




Effective Control Of Waterside Corrosion and Heat Transfer Efficiency in Chemical Plant Cooling Systems

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All chemical plants throughout the world incorporate cooling systems as critical components in the manufacturing process. And for each and every type of facility, part of the corporate formula for ensuring adequate profit margins and long-term economic viability involves good engineering design and construction of these cooling systems and their safe and effective operational control.

Control starts with clean waterside surfaces, regular maintenance, and a good housekeeping program. It is easier and significantly less expensive to keep a clean system clean than to stop a dirty system from getting dirtier. It is also safer, in terms of reducing health risks to plant operators and other facility workers and in limiting potential exposure to subsequent legal action, to take a proactive approach to the operational maintenance of cooling systems.

Although this article is primarily concerned with effective control of waterside corrosion and heat transfer efficiency in cooling systems, the fact is, engineering safety and the safety of process workers are intimately bound up in providing the necessary degree and quality of operational control. Effective waterside control and cooling system safety issues are not separate discussion topics. They are mutually inclusive.

Cooling Systems and Associated Waterside Problems

Before we can consider an effective control, the first aspects to consider are cooling systems as an entity and the waterside problems common to all systems—corrosion, fouling and deposition. Also, a very specific type of safety problem that can easily develop as a consequence of a failure to provide the necessary degree and quality of control is the growth of *legionella sp.* organisms. This situation, in turn, creates unsafe conditions and the risk of Legionnaires' disease.

Water cooling systems are designed to provide an efficient means of transferring, transporting, and dissipating heat, and many of the problems affecting operational efficiency and the fabric of the system that may lead to increased health and safety risks are associated with corrosion, fouling, and deposition within the systems' water wetted areas. As a consequence, these important factors should be proactively managed.

The heat exchanger (being the primary source of heat extraction) requires close attention to maintain clean conditions, protect the tubing and tube sheets, and minimize restrictions on heat transfer to the bulk water. However, system design and construction materials, water treatment chemistry, environmental legislation, and perceptions of quality and service have changed in recent years, which means that cooling towers, evaporative condensers, pumps, pipe-work, valves, filters, and screens also need to be considered. In fact, the entire cooling system needs to be managed as a whole, with no obvious weak links left to chance.

In a similar vein, technical discussions on issues such as corrosion, carbonate scaling, and microbiological control often tend to consider these topics as individual problems that are somehow unrelated to each other. But the practical reality is that these subjects are inter-related, and consequently, management must consider each specific problem and control measures in the light of the complete dynamic cooling water system.

Finally, some comments on terminology, as many terms have become interchangeable (such as deposition and fouling, which can mean different things to different people). While strict definitions may be of benefit, they remain difficult to provide, especially as recognition grows within the industry of the very significant and deleterious role that biofouling plays in trapping inorganic deposits, fouling the waterways of cooling systems, and promoting certain corrosion processes.

- *Corrosion* is an electrochemical process whereby the oxidation of metals or alloys to their (lower energy state) oxides or cations takes place, resulting in a loss of mechanical or structural strength and metal wastage. Corrosion takes many forms and includes biocorrosion, which is corrosion at the water-metal interface of a biofilm.
- *Fouling* produces dirty and inefficient cooling systems, impeding the flow of cooling water. It involves the physical adherence to surfaces and mutual entanglement of insoluble salts, corrosion products, oils, fats and other process contaminants, air-blown debris, and other substances. Where fouling involves bulky matrixes of microbiological origin (biomass), it is often termed biofouling and involves the formation of biofilm.
- *Deposition* involves the formation and precipitation of crystalline scales and the throwing down, within critical parts of the cooling system, of silt, sand, muds, and sediments; all these deposit components have the effect of reducing the rate of heat transfer. Corrosion can also occur under deposits.
- A *biofilm* or *slime* is a biological matrix of micro-organisms, their excretion products, and trapped particles. (N.B. dental plaque is a biofilm).

Exploring Waterside Problem Areas

a. Corrosion

Most cooling systems are primarily constructed of carbon steel, which is subject to strong corrosive influences that will reduce its inherent, relatively high-energy state gained during manufacture back down to the naturally lower energy state of iron oxide(s). (There is initially no area of thermodynamic stability between the steel and the water with which it is in contact.) Most other metals in the cooling system are subject to similar corrosive influences, although of reduced intensity due to their more corrosion-resistant (or noble) properties.

