



Microbially influenced corrosion of stainless steel 304 under halogenated fluids  
by Vivek Agrawal

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Environmental Engineering  
Montana State University  
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Abstract:

The focus of the research was significant pitting corrosion which occurred under biofilm deposits on the cooling water side of 304 (16 ga) stainless steel heat exchanger tubing in an open, recirculating, cooling tower system (RCT) in a methanol plant. The corrosion morphology was characterized by pitting of two types: (1) large, round surface pits, and (2) small surface pits leading to subsurface caverns and tunnels.

The main objectives of this study were to simulate these corrosion phenomena in the laboratory and to observe the effect of operating variables on corrosion. The make-up water from the RCT system was used as nutrient feed in the laboratory experiments. RotoTorque reactors were fed continuously with make-up water at different dilution rates which influences biofilm accumulation. The make-up water was enriched with biodegradable carbon (methanol) to recirculating water strength to simulate the effect of cycles of concentration in the Methanol plant RCT system. Chlorine was added as a biocide once a day.

A computer model of the RCT system was developed to mathematically simulate the general system behavior under different operating conditions. The computer simulations were used to "numerically experiment" with the recirculating cooling water as opposed to the make-up water which was the only reasonable choice for laboratory experimentation for two reasons: (1) the source water for cooling at the plant was modified between the times of the corrosion episodes and the laboratory experiment and (2) the recirculating water at the plant during this laboratory study was receiving high dosages of biocide which altered its quality considerably.

Field experiments were also conducted in the Methanol plant RCT system make-up water line.

No conclusive evidence of MIC was observed of any kind from the laboratory or field experiments. No significant corrosion was observed in the laboratory experiments. The stainless steel 304 coupons installed in the industrial RCT system experienced no corrosion. The cooling source water has changed since the failures occurred. The new source water is of higher quality. In addition, biocide is dosed at relatively high levels to the RCT. No failures have been observed with these new conditions. However, from the experimental results, we conclude that poor water quality alone was not the cause of failure of stainless steel heat exchanger tubing in the RCT system.

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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## ABSTRACT

The focus of the research was significant pitting corrosion which occurred under biofilm deposits on the cooling water side of 304 (16 ga) stainless steel heat exchanger tubing in an open, recirculating, cooling tower system (RCT) in a methanol plant. The corrosion morphology was characterized by pitting of two types: (1) large, round surface pits, and (2) small surface pits leading to subsurface caverns and tunnels.

The main objectives of this study were to simulate these corrosion phenomena in the laboratory and to observe the effect of operating variables on corrosion. The make-up water from the RCT system was used as nutrient feed in the laboratory experiments. RotoTorque reactors were fed continuously with make-up water at different dilution rates which influences biofilm accumulation. The make-up water was enriched with biodegradable carbon (methanol) to recirculating water strength to simulate the effect of cycles of concentration in the Methanol plant RCT system. Chlorine was added as a biocide once a day.

A computer model of the RCT system was developed to mathematically simulate the general system behavior under different operating conditions. The computer simulations were used to "numerically experiment" with the recirculating cooling water as opposed to the make-up water which was the only reasonable choice for laboratory experimentation for two reasons: (1) the source water for cooling at the plant was modified between the times of the corrosion episodes and the laboratory experiment and (2) the recirculating water at the plant during this laboratory study was receiving high dosages of biocide which altered its quality considerably.

Field experiments were also conducted in the Methanol plant RCT system make-up water line.

No conclusive evidence of MIC was observed of any kind from the laboratory or field experiments. No significant corrosion was observed in the laboratory experiments. The stainless steel 304 coupons installed in the industrial RCT system experienced no corrosion. The cooling source water has changed since the failures occurred. The new source water is of higher quality. In addition, biocide is dosed at relatively high levels to the RCT. No failures have been observed with these new conditions. However, from the experimental results, we conclude that poor water quality alone was not the cause of failure of stainless steel heat exchanger tubing in the RCT system.

## INTRODUCTION

Problem Characterization

Microorganisms exhibit a tendency for adsorbing to and colonizing surfaces which are submerged in aquatic environments. The immobilized cells grow, reproduce, and produce extracellular polymeric substance (EPS). The EPS frequently extends from the cell, forming a tangled mass of fibers lending structure to the entire assemblage known as biofilm. Biofilms tend to grow on almost any surface including teeth, concrete, plastic, and metal surfaces.

