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The study of marine corrosion of copper alloys in chlorinated condenser cooling circuits: The role of microbiological components

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ABSTRACT

The present paper reports the on-line monitoring of corrosion behavior of the CuNi 70:30 and Al brass alloys exposed to seawater and complementary offline microbiological analyses.

An electrochemical equipment with sensors specifically set for industrial application and suitable to estimate the corrosion (by linear polarization resistance technique), the biofilm growth (by the BIOX electrochemical probe), the chlorination treatment and other physical-chemical parameters of the water has been used for the on-line monitoring.

In order to identify and better characterize the bacteria community present on copper alloys, tube samples were collected after a long period (1 year) and short period (2 days) of exposition to treated natural seawater (TNSW) and natural seawater (NSW).

From the collected samples, molecular techniques such as DNA extraction, polymerase chain reaction (PCR), denaturing gradient gel electrophoresis (DGGE) and identification by sequencing were performed to better characterize and identify the microbial biodiversity present in the samples.

The monitoring data confirmed the significant role played by biofouling deposition against the passivity of these Cu alloys in seawater and the positive influence of antifouling treatments based on low level dosages.

Molecular analysis indicated biodiversity with the presence of *Marinobacter*, *Alteromonas* and *Pseudomonas* species.

1. Introduction

Due to their corrosion resistance, mechanical ductility, excellent electrical and thermal conductivity, copper alloys are used extensively as condenser and heat exchanger tubing materials in power plants [1,2]. Nevertheless, Cu alloys when immersed in seawater are quickly covered by colonies of bacteria which, unlike macrofouling organisms, are not affected by the toxicity of copper, since these are protected by a mucopolysaccharide matrix [3].

Microbial communities (biofilm) rapidly colonize and strongly adhere to metal surfaces that are in contact with seawater together with other organic matter dispersed and adsorbed, corrosion products, algae and other microorganisms, resulting in a big complex microfouling [4].

Concentration under biofilms of chloride or other aggressive anions and corrosive active compounds/environments produced by microorganisms, such as reduced pH, dissolved CO_2, organic acids, anaerobic sulfide and acidic polysaccharides can lead to disruption of passive layer that would otherwise protect the metal surface [5].

Secreted by biofilm, extracellular polymeric substances (EPS), e.g. copper binding proteins [6], can accelerate corrosion of copper and copper alloys. EPS acts as binding agents for copper ions that otherwise inhibit microbial growth.

Biofilm, therefore, can modify the electrochemical characteristics of metals surface [7,8] and cause physical degradation/deterioration called microbiologically influenced corrosion (MIC) or bio-corrosion [9].

MIC is associated to loss of production, damage in expensive equipment and increased maintenance costs in power plants.

From a review conducted in Italian power plants [10] and from other recent inquiries results indicate that more than 50% of the corrosion cases of the condenser tubes might be prevented keeping the equipment in good clean conditions during the plant operation.

Recommended industrial practices suggest treating the condenser tubes with cool and chlorinated water for some weeks before the first start of operation, while during the regular operation it is committed to use in the cooling circuits an efficient antifouling treatment.

Recent studies [11] confirmed the recommendations documenting that microbial activity affects negatively both the formation and the stability of protective layer on Cu based alloys (the traditional materials for the tubing of condenser of power plants that use seawater as coolant). In the last years, the detection of many failure events in condensers

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drove the achievement of experimental monitoring setup regarding these phenomena.

For this purpose measurements were carried out in on-plant circuits, by using electrochemical tools (a biofilm sensor named BIOX and a corrosion probe, both described in the following chapters) that were successfully tested in several previous experiments with different characterized environments and industrial sites [12,13].

Some species of *Pseudomonas, Sphingomonas, Pseudomonas paucimobilis, Rhodotorula, Flavobacterium, Acidovorax delafieldii, Cytophaga johnsonae, Micrococcus kristinae, Acidovorax* and *Sphingomonas* have been identified in biofilms that cause MIC in copper pipes [14–17].

In order to identify and better characterize the bacteria community present in the metal tubes, CuNi 70:30 (70% Cu, 30%Ni) and Al brass samples (76% Cu, 22% Zn and 2% Al) were collected after a long period (1 year) and short period (2 days) of exposition to natural treated seawater (NTSW) and natural seawater (NSW), molecular techniques including DNA extraction, PCR of 16S rRNA gene and DGGE and sequencing were used.

2. Materials and methods

2.1. Monitoring system

A monitoring system was set up in a cooling circuit bypass of a marine power plant located on the Tyrrhenian Italian coast in order to monitor the corrosion (by linear polarization resistance [LPR] technique), the biofilm growth (by the BIOX electrochemical probe described below), the antifouling (biocide) treatment and other electrochemical and physical-chemical parameters of the seawater. Industrial equipment with sensors specifically set for industrial application was used [11] (Fig. 1).

This bypass was set in order to study two different conditions: the natural seawater (NSW), collected before the antifouling treatment of condenser, and the seawater exiting the condenser and treated by biocide (TNSW).