A wide variety of situations can induce or accelerate corrosion processes. These include the proximity of dissimilar metals, the introduction of acids or aggressive chemicals into the cooling water, the scrubbing of gases and other materials from the air, fouling and deposition, microbiological infestations, process leaks, and others. Microbiological corrosion by sessile, slime-producing organisms, such as iron and sulfur bacteria, is particularly important, and the organisms also contribute to potential health risks. Thus, management of the entire cooling system is vitally important in reducing both the overall rate of corrosion to an acceptable level and specific corrosion processes in critical areas. Corrosion cannot be totally stopped or eliminated.

The corrosion of steel or other metals takes place when an electrochemical cell is established in the cooling system, employing the water as an electrolyte, and two different electrochemical processes occur on the metals (anode and cathode), or when two metals are coupled together. Corrosion occurs on a metal due to variations in oxidation potential on the metal surface (*microanodes* and *microcathodes*), such as irregularities in the metal's crystalline structure or stresses caused during the finishing stages of manufacture. The metal or metal area

having the lowest potential becomes the anode. It is at the anode that oxidation takes place, with the metal suffering a loss of electrons and an increase in positive charge. The resulting metal ions (positive charge) dissolve in the water electrolyte and thus metal waste occurs. At the cathode, a variety of reduction reactions take place, including the reduction of hydrogen ions (the gaining of electrons) to produce hydrogen gas.

In general, the lower the anode potential, the more base the metal and the higher the rate of corrosion. In untreated cooling water electrolyte, high levels of total dissolved solids, conductivity, or temperature tend to increase the rate of corrosion. Also, high concentrations of chloride or sulfate ions, dissolved gases such as O_2 , CO_2 , H_2S , NH_3 , foulants containing certain species of bacteria, or silt can and will increase the rate of corrosion.

The CaO/CO_2 equilibrium and the O_2 content of cooling water are recognized as being major factors in determining potential corrosion rates. Corrosion always tends to be more severe when the metal surface is shielded by foulants or semiporous deposits such as silt and muds, as various forms of selective corrosion can take place, including crevice corrosion, under-deposit corrosion, and tuberculation, which are all forms of *concentration cell corrosion* and involve oxygen to a greater or lesser extent. Also, chloride, in particular, reduces the corrosion resistance of many metals, especially those that naturally and strongly passivate to form a protective oxide layer (such as stainless steel and aluminum) by attacking the passivated film. High chlorides increase the risk of stress corrosion cracking in austenitic stainless steel, as well as the general rate of corrosion, and will attack in localized areas, often causing pitting-type corrosion.

Simple corrosion rate methods may only determine general corrosion, which tends to be uniform and not particularly representative of other complex corrosion reactions occurring in inaccessible parts of the cooling system where foulants and deposits may be present. These reactions are far more damaging to both operational efficiency and the integrity of the system, hence the emphasis on good housekeeping and overall cooling system management.

Today, heavy mill zinc galvanized (HMG) factory-fabricated steel towers are very popular due to relatively

low construction costs and increased flexibility of sizing and application. However, the demise of strongly passivating chromate treatments, an increased use of poorer quality water sources with higher levels of contaminants and pH, plus a demand for higher recirculating water operating cycles and a generally poor understanding by engineering contractors of the need for effective cleaning and passivation programs at the startup of new systems, have all contributed to the widespread resultant problem of white rust corrosion and reduced equipment operating life. Better engineering design and good startup programs are needed to manage white rust problems.

Cooling system pipe-work and components can also suffer corrosion and damage (such as cavitation, erosion, and stress corrosion) under a variety of operating conditions and from many causative agents. Some common types of corrosion risks are shown in Table 1.

