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MICROBIAL FOULING AND ITS CONTROL: A PHENOMENOLOGICAL APPROACH

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ABSTRACT

Biofouling is a major concern to the power industry because of its effect on plant performance and its effect on useful lifetime of certain types of plant equipment (e.g., condensers, fan coolers). Biofouling is controlled most often by application of chlorine. The determination of a chlorine application rate must consider the concentration necessary for effective biofouling control while minimizing the chlorine concentration released to the receiving waters at the plant site.

The objectives of this paper are to stress the following concepts:

1. The critical role of cooling water organic carbon (OC) in microbial fouling and its influence on control with oxidizing biocides.
2. Mass transfer and diffusion are generally the rate-limiting steps in the chlorine-biofilm reactor.
3. An instrument is necessary to assess effective chlorine dosage for control of fouling biofilms while minimizing chlorine discharge to the environment.

ACKNOWLEDGMENTS

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INTRODUCTION

Biofouling refers to the undesirable accumulation of a biotic deposit on a surface. The deposit may contain micro- and macroorganisms. This proposal will focus on microbial fouling biofilms which consist of an organic film composed of microorganisms embedded in a polymer matrix of their own making. The extracellular polymer substances (EPS) are presumed to be largely composed of polysaccharides along with glycoproteins and, sometimes, nucleic acids. The composite of microbial cells and EPS will be termed a biofilm. Complex fouling deposits, like those found in operating heat exchangers, often consist of biofilms in intimate association with inorganic particles (1), crystalline precipitates or scale (2), or corrosion products (3). These complex deposits often form more rapidly and are more tightly bound than biofilms alone.

Fouling biofilms impair the performance of process equipment. They can form in any fluid flow conduit and increase fluid frictional resistance (4). In addition, biofilms in heat exchangers can increase heat transfer resistance (1, 5, 6). Biofouling may also accelerate corrosion of the surface beneath the biofilm (7, 3).

Fouling in heat exchangers may cost the United States billions of dollars annually (8). Zelver et al. (1) have documented a case of biofouling at a nuclear power plant in which heat transfer rate in a fan cooler decreased by 30% due to biofouling in a 30 day period. Subsequent tests indicated continued increase in fouling over a 6 month period. The testing at this plant was partially prompted by microbially-mediated corrosion problems accompanying the biofouling so two alloys (90-10 Cu-Ni and AL-6X stainless steel) were tested in parallel. Rate and extent of fouling on AL-6X was greater than on the Cu-Ni under the test conditions. In another study at a Canadian power plant site, biofouling decreased heat transfer rate in a condenser by 30% over a two month period (9). The plant design had allowed for a 15% decrease due to fouling.

FOULING BIOFILMS

Rate and extent of fouling biofilm accumulation is the net result of four fundamental processes (10) frequently occurring simultaneously:

1. Transport of organics and cells to the wetted surface
2. Adsorption and firm adhesion of the cells to the wetted surface
3. Microbial cell growth and EPS formation at the wetted surface and within the biofilm
4. Partial detachment of biofilm material primarily due to fluid shear forces

The rate and extent of fouling biofilm development has been the subject of numerous laboratory and field investigations. The variables influencing fouling biofilm formation which have been studied the most include:

1. Initial surface conditions (11, 12, 13)
2. Selected water quality parameters including organic carbon concentration (14, 15, 16, 17)
3. Fluid velocity (14, 18, 19, 20, 1, 21)
4. Water temperature (14, 20, 18, 21)
5. Tube alloy (3, 22)
6. Tube wall temperature (14)

TRANSPORT AND ADSORPTION

Microbial cells enter a condenser tube with the cooling water. The cells are transported from the water to the tube wall by a variety of mechanisms (10) whereupon a small number of them adsorb. The adsorbed cells become firmly attached with time, generally through the mediation of EPS.

In the absence of microbial growth, numerous investigators (23, 24, 25) have observed that a saturation condition results in which cells are distributed rather sparsely over the substratum. Mathematical modelling of the biofouling process (Bakke and Yeh, unpublished results) demonstrates the relatively small accumulation which occurs due to adsorption in the absence of growth, i.e., substrate concentration almost zero ... 0.2 mg l^{-1} (Figure 1). The surface density of adsorbed cells may be a function of fluid velocity or shear stress at the substratum (Table 1). In a flowing system, the saturation coverage of the substratum is quite low (< 5% of the surface area). Consequently, no significant biofilm is likely to accumulate if recruitment of microorganisms from the cooling water is the only mechanism.

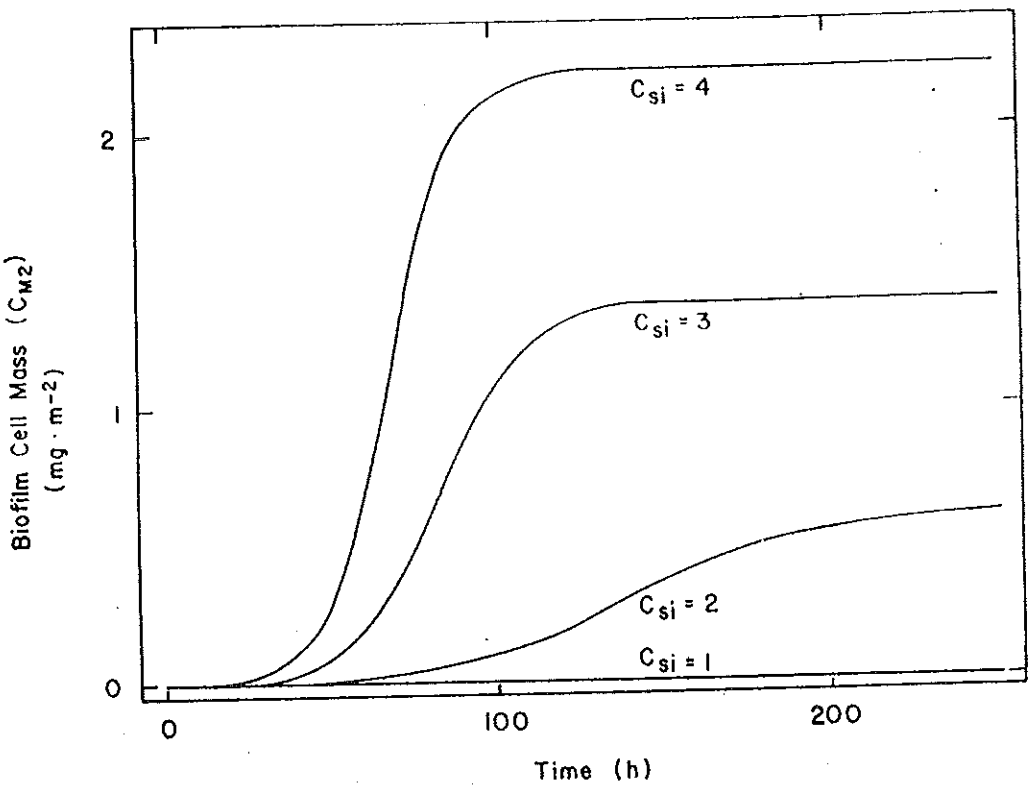


Figure 1. The influence of inlet OC concentration (g m^{-3}) on fouling biofilm progression.

TABLE 1

SATURATION COVERAGE OF A SUBSTRATUM BY MICROORGANISMS AS A FUNCTION OF FLOW REGIME
(A pseudomonad was used by each investigator.)

Substratum	Flow Regime	Saturation Coverage	Reference
polystyrene	quiescent	40	23
glass	laminar	1-5	24
glass	turbulent	0.1	25

How, then, do fouling biofilms accumulate to the extent that they influence heat transfer in a condenser tube? Biofilms accumulate as a result of growth and other metabolic processes.

METABOLIC ACTIVITY WITHIN THE BIOFILM

Fouling biofilms accumulate to a troublesome extent as a result of metabolic activities including cellular reproduction and product formation (e.g., EPS formation) within the biofilm. Therefore, the adsorbed

cells reproduce and produce EPS some of which remains in the biofilm while the remainder detaches. The driving force for the microbial metabolic processes is chemical or radiant energy. In condenser tubes, only chemical energy is available and is most often in the form of organic compounds from which the microorganisms (heterotrophs) obtain both energy and carbon.

Organic Carbon (OC) as the Energy Source

OC drives virtually all microbial processes in a condenser tube. Organic carbon (OC) is present in all cooling waters and is frequently classified as total organic carbon (TOC) which equals the sum of soluble organic carbon (SOC) plus particulate organic carbon (POC). Seawater off the coast of Hawaii contains on the order of 1 mg TOC l^{-1}. Total organic carbon in cooling water from an industrial, "zero discharge", recirculating cooling tower system has been measured at approximately 500 mg l^{-1} (26). Untreated municipal sewage contains on the order of 200 mg TOC l^{-1}.