Biofilms serve beneficial purposes in natural environments and in some modulated systems (e.g., removal of contaminants from natural flowing streams, trickling filters and rotating biological contactors). Biofilms can, however, impair the performance of process equipment. They can impede the flow of heat across the surface, increase fluid frictional resistance at the surface, and enhance corrosion rate at the surface.

Significant, costly, localized corrosion of the cooling water side surfaces of stainless steel (SS) heat exchanger tubing has occurred repeatedly (Puckorius, 1983) in condensers in open, recirculating, cooling tower systems (Figure 1). The problem is faced by industries including the chemical, petroleum, and power industry. Repeated and frequent failures of condensers have cost several billion dollars in inspection, repairs, interim, and final replacement (Tatnall, 1981).



Figure 1. Scanning Electron Micrograph (SEM) of a corrosion pit from a section of 304 stainless steel heat exchanger tubing (x43) from a plant which has suffered similar problems (photograph provided by Tatnall, Dupont, Delaware).

#### Problem

The focus of this study was pitting corrosion under biofilm deposits on the cooling water side of a SS 304 heat exchanger tubing in an open, recirculating, cooling tower/condenser system of a Methanol plant (RCT system). The corrosion failures were very costly and occurred in 1982. Since then, the source of cooling water has changed as well as RCT operation and the failures have not occurred again.

Research Goal and Objectives

The goal of the research was to determine the controlling mechanism and factors influencing pitting corrosion on SS 304 heat exchanger tubing in the RCT system at the Methanol plant during the failures of 1982. The specific objectives were as follows:

1. Develop a laboratory system for simulating the corrosion phenomenon observed in the RCT system heat exchanger tubing.
2. Evaluate the effect of operating variables (biocide, cycles of concentration, and substrate loading rate) on the observed corrosion phenomenon in the laboratory.
3. Develop a RCT model for performing computer simulations to integrate laboratory results with observations in the RCT system.

## LITERATURE REVIEW

The durability, versatility, and economics of SS 304 have made it one of the most widely used alloys in the chemical, petroleum, and power industries. However during the last few decades, it has become apparent that SS 304 is susceptible to MIC phenomena. Although the exact mechanism of MIC is still not fully understood, corrosion influenced by bacteria is a widely accepted and costly phenomenon.

The literature review focuses on surface morphology and physical characteristics of SS 304, properties of biofilms and treatments for their control, and the possible role of biofilms in the corrosion of SS 304.

Biofilm Formation: A Process Analysis

The adsorption of bacteria is a general phenomenon encountered in natural environments with important ecological implications. Bacterial adsorption to surfaces offers survival advantages because of increased nutrient availability, particularly in fast flowing and nutrient-deficient habitats. The adsorbed cells reproduce and form extracellular polymers leading to the formation of biofilm. Accumulation of biofilm at the surface is the net result of the following fundamental processes (Characklis, 1981):

1. Adsorption of organic molecules to the surface forming a conditioned surface.
2. Transport of microbial cells to the conditioned surface.
3. Microbial transformation (growth, reproduction) at the

surface.

4. Partial detachment of biofilm due to fluid shear stress.

Biofilm formation is not a sequence of the above rate processes occurring individually but rather the net result of these processes occurring simultaneously. At specific times in the overall development, certain rate processes contribute more to biofilm accumulation and activity than the others.

#### Control of Biofilm Accumulation

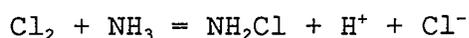
Biological fouling in cooling water systems is the result of excessive growth and development of different members of the lower life forms, namely algae, bacteria, and fungi.

Many different types of chemical agents are employed for microorganism control in recirculating cooling water systems. The primary purpose of the chemical agent is to kill and/or inhibit the growth and accumulation of organisms. If a given toxicant or biocide is present in sufficient quantity the microorganisms will be killed. Biocides also cause the detachment of biofilm from the surface thus keeping the system surfaces relatively free of microbial populations and minimizing biofouling and other related phenomena. The scope of this literature review is restricted to one biocide, chlorine.