The regular antifouling treatment carried out in this plant uses intermittent dosages of 1–2 mg/l of a commercial product based on sodium hypochlorite, in order to have a total residual oxidant concentration of 0.4–0.8 mg/l in the water exiting the condenser. The dosing occurs every 6 h, each lasting 0.5 h–1 h, depending on the season.

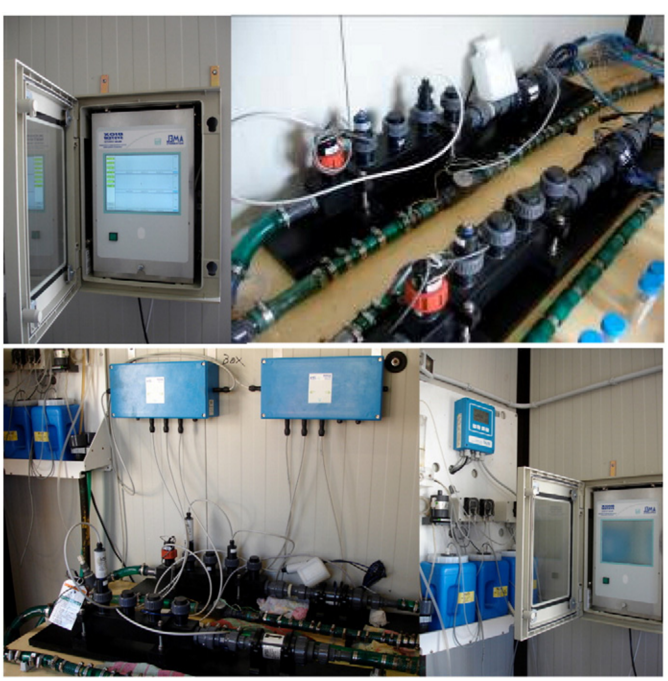

Fig. 1. Probes of the electrochemical integrated monitoring system installed in a power plant (BIOX probe in the frame).

2.1.1. Biofilm growth (BIOX probe)

The signal is provided by the electrochemical sensor named BIOX, a bio-battery made by a stainless steel and Zn electrodes connected by a high value resistance [13]. It reveals the biofilm presence starting from a very little biofilm amount developed on a few percent of the whole electrode surface. When bacteria density on the surface reaches a value near to 10^7 b/cm^2 (counting the cells in SEM micrographs) the electrical signal goes on saturation (around 1.2 mV), corresponding to a signal increase of more than 0.5 V from the base value [12].

2.1.2. Antifouling treatments

The antifouling treatments are monitored with the electrochemical probe BIOX, its cathode (stainless steel) being sensitive to the effect of strong oxidants, as well as to the effect of the biofilm growth. The oxidant species (chlorine, bromine, chlorine dioxide, peracetic acid, hydrogen peroxide and others biocides) act as additional cathodic processes in the electrochemical probe, increasing the galvanic current circulating as biofilm [13].

Oxidant detection is fast, while biofilm response is quite long, due to the long time (days) required for bacteria to colonize the complete surface of the electrodes [10,11].

The residual oxidant into the water bulk is measured by a colorimetric device using DPD (*N,N*-diethyl-*p*-phenylendiamine) method (according to ISO 7393-2). The comeback of the two on-line systems, BIOX and the colorimetric instrument, results in a good agreement.

2.1.3. Corrosion rate

The corrosion rate is estimated by a linear polarization resistance (LPR) probe that uses the electrochemical configuration of the cell with 5 tubular electrodes designed to maintain a symmetric circulation of the polarization current, keeping the working electrodes in the same conditions (flow rate and geometry) as the real operating condenser tubes [10]. The probe is in agreement with the ASTM G96-90(2001)-mode B and ASTM G102-89(1999). The software calculates the corrosion rate (V_{cor}) expressed in μm/year (Eq. (1)) using the correlation factor $B = 250$ as experimentally determined comparing the integral of the inverse of polarization resistance (R_p) vs. time and the weight loss of the same electrode during many trials.

$$V_{cor}(\mu m/year) = \frac{B}{R_p(k\Omega) \cdot Surface(cm^2)} \quad (1)$$

2.1.4. Other parameters

Other physical–chemical parameters of the water: flow rate, temperature, turbidity, corrosion potential of interested material and seawater redox potential are also measured by using industrial on-line sensors.

2.2. Molecular biology

2.2.1. DNA extraction

Biofilm from CuNi 70:30 and Al brass samples was collected by transferring the samples to sterile Petri dishes and rinsed with 0.9% NaCl. The rinsed-off solution was collected in sterile 1.5 ml Eppendorf tubes and centrifuged for 5 min at 13,000 ×g (Heraeus Fresco 21, Thermo Scientific, UK). Supernatant was discarded and total DNA was isolated with the PowerBiofilmTM DNA isolation kit (Mo BIO Laboratories, UK) according to the manufacturer's instructions.

The kit uses a bead beating technique and incubation at 65 °C for 5 min in aiding to breakdown biofilm extracellular polymeric substance matrix.