



Antifouling strategies and corrosion control in cooling circuits



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ABSTRACT

Biofouling and corrosion phenomena dramatically reduce the functionality of industrial cooling circuits, especially in marine environments. This study underlines the effectiveness of a low level chlorination treatment of seawater to prevent biological fouling and biocorrosion.

Reported examples emphasize the reaction of chlorine with bromide, ammonia and organic compounds in seawater and the effectiveness of a treatment performed in such a way to guarantee a residual concentration lower than 3 μM at the outlet of the condensers.

In a brief review of antifouling strategies, alternatives to chlorination and the monitoring approach able to optimize the treatments are also reported.

An integrated, on-line system based on electrochemical probes (Biox system and a linear polarization resistance probe) demonstrated to be sufficient to monitor in real time: corrosion, biofilm growth and chemical treatments based on chlorine or alternative oxidant products (chlorine dioxide, etc.).

A careful electrochemical monitoring and the optimized treatments help the plant operators of industrial cooling circuits prevent the decay of the equipment performance, allowing at the same time the control of the halogenated by-products formation.

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1. Introduction

The settlement of macrofouling in cooling canals and the formation of biofilm on surfaces of heat exchangers are the two main causes that dramatically reduce the functionality of the cooling circuits, especially in marine environment.

As a matter of fact, the efficiency and availability of a power plant depend to a great extent on the integrity and cleanness of the condensers. Indeed, more than 5% of its efficiency can be lost due to biological films. At worst, the power units using seawater as coolant must be shut down if macrofouling (mussels, serpulids, algae etc.) plugs the tubes of condensers [1].

Biofilm is the first layer of biofouling growing on the surface of wetted structures in contact with natural waters. When its growth is not well controlled, biocorrosion (microbial corrosion MIC) can occur. Many metallic materials commonly utilized in plants are affected by MIC, like stainless steel and copper alloys (common materials for heat exchangers). Copper alloys are not an exception because biofilms can protect microorganisms from the toxic effect of copper dissolution [2]. Heater exchangers in titanium do not suffer from MIC, but the inhibition of heat transfer can become an unacceptable phenomenon under biofouling.

Corrosion rate, especially after the biofilm overcomes the first phase of its development, was found to be not directly correlated to parameters such as the biofilm thickness, its roughness, or the number of settled microorganisms [2].

A previous survey conducted by European specialists (BRRT – CT98-5084, UE program 1999–2003), based on their personal experience concluded that many techniques can be employed successfully for corrosion monitoring in the laboratory, few of them suitable on-field. Some of the methods are very effective for monitoring biofilm, others for monitoring corrosion; even though none of them can be used alone to effectively follow the development of microbial attacks in all the possible combination of metals, environments, and biofilms. Nevertheless, the recent successful experiences in the industrial application of integrated electrochemical probes for the biofilm and corrosion monitoring suggest that the electrochemical approach can be suitable enough for helping plant operators in the conduction of antifouling/anticorrosive treatments [3]. The best available technology (BAT) for industrial cooling circuits (Reference Document of Directive 2008/1/EC) acknowledged the effort in innovation of the monitoring tools and strongly emphasizes their role, especially for just existing plants with cooling circuits that employ corrodible materials (as copper alloys and steel) still needing of chemical treatments as chlorination. The on-line monitoring tools, in fact, concern the way a circuit is operated and maintained preserving the performance of heat exchange facilities and minimizing environmental impact due to the chemical treatment.

Specific experiences with the integrated electrochemical monitoring of copper alloy condenser tubes were recently conducted in the context

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of the Initial Training Network on biocorrosion (BIOCOR-ITN) [4]. In the same networking context of BIOCOR-ITN (Sub-Program N. 3), the antifouling strategies are also approached by the study of crucial chemical–physical parameters potentially involved in the inhibition of biofilm development on material widely used for heat exchange (copper alloys, stainless steel and titanium), exposed to marine or fresh water. The control of the biomolecules adsorption (the first step in biofilm formation) is pursued in these studies by modifying the surface properties of the material (hydrophobicity in particular) [5,6]. Concerning the copper alloys, a fundamental electrochemical approach was associated with surface analysis [7]. Bovine Serum Albumin (BSA) as a model protein was used in the studies, due to the low cost and a good knowledge of its properties [8]. Studies by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ions mass spectrometry (ToF-SIMS) are reported in this issue [9].

2. Cleaning methods

Cleaning methods have to be adopted in large power stations as well as in the other smaller industrial cooling circuits suffering from biofouling settlement, mainly including physical screening, physical cleaning other than chemical dosing [1].

The mechanical cleaning of the equipment and a water filtration (by rotating filters and mussels filters) are the most commonly used processes. They include the continuous cleaning of the condensers tubes by solid balls or brushes, manual cleaning, use of trash rakes, filters with meshes of different widths.