But OC concentration, although the critical factor in batch microbial growth, is not as important as OC loading rate to the biofilm surface when the concern is condenser fouling. Loading rate is defined as follows:

$$\text{loading rate} = \frac{\text{volumetric flow rate} \times \text{inlet OC concentration}}{\text{wetted surface area}} = \frac{F\,C_{si}}{A} \qquad (1)$$

or, multiplying and dividing by volume, V

$$\text{loading rate} = \frac{D\,C_{si}}{(A/V)} \qquad (2)$$

where F = volumetric flow rate ($L^3\ t^{-1}$)
V = tube volume (L^3)
A = tube surface area (L^2)
C_{si} = inlet organic carbon concentration ($M\ L^{-3}$)
D = F/V = dilution rate (t^{-1})
D^{-1} = residence time (t)

The influence of OC loading rate on biofilm accumulation has been calculated from a mathematical model based on laboratory experiments and is indicated in Figure 2. The OC concentration is 20 mg l^{-1}. Higher dilution rates mean higher OC loading rates to the biofilm and result in increased biofilm accumulation.

In a condenser tube, growth of microorganisms in the liquid phase is essentially zero for at least two reasons:

1. Inlet OC concentration, C_{si}, is generally low
2. Liquid residence time in the condenser tube, D^{-1}, is only a few seconds

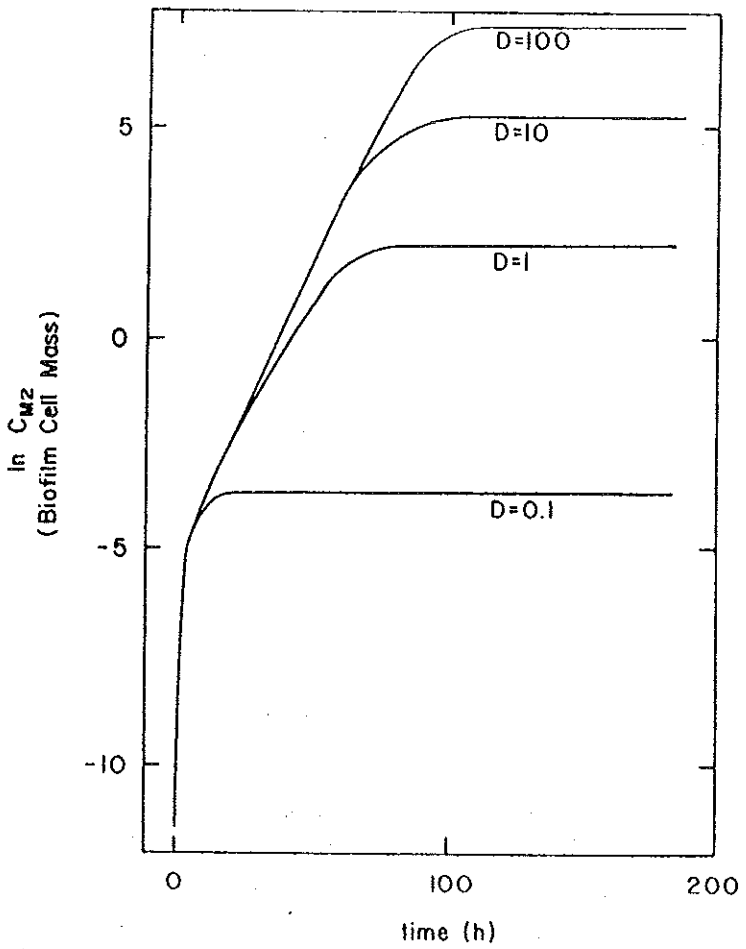


Figure 2. The influence of dilution rate (h^{-1}) on fouling biofilm progression. Note the logarithmic scale of the ordinate.

Biofilm growth at the expense of the OC, however, can be quite extensive. A comparison of a batch growth system (e.g., a test tube) versus a continuous flow condenser tube is provided in Figure 3. The biomass produced in the test tube is essentially negligible compared to that produced in the condenser tube biofilm. Of course, all the biofilm produced does not accumulate in the condenser tube. A significant fraction detaches and exits the condenser. The detached biomass is primarily responsible for the biomass found dispersed in the water phase.

The effect of varying inlet OC concentrations has been modelled (Figure 1). At high OC (> 20 mg l^{-1}), oxygen may become limiting and portions of the biofilm may be anaerobic.

The organic compounds also represent a significant portion of the chlorine demand in a cooling water (see below). Thus, an increase OC content in cooling water not only contributes to increased biofouling but also reduces the effectiveness of a given chlorine concentration in controlling biofouling.

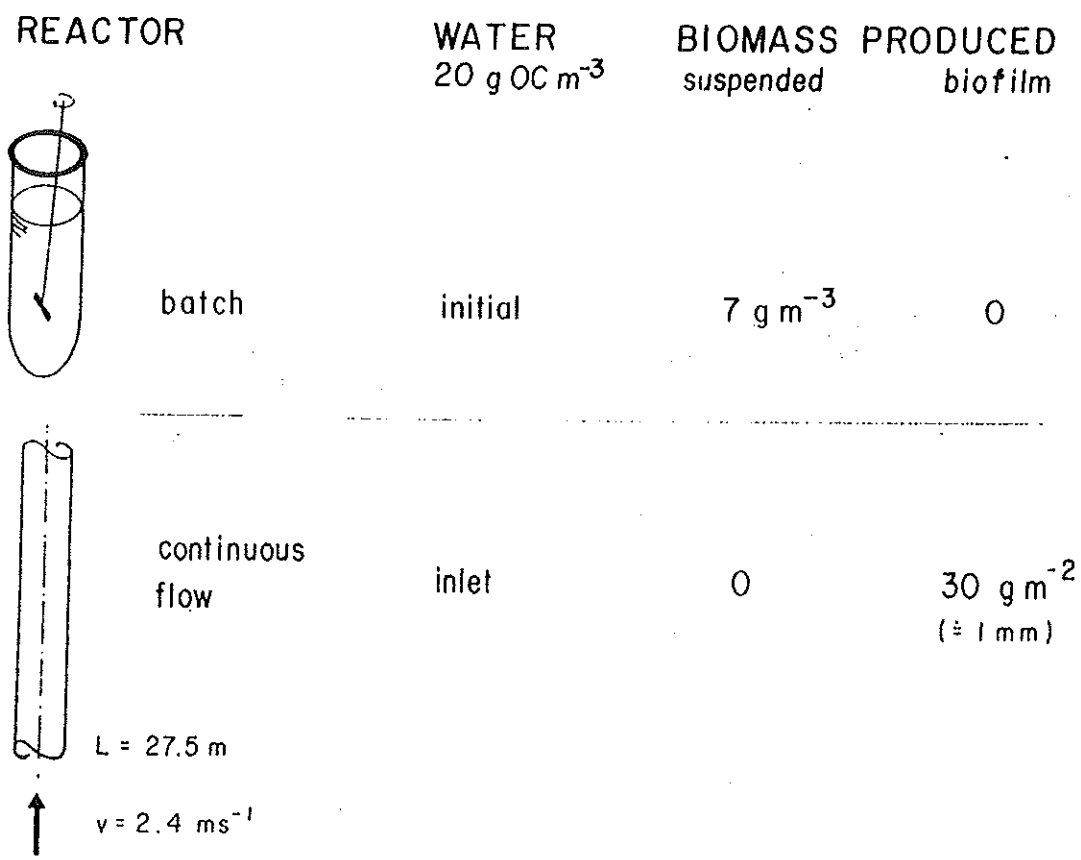


Figure 3. A comparison between dispersed biomass production in a test tube (a closed, batch system) and biofilm production in a condenser tube (an open, continuous flow system) over a 24 h period.

Correlation of OC with Biofouling

There are some limited data which suggest that biofouling correlates with TOC in the cooling water. Battaglia et al. (27) measured TOC concentrations at several power plants and related them qualitatively to the biofouling problem experienced at the site. No significant quantitative conclusions resulted because of other confounding factors. As suggested above, OC loading rate may be more indicative of microbial fouling potential than concentration. Therefore, it may be necessary to include flow rate (i.e., fluid velocity) in the calculation.

However, fluid velocity also influences detachment (15) which reduces the net biofilm accumulation (Figure 4). Characklis (14) has demonstrated the combined influence of OC and fluid velocity on rate of fouling biofilm development in a laboratory system (Figure 5). Equation 2 indicates the dependence of loading rate on surface area to volume ratio in the condenser. Therefore, there may be a strong interactive influence on fouling biofilm development between OC concentration, fluid velocity, and available surface area.