Table 1: Type of corrosion risk in cooling water

Metal	Impact of Corrosion
Steel	Stagnant water tends to induce local attack.
	Fouling induces concentration-cell type corrosion.
	High Cl^- and SO_4^{2-} tends to increase risks of pitting.
	O_2 saturated water may induce general corrosion.
	Fouling by slime-producing bacteria and the presence of SO_4^{2-} induces corrosion due to sulfate reducing bacteria.
	Coupling with noble metal causes galvanic corrosion.
Iron	A low pH induces rapid, acid-induced wastage and pitting corrosion.
	Presence of some O_2 , plus deposits and low flow, stimulates tuberculation.
SS	Soft water, low pH, H_2S can stimulate graphitization.
	Vulnerable to depassivation from high Cl^- .
Brass	Residual or applied stress with Cl^- induces SCC.
	Ammonia produces cracking & wastage.
Zinc	High velocity can induce erosion-corrosion (>6 fps)
	Uninhibited brass suffers dezincification.
Al	High alkalinity causes white rust.
	pH over 9 with OH^- causes rapid corrosion

b. Scales, Sludges, Inorganic Deposits, and Foulants

Effective cooling system management is seldom better demonstrated than by the clean physical appearance of cooling towers and other visible components and the continuously efficient operation of heat exchangers. The physical lack of any crystalline scales or corrosion deposits on heat-exchange surfaces, or the buildup of

muds, silt, precipitated salts, sludges, biofilm, or other foulants anywhere within the system, is a difficult objective to achieve due in part to the problems of anticipating and controlling the effects caused by the sheer number of variables present.

- Scaling refers to the crystalline growth of a variety of insoluble salts or metal oxides, which are usually deposited as a hard, adherent layer or layers on heat transfer surfaces. This is extremely undesirable because all crystalline scales reduce the rate of heat transfer and therefore seriously reduce the efficiency of the overall cooling system. Scales from individual salts vary in their heat transfer insulating effects, but most adherent deposits found on heat transfer surfaces consist of one or two predominant salts (such as calcium carbonate or calcium phosphate) intimately combined with a variety of lesser amounts and types of scales, together with some corrosion debris and other fouling matter. Suffice to say that a small buildup of scale generally produces a detrimentally large reduction in heat transfer. Also, scales can exhibit shielding effects, thus increasing the risk of corrosion through differential oxygen concentration cells. A buildup of scale deposits will also tend to directly impede the flow of cooling water, as well as act as a key for the accumulation of muds, silt, and biomass. Thus, the buildup of a deposit acts as an indirect foulant. Scaling also compromises engineering safety, as microorganisms can grow and reproduce under deposits. In some countries with stringent legislative *legionella* control programs, it is necessary to employ water softeners in all hard-water areas to prevent the development of scales and thus, minimize the risk of legionellosis.
- Sludge is another common term used to describe the soft deposits or water-based suspensions containing variable mixtures of mud, clays, sand, silt, colloids, biomass, oil and grease, and precipitated salts in an amorphous form. Sludge often occurs in low-flow areas such as heat exchanger water boxes, pipe bends, hot and cold wells, or cooling tower sumps, where it acts as a primary foulant by impeding water flow. In critical components such as heat exchangers, sludge deposits not only foul the unit, but also, in concert with scales, can reduce heat transfer or provide shielding effects for corrosion, including biocorrosion. Some sludge can and will result from the precipitation of salts due to supersaturation in the main body of

the cooling water (i.e., they exceed their respective solubility limits, and bulk water precipitation occurs). In addition, oil or other process materials can leak into the cooling system, adding to the foulant load. The source of most sludge and other foulants, however, is from the surrounding environment. Air-blown leaves, sand, dust, and dirt; the infiltration of microbiological organisms; the air scrubbing effects of the cooling tower; and the photosynthesis of algae in exposed bodies of water, such as cooling tower, open distribution-basins, or cold wells, are mechanisms for the (almost continuous) onslaught of cooling system contamination and fouling. Anything practical that can be done to prevent or minimize the ingress or the effects of these contaminants is a vital part of cooling system management and is to be encouraged.

Analysis of most crystalline scale deposits and mineral foulants taken from the waterside of cooling systems shows, not unexpectedly, considerable variation in composition. The analysis normally reveals the presence of mixtures of several salts and metal oxides originally derived from water impurities or corrosion processes. Some minerals commonly found include those shown in Table 2.