Physical methods can be regularly used for the anti-fouling treatment in cooling systems with an appropriate design, consisting mainly of:

- maintenance of velocities high enough to avoid the fixation of organisms (velocity $> 2 \text{ m s}^{-1}$);
- temperature increase: raising the temperature of the cooling water (40 °C for a few hours).

Many plants are provided with a continuous cleaning system based on the circulation into the condenser tubes of balls made of spongy rubber, having the same density of water and a diameter slightly larger than the bore of the condenser tubes. This type of treatment often is associated synergistically to chemical treatment. It is particularly effective for the prevention of microfouling, and it is one of the recommendable methods as BAT for cooling water circuits.

3. Chlorination

The most common biocide for chemical anti-biofouling treatments used in the industrial waters is chlorination. The term “chlorination” is often used inappropriately by the plants operators in referring to the dosage/production of other oxidant species than chlorine (or hypochlorite), as the alternative product chlorine dioxide.

Furthermore, in the case of seawater, where the concentration of bromide is naturally as high as 0.87 mM, the oxidative power of chlorine dosed is quickly transferred to bromide, with the equilibrium of the reaction (1) fast moving on the right, converting the “chlorination” in a “bromination”.



The by-products formed from the reaction of chlorine with ammonia group are showed in the reactions (2–6). Stoichiometric ratios of reactions 1–6 depend on temperature, reaction time, the pH and the initial ratio of reactants [10,11].

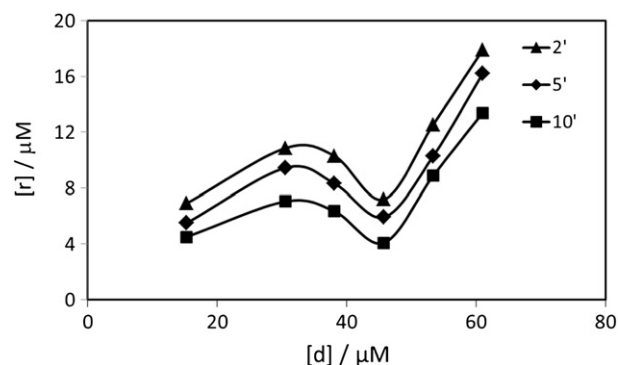
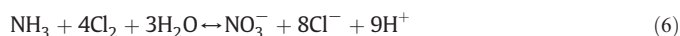
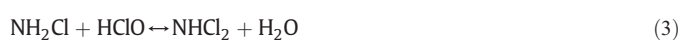


Fig. 1. Residual oxidant [R] as function of chlorine dosage [D] at different contact times (2, 5, 10 min) in seawater sampled from the cooling circuit of a power plant in Italy (Adriatic sea).



Finally, the chlorine (like all other strong oxidants), reacts with a large amount of other compounds, both organic and inorganic (reducing agents such as hydrogen sulfide, ferrous ions, manganous ions, and nitrite ions). These reactions constitute the “chlorine demand” of water (the difference of concentration dosed and the residual oxidant measured after a fixed time, expressed as Cl_2). Due to the high content of biological organics (especially during the summer time), which forms ammonia groups after the degradation of proteins, the chlorine demand of seawater is normally able to exhaust in few minutes almost completely the dosed active chlorine, that usually is less than 50 μM ($1\text{--}3 \text{ mg l}^{-1}$). The typical degradation trends are shown in Fig. 1, where the increasing concentration of dosed chlorine (d) at abscissas and the corresponding trends of residual oxidant concentration (r) at ordinates are presented. The percentages of consumed chlorine are reported in Table 1. The percentage of consumed chlorine in the case of distilled water (control) added with the lower chlorine concentration of 15.25 μM , is also reported in Table 1 for comparison.

The data of Fig. 1 and Table 1 refer to the residual oxidant concentrations of chlorine (free and combined with ammonia) at 24 °C, measured after different times (2, 5 and 10 min) from the addition of different sodium hypochlorite concentrations. Seawater was sampled at the inlet of a cooling circuit before any chemical treatment.

The colorimetric method based on the reaction of the oxidant compound with DPD (N,N-diethyl-p-phenylendiamine) measuring the total oxidant concentration (TRO) according to ISO 7393-2 standard was used for measurements. The sensitivity to concentrations as low as 0.4 μM (0.03 mg l^{-1}), with a pink coloring visible for human eye, make this method the widely used standard, friendly for not skilled plant operators as well.

The maximum % of chlorine decay achieved when the chlorine dosage was increased at 45.76 μM (3.25 mg l^{-1}) is the typical “Break-point” [10] due to the oxidation of chloramines (reactions 3–4) suddenly formed after the chlorine dosage in presence of nitrogenous compounds (reaction (2)). After the “Break-point”, where the value depends on the concentration of inorganic

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