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EXPERIENCES OF ON-LINE MONITORING OF MICROBIAL CORROSION AND ANTIFOULING ON COPPER ALLOYS CONDENSER TUBES

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ABSTRACT

In spite the toxic effect of Cu, copper alloys are notably exposed to microbial corrosion in condensers of marine power plants circulating sea water rich with mud, the typical condition of portual areas. The mud incoming occurs especially in consequence of storms and adverse climate conditions. Intermittent chlorination is the widest employed treatment for the prevention of biofilm in cooling circuits of industrial plants.

In recent years, the detection of many failure events in condensers drove the experimental monitoring setup regarding these phenomena.

The present paper reports the on-line monitoring of corrosion behavior of the CuNi 70/30 alloys during the first year of operation in two different test lines: with and without chlorination treatment. The results confirm that chlorination treatments promoted the formation of a protective layer on Cu based alloys, decreasing the corrosion rate to acceptable values less than 5 µm/y.

An innovative electrochemical, integrated equipment, with wireless sensors specifically set for industrial application and suitable to monitor 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.

Keywords: Biofilm; Chlorination; Copper alloys, CuNi 70/30; Condenser tubes; on-line monitoring, corrosion monitoring, antifouling monitoring.

1. INTRODUCTION

Biofilm formation can cause problems in many branches of industry, such as in industrial water systems and process industries. It may cause energy losses and blockages in condenser tubes, cooling fill materials, water/wastewater circuits, heat exchange tubes and on ship hulls.

A power plant can loose more than 5% of its efficiency due to biological films and, at worst, the power units must be shut down if macrofouling plugs the tubes of condensers [1]. Up to 20% and more of all the corrosion damages of heat exchangers are generally attributed to microbial corrosion. From a survey conducted in Italian power plants, and from other recent inquiries, results that more than 50% of the corrosion cases of the condenser tubes might be prevented keeping the equipments in good clean conditions during the plant operation [1].

The corrosion behavior of condenser alloys is influenced by various parameters, including alloy composition, metallurgical effects, temperature, flow velocity, oxygen content and impurities in cooling water , type of chlorination treatments, the presence of filters and on-line mechanical cleaning systems, etc.

Typically, chlorine dosages (intermittent or continuous) are used to prevent biofouling. 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 [2] confirmed the recommendations, documenting that microbial activity negatively affects both the formation and the stability of protective oxide layers on Cu based alloys (the traditional materials for the tubing of condenser of power plants that use seawater as coolant). An important development of biofilm on CuNi 70/30 in the early stages of operation may induce localized corrosion so extensive as to require the replacement of tubes.

From thermodynamic point of view, the strong oxidant action of chlorine should promote corrosion of copper alloys [3, 4] but it exhibits a good range of safety with a threshold which guarantees the best benefit and avoids the possible negative effects. Although it must be considered the fact that the behavior of each material could result quite different.

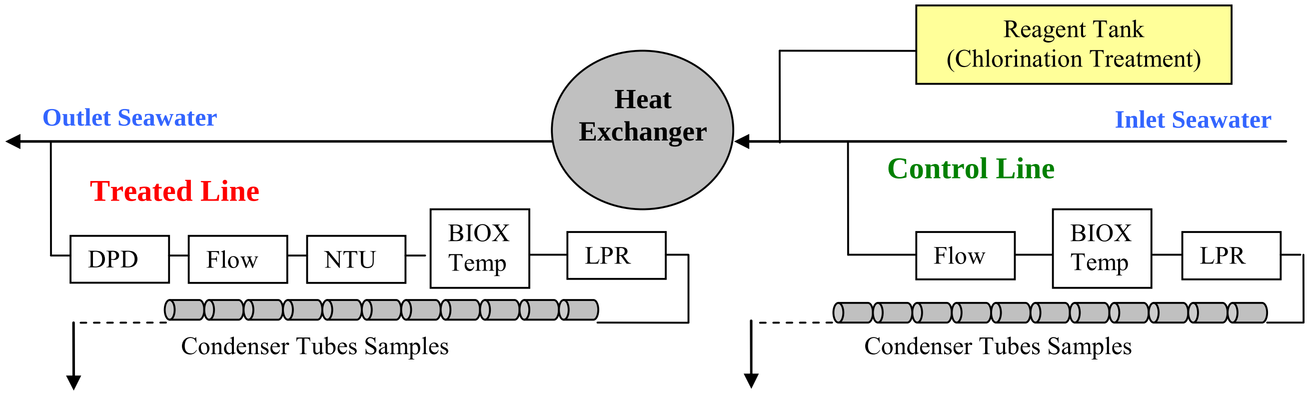

Figure 1: Schematic of the two hydraulic test lines (control and treated) in the cooling circuit bypass.