Table 2: Common mineral components of deposits and foulants

Salt/ Oxide	Mineral	Formula
Calcium carbonate	Aragonite	CaCO_3
	Calcite	CaCO_3
Calcium phosphate	Hydroxyapatite	$\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$
	Tricalcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$
Calcium sulfate	Anhydrite	CaSO_4
	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
	Hemihydrate	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
Copper oxide	Cuprite	Cu_2O
Iron carbonate	Siderite	FeCO_3
Iron oxide	Haematite	Fe_2O_3
	Alpha iron oxide (paramagnetic)	$\alpha\text{Fe}_2\text{O}_3$
	Gamma iron oxide (ferromagnetic)	$\gamma\text{Fe}_2\text{O}_3$
	Lepidocrocite	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
	Magnetite	$\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O}$
Iron sulfide	Troilite	FeS
Magnesium hydroxide	Brucite	$\text{Mg}(\text{OH})_4$
Magnesium phosphate	Magnesium hydroxy phosphate	$3\text{Mg}_3(\text{PO}_4)_2 \cdot \text{Mg}(\text{OH})_2$
Magnesium silicate	Serpentine	$3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Silica	Crystoballite	SiO_2
Zinc carbonate	White rust	ZnCO_3

c. Legionellosis

With cooling towers or evaporative condensers (along with other types of equipment producing a water aerosol) where effective control of waterside corrosion and heat transfer efficiency is not maintained, engineering safety becomes compromised and the conditions required for *legionella* growth and transmission may be created.


Legionnaires' disease and Pontiac fever, which are both forms of legionellosis, are caused from the inhalation by susceptible individuals of certain serotypes (varieties)

of the gram-negative bacilli *Legionella pneumophila*, and also by some other species/serotypes. The mode of transmission is usually through water droplets containing the organisms. Organisms can also be found in buildings' potable water storage and distribution systems, such as hot water storage tanks (calorifiers), especially those designs that permit stratification of hot stored water and cold makeup water.


Legionellosis is a type of pneumonia. It was first identified after the 1976 Convention of the American Legion in

Pennsylvania, when over 200 people were taken ill and 34 subsequently died. The species most commonly associated with disease outbreaks is *Legionella pneumophila serotype 1*, which appears to be the most pathogenic of the genus. At its onset, Legionnaires' disease is characterized by a high fever, chills, headaches, and muscular pain. A dry, nonproductive cough develops, and most patients suffer breathing difficulties. A third of the patients suffer from diarrhea and/or vomiting and half become confused or delirious. In outbreaks, the fatality rate is typically around 20%. Although most people make a complete recovery, some can suffer long-term symptoms. If recognized in its early stages, the disease can be effectively treated with antibiotics such as erythromycin. Legionnaires' disease is frequently characterized as an "opportunistic" disease, meaning that it most frequently attacks individuals who have an underlying illness or have weakened immune systems. The most susceptible people include the elderly, smokers, and immunosuppressed individuals. People with chronic obstructive pulmonary disease (COPD), organ transplant patients, and individuals on corticosteroid therapy are also at elevated risk.

Legionella bacteria may also cause other forms of legionellosis, such



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as Pontiac fever, which is a short, self-limiting, flu-like illness that has no long-term effects. Pontiac fever develops rapidly (within 5 hours to 3 days) and lasts for 3 to 5 days. The attack rate is high, typically around 95%. It produces headaches, nausea, vomiting, aching muscles, and a cough, but no pneumonia develops.

Since 1976, much has subsequently been learned about the *legionella* organism responsible for the Pennsylvania outbreak. Within the *genus Legionella*, over 30 species and 47 serologically distinct groups (serotypes) have been identified. As *legionella* bacteria are widespread in the environment, it becomes apparent that the organism may be easily introduced into water systems from the air or water supply or from ingress of foreign matter into a water system.

Precise information on the number of cases of legionellosis occurring each year around the world is very difficult to obtain due to a lack of any common reporting procedures and significant under-diagnosis and under-reporting in most countries. In the United States, estimates given are typically in the range of 25,000 to 50,000 cases per year, although the number of annual reported cases of legionellosis is only around 1,000. (Compare this with the approximately 16,000 cases of tuberculosis reported per year in the United States). A global estimate is perhaps a minimum of 250,000 cases per year, resulting in probably 10,000 to 20,000 annual deaths worldwide.