The quality of the OC will also influence biofouling and cause scatter in any attempted correlation. For example, the rate and extent of OC biodegradability will influence biofouling. Glucose will be consumed

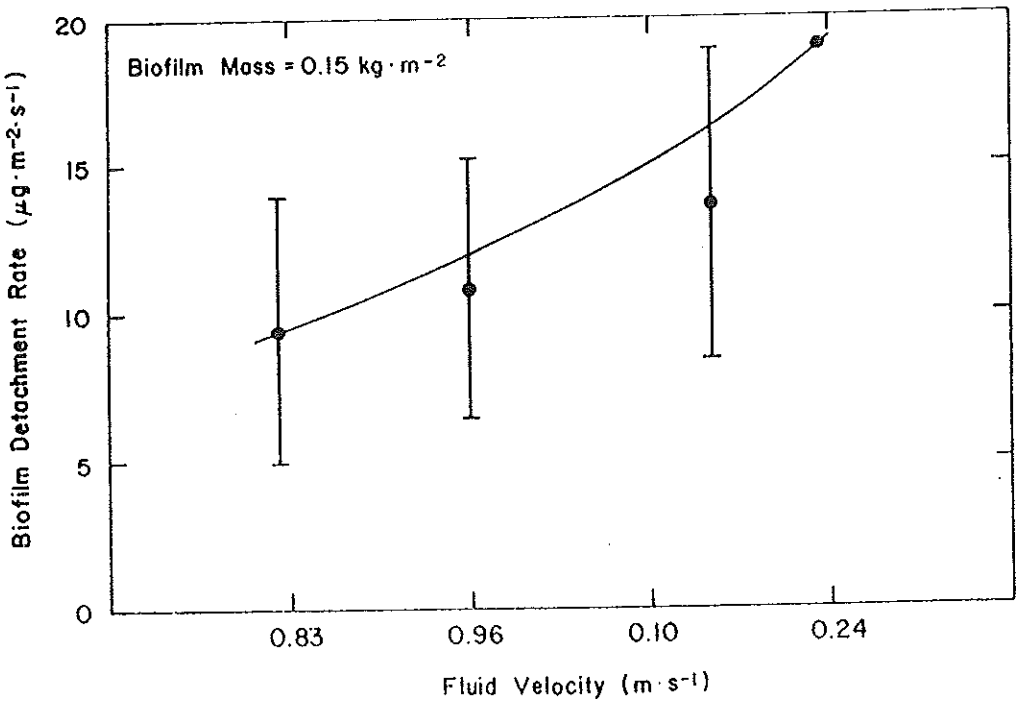


Figure 4. The influence of fluid velocity on biofilm detachment rate. Data were obtained from a rotating annular reactor (15) in which the fluid velocities correspond to shear stress in the ranges 2-3 N m^{-2}. The fitted line corresponds to the dependence of shear stress on velocity (α $v^{1.75}$).

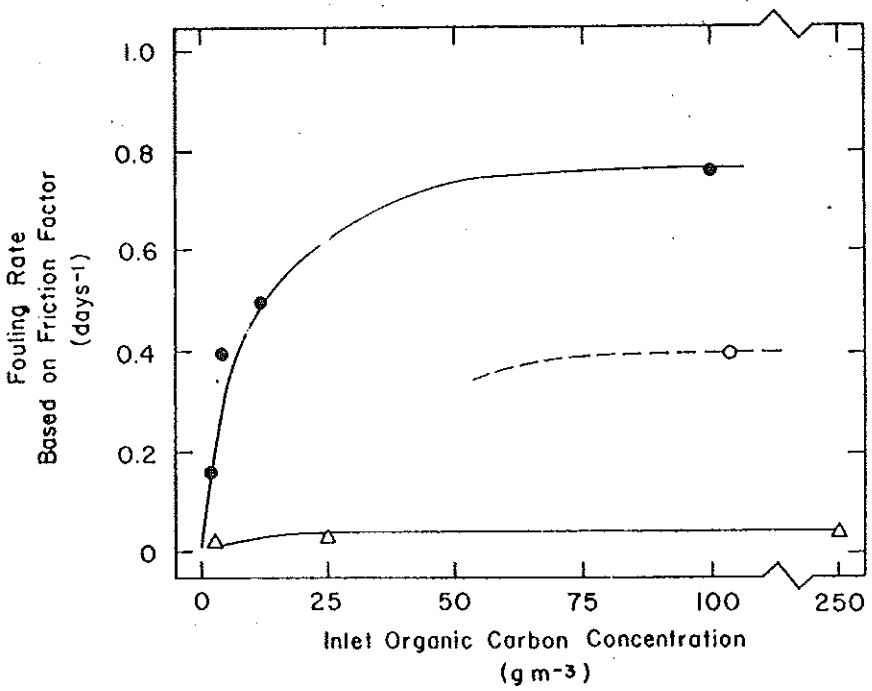


Figure 5. The influence of inlet OC concentration and fluid velocity on rate of biofouling in a laboratory system (0.5 in ID tube) (14).

much more rapidly than cellulose (polymerized glucose) at the same OC concentration. Particulate organic carbon (POC) will generally be degraded slower than the soluble organic carbon (SOC). An assay similar to the Biochemical Oxygen demand (BOD) test may be necessary to more accurately assess the influence of OC quality on biofouling. Another complicating process, adsorption of colloidal organic particles, can contribute to the accumulation of the fouling deposit even though it is not a direct result of metabolic activity in the biofilm.

Suspended solids concentration provides another confounding factor influencing the rate and extent of biofouling. Battaglia et al. (27) indicate that high suspended solids content frequently accompanies low biofouling rates even in the presence of significant OC. Suspended solids apparently scour the tube surfaces inhibiting biofilm accumulation.

Biofouling is generally more of a problem in summer months when temperatures are higher. High temperatures generally increases the rate of a biological processes. However, two other factors may be indirectly causing the observed increase in biofouling during summer. Dilution rate (i.e., fluid velocity) in the condenser frequently is increased to provide a higher cooling capacity in the summer months. But higher dilution rates increases OC loading rate and increases detachment rate. Which process controls? In addition, higher rates of primary productivity can occur in natural waters which increases the OC concentration (and OC loading rate) in the condenser.

In summary, the simple correlation of biofouling with organic carbon concentration in the cooling water is fraught with difficulties. However, OC is a good indicator of the potential for biofouling and is a most critical factor in any model seeking to predict biofouling.

DETACHMENT

Fluid velocity (shear stress) strongly influences detachment of biofilm (Figure 4). As the biofilm accumulates, the fluid forces shear off more cells until biofilm production equals biofilm detachment and a pseudo-steady state is established. The biofilm accumulation at steady state is dependent on both OC loading rate and fluid velocity (Figure 6). The same two variables significantly influence the rate of biofouling as well (Figure 5).

Fluid velocity can also influence mass transfer rate from the liquid to the biofilm. At lower velocities mass transfer may be rate limiting for biofilm accumulation. Therefore, increasing velocity increases OC flux to the biofilm and increases biofouling. At high velocities, detachment controls biofilm accumulation so that increasing velocity will decrease biofouling. As a result, there may be an optimum velocity for biofouling in a given condenser tube (Figure 7). Mass transfer may be the rate-limiting step in the chlorination process for fouling biofilm control because the reaction between the chlorine and biofilm is so rapid (see below).

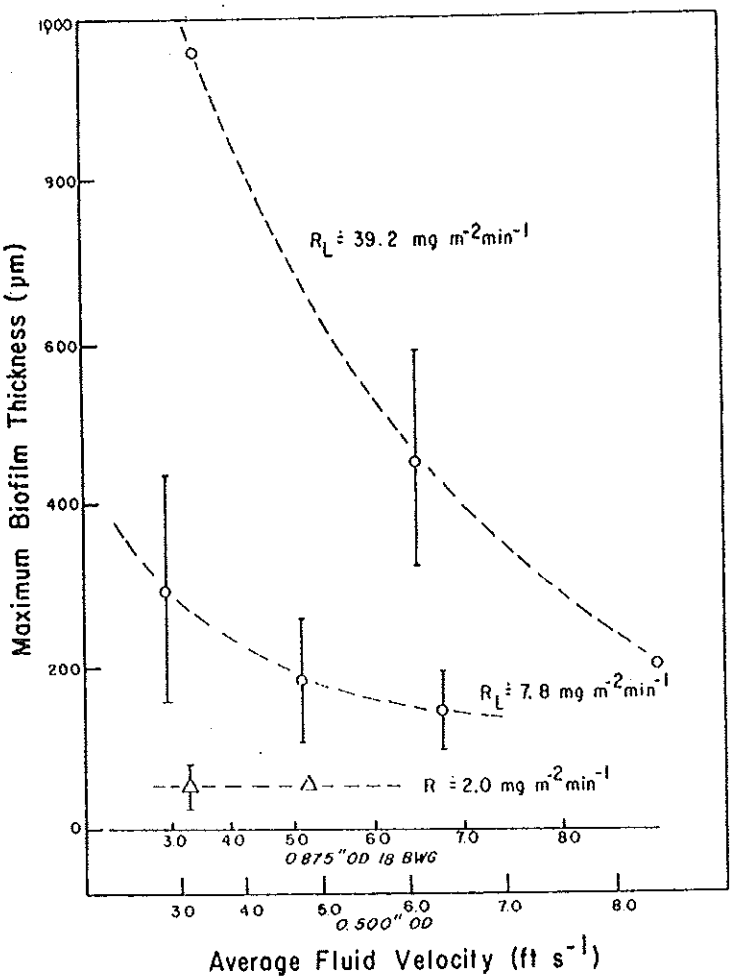


Figure 6. The influence of inlet OC concentration and fluid velocity on maximum biofilm thickness attained in a laboratory system (0.5 in ID tube) (14).