Chlorine is one of the most widely employed agents for control of microbiological deposits in recirculating cooling water systems and is frequently the most economical treatment method. Chlorine is highly toxic and has traditionally been employed in RCTs on an intermittent (shock fashion) basis. However in recent years, continuous low dosage treatment has also been widely practiced.

Unfortunately, chlorine has also been found to be one of the most damaging materials to both metal and non-metal parts of the cooling tower system (Cooling Water Treatment Manual, NACE, 1971). Widely accepted practice suggests that the free chlorine residual be less than  $1E-3$  kg/m<sup>3</sup> in the hot return line to the tower.

The effectiveness of chlorine is decreased by the presence of organic matter including biomass, reducing agents such as hydrogen sulfide, and chemicals containing reactive nitrogen, e.g., ammonia:



An ammonia plant located near the RCT system at the Methanol plant can produce similar effects in the system under study. Thus, when the wind is from the direction of the ammonia plant, much of the chlorine is in the form of chloramines. Chloramines do not disinfect suspended cells as effectively as free chlorine. However, there are indications that chloramines are more effective against biofilms.

The rate of chlorine transport to the biofilm through the bulk water depends on the concentration of chlorine in the bulk water, the concentration of chlorine-demanding compounds, and the intensity of the turbulence in the system. The chlorine concentration in the bulk water is the net result of the chlorine addition rate minus the chlorine demand rate of the water. Sufficient chlorine must be added to the water to satisfy all these reactions, collectively known as "chlorine demand", and to allow a suitable concentration of residual chlorine to persist in the water.

### SS 304: Metal Structure and Corrosion Resistance

Stainless steel is an iron-base alloy containing more chromium than the 12 per cent necessary to produce passivity but less than 30 per cent. SS 304 belongs to the class of austenitic steels. Austenitic steel exhibits a wide range of mechanical properties, making it one of the most widely used alloys. Austenitic steel is manufactured by annealing at elevated temperatures high enough to avoid carbide precipitation, usually above 1850°F. The steel is cooled rapidly from the annealing temperature to avoid austenitic transformation. Chromium-containing SS are generally made austenitic by the addition of nickel, a strong austenite stabilizing agent. Manganese and nickel are added to retain the austenite at room temperature.

Pitting and crevice corrosion occurs in SS resulting from a highly localized breakdown in the passive oxide film protecting the surface and followed by electrochemical action. The presence of chlorides has been hypothesized to be a major cause of pitting and crevice corrosion. Collection or accumulation of solids on surfaces is also conducive to pitting (Source Handbook of Stainless Steels, American Society for Metals Publications, 1977).

### Corrosion of SS 304 in Absence of Bacteria

Most metals in their pure form are unstable in many environments and tend to revert to corresponding oxides or other stable combinations from which they were derived, i.e., they corrode.

Electrochemical theory indicates that a difference in potential must exist between two or more points and current must flow for corrosion to occur. A difference in potential can be caused by several factors including difference in concentration of dissolved oxygen at one point compared with another, difference in composition, and slag inclusions.

When corrosion occurs, metals go into solution at anodic areas as metal hydroxide. This is an oxidation reaction. One or more reactions occur at cathodic areas (reduction reactions). Hydrogen ions are reduced to atomic hydrogen by taking on the available electrons. The atomic hydrogen combines to form hydrogen gas at cathodic areas. If this monomolecular layer of hydrogen gas is not disturbed, polarization will occur and the corrosion reaction will be suppressed. The hydrogen layer can be destroyed by either mechanical or chemical means, or both.

SS 304 does not corrode in neutral pH water free of oxygen. However cooling water is usually saturated with dissolved oxygen and is high in concentration of dissolved and particulate materials. These factors tend to enhance corrosion. Other factors influencing the corrosion of SS are temperature, rate of water flow, pH, chloride concentration and carbon dioxide concentration.

If the metal hydroxide is relatively soluble, as in the case of ferrous hydroxide, it will remain in solution until the solution becomes saturated, and then separate out. More ferrous ions can diffuse through the precipitated ferrous hydroxide ( $\text{Fe}(\text{OH})_3$ ), and can be oxidized and precipitated as it reaches the oxide-water interface. An active anode continually produces ferrous ions which diffuse and electrochemically migrate toward the water- $\text{Fe}(\text{OH})_3$

interface at much greater rates than oxygen can diffuse through the deposit towards the corroding metal surface. Thus, the cell continues to function as a differential aeration cell. The result is that a small pit is formed at the anodic area, covered with a canopy of deposited material called a tubercle.

