	26.67	16.47
Std. Dev.	431.59	1188.75	194.70	1202.95	: 6.90	1 4.52	3.31	10.06
	:			i				
269-370-371	1	1	1	:	:	1	t :	1
Averade	912.50	472.92	456.25	314.84	1 6.50	10.29	28.50	6.52
Cha Dav	167.57	28.09	145.20	33.47	1 5.48	4.17	1 3.50	10.20
	!	!	!	1				
	•	•	• -				i	
3/2-3/3-3/4				. 601 67			29 50	6.46
Average	1 912.00					1 2 47		
Std. Dev.	103-19	110.39	1 72.04	/3.0/	. 2.//	4.4/		
375-376-377		1	1					
Average	993.75	1672.50	1321.25	:737.50	1 7.88	1 11.48	30.00	10.47
Std. Dev.	1 57.40	66.76	1 29.50	: 49.18	: 5.24	3.43	3.56	10.07
	يقبعه والتركي سيتبيون	ک کا بردون کا کک	بحل وداحم وي	بي بي بر اي اي اي اي اي	بوجنبك المعي			-
379-379-380	1 ·	:	1	t	1	1	1	ł
Average	11,082.50	1763.00	1317.50	1760.00	: 5.88	9.62	:30.33	:6.52
Std. Dev.	1 80.97	64.81	1 23.58	64.42	3.61	2.09	3.33	10.04
						:	;	:
391-392-292	i	1	1	1	:	1	:	1
	11.115.00	1800-00	1315 00	1785.00	4.20	8.80	30.00	16.50
AVERAGE Cha D-	1 20 00	1 10 71	1 21 21		1 1.77	1 3.02	2.00	10.00
sta. Dev.	¥8.02 نات ا	1 100/1	• ••••		1	!		
384-385-386	1		1		:			
Average	11,138.57	1835.71	1302.86	1802.00	1 0.3/			10.31
Std. Dev.	1 55.04	1 67.90	39.63	38.68	i 2. 91	2.32	1.33	10.03
				i				
387-388-389	1	1	1	۱.				
Average	11,161.00	1768.00	1393.00	1767.50	1 5.26	1 7.52	127.73	16.50
Std. Dev.	1 141.22	1 85.59	1 60.30	1 37.00	: 2.04	1 1.37	0.25	10.00
		!		!			1	
390-391-392	1	1	t	1	1 .	1	រ ៖	l
	11.065.00	1729.39	1335.67	806-00	: 9.14	: 8.81	129.33	18.51
inverdye Idha Baa	1 07 01	1105 57		1 73-10	4.22	1 3.79	1 1.87	10.02
ista. Jev.	1 7/.21	103.32	- 38.09	1	· ···	· · · · · · · · · · · · · · · · · · ·	1	1
	, 			:		1	1	1
293-394-395	1					9.07	129 22	
:Average	11,092.50	1768.75	1323.75	1832.50	. 0.3/		1 1 00 -	
Std. Dev.	: 53.68	1 60.89	: 45.09	1 78.54	1.99	1 1.31	1.63	10.00
	•	•	1	1	1		i	i