Despite the needs of chlorination, a special attention must be paid on the environmental concerns deriving from the possible formation of toxic chlorine by-products (alomethans) [5].

Indeed, following the discovery of the presence of by-products toxic for the environment and human health, the concentration of chlorine allowed to industrial discharge has been drastically reduced all over the world.

Sustainable treatments and a careful control of their effects (in terms of environmental impact as well as the performance of materials) are becoming now mandatory in the operational practice of industrial cooling circuits.

Accordingly with these needs, an integrated multi-parameter monitoring equipment, specifically set for industrial application, was set up and used in power plants to control the passivity of copper alloys and the effect of chlorination treatments in the formation and stabilization of these protective oxide layers.

The on-line monitoring of few electrochemical parameters results useful enough as early warning to help the plant operators of industrial cooling circuits in the optimization of chlorination treatment and to guarantee the efficiency/availability of the condenser tubes.

The monitoring approach of the integrated system and some relevant data related to CuNi 70/30 are presented and discussed in the present paper. chlorination treatments on condenser tubes. The results of the monitoring campaigns confirmed the relevant role of biofouling against the formation of protective oxide layers on the surfaces of copper alloys exposed to seawater and, vice-versa, the positive influence of chlorination treatments.

2. MATERIALS AND METHODS

An experimental circuit was installed in an Italian power plant, with the main objective of monitoring the corrosion behavior of Cu-Ni 70/30 alloys.

A bypass in the condenser (schematic in Figure 1) was set to study two different conditions: the outlet water from the condenser (treated line) and inlet seawater, before the chlorination treatment, with any kind of treatment (control line).

The integrated monitoring system

A laboratory assembled devices (first) and the commercial version of the monitor system (finally) was used to perform the test campaign in the power plant cooling circuit.

Rugged electrochemical tools (described in follow) are the key tools of the integrated hardware composing the monitoring system used, permitting the on-line control of:

- the corrosion rate (by a tubular probe using electrochemical LPR technique),
- the biofilm growth (by BIOX electrochemical probe),
- the chlorination treatment (by BIOX electrochemical probe and colorimetric device),
- the water temperature,
- the water flow,
- other physical-chemical parameters (turbidity and corrosion potential).

Fig 2 shows details of the commercial system used (AMEL, model 1310CU) operates with full wireless set of probes, in remote control (via GSM modem).

The wireless modality is very useful where the electrical supply is not available and the environmental conditions result extreme for electronic components, as usual in many parts of industrial cooling circuits. Furthermore, the remote control permits to supervise several plants in simultaneous with a single workstation.

Specific software allows the on-line visualization and storage of the measurements, giving a continuous adjourned trend of the parameters.

Some specimens cut from the operated condenser tubes complete the hydraulic test line, so to make possible periodic visual observation, weight loss determination and other off line specific analyses.

Figure 2: a) View inside of the experimental circuit box (b) the computer display and (c) two hydraulic lines (Control and Treated) with CuNi 70/30 specimens and probes.

Electrochemical tools

The corrosion rate is estimated by a Linear Polarisation Technique (LPR) probe that uses the electrochemical configuration of the cell with 5 tubular electrodes shown in Figure 3. The electrochemical cell is built using five specimens cut from a condenser tube. The cell is in agreement with the ASTM G96-90(2001)-mode B and ASTM G102-89(1999) standards and it is designed to maintain a symmetric circulation of the polarization current, keeping the working electrodes in the same conditions (flow rate ad geometry) of real operating condenser tubes.

The software calculates the corrosion rates expressed in µm/year using a correlation factor between the electrochemical data and the weight losses determined experimentally (comparing the integral of the inverse of polarization resistance (Rp) vs. time and the weight loss of the same electrode). The variation of such a factor, using different specimens for increasing exposition times to seawater, is less of 20% (based on the experience of several previous campaigns), negligible for practical purposes.