Corrosion may also occur as a result of differences in oxygen concentration in contact with a metal surface due to the presence of insoluble deposits. The covered metal surface is reached by a solution containing smaller amounts of dissolved oxygen and continues to corrode, while the adjacent metal surface in contact with oxygen-rich solution, acting as a cathode, is protected.

#### Corrosion of SS 304 in Presence of Bacteria

The corrosion resistance of SS 304 in industrial water systems can be greatly influenced by biological factors. Corrosion of SS 304 induced by bacteria is a widely recognized phenomenon in the pulp and paper industry and in cooling systems among others.

Several theories have been proposed to explain the mechanism of microbially influenced corrosion (MIC) of SS 304. MIC is believed to be initiated at sites of inclusions on the metal surface resulting in concentrated metal chloride formation. Mollica et al. (1987) and others reported aerobic bacteria settlement on the stainless steel surfaces leading to an increased oxygen reduction rate causing enhanced localized corrosion propagation rate. Some of the bacteria identified with MIC of SS 304 surfaces are described below.

### Filamentous Iron Bacteria (Fe/Mn-oxidizers)

Filamentous iron bacteria, typified by Sphaerotilus, oxidize dissolved ferrous iron to insoluble ferric hydrate, which forms a common sheath for several cells and produces a characteristic stalk-like, filamentous form. Some species can oxidize and concentrate even manganese. Filamentous iron bacteria have been hypothesized to be responsible for the common hollow, tubercles seen at the site of corrosion. They are aerobic and create oxygen depletion under the tubercles (Tatnall, 1981).

Gallionella, another "iron bacterium" tends to concentrate chlorides, with the result that deposits are rich in ferric and manganic chlorides which act like dilute HCl causing pitting corrosion of stainless steel.

Ghiorse (1984) has pointed out that metal oxidation has not been demonstrated in some cases and that certain microorganisms can catalyze the oxidation of metals. Other microorganisms accumulate abiotically oxidized metal precipitates. Metal oxidizing organisms create environments for the accumulation of chloride ions (to maintain charge neutrality) and form acidic ferric chloride and manganic chloride, which are highly corrosive to SS 304. Further pit development is enhanced as an oxygen concentration cell develops. Also, metal-oxidizing organisms efficiently scavenge oxygen and, therefore, provide conditions for the growth of obligate, anaerobic bacteria.

### Acid Producing Bacteria

Acid producers, typified by Clostridia, produce short-chain organic acids by either fermentation or acidogenesis. The localized

acidic attack can create a localized low pH environment, initiating the corrosion of metal surface at those sites.

#### Sulfate Reducers (SRB)

Von Wolzogen Kuhr and van der Vlugt (1934) proposed the cathodic depolarization theory for SRB corrosion. The theory suggests that hydrogenase catalyzed the hydrogen reduction reaction on the iron surface. King and Miller (1973) supported the hydrogenase theory but proposed that the cathodic depolarization occurred on the iron sulfide instead of the iron surface. Costello (1974) reports that Desulfovibrio desulfuricans produces  $H_2S$  which directly depolarizes the cathode. In summary,  $H_2S$  corrosion is under kinetic control and the sulfide film seems to play an important role in the anaerobic corrosion process both in biotic and abiotic systems.

## DESCRIPTION OF THE INDUSTRIAL SYSTEM

The RCT system was analyzed on a continuum of scales ranging from the microscale to the macroscale (Figure 2). Microscale ( $\leq 10^{-3}$  m) analyses address the structure, composition, and processes occurring within the fouling deposit and at the interface between the fouling deposit and the metal alloy (i.e., the substratum). At the mesoscale ( $10^{-3}$ -10 m), the influence of hydrodynamics and geometry (e.g., circular tube) was considered. At the macroscale ( $> 10$  m), the system design and operation (e.g., hydraulic residence time, cycles of concentration) determine the bulk environmental conditions (e.g., water quality, temperature, etc.) in which the fouling and corrosion take place.