•

TABLE	J -1		C01	NTI	NUED
	AVERAGE	COOLING	TOWER	WATER	QUALITY

ll Run #	1 Total	1 Ca	i Ng	Sulfate	l Poly	l Ortho	Silica	ł	1	t
	l Hard.	l Hard.	l Hard.	as	l Phospt	Phospt	l as i	PH	I TOTAL	: SOLUBLE
Average	las CaCO3	las CaCC3	las CaCO3	S04	l as PO4	l as PO4	I SiO2		I IRON	I IRON
i 310. yev	i ppm '	i ppm	i ppm Veneense	i ppm '	: ppm !	i ppm !	i ppa I		1	1
1396-397-398		Ì	1	1	:	! !				!
Average	11,120.38	827.31	293.08	848.46	5.49	4.28	27.62	8.50		
Std. Dev.	66.66	77.13	1 43.48	69.71	2.38	1 1.66	: 0.84	0.00	ł	1
1399-400-401	·{ !	· + + !	· !	*~~~~~~~ !	 !	* 	• • • • • • • • 		1	:
Average		677.21	354.81	728.08	6.73	1 5.91	24.04	8.50	1	1 !
IStd. Dev.	1 52.26	43.57	44.55	38.56	3.65	3.90	2.22	0.00	1	
				*******				*	l	1
1402-403-404	1 284 66	1 021 00	1 443 66 1	052.00		1			1	1
IAVErage 15ta Dav	11,204.00	1 031.04	i 443.00 i 1 26.21 !	932.00	i 6.00	i 3,48 ! 2,25	i 26.00 i ! 0.00 i	0.00	i	1
					£104 +				• 	
1405-406-407	I	I	1 1	1 1		1		1		l
i Aver age	11,263.75	1 840.00	423.75	987.50	4.70	3.33	29.88 1	8.50		l
IStd. Dev.	43.57	43.58	38.79	92.70	1.69	0.63	1.36 1	0.00		
408-409-410	; !		1							
Average	11.308.57	837.66	470.71 1	975.00	9.19	8.21	20.83	7.46	1.94	
IStd. Dev.	1 109.32	49.65	69.15	32.79	5.19	3.95	6.14 1	0.04	0.14	l 0

411-412-413	1	; !	1 1							
Aver age	11,140.00	1 730.00	1 410.00 i	913.33	5.76	5.30	26.33 1	7.50	1.9	
lStd. Dev.	27.39	23.45	31.62	53.75	1.98	0.99	1.70 1	0.00	0.13	0
		Į			{	*****				
:	 		;	********			 	[[
Average	. 960.00	639.00	321.00 1	714.00	5.82	5.40	22.00	7.51	3.74	٥
IStd. Dev.	50.20	42.00	66.80 1	37.20	1.14	1.16	3.85 1	0.05 1	0.17	Ŏ