Managing Process Safety, Risk, and Costs by Controlling Waterside Problem Areas

It is well understood that chemical plants need to be operated safely and efficiently with a proactive approach, and, while cooling systems do not present the same level of risk as a chemical reactor, effective cooling water management, planned preventative maintenance, and good housekeeping practices remain important functions if safety issues and costs are to be properly managed. In turn, no overall cooling water treatment program can fully deliver its promised benefits unless effective control is exercised, which should encompass areas such as:

- Adherence to a quantifiable technical and administrative servicing standard.
- The setup and administration of log books and maintenance schedules.
- Specific adherence to mandatory regulations and OSHA guidelines.

- Pre-commission cleaning and system passivation prior to program startup.
- The setup and utilization of dosing and control equipment.
- Chemical inhibitor monitoring, including operational analysis and control work.
- Biological contaminant monitoring and *legionella* control recordkeeping.
- The use of real-time monitoring and control software systems, where appropriate.
- Program troubleshooting, results interpretation, program adjustment, and visual inspections.

All treatment programs produce the best results in clean, well-maintained cooling systems, and, whereas maintenance management activities ensure cooling system functional performance, good housekeeping ensures that the cooling system remains in a clean, hygienic, and safe condition. Some practical aspects of good housekeeping include:

- All debris should be regularly removed from the vicinity of the cooling towers.
- Action is required to prevent the ingress of sand, silt, muds, and other foulants.
- Algal biomass or other visible fouling should be removed from the cooling tower before any clogging of nozzles, fill-packs, or other water distribution components takes place.
- Screens should be maintained in a clean condition to remove silt and algae.
- Cooling systems should be drained and cleaned on a regular basis (normally twice per year).
- Regular visual inspections should be carried out.
- Incorporate drain valves on the water side of heat exchangers to periodically remove sludge.
- Store small quantities of antifoam, mud remover, and emulsifier (or demulsifier) to deal with any process contamination and emergency problems.

a. Specific Corrosion Control

Effective control of the corrosion process in cooling systems can be achieved in a number of ways, including the following methods:

1. The wider use of strongly corrosion resistant metals.
2. The formation of natural or deliberate protective films on metal surfaces using passivation or galvanizing techniques.

3. The use of chemical corrosion inhibitors such as molybdate, zinc, orthophosphate, phosphonates, and azoles as part of a treatment program.
4. Modification of the circulating water chemistry to a specified balance point or range.
5. Good housekeeping practices.
6. Cathodic protection.
7. Excellent microbiological control.
8. The use of paints and coatings.
9. Deaeration in a closed loop, which is typically practical, provided that the system really is closed. (Note: Many are not, and enhanced oxygen corrosion results.)

Usually, a combination of techniques is used on an ongoing basis, and monitoring is maintained to provide both an early warning of potential problems and a degree of reassurance to all parties involved. Where, for example, a high-chloride makeup water is used, it is necessary to be scrupulous in maintaining clean metal surfaces in the cooling system by employing more frequent physical cleaning and using side-stream filters, polymer dispersants, and biodispersants. Raising the level of chemical inhibitor treatment is a further and usually beneficial response.

b. Specific Control Over Deposition and Fouling

Corrosion takes many forms but is always an electrochemical process, whereas deposition and fouling are often combinations of both chemical and physical processes involving inorganic and organic contaminants, and their effective control tends to be much more of an art rather than a science. The development in recent years of a wide range of modern organics, often with novel multifunctional chemistries that can act under difficult and stressful operating conditions, has done much to improve the armory of tools to be used in keeping cooling systems clean. The types of organics employed include phosphonates; phosphinocarboxylates; polymaleates; and acrylic acid based homo-polymers, co-polymers, and terpolymers. They primarily function as:

- Deposit control agents or antiscalants to inhibit the deposition of calcium carbonate and other alkaline earth salts.
- Dispersants or antifoulants (sludge fluidizers, biodispersants, or mud treatments) to control the physical adherence of insoluble salts, corrosion products, oils, fats, process contaminants, biofilms, and biomass onto heat transfer and other water wetted surfaces.