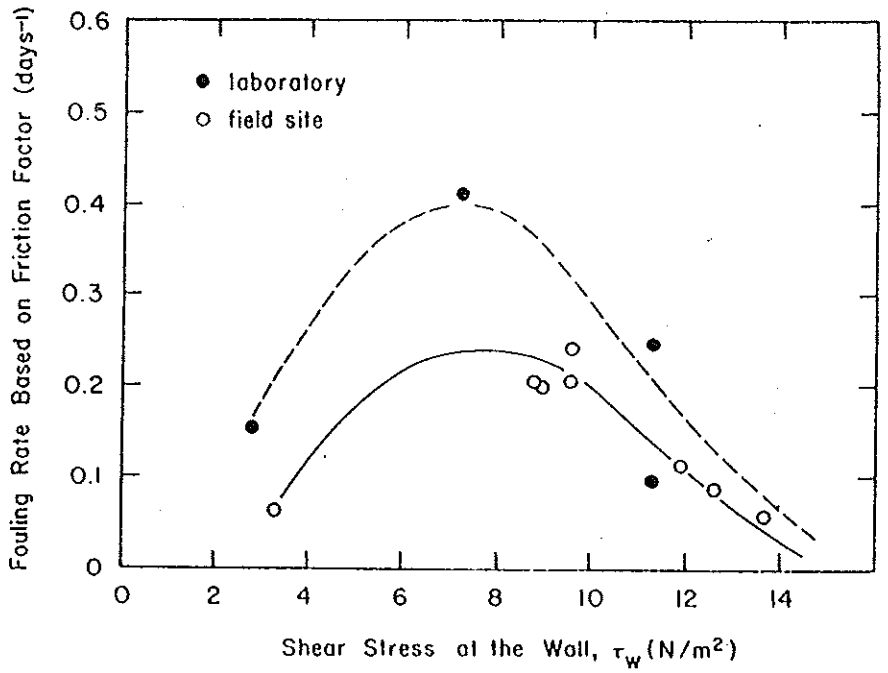


Figure 7. The influence of fluid velocity (shear stress) on rate of biofouling (based on change in frictional resistance) in a laboratory system (0.5 in ID tube) and at a power plant site.

CONTROL OF FOULING BIOFILMS BY CHLORINATION

Biofouling is controlled by a wide variety of physical and chemical means (28, 27, 29). However, the most effective and most commonly used method for controlling and/or preventing biofouling is chlorination. Recently, concern over the toxicity of chlorine (30) and some of its reaction products (31) has stimulated a search for alternatives (27, 32, 31, 33). Nevertheless, chlorination is still widely practiced in power plants and in process plants for minimizing the negative effects of biofouling (27).

Chlorine itself is used in a variety of ways to control biofouling. It is applied as chlorine gas, hypochlorite ion, chlorine dioxide, and is electrochemically generated in sea water. Chlorine is used in once-through systems or in recirculating cooling towers; applied continuously or in shock dosages. It is used in fresh water systems and sea water; in clean water and in contaminated water containing high levels of oxidizable materials.

Although biofouling is most often controlled by addition of chlorine, its use has disadvantages as well as advantages. Constraints placed on the use of chlorine have often limited its success in biofouling control. These constraints include:

1. Cost Effectiveness. This may be a factor in once-through or recirculating cooling systems where extremely high chlorine demand exists.

2. Corrosion. Some condenser materials are vulnerable to corrosion induced by high chlorine concentrations. In recirculating cooling tower systems which operate at high cycles of concentration, organic compounds concentrate to high levels and microbial cells accumulate leading to severe biofouling problems. Addition of chlorine in large quantities leads to corrosive levels of chloride as a result of chlorine reduction (26).

3. Environmental Regulations. Environmental concerns limit the concentration of chlorine that can be released to receiving waters.

Chlorine and other strong oxidizers (chlorine dioxide, ozone, bromine compounds) are superior microbial fouling control agents because they effectively disrupt and loosen fouling deposits. Chlorine, in the water phase, can also inactivate microbial cells (disinfect) and oxidize microbial nutrients rendering them relatively useless for support of microbial growth. When chlorine contacts biofilm, the following processes are observed to occur:

1. detachment of biofilm
2. dissolution of biofilm components
3. disinfection

Chlorine is consumed in all of these reactions. Limited observations suggest that the following factors influence the rate and extent of the chlorine-biofilm reaction:

1. Turbulent Intensity. Transport of chlorine from the bulk water phase to the water-biofilm interface is the first step in the chlorine-biofilm interaction. Transport rate increases with increasing chlorine concentration and turbulence. Practically, turbulent intensity may be increased by an increased flow rate as proposed in some targeted chlorination systems.

2. Chlorine Concentration at the Water-Biofilm Interface. Transport of chlorine within the biofilm or deposit is a direct function of the chlorine concentration at the interface. Transport rate (or diffusion) in the biofilm can be increased by increasing the chlorine concentration at the water-biofilm interface. Environmental regulations place a limit on effluent chlorine concentration. However, previous measurements in our laboratory suggest that periodic dosing of high chlorine concentrations will be more effective than low concentration continuous dosing assuming the same long-term chlorine application rate for both cases. Proposed targeted chlorination systems, if superimposed on such a short duration-high concentration treatment, may minimize the chlorine concentration reaching the receiving waters while maximizing chlorine concentrations at the water-biofilm interface.

3. Composition of the Fouling Biofilm. Reaction of chlorine within the biofilm is dependent on the organic and inorganic composition of the biofilm as well as its thickness or mass. Very little published information is available regarding the chlorine demand of biofilms other than that reported by our laboratory. This is surprising since the main objective of biofouling control is to react the chlorine with the biofilm. Disinfection (i.e., killing of microbial cells) in potable water systems is effective at low chlorine concentrations. However, in well-developed biofilms much of the material is EPS which competes effectively for available chlorine within the biofilm thereby reducing the amount available for killing cells.

4. Fluid Shear Stress at the Water-Biofilm Interface. Detachment and reentrainment of biofilm, primarily due to fluid shear stress, accompanies the reaction of biofilm with chlorine. Detachment of biofilm due to chlorine treatment has been observed but the rate and extent of removal as a function of chlorine application and fluid shear stress in the tube has not been determined. Fluid shear stress in the tube could conceivably be increased using the targeted chlorination concepts currently being investigated.

5. pH. The hypochlorous acid-hypochlorite ion equilibrium may be critical to performance effectiveness. HOCl apparently favors disinfection while OCl^- apparently favors detachment. The equilibrium can be manipulated in recirculating cooling systems where pH is controlled.

Summarizing the above statements, a chlorination treatment program at a power plant may be improved by the following measures:

1. Increase Chlorine Concentration at the Water-Biofilm Interface. Most practically, this is accomplished by increasing chlorine concentration in the water phase. However, another possibility is to "target" chlorination at the water-biofilm interface. For example, reduction of the bulk water chlorine demand is generally a difficult, costly task. But if chlorine can be injected in the viscous sublayer region, the chlorine demand of the water will have significantly less effect on the process. This procedure may be possible with special nozzles in a targeted chlorination scheme.

2. Increase Fluid Shear Stress at the Water-Biofilm Interface. This requires increasing fluid flow rate, especially during chlorination periods, which may be convenient with a targeted chlorination system.

3. Use pH control to favor hypochlorite ion-promoted detachment with well-developed biofilms and hypochlorous acid disinfection with thin films. An interesting alternative would be to alternate between continuous chlorination at pH 6.5 and "shock" chlorination at pH 8.

These recommendations are based on observations from the literature and may lead to more effective use of chlorine for biofouling control. However, these recommendations are, for the most part, speculation since they are based on incomplete or fragmented experimental results. In fact, the processes contributing to the short- and long-lived effectiveness of a chlorination program for biofouling control are not well understood.

The work that has appeared in the literature on predicting the fate of chlorine in cooling water is primarily based on chemical studies and equilibrium or kinetic models (34, 35, 36, 37). These studies have concentrated on equilibrium or kinetic measurements of chlorine demand of the cooling water and have ignored the reaction of chlorine with the fouling biofilm at the heat exchanger surfaces. These studies have also ignored the influence of potential mass transfer limitations in a condenser tube. Consequently, the results have not always been successful (37) and chlorine minimization programs are still relied on in most cases (38) for determining chlorination application rates. However, chlorine minimization studies are costly and cannot account for seasonal changes in water quality and variations in power demand which influence the effectiveness of chlorine for biofouling control.

Despite the importance of biofouling control to power plant operation and maintenance, as well as the apparent effectiveness of chlorine, the stoichiometry and kinetics of biofouling control with chlorine (and other oxidants) have never been addressed. In fact, a targeted chlorination project has been stymied by lack of dependable rate and stoichiometric information on the chlorine-biofilm reaction. If the nature of the stoichiometry and kinetics of the chlorine-biofilm process were known, procedures for establishing a continuing, efficient, cost effective, environmentally compatible chlorination program could be developed. This same data would be invaluable in testing programs such as the targeted chlorination studies and others planned in the future. Such information would also be useful in comparing novel physical, chemical, and even biological methods for biofouling control.