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TABLE J-1 CONTINUED' AVERAGE COOLING TOWER WATER GUALITY

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**********		*******		25523232888	*******				*********
::: :::::::::::::::::::::::::::::::::	Total 1	Ca 1	Ka I	Sul fata :	Pely I	Orthe 1	Silica I	: :	•
{ ! }	Hard. 1	Hard. 1	Hard. 1	15	Phospt 1	Phospt 1	45 1		TOTAL I
11 Average 🗍	as CaCO3	as CaCO3 1	as CaCO3 1	504 ° 1	as P04 1	as P04 1	8102 1	: 1	ERON 1
11 Std. Dev I	i ppa i	ppe 1	ppe l	i ppe l	ppe !	ppe 1	ppe 1	: :	:
;									
: 1417-419	l 1	I 1				1		: :	l 1
!lAverage	1,225.83	1 753.67	470.42	853.33	2.26	9.75	22.57	1 7.61	3.04 ;
liStd. Dev. I	167.43	1 76.54	99.78	125.49	1.01	2.64	3.77	0.03 1	1.15
;;	*******						*******		
::420-422	:	:	i 1					: 1	: :
l:Average 🔡	1,076.00	645.00	431.00	722.00	4.33	: 0. 10	22.83	7.45	2.78
liStd. Bev.	125.82	90.00	61.50	55.08	1.84	2.77	1.47	0.15	.75 :
		********			*******	********			*******
: :423-424									
: Aver age	890.13	538.13	360,00	635.00	Z.79	11.66	21.51	7,40	2.69
I:Std. Bev.	102.50	91.92	99.50	88.96	1.20	3,34	1.93	: 0.33	0.59 :
	••••••	******							
: :423-425							i 		
i laver åge	977.08	6 622.50	332.92	; /66.67	i Z.80	8.93	18.22	: 7.53	2.52
:: 5t3. 3ev.	i 61.29	z 7.68	48.85	55.87	. 9,85	i 1.43	i V.36	. U.03	0,43
	; • • • • • • • • • • • • • • • • • • •	;	********		; -+=+===== ;	,	, ,		;;
: :42/*429 	i 11 AAA AA	i 1 /10 1/	994 44	i 944	, , , , , , , , , , , , , , , , , , ,		•	<i></i>	
t faver ege	15,008,73	i 622.86	i 3/9.5/	: /J2.14 . /m fm /	i i.14 i i.44	• 8.81 • • • •	* 41.44 * * A4	· /.30	1 61813 1 7 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
i 1369. 984.	1 0J./7	33.43	43.24	a 87.63	. 1.VJ	· 1,30	. d.V9 !	• ••••	, 3,9/ j !
11470-499					•	•			
11400-144		. 607 AA	967 88		1 7.47	10.19	18.35	. 7.41	2.75
TIRVERAGE	69 9/ 101 30	1 003.00 ·	· 30/.3V		1 1.76	1.40	4.68	1 0.17	0.67 1
*********		!	· 31.94 ·						
1 477-435					:		•	:	1
!! Avarana	1 999.17	1 600.83	381.67	1 675.01	2.11	9.43	16.40	7.43	4.45
1:Std. Tov.	45.60	41.27	: 35.62	1 31.62	1 1.01	2.61	1 3.01	1 0.08	0.79 1
!!	!	! ••••••	· ••••••	:	!				
1 1476-478	•		•	•	L	1	•	•	• •
I'Averana	11.073.33	1 745.00	1 327.78	t 632.00	1 20	: XC	; 34.67	: 7.50	: 80 :
1:Std. Bov.	1 19.72	47.43	92.77	1 112.54	1	1	: 3.06	1 0.00	
!!		!	!		[
1 :479-441		!		•	i	1	1	1	
I Average	11.073.50	1 709.60	1 249.50	1 744. 3 0	1 NG	1 10	27.25	: 7.49	2.96 1
LiStd. Bav.	1 105.31	1 14.94	1 95.80	1 37.35	1	1	1 2.43	1 0.09	0.64 1
1 !	!	:	!	!			¦		; • • • • • • • • • • • •
: :442-444	Ì	i .		•	t	1	t	1	r 1
LAverage	11,040.83	1 665.83	425.00	745.00	t NC	t XC	1 24.20	1 7.50	: 3.72 !
119td. Bev.	1 75.39	63.67	1 36.88	76.88	1	:	1 1.10	1 0.03	1 0.64 1
		{		{		¦	:		;
1 : 445-447	1 '	:	:	1	۱	:	t	1 .	: 1
l lAverage	11,070.33	1 703.23	375.00	727.78	1 80	I NO	22.40	1 7.59	3.07 1
115t4. Bev.	1 44.65	27.50	1 49.75	1.33	1	:	1 0.89	1 8.05	0.3 1
				:	¦	******	*******		
1 :448-450	I	:	:	1	:	:		1	
l lAver age	11,115.56	1 735.56	1 379.44	1 748.89	1 80	I XO	24.08	1 7.63	Z.94
119td. Jev.	1 115.88	1 - 54.97	1 63.42	1 137.15	1	1	1 2.15	1 0.06	1.16.
*********		;	}	¦				¦	
1 1451-453	1	1 j -	:	1	1			1	
1 Average •	11,022.86	1 657.14	1 365.71	1 714.29	1 5.16	1.63	1 29.67	7.62	4.89
liste. Tev.:	1 78.47	1 - 46.18	1 66.67	1 72.77	1 1.71	. 0.70	: 4.93	1 0.06	3.23
	1			1		;			[+
1:454-456	1	1	1 -	1			i	i , ,	
" l'Aver age	1	1 , 720.50	1 391.11	1 786.77	1 4.91	i 7.43	i 48.90.	i 7.57 I A A4 -	· 3.79 i
tiStd. Dev.	1 77.42	1. 45.00	1 39.59	1 44.72	: 1.94	I 1.64	i 3.78 1	1 V.V7 . 1	
							i	i	,-
1457-458	1	1 (A	1	1	1	i	i .	• • •	
1 Avar age	11,111.49	1 712.00	1 297.50	1 805.00	1 5.33	I U.44	i 29.67	• 7.62	i 3.31
:Std. Jev.	: 21.91	1 23.61	1 37.78	1 10.49	1 1.10	I 1.05	i 1.30	i 9.95	i 1.03
{!	******			;	*		i		;;

APPENDIX K

AVERAGE SYSTEM FLOWRATES

	T	A	9	L	Ε	1	K-1
AVERAGE	F	Ľ)₩-	RF	ITE	S	(LITERS/DAY)