These chemicals, in the form of liquid formulated blends, are added continuously to the cooling system at low feed rates and in proportion to the system makeup water requirements. The precise formulation and feed requirement for corrosion inhibitors, deposit control agents, antifoulants, stabilizers, sequestrants, metal surface cleaners, and other chemical treatment components is based on achieving a particular water chemistry balance, fairly specific for the particular design of the cooling system and the operating circumstances.

Additionally, various microbiocides are periodically employed. These are also antifoulants and may have biostatic or biocidal properties depending upon feed rate frequency and system-water volume concentration. Types of microbiocides employed include chlorine, bromine, isothiazoline, glutaraldehyde, polymeric quaternary ammonium compounds, and tertbutylazine.

c. Specific Control of *Legionella* and Other Safety and Health Risks

Given suitable conditions for growth, almost any water system is likely to be at some degree of risk for contamination with the *legionella* bacteria at some point. The organism is often present in small numbers in fresh water and has been commonly identified in many potable water sources, albeit only in very small numbers. They can enter chemical plant cooling systems (and other types of water systems) and, unless adequate precautions are taken, they may colonize and reach large numbers, which presents a risk to human health if inhaled by susceptible individuals.

Aerosol formation is the consequence of the normal operation of evaporative condensers and cooling towers used in chemical plants (and certain domestic water services equipment such as shower/spray systems). Bacteria from these water systems may be inhaled whenever an aerosol is produced, increasing the risk of exposure. Poor water-system designs, installations, maintenance, and management are typically associated with illnesses and fatalities, which are usually preventable.

It is suspected that water supply mains are the most likely source for *legionella*, although potable water itself has never been found to be the prime cause of any infection or outbreak. Additionally, there is no evidence that

well managed and maintained cooling systems provide any significant risk of exposure to legionellosis.

Although the statistics of legionellosis may be disputed by some authorities, the level of reported cases in some countries, such as the United Kingdom and Australia (and the associated media coverage), has been sufficient for their governments to implement codes of practice and regulations to reduce the risks to the public at large of contracting legionellosis. As information concerning the organism became available and awareness grew in the 1980s, the level of reported cases rose dramatically, prompting government action. Some local authorities have additionally required the registration of all cooling towers and evaporative condensers located within their jurisdiction. Breach of *legionella*-related health and safety laws or specific regulations have led many companies, their directors, and water treatment service company contractors to court. Poor risk assessments and risk control measures that fail to ensure, as far as reasonably practicable, the safety of employees and visitors is a punishable offense in these countries.

More recently, in the United States, OSHA has decided to issue recommendations for controlling the risks of growth and transmission of the *legionella* organism. These OSHA recommendations are very similar to those of other countries and have been posted online at <http://www.osha-slc.gov/TechMan-data/III-7.html>. The emphasis is on risk identification and assessment, planned preventative maintenance practices, good water treatment programs (including the use of suitable chemicals, regular testing, and technical support services), reporting and documentation of actions taken, and training. Risk assessment looks at issues such as:


- The cooling tower location, with regard to its proximity to a susceptible population.
- The design and operating characteristics of the cooling system (and especially the tower itself), which determines the risk of a high concentration of *legionella* and other potentially pathogenic microorganisms. A risk control measure may, for example, ensure that cooling tower drift eliminators are actually effective in preventing the dispersal of water droplets that could potentially contain *legionella* organisms

- The water treatment program (or lack thereof), including the type and feed rates of chemicals employed, results obtained, maintenance management, and field technical services.

Key features of legionellosis control programs tend to include:

- Systematic use of biocides.
- Periodic (at least monthly) microbiological analysis.
- Routine monitoring and systematic documentation.
- Periodic inspection and cleaning of all cooling tower components.

Summary

The effective control of waterside corrosion and heat transfer efficiency in chemical plant cooling systems through a proactive management approach is vital, and the consequence of foreign regulations and new OSHA recommendations has meant that the control of *legionella* has become an additional and very important safety consideration in chemical plants worldwide (and for industry as a whole). Since a major objective in avoiding legionellosis is keeping water systems clean and deposit free, there is no conflict between the objectives of effective control of waterside corrosion and heat transfer efficiency and engineering safety. 

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