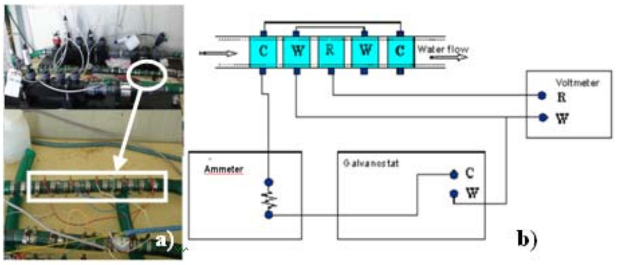

Figure 3: a) Electrochemical cell; b) schematic representative of Linear Polarization Resistance Technique (LPR).

The biofilm growth is valuated by the specific electrochemical probe BIOX [7], consisting in a special tubular electrochemical "battery" (Fig. 4) whose current density increases when the biofilm colonizes its stainless steel cathode. The biofilm growing on the BIOX probe surface changes the electrochemical characteristics at the metal-biofilm interface accelerating the cathodic discharges of oxygen. The electrochemical sensors show a very high sensitivity to the biofilm growth during the early phase of its development. The signal provided by the electrochemical sensor reveals the biofilm presence starting from a very little biofilm amount developed on a few percent of the whole electrode surface. When bacteria density reaches a value close to 10^7 bacteria/cm^2, the electrical signal goes in saturation, corresponding to a signal increase of more than 0.5 V from the base value.

Industrial BIOX systems completed of dedicated computer, flow meter and temperature meter are operating since 1990 in many thermal power stations to optimize antifouling treatments [8].

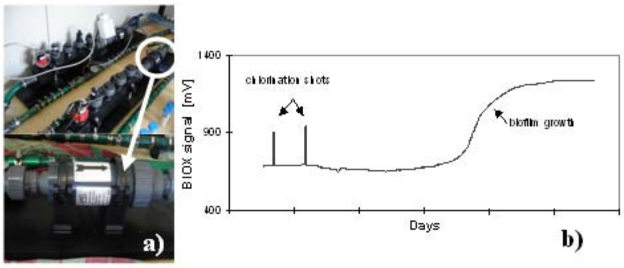

Figure 4: a) BIOX system b) typical trend of BIOX signal (chlorine dosages and biofilm growth).

The chlorination treatment of condenser is monitored in two ways: roughly, with the electrochemical probe BIOX, being its cathode sensitive to the cathodic effect of strong oxidants, as well as to the cathodic effect of the biofilm growth [8].

The oxidant species (chlorine, bromine, chlorine dioxide, peracetic acid, hydrogen peroxide and others biocides) act as additional cathodic processes, increasing the galvanic current circulating in the electrochemical probe, like the biofilm.

Oxidant detection is rapid while biofilm response is quite long, because the long time required for bacteria to colonize the complete surface of the electrodes.

Under regular operational conditions, the BIOX software permits to distinguish in a simply way the contribution of both phenomena, by viewing the probe output responses with respect to time.

The sensitivity of BIOX to the oxidant is limited to the concentration able to diffuse on the electrode surface, depending of the cleaning condition of the probe so, in order to measure also the concentration of the oxidant into the water bulk, a colorimetric device was added to the monitoring probe set. That system (AMI Codes of SWAN, [9]), is based on DPD (N, N-diethyl-p–phenylendiamine) method (according to ISO 7393-2). In Fig. 5 it is reported a trend of BIOX signal compared to that of a colorimetric instrumentation. Roughly, in the range of 0.1 – 1 mg/l of total residual oxidant in the water, the response of the two on-line instrumentation results in a good agreement.

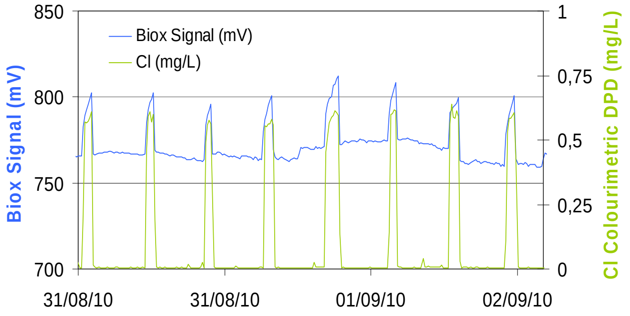

Figure 5: BIOX signal trends and the residual oxidant concentration in seawater measured with the on-line instrumentation based on DPD colorimetric method.