RUN Ø	AVG STD DEV	EVAPORA- Tion	CITY WATER	BLON Down	FORTIFY Solution	INHIBI- : Tor :
302-4	AVG STD DEV	184.4 6.6	254.2 9.8	175.2	103.9	3.46
305-7	AVG STD DEV	195.5 24.7	269.9	150.6 4.6	103.3	2.94
308-9	STD DEV	224.4	283.2 33.3	165.9 8.3	100.8 5.9	3.50 1.42
310	STD DEV	197.6 28.9	261.0 42.7	164.0 2.0	83.9 26.7	2.90 0.91
511-2 	I AV6	190.5	297.6 11.6	169.4 6.1	8.1	3.12 0.81
31625	STD DEV	8.7 190.5	12.1	100.7	69.J 1.0	0.68
316-7	LSID_DEV_	10.6	10.4	3.6	2.2	0.69
320-1	L_SID_DEY_	7.7	7.8	1.9	0.9	0.50
322-3	L_SIQ_DEY_	7.3 193.3	8.6 296.7	2 4 168.3	1.3 61.0	0.78
324-6	STO DEV AVG	8.0 194.4	9.0 296.1	<u> </u>	63.3	0_61 3_59
327=9	AVG	171.8 16.7	268.5 16.0	169.4	7.2 64.2	<u> </u>
330-2	AVG STD DEV	170.9	275.5	170.6	63.7	0.36
333-3	AVG	169.8 5.3	272.9	166	61.3	5.40 0.32
336-8	: AVG : STD DEV	184 7.4	273.I 11.0	134.5 9.7	39.8 1.6	3.5 0.27
339-41	: AVG : STD DEV	179.7 8.3	283.6 10.6	171.2	60.7 1.6	3.83 0.32
342-4 sr:2-8	: AVG :_SJD_DEY	169.9	282.0	179.0	60.3	3.32
,~	: AVG : SID DEY_	6.1	7.3	0.9	5.0	0.42

TABLE : K-1 Continued AVERAGE FLOW-RATES (LITERS/DAY)

	RLIN #	AVG	EVAPOR! C	ΤΥ : BLOW	FORTIF:	INHIBI
11		STD DEV	I TION WA	TER I DOWN	SOLUTI	TOR I
: 1						
11	348-349-350	I AVG	156.6 126	0.4 .172.2	: 62.7	2.2 1
11		STD DEV	6.4 1 1	1.4 2.6	1 5.1 1	1.5 :
: 1	351-352-353	AVG	1169.5 (27	1.2 1164.2	1 56.8	2.4
11		STD DEV	18.7 1 3	2.1 29.0	4.8	1.3
11	354-355-356	AVG	166.7 (27)	3.6 1165.4	1.55.0.1	3.1 :
: ;		STD DEV	25.7 3	1.7 11.3	2.5	0.3 ;
11	357-358-359	AVG	1174.2 1270	0.8/157.3	1 57.5 1	2.9 ;
::		STD DEV	1 24.0 1 3	3.8 1. 21.9	1 4.8	1.0 ;
11	360-361-362	AVG	156.6 127	1.4 (184.3	65.4	0.0 1
11		STD DEV	1 27.6 1 2	B.4 ¦ 11.2	1 0.9	0.01
11	363-364-365	AVG	1175.2 127	4.9 :173.6	1 65.6 1	0.0 :
11		STD DEV	13.8 1	3.9 1 4.9	1.1	0.01
11	366-367-368	AVG	152.5 126	9.6 1166.1	40.1	0.5
11		STD DEV	1 18.6 1 1	3.3 1 8.3	8.4	1.2
11	369-370-371	AVG	1114.2 125	1.7 1172.5	: 30.9	1.8
11		STD DEV	24.6 2	5.8 5.7	6.4	1.6
11	372-373-374	: AVG	1128.3 126	0.1 175.2	50.1	1.0
		STD DEV	1 28.4 1 4	4.8 1.3	: 7.0	1.4
11	375-376-377	AVG _	143.6 26	4.4 1174.1	48.3	2.0
11		STD DEV	1 3.6 1	7.1 2.8	1 8.6	1.6 :
11	378-379-380	AVG	(131.6 24)	5.8 :174.9	1,53.9	2.7 ;
11		STD DEV	1 17.0 1 1	7.2 : 2.3	1 8.0	1.1 1
11	381-182-383	AVG	139.8 125	9.8 1173.9	49.4	0.0
11		STD DEV	5.8 (5.4 0.1	1 0.3 1	0.01
11	384-385-386	AVG	1135.6 125	4.2 174.3	50.8	1.1 1
::		I STD DEV	1 6.6 1 0	5.8 1.6	1 2.2	1.4
11	387-388-389	AVG	1126.0 124	7.6 1183.3	1 56.2 1	2.2 :
13		STD DEV	9,4 1 1	5.9 8.1	4.4	1.6 1
11	390-391-392	AVG	:133.3 :24	B.2 :171.0	46.8	3.0 1
11		STD DEV	1 29.7 1 3	4.1 : 8.2	1 11.6	0.5
11	393-394-395	I AVG	1107.1 121	3.8 :172.8	1 57.8 1	1.8
::		STD DEV	7.0	5.6 1.1	: 7.2 :	1.5