A PROCESS ANALYSIS

Chlorine has been widely used as a disinfectant to kill microorganisms in water treatment. Originally, chlorine was thought to control biofouling by "killing" microbial cells (i.e., disinfecting). Recently, however, experimental results have indicated that chlorine also oxidizes and depolymerizes the EPS in the biofilm causing destruction of the biofilm matrix and its detachment from the surface (39). There is still some controversy over which mechanism is responsible for chlorine's superior effectiveness in fouling control (40).

Transport and reaction of chlorine in a tube with turbulent flow is perceived to occur as a result of the following processes (Figure 8):

1. Chlorine species entering the tube react with chlorine-demanding components (viable cells and chemical compounds) in the bulk water.

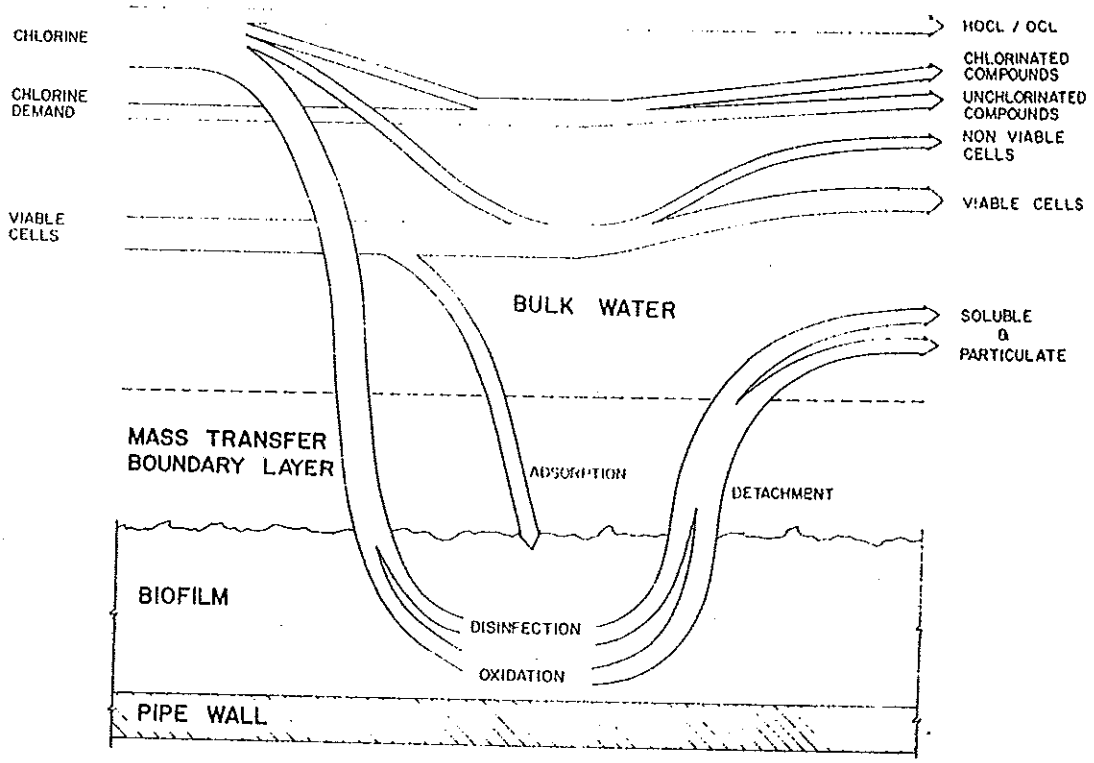


Figure 8. Processes occurring during biofouling control with chlorine or other strong oxidizer.

2. Chlorine species are transported through the bulk fluid to the water-biofilm interface.

3. Chlorine species diffuse and react within the biofilm.

Since both "solid" (i.e., the biofilm and the metal substratum) and liquid phases are present, the chlorine-biofilm reaction can be termed a heterogeneous process. In heterogeneous systems such as this, there is a high probability that transport rates will limit the overall rate of reaction. This includes transport of reactants and products within each phase and across phase boundaries.

Transport of Chlorine in the Water Phase

The rate at which chlorine is transported to the biofilm depends on the concentration of chlorine in the bulk water and the intensity of turbulence.

The concentration of chlorine in the bulk water is related to its application rate minus the chlorine demand rate of the water. If the chlorine concentration at the biofilm interface is the same as its concentration in the bulk water, then the concentration in the water drives the reactions of chlorine within the biofilm. If chlorine reacts with the biofilm relatively rapidly, the concentration at the interface will be low and physical transport of chlorine to the interface may limit the rate of the overall process within the biofilm.

By increasing the intensity of turbulence through increased flow rate, both the transport rates in the bulk water and the concentration at the interface will increase. In the bulk water, chlorine is transported in the radial direction in the tube primarily by eddy diffusion (i.e., convective mechanism). Several investigators have observed that increasing turbulence results in increased chlorine reaction rates (41, 20, 42). Novak (20) observed a first order rate with respect to chlorine concentration which indicates either a first order reaction or a mass transfer limitation (Figure 9). Under what circumstances is chlorine delivery to the site of biofouling control rate-limited by mass transfer in the water, diffusion in the biofilm, or reaction in the biofilm? The answer to this question impacts significantly the choice of chlorine application mode (e.g., continuous application vs. shock or periodic application).

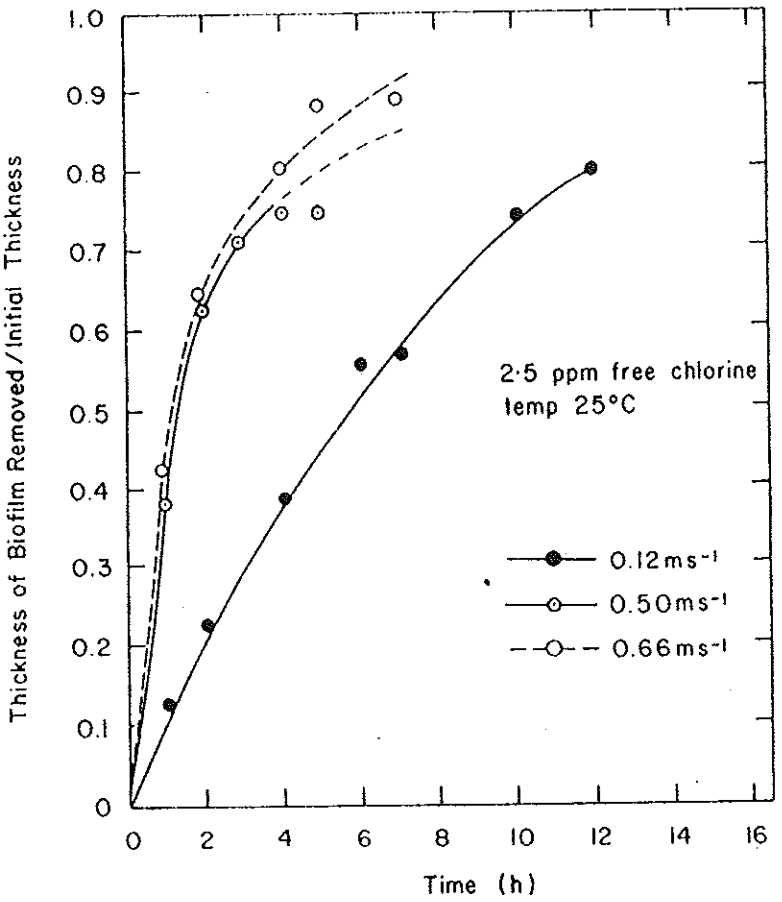


Figure 9. The influence of fluid velocity on biofilm removal with chlorine (42).

Transport of Chlorine in the Biofilm

The transport of chlorine within biofilms occurs primarily by molecular diffusion. Since the composition of biofilms is from 96% to 99% water, the diffusivity of chlorine in biofilm is some fraction of its diffusivity in water. In biofilms of higher density, or in those containing microbial matter associated with inorganic

scales, tubercules, or sediment deposits, diffusion of chlorine may be relatively slow. Obviously, diffusion of chlorine through a deposit determines its "penetration" and, hence, its overall effectiveness.

Reaction of Chlorine in the Water Phase

The reaction of chlorine in the water phase is generally referred to as the "chlorine demand" of the water. The chlorine demand is due to soluble oxidizable inorganic compounds, soluble organic compounds, microbial cells, and other particulates in the water. These oxidizable species compete with the biofilm for available chlorine and often reduce the effectiveness of biofouling control. Both the extent and rate of chlorine demand determine the amount of chlorine available for biofouling control. Present methods for measuring chlorine demand measure only how much chlorine is consumed, i.e., a stoichiometric quantity. The rate of chlorine demand (i.e., how fast chlorine is consumed) would be a more useful quantity in assessing its effect on biofouling control.

Bongers (40) measured the rate of decay of chlorine in estuarine waters and found it to occur in three phases. He found that during phase one, free chlorine decreased to about half of its original concentration in 30 seconds. Two successive but distinct phases had rates of decay which were significantly slower. These data imply that reactions in the water phase cannot necessarily be modeled by a single simple first order rate expression. On the other hand, if total residence time in the tube is less than 30 seconds, only the first phase chlorine demand is relevant.