Macroscale: RCT System

The RCT system is located near Beaumont Texas, several miles from the Gulf of Mexico. Topography is flat, and the water table high. Swamps, bayous, sloughs, and estuaries are numerous. Surrounding vegetation is dominated by water oaks and southern pine. Ambient temperature ranges from 4 to 35°C with an average annual temperature of 19 to 21°C. Humidity ranges from 65-90 %.

The work site contains several plants including methanol, aniline, ammonia, and two specialty-polymers. The Methanol plant is located in the southwest corner of the site with the ammonia plant located nearby.

The cooling water source (make-up water) for Methanol plant is a canal which is fed by the Neches River and Pine Island Bayou.

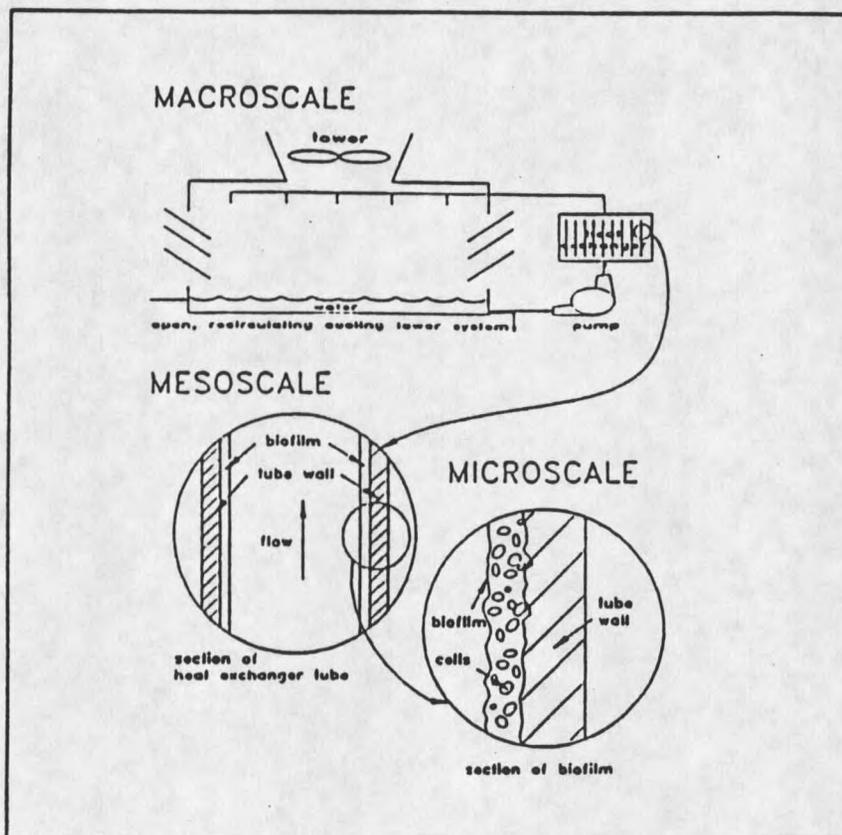


Figure 2. The relationship of engineering scale to interfacial microbial processes.

Temperature of the make up water at RCT inlet varies between 20 to 34°C. The RCT system is fed with untreated canal water. All other plants on site receive canal water that is clarified before use as make-up. Analytical results of the canal water near the plant before and after the shift to Pine Island water (Appendix D) are reported in Table 12. It is important to note that the failures occurred before the shift to Pine Island water. No large variation in canal

source water quality is obvious on a seasonal or yearly basis (Appendix D, Table 13). The water quality has improved significantly since the time of the corrosion failures.

The cooling tower system is an open, recirculating, forced-draft type with shell-and-tube condensers, including the two main crude condensers which operate in parallel (Figure 3). Several smaller condensers also operate in the system. The piping from the RCT basin to the crude condensers is cement-lined carbon steel with the bulk of the system piping made of reinforced concrete.

The system is operated with a volume,  $V$ , of water. The warm water return,  $Q_R$ , is pumped from the basin through a series of heat exchangers to the plenum at the top of the cooling tower. From the plenum, the water is distributed uniformly through an assembly of spray-nozzles over the interior of the structure which contains splash packing or fill material, constructed of slats stacked in decks and spaced in staggered rows. Water splashes from row to row, breaking into droplets, at a fixed rate. This rate is called the "water loading" rate of the tower.

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



















































































































































































