TABLE : K-1 Continued AVERAGE FLOW-RATES (LITERS/DAY)

					****				. æ :		
11 RUN #		AVG STD D	EV	IEVAPO	ORI CITY N WATER	I BLOW		FORTIF		INHIBI TOR	1
	-			- ;		- ;	- 1		- ; -		ł
11396-397-398	1	AVG		1129.8	B 1231.4	1170.6	ł	60.4	;	2.5	ł
11	1	STD	DEV	1 6.1	1 1 7.9	1 2.6	ł	6.6	ł	0.6	1
11399-400-401	t	AVG		1108.6	5 1214.8	1172.9	ł	58.9	ł	3.0	ł
1 3	;	STD	DEV	1 10.3	3 : 12.0	: 3.8	1	3.9	I	0.3	ł
11402-403-404	ł	AVG		1146.0	0 1233.6	1170.5	1	75.1	ł	2.9	ł
11	ł	STD	DEV	40.	1 43.9	1 3.9	ł	0.7	ł	0.3	:
11405-405-407	ł	AVG		1168.2	2 1257.2	1168.6	l	71.8	ł	3.0	ł
11	ł	STD	DEV	1 27.1	7 32.8	4.0	1	5.1	1	0.2	ł
11408-409-410	ł	AVG		1143.8	8 1218.9	1168.3	ł	70.0	ł	2.7	l
11	ł	STD	DEV	1 21.0	0 44.7	1 12.3	1	9.9	ł	0.9	ł
11411-412-413	ł	AVG		135.1	1 1241.4	1169.9	ł	55.3	ł	3.2	ł
11	ł	STD	DEV	1 9.9	9 15.6	1 7.3	ł	4.0	ł	0.2	ł
11414-415-416	ł	AVG		1152.1	1 1262.0	1171.2	ł	53.8	ł	5.0	1
11	ł	STD	DEV	1 23.9	9 1 20.4	1 8.7	ł	2.5	ł	0.3	ţ.
: !											ł

TABLE : K-1 Continued AVERAGE FLOW-RATES (LITERS/DAY)