Temperature has been shown to significantly affect both the rate and extent of chlorine consumption in sea water (43). Consequently, bulk water temperature may affect fouling control where there is significant chlorine demand. To what extent does temperature or a temperature gradient affect biofouling control with chlorine? Does temperature, which varies significantly in heat exchanger tubes (radially and axially), significantly influence the rate of chlorine demand.

Reaction of Chlorine with the Biofilm

Chlorine reacts with various organic and reduced inorganic components within the biofilm. It can disrupt cellular material and inactivate cells (disinfect). In well developed biofilms, its greatest apparent effect is reaction with EPS (primarily polysaccharides) which are responsible for the physical integrity of the biofilm (39). A series of studies (44, 39, 14) have estimated the process rate and process stoichiometry of the reaction of chlorine with immobilized biofilm. However, these data include variations resulting from poorly defined chlorine demand in the bulk water and microbial populations in the biofilm.

Bacterial flocs and biofilms that are rich in EPS exhibit a more rapid, ultimately greater, chlorine demand than cells with little associated EPS (39). One possible explanation is derived from the observation that hypochlorite ion attacks glucose polysaccharides with extensive oxidation at the C_2 and C_3 positions of D-glucose units, which results in cleavage of the C_2-C_3 bond (45, 46). Depolymerization can result from the inductive effects of this oxidation, from direct oxidative cleavage of the glucosidic bond, or from degradation of the intermediate carbonyl compound.

Most of what is known about chlorine disinfection is derived from water treatment studies. It is generally agreed that chlorine disinfects by inhibiting enzymatic processes within the bacterial cell (47). Chlorine has been found to be more effective as a disinfectant at pH 6.0 to pH 6.5. Hypochlorous acid predominates at these pH values. It is postulated that the hypochlorous acid molecule, which is electrically neutral and has a smaller solvation shell than the hypochlorite ion, can readily pass through cellular membranes while the hypochlorite ion cannot. Characklis et al. (48) found that high pH improved biofilm destruction by chlorine suggesting that hypochlorite ion is more effective at depolymerizing the biofilm.

Reaction of Chlorine with the Condenser Tube

The condenser surface may also exert a chlorine demand. Characklis and Zelver (3) have documented the chlorine demand of a copper-nickel alloy as contrasted with titanium which exerted no such demand. Lewis (49) also found that Cu-Ni reacts with chlorine. The chlorine demand may be directly related to the significant corrosion observed in seawater studies when copper-nickel alloys are chlorinated regularly (Fischer, personal communication). This may be due to stoichiometric reaction of the tube alloy with chlorine, or removal of a protective oxide coating from the alloy, rendering the underlying metal vulnerable to other corrosion reactions. However, the chlorine demand may not be related directly to corrosion since metal ions such as Cu(II) have been shown to catalyze chlorine decomposition (50) to chloride. How much does metallurgy affect chlorine demand and chlorine's effectiveness in destroying biofilm? How do chlorination and biofouling affect corrosion rates in heat exchangers?

BIOFILM REMOVAL AND/OR DESTRUCTION

The reaction of chlorine with biofilm produces an immediate response in the bulk water by increasing turbidity and the soluble organic constituents (39). A significant removal of biofilm is evidenced by a decrease in biofilm thickness (48, 42) and a decrease in fluid frictional resistance (14, 39, 41). Inactivation of the biofilm with a nonoxidizing poison does not result in any biofilm removal (39). The results suggest that hypochlorite oxidizes EPS within the biofilm resulting in EPS depolymerization, dissolution, and detachment. Characklis et al. (48) reported that biofilm detachment resulting from chlorination is much higher between pH 7.5 and 8.5 than between pH 6 and 7 where disinfection is optimum. These data are consistent with data for chlorination of polysaccharides such as starch, which is optimum at pH > 7 (51). Similar data are not available for monochloramine, dichloramine, or other N-chloro compounds.

Chlorine "enhancers" are sometimes added to improve chlorination performance. Supposedly, these compounds increase penetration of chlorine into the biofilm. If this is true, the removal of biofilm from the surface should be enhanced. Are chlorine "enhancers" effective? Under what circumstances are they effective?

Chlorine concentrations as high as 20 mg/l applied several times a day may be needed to effectively control biofouling at a power plant (27). The criterion for dosage is frequently the residual concentration in the outlet water. By maintaining a residual at the outlet, chlorine demand in the water is presumably overwhelmed. Typical chlorine residuals in the outlet range from 0.1 to 0.5 mg/l for effective performance.

However, the mass transfer limitations described earlier suggest that, despite a chlorine residual in the outlet, the region of the pipe near the bulk water-biofilm interface may be devoid of chlorine. If so, biofouling control effectiveness may be poor even when a measurable chlorine residual is measured in the outlet. Under what conditions is maintenance of a chlorine residual in the outlet sufficient to eliminate the effect of chlorine demand in the condenser? Is the chlorine residual in the outlet sufficient as a criterion for biofouling control effectiveness?

Fluid shear forces may play a major role in the removal of biofilm. Several investigators (41, 42, 20, 14) measured a higher rate of chlorine uptake by biofilms and a greater amount of biofilm removed when the fluid shear stress was increased. The authors suggest that greater shear force may have the following effect:

1. Increased mass transfer of chlorine from the water to the biofilm

2. Disrupts the biofilm during chlorination, reentraining reaction products in the water phase and exposing new biofilm surfaces for chlorine attack

3. Increasing shear force (fluid velocity) also reflects a thinner viscous sublayer in the tube. The viscous sublayer is a region of low shear force and biofilm within the viscous sublayer will not be disrupted to a great extent unless the shear force is increased. Timperley (52) has commented on this effect of mean flow velocity on the cleaning of biofouled tubes.

Observations indicate that a residual biofouling deposit remains even after repeated chlorine treatment. This has important consequences for subsequent regrowth of the biofouling deposit.

BIOFOULING CONTROL THROUGH DISINFECTION

Low level chlorination can significantly reduce viable microbial cells in water and destroy some of the nutrients necessary for cell growth. It is effectively used to maintain drinking water quality at residual concentrations as low as 0.03 mg/l (53). It is also effective in controlling attachment and growth of microorganisms in heat exchanger systems (40). Low level chlorination, however, is not sufficient to prevent attachment of surviving viable cells to heat exchanger walls. Low level, continuous chlorination can be used to slow down microbial fouling but rarely eliminates it. Concentrations of chlorine high enough to make these systems aseptic would be prohibitively expensive and create unacceptable environmental damage.

BIOFILM "REGROWTH"

Numerous investigators (14, 41, 20, 42, 49) and plant operators have observed a rapid resumption of biofouling immediately following chlorine treatment and have termed this phenomenon "regrowth." Figure 10 (49) illustrates this phenomenon. Regrowth may be due to one or all of the following reasons:

1. The remaining biofilm contains enough viable organisms to preclude any lag phase, observed on clean tubes, in resumed fouling biofilm formation after shock chlorination.

2. The remaining biofilm imparts an increased relative roughness to the tube surface and, thus, enhances transport and adhesion of microbial cells and other compounds to the surface. The roughness of the deposit also provides a "stickier" surface.

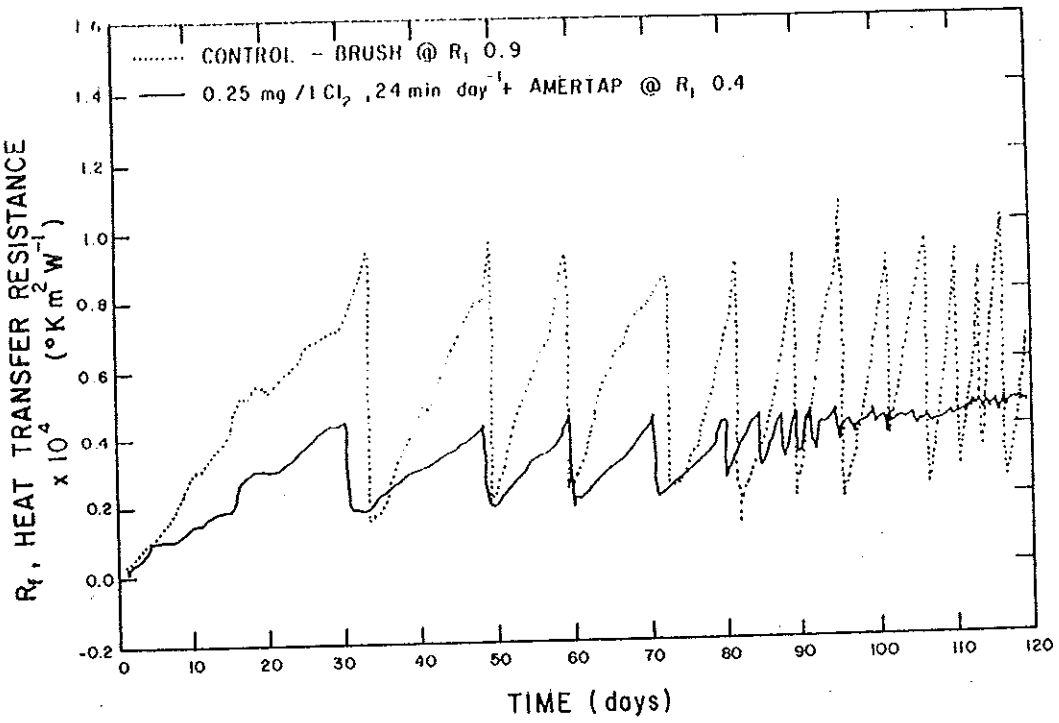


Figure 10. Fouling resistance on Alclarol 3003 aluminum tubes treated as shown when heat transfer resistance reached the maximum desired level (0.4-0.9) (49).