	================			========			======	=
I RUN 🛊	I AVG	EVAPOR: CITY	I BLOW	FORTIF	INHIBITOR	INHIBITOR	IRON	1
;	STD DEV	I TION IWATER	I DOWN	SOLUTI	PHOSPHATE	COPOLYMER	1	1
¦		-	- !	:		;		1
417-19	I AVG	1146.7 1248.6	173.1	63.6	! 0.0	1 0	4.01	;
:	STD DEV	12.4 21.8	7.9	13.8	0.0	: 0	1.02	ł
:420-22	I AVG	1151.5 1260.8	1170.8	48.7	1.8	: 3.08	13.38	ł
:	STD DEV	8.6 10.2	9.6	10.3	1.8	1.06	10.52	ł
423-24	I AVG	48.0 1152.3	1173.9	: 58.1	0.6	: 3.33	13.24	ł
!	STD DEV	1 11.8 1 7.1	6.2	7.1	1.4	: 0.23	:0.31	ł
: 425-26	I AVG	1 59.2 170.3	176.4	1 55.4	0.0	3.29	13.38	;
1	STD DEV	15.1 15.0	1.3	5.7	0.0	0.21	10.64	;
:427-2 9	I AVG	1152.2 1257.5	174.7	54.3	: 0.0	2.93	12.78	ł
:	STD DEV	1 15.3 26.1	1.4	1.7	: 0.0	1.37	10.21	ł
:430-32	I AVG	1 90.3 1195.0	1170.0	: 53.8	2.4	: 2.85	14.58	ł
:	: STD DEV	47.1 44.5	: 8.5	: 3.0	1.5	1 2.54	1.45	ł
:433-35	I AVG	1157.3 1267.5	167.9	55.1	1.0	: 3.11	16.53	ł
:	: STD DEV	1 5.2 6.0	4.5	: 4.9	1.5	: 0.4	10.97	!
:436-38	AV6	1154.4 1269.4	:171.0	: 61.6	I NO	I NO	I NO	ł
:	STD DEV	: 5.8 : 10.5	: 2.0	: 7.7	•	1	:	ł
439-41	AV6	1198.9 1294.3	170.4	: 66.8	I NO	I NO	4.6	!
:	STD DEV	10.3 115.7	: 8.5	6.2	!	1	:0.77	ł
442-44	AVG	1155.5 1250.7	168.4	65.6	I NO	I NO	13.99	ł
:	STO DEV	: 30.3 : 23.7	6.5	4.5	1	1	:0.43	ł
:445-47	: AVG	136.2 237.6	173.7	: 63.9	I NO	I NO	13.41	ł
1	STD DEV	1 19.5 1 22.1	11.4	1 3.5	1	1	10.81	ł
:448-50	I AVG	1112.8 1213.1	:168.2	: 60.7	NO NO	I NO	13.95	;
:	STD DEV	1 21.7 1 25.0	6.6	8.8	1	1	10.79	ł
:451-53	AV6	1152.6 1248.4	168.0	: 62.0	2.3	I NO	4.27	!
1	STD DEV	: 30.1 : 26.9	1 11.6	; 7.8	1.1	1	12.37	1
454-56	AV6	1154.5 1265.2	185.1	; 75.4	1.1	: NO	4.46	1
1	STD DEV	10.1 20.0	16.5	5.1	0.2	1	10.89	1
1457-59	I AVG	1 58.2 1164.8	1175.6	7.8	1.7	I NO	13.83	ł
1	STD DEV	1 27.5 28.8	1 15.6	1.4	0.9	1	10.79	:
=======	2222222222		3222222	========			======	:=

APPENDIX L

PLOTS OF CORRELATIONAL CURVES

- Figures M-1(a-h) Correlational of -lnød vs velocity at a constant surface temperature for 8 sets of different water qualities.
- Figures M-2(a-q) Correlation of -ln(00/Fv) vs [1/(Ts+460)] [10⁽³⁾) for the 17 different water qualities observed in Table VI-2.
- Figures M-3(a-q) Curves of Constant Velocity on Grid of Time Constant vs Surface Temperature for the 17 different water qualities observed in Table VI-2.
- Figures M-4(a-q) Curves of Constant Velocity on Grid of (Time constant x shear stress) vs Surface Temperature for the 17 different water qualities observed in Table VI-2.

PLOTS OF CORRELATIONAL CURVES

Figures L-1(a-h) Correlational of -lnød vs Velocity at a constant surface temperature for 8 sets of different water qualities.









PLOTS OF CORRELATIONAL CURVES

Figures L-2(a-o) Correlation of -ln(00/Fv) vs [1/(Ts+460)] [10³) for the 15 different water qualities observed in Table VI-2.



















PLOTS OF CORRELATIONAL CURVES

Figures L-3(a-o) Curves of Constant Velocity on Grid of Time Constant vs Surface Temperature for the 15 different water qualities observed in Table VI-2.





Figure L-3d Surface Temperature(F)



Time Constant 8c (hour)

















PLOTS OF CORRELATIONAL CURVES

Figures L-4(a-o) Curves of Constant Velocity on Grid of (Time Constant × Shear Stress) vs Surface Temperature for the 15 different water qualities observed in Table VI-2.