3. The chlorine preferentially removes EPS and not biofilm cells, thus leaving biofilm cells more exposed to the nutrients.

4. EPS is rapidly created by surviving organisms as a protective response to irritation by chlorine.

5. There is selection for a chlorine resistant organism (e.g., one which normally produces excessive amounts of EPS) which proliferates on successive chlorinations.

Rapid regrowth has also been observed on walls of water distribution systems (54, 55). These authors demonstrated that bacteria previously exposed to chlorine were more resistant to chlorine than those never exposed. This is consistent with the latter two hypotheses.

After extended periods of repeated chlorination, a refractory material has been noted in several investigations (14, 56). The deposit increases in ash content with repeated chlorination and, in several cases, an inordinately high content of manganese has been observed.

The refractory deposit has an apparent inhibitory effect on macrobial fouling (56). However, this refractory material may accumulate to such an extent that it impedes heat transfer and is not affected by chlorine. What is the rate and extent of accumulation of refractory material and how is it influenced by tube alloy and water quality? How does the refractory material affect subsequent biofilm development? What is the most effective way to inhibit or remove the refractory material? If the refractory material inhibits

further biofouling, how can a thin film be maintained which does not significantly influence heat transfer as fluid frictional resistance?

USE OF FOULING MONITORS

Let's assume you are asked to control pH in a recirculating cooling tower system in which the pH of the process water varies considerably with the seasons and even with climatic conditions. You are given a storage tank of acid and a storage tank of base with the ancillary pumps, flow meters, valves, etc. Before any effective pH control is possible, however, you will need a pH electrode. The electrode reading will provide feedback (manual or automatic) so that you can assess the necessary flow rate or amount of acid or base addition. In a similar manner, a fouling monitor is needed to determine the necessary amount of chlorine needed to control biofouling and still operate within the environmental regulations. In other parts of this paper, I have indicated the numerous factors which influence (1) the rate and extent of biofouling and (2) the chlorine demand of the cooling water and fouling biofilm. Both variables significantly affect the efficient operation of power plant condensers. Therefore, determining an effective chlorine dosage (chlorine minimization) can be a hassle. The problem is complicated further by the fact that the effective chlorine dosage changes with season and other uncontrollable factors.

A fouling monitor, combined with a device for measuring rate of chlorine (or other oxidant) demand, will permit the frequent evaluation of a dosing frequency, duration, and concentration. The costs for fouling monitors vary considerably depending on their level of sophistication and the accessories provided. However, the cost of the most expensive fouling monitor pales in relation to energy losses, downtime, and even chemical costs related to fouling processes. Other papers in this symposium will deal with fouling monitors and their usefulness in more detail.

CONCLUSIONS

Organic carbon (OC) in the cooling water is a pivotal variable when considering biofouling in a power plant condenser:

1. OC provides the energy or driving force for biofilm accumulation in the condenser.
2. OC provides a significant fraction of the chlorine (oxidant) demand in the cooling water which can limit the effectiveness of a given chlorine dosage.
3. A fouling monitor is useful and necessary for regular evaluation of a chlorination (biofouling control) program.

A process engineering approach, including the contribution from aquatic chemistry and microbiology, provides a relatively simple, flexible and effective program for controlling biofouling in power plant condensers. Further investment in research and testing will improve these methods with extremely rapid returns.

REFERENCES

1. N. Zelver, F. R. Flandreau, W. H. Spataro, K. R. Chapple, W. G. Characklis, and F. L. Roe. Analysis and Monitoring of Heat Transfer Tube Fouling. Denver, CO: Joint Power Generation Conference, 1982, 5pp.

2. M. H. Turakhia, K. E. Cooksey, and W. G. Characklis. "Influence of Calcium-Specific Chelant on Biofilm Removal." Appl. Env. Microbiol., Vol. 46, pp. 1236-1238

3. W. G. Characklis and N. Zelver. Biofilm Development and Control in Simulated Shipboard Condenser Tubes. David Taylor Naval Ship Research and Development Center, 1983, 203pp.

4. B. F. Picologlou, N. Zelver, and W. G. Characklis. "Effect of Biofilm Growth on Hydraulic Performance." J. Hyd. Div., ASCE, Vol. 106, No. HY5, pp. 733-746.

5. W. G. Characklis, M. J. Nimmons, and B. F. Picologlou. J. Heat Transf. Engr., 1981, Vol. 2, pp. 23-37.

6. M. H. Turakhia, W. G. Characklis, and N. Zelver. "Fouling of Heat Exchanger Surfaces: Measurement and Diagnosis." Heat Transfer Engineering, Vol. 5, pp. 93-101.

7. W. G. Characklis, N. Zelver, C. H. Nelson, R. O. Lewis, D. E. Dobb, and G. K. Pagenkopf. Influence of Biofouling and Biofouling Control Techniques on Corrosion of Copper-Nickel Tubes. CORROSION/83 Symposium: Corrosion Induced by Bacteria, 1982, 203pp.

8. D. Lund and C. Sandu. "State-of-the-Art of Fouling: Heat Transfer Surfaces." Proc. Fundamentals and Applications of Surface Phenomena Associated with Fouling and Cleaning in Food Processing (B. Hallstrom, D. B. Lund and Ch. Tragardh, eds.). Madison, WI: Dept. of Food Science, University of Wisconsin, 1981, pp. 27-56.

9. W. G. Characklis and J. A. Robinson. Development of Fouling Control Program. Final Report, Canadian Electrical Association, 1984, No. 219 G 388.

10. W. G. Characklis. "Fouling Biofilm Development: A Process Analysis." Biotech. Bioeng., 1981, Vol. 23, pp. 1923-1960.

11. R. E. Baier. "Influence of the Initial Surface Condition of Materials on Bioadhesion." Proc.: Third International Congress On Marine Corrosion and Fouling (R. F. Acker et al., ed.). Gaithersburg, MA, 1972, pp. 633-640.

12. K. C. Marshall. "Mechanisms of Adhesion of Marine Bacteria to Surfaces." Proc.: Third International Congress On Marine Corrosion and Fouling (R. F. Acker et al., ed.). Gaithersburg, MA, 1972, pp. 625-633.

13. R. Neihof and G. Loeb. "Molecular Fouling of Surfaces in Seawater." Proc.: Third International Congress On Marine Corrosion and Fouling (R. F. Acker et al., ed.). Gaithersburg, MA, 1972, pp. 710-718.

14. W. G. Characklis. Biofilm Development and Destruction. Palo Alto, CA: Final Report, Electric Power Research Institute, EPRI CS-1554, 1980, 311pp.

15. M. G. Trulear and W. G. Characklis. "Dynamics of Biofilm Processes." J. Wat. Poll. Contr. Fed., 1982, Vol. 54, pp. 1288-1301.

16. J. E. Duddridge, C. A. Kent, and J. F. Laws. "Bacterial Adhesion to Metallic Surfaces." Progress in the Prevention of Fouling in Industrial Plant. Nottingham University, Nottingham, England: Corrosion Science Division, Institution of Corrosion Sciences and Technology, 1981, pp. 127-153.

17. W. A. Corpe. "Marine Microfouling and OTEC Heat Exchangers." Proc. Ocean Thermal Energy Conversion (OTEC) Biofouling and Corrosion Symposium (R. H. Grey, ed.), Washington, D.C., 1977, pp. 31-34.

18. T. R. Bott and M. M. V. P. S. Pinheiro. "Biological Fouling-Velocity and Temperature Effects." Can. J. Chem. Eng., 1977, Vol. 55, pp. 473-474.

19. D. W. S. Harty and T. R. Bott. "Deposition and Growth of Microorganisms on Simulated Heat Exchanger Surfaces." Fouling of Heat Transfer Equipment (E. F. C. Somerscales and J. G. Knudsen, eds). Washington, D.C.: Hemisphere Publishing Corp., 1981, pp. 334-344.

20. L. Novak. "Comparison of the Rhine River and the Oresund Sea Water Fouling and Its Removal by Chlorination." J. Heat Transfer, 1982, Vol. 104, pp. 663-669.

21. K. Pederson. "Development and Regulation of Microbial Biofilms in Flowing Water Systems." Goteborg, Sweden: Ph.D. Thesis, University of Goteborg, 1982, 73pp.

22. A. Eaton, C. Chamberlin, and M. Cooney. "Colonization of Cu-Ni Surfaces by Microfouling Organisms." Condenser Biofouling Control (J. F. Garey et al., eds.), Ann Arbor, MI: Ann Arbor Science 1980, pp. 105-120.

23. M. Fletcher. "The Effects of Culture Concentration and Age, Time, and Temperature on Bacterial Attachment to Polystyrene." Can. J. Microbiol., 1977, Vol. 23, pp. 1-6.

24. M. S. Powell and N. K. H. Slater. "The Deposition of Bacterial Cells to Solid Surfaces." Biotech. Bioeng., 1983, Vol. 25, pp. 891-900.

25. C. H. Nelson, J. A. Robinson, and W. G. Characklis. "Bacterial Adsorption to Smooth Surfaces: Rate, Extent, and Spatial Pattern." Biotech. Bioeng., 1985 (in press).

26. J. V. Matson and W. G. Characklis. "Biofouling Control in Recycled Cooling Water with Bromochlorodimethylhydantoin." J. Cooling Water Institute, 1983, Vol. 4, No. 1, pp. 27-32.

27. P. J. Battaglia, D. P. Bour, and R. M. Burd. Biofouling Control Practice and Assessment. Palo Alto, CA: Final Report, Electric Power Institute, EPRI CS-1976, Project 1132-1, 1981, 212pp.

28. Anon. Possible Alternatives to Chlorination for Controlling Fouling in Power Station Cooling Water Systems. Final Report, Marine Research, Inc., 1976.

29. J. Graham. Biofouling Control Assessment—A Preliminary Data Base Analysis. Palo Alto, CA: Final Report, Electric Power Research Institute, EPRI CS-2469, Contract TPS 80-739, 1982, 235pp.

30. L. W. Hall, Jr., G. R. Helz, and D. T. Burton. Power Plant Chlorination: A Biological and Chemical Assessment. Ann Arbor, MI: Ann Arbor Science Publishers in cooperation with Electric Power Research Institute, EPRI EA-1750, 1981.

31. J. R. Trabalka and M. B. Burch. "Investigation of the Effects of Halogenated Organic Compounds Produced in Cooling Systems and Process Effluents on Aquatic Organisms." Water Chlorination: Environmental Impact and Health Effects (R. L. Jolley, H. Gorchev and D. H. Hamilton, eds.). Ann Arbor, MI: Ann Arbor Science Publishers, 1980, Vol. 2, pp. 163-173.

32. T. D. Waite and J. R. Fagan. "Summary of Biofouling Control Alternatives." Condenser Biofouling Control (J. F. Garey et al., eds.). Ann Arbor, MI: Ann Arbor Science, 1980, pp. 441-462.

33. D. T. Burton. "Biofouling Control Procedures for Power Plant Cooling Water Systems." Condenser Biofouling Control (J. F. Garey et al., eds.). Ann Arbor, MI: Ann Arbor Science, 1980, pp. 251-266.

34. R. L. Zielke and S. K. Macey. "Validation of a Kinetic Model to Predict Residual Chlorine in Fresh Water." Water Chlorination: Environmental Impact and Health Effects (R. L. Jolley, W. A. Brungs and R. B. Cumming, eds.). Ann Arbor, MI: Ann Arbor Science, 1980, Vol. 3, pp. 445-451.

35. R. Sugam and G. R. Helz. "Sea Water Chlorination: A Description of Chemical Speciation." Water Chlorination: Environmental Impact and Health Effects (R. L. Jolley, W. A. Brungs and R. B. Cumming, eds.). Ann Arbor, MI: Ann Arbor Science, 1981, Vol. 3, pp. 427-433.

36. W. R. Haag and M. H. Lietzke. "A Kinetic Model for Predicting the Concentrations of Active Halogen Species in Chlorinated Saline Cooling Waters." Water Chlorination: Environmental Impact and Health Effects (R. L. Jolley, W. A. Brungs and R. B. Cumming, eds.). Ann Arbor, MI: Ann Arbor Science, 1980, Vol. 3, pp. 415-426.

37. G. R. Helz, R. Sugam, and R. Y. Hsu. "Chlorine Degradation and Halocarbon Production in Estuarine Waters." Water Chlorination: Environmental Impact and Health Effects (R. L. Jolley, H. Gorchev and D. H. Hamilton, eds.). Ann Arbor, MI: Ann Arbor Science, 1978, Vol. 2, p. 209.

38. R. D. Moss, H. B. Flora II, R. A. Hiltunen, C. V. Seaman, N. D. Moore, and S. H. Magliente. "A Chlorine Minimization/Optimization Study for Condenser Fouling Control." Third Conference on Water Chlorination: Environmental Impact and Health Effects. Colorado Springs, CO, October 1979.

39. W. G. Characklis and S. T. Dydek. "The Influence of Carbon-Nitrogen Ratio on the Chlorination of Microbial Aggregates." Water Research, 1976, Vol. 10, pp. 515-522.

40. L. H. Bongers and D. T. Burton. "Bromine Chloride—An Alternative to Chlorine for Fouling Control in Condenser Cooling Systems." Washington, D.C.: U.S. Environmental Protection Agency, EPA-600/7-77-053, 1977.

41. G. Norrman, W. G. Characklis, and J. D. Bryers. "Control of Microbial Fouling in Circular Tubes with Chlorine." Dev. Ind. Microbiol., 1977, Vol. 18, pp. 581-590.

42. P. C. Miller and T. R. Bott. "The Removal of Biological Films using Sodium Hypochlorite Solutions." Progress in the Prevention of Fouling in Industrial Plant. Nottingham University, Nottingham, England: Corrosion Science Div., Institution of Corrosion Science and Technology, 1981, pp. 121-136.

43. G. T. F. Wong. "The Effect of Temperature on Dissipation of Chlorine in Seawater." Water Chlorination: Environmental Impact and Health Effects. Ann Arbor, MI: Ann Arbor Science Publishers, 1980, Vol. 3, pp. 395-406.

44. W. G. Characklis. "Effect of Hypochlorite on Microbial Slimes." Proc., 26th Industrial Waste Conf. Purdue University, 1971, pp. 171-181.

45. C. H. Hullinger. "Hypochlorite-Oxidized Starch." Methods in Carbohydrate Chemistry (R. L. Whistler and M. L. Wolfram, eds.). New York: Academic Press, 1963, pp. 313-315.

46. R. L. Whistler, E. G. Linke, and S. Kazeniac. "Action of Alkaline Hypochlorite on Corn Starch Amylose and Methyl 4-o-Methyl-D-Glucopyranosides." J. American Chemical Society, 1956, Vol. 78, No. 18, pp. 4704-4709.

47. O. Wyss. "Disinfection by Chlorine: Theoretical Aspects." Water and Sewage Works, 1962, Vol. 109, No. 12, pp. R155-R158.

48. W. G. Characklis, M. G. Trulear, N. Stathopoulos, and L. C. Chang. "Oxidation and Destruction of Microbial Films." Water Chlorination: Environmental Impact and Assessment (R. L. Jolley, ed.). Ann Arbor, MI: Ann Arbor Science, 1980, Vol. 3, pp. 349-368.

49. R. O. Lewis. "The Influence of Biofouling Countermeasures on Corrosion of Heat Exchanger Materials in Seawater." Material Performance, 1982, pp. 31-38.

50. M. W. Lister. "Decomposition of Sodium Hypochlorite: The Catalyzed Reaction." Can. J. Chem., 1956, Vol. 34, pp. 479-488.

51. R. L. Whistler and R. Shwenger. "Oxidation of Amylopectin with Hypochlorite at Different Hydrogen Ion Concentrations." J. American Chemical Society, 1957, Vol. 79, No. 24, Dec. 20, pp. 6460-6464.

52. D. Timperley. "Effect of Reynolds Number and Mean Velocity of Flow on the Cleaning-in-Place of Pipelines." Proc., Fundamentals and Applications of Surface Phenomena Associated with Fouling and Cleaning in Food Processing (B. Hallstrom, D. B. Lund and Ch. Tragardh, eds.). Madison, WI: Dept. of Food Science, University of Wisconsin, 1981, pp. 402-412.

53. J.-L. Biros and H. Lamblin. "Reduction of Residual Chlorine by Intensive Monitoring of Bacterial Population in Supplied Water." Water Chlorination: Environmental Impact and Health Effects (R. L. Jolley, W. A. Brungs and R. B. Cumming, eds.). Ann Arbor, MI: Ann Arbor Science, 1980, Vol. 3, pp. 743-755.

54. H. F. Ridgeway and B. H. Olson. "Chlorine Resistance Patterns of Bacteria from Two Drinking Water Distribution Systems." Appl. Envi. Microbiol., 1982, pp. 972-987.

55. J. D. Berg, A. Matin, and P. Roberts. "Effect of Antecedent Growth Conditions on Sensitivity of Escherichia coli to Chlorine Dioxide." Appl. Envi. Microbiol., 1982, pp. 814-819.

56. D. C. Mangum and B. P. Shepherd. Methods of Controlling Marine Fouling in Sea Water Desalination Plants. Final Report, Office of Saline Water, U.S. Dept. of Interior, Contract No. 14-30-2829, 1973, 124pp.