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APPENDIX M

SOLUBILITY INFORMATION

As a guide to cooling tower water treatment, McCoy (23) calculates the solubility of the scaling compounds at standard conditions, then suggests that concentrations be held lower than the calculated saturation values. Using only the hydrogen phosphate complexes and the solubility product of $Ca_{\oplus}(PO_{+})_{\oplus}$, he calculates the saturation concentration of $Ca_{\oplus}(PO_{+})_{\oplus}$.

Herbig (12), collected solubility data for the cooling tower constituents. Using these data he generated saturation curves for different potential precipitant. An example of such curves is Figure M-1.

Table M-1 lists the solubility products constant at three different temperatures (130, 145, 160°F) for the cooling water constituents. This table is adapted from Herbig (12) with the iron solubility products constants calculated during the course of this investigation.

Humphris() reported information on the solubility of calcium phosphate in a cooling tower and an equation was derived from these data for predicting cooling water conditions. Figure M-2 is a nomogram produced from the derived equation.

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Figure M-l Saturation Curves of Calcium and Orthophosphate in Solution with Respect to Calcium Phosphate

TABLE M-1

<u>Equilibrium Equations</u>

LOG K VALUES

			<u>130°F</u>	<u>145°F</u>	<u>160°F</u>
1.	[MgOH+] [H+] [Mg ²⁺]	= K1	-11.29	-11.12	-10.96
2.	<u>[MgSO₄_aq]</u> [Mg ^{æ+}][SO ^{æ-}]	= K2	2.59	2.67	2.74
з.	[H+] [OH]	= K	-13.15	-12.95	-12.78
4.	[MgP0;;] [Mg ^{జ+}][P0;:]	= Ka	3.40	3.40	3.40
5.	<u>[MgHPO₄_ag]</u> [Mg≅+][HPOद=]	= K4	1.8	1.8	1.8
6.	<u>[Ca^{e]3}[PO君~]</u> = [Ca ₃ (PO4) ₂] ₅	= Ks	-31.24	-32.33	-33.59
7.	<u>[H+][H</u> ⊵PO₄∄ [H₃PO₄]	= K.	-2.3Ø	-2.36	-2.41
8.	<u>[H+][HPO╃-]</u> [H _≈ PO₄Ĵ	= K-,	-7.19	-7.20	-7.23
9.	<u>[H+][P0⊉-]</u> [HPO # -]	= Kø	-11.90	-11.78	-11.65
1Ø.	<u>[CaPO</u> ₄] [Ca≋+][PO2=]	= Kç	6.66	6.71	6.76
11.	<u>[CaHPO₄ aq]</u> [Ca ^{æ+}][HPO╦]	= K1Ø	3.23	3.68	4.21
12.	<u>[CaH∍PO‡]</u> [Ca [#] +][H ₂ PO∓]	= K ₁ 1	.72	.8	.92

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13.	<u>[CaSO4aq]</u> = [[Ca ²⁺][SO2 ⁻]	K12	2.42	2.47	2.51
14.	<u>[FePO₄•2H¤O]</u> _₩ [H+] [Fe ³⁺][HPO╤-][H2O] [;]	_= K ₁₀	16.Ø4	16.137	16.23
15.	<u>[FePO₄]_@[H+]</u> [Fe ³⁺][HPOद=]	= K ₁₄	16.63	16.804	16.97
16.	<u>[FePO₄•2H₂0]</u> [Fe ³⁺][PO⋧ [_]][H ₂ 0] ²	= K ₁₅	24.13	24.290	24.44
17.	<u>[FePO₄•2H2O]</u> [Fe ³⁺][POZ ⁻][H _e O] ^e	= K1¢	28.15	28.189	28.22
18.	<u>[FePO₄]</u> . [Fe ³⁺][PO컱]	= K _{1.7}	28.74	28.86	28.96
19.	<u>[FePO4]#[H+]2</u> [Fe ³⁺][H2PO41]	= K ₁ .e	9.493	9.68	9.86
2Ø.	<u>[Fe(OH)_@]_#[H+₃ª</u> [Fe ³⁺][H ₂ O] ³	= K₁;	-2.13	-1.80	-1.48

* Brackets indicate activities.

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Figure M-2 Precipitation Nomogram

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