Other physical-chemical parameters of the water: turbidity and temperature are also measured. Turbidity increases as a result of suspended solids in the water that reduce the transmission of light (suspended solids ranges from clay, silt, and plankton). A nephelometer measures the intensity of light scattered by suspended solids, in the range of 0-100 Nephelometric Turbidity Units (NTU), with a sensitivity of 0.2 NTU. A temperature electronic sensor as well as a nephelometer probe is integrated in the same instrumentation (produced by AMEL, Fig. 2).

Materials: some specimens of the same CuNi 70/30 alloy, cut from new and operated condenser tubes, were inserted in the test lines. The chemical and physical-chemical characteristics of condenser tubes are reported in Table 1.

Table 1: Composition, heat exchange coefficient and density of CuNi 70/30 condenser tubes.

Alloy	Chemical analyses (%)						
Cu/Ni 70/30	Cu	Zn	Ni	Al	As	Fe	Mn
	68.5	-	30	-	-	0.7	0.8
	Heat exchange coefficient (cal·cm·cm-2s-1C-1)					**Density (g/cm3)**	
	0.07					8.8	

Operating conditions

The cooling circuit of the plant is affected by significant daily/weekly influxes of slime and mud, which caused extensive microfouling accumulation in the tubes that cannot be mitigated by the operating mechanical filters (sited before the condenser).

A regular antifouling treatment is carried out, using intermittent dosages 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 hours, each lasting 0.5-1 hours, depending on the season.

3. RESULTS OF THE MONITORING CAMPAIGNS

The experimental data of the integrated monitoring conducted on several specimens of a CuNi 70/30 condenser tube of power plants confirmed the relevant role played by biofouling deposition against the passivation of the CuNi 70/30 alloy in seawater and the positive influence of chlorination treatments based on short, intermittent and low level dosages.

The chlorination treatment applied regularly since the beginning of the condenser operation resulted effective enough and the corrosion was reduced to negligible values, under 5 µm/y (by monthly weight loss) after about one month of the exposition to seawater.

The monitoring of corrosion rate highlights the occurrence of significant and frequent peaks in the corrosion rate of the specimen in the unchlorinated line, and a quite constant and low value of corrosion rate of the chlorinated ones. Long time monitoring trends were already reported in detail in a previous work [2].

The figure 6 shows data of a short period of monitoring of new specimens at the beginning of their exposition at seawater in both the test lines, when a new and first biofilm layer start to growth on all the surfaces of the unchlorinated line. The graph underlines the occurrence of high values of corrosion rate (CR) of the unchlorinated specimens. The corrosion monitored by the LPR probe was in agreement with the high weight losses calculated.

The trend and the variability of the BIOX signal peaks in the figure 6 documents how it is difficult to maintain a constant concentration of residual oxidant into the water and to get a total control of biofilm activity, in spite of the constant dosing of the chlorine. Indeed, the chlorine demand of the water (mainly due to its reactions with the organics dissolved into the water) can change during the same day also, and this fact is one of the causes that can justify the variability of the oxidant concentration that reaches the metal electrode of the BIOX probe.

The graphs in fig. 7 underline the weak, but detectable noise on the corrosion rate trend in coincidence with the dosages of chlorine. The peaks, due to chlorination, do not influence significantly the weigh loss of specimens, indeed, the corrosion resulted systematically less than 5 µm/y.

The quite stable base line value of BIOX signal around 650-700 mV confirmed that chlorination treatment was enough to strictly control the biofilm growth. During the winter month of February, a small increase of the BIOX signal was detected in correspondence with two important monitored parameters: increase of the incoming slime (detected by the Nephelometer) and temperature enhance (Fig. 8).

It is also visible the occurrence of significant and frequent peaks in the corrosion rate of the specimens in the control line, contrasting with the relatively constant corrosion rate of the treated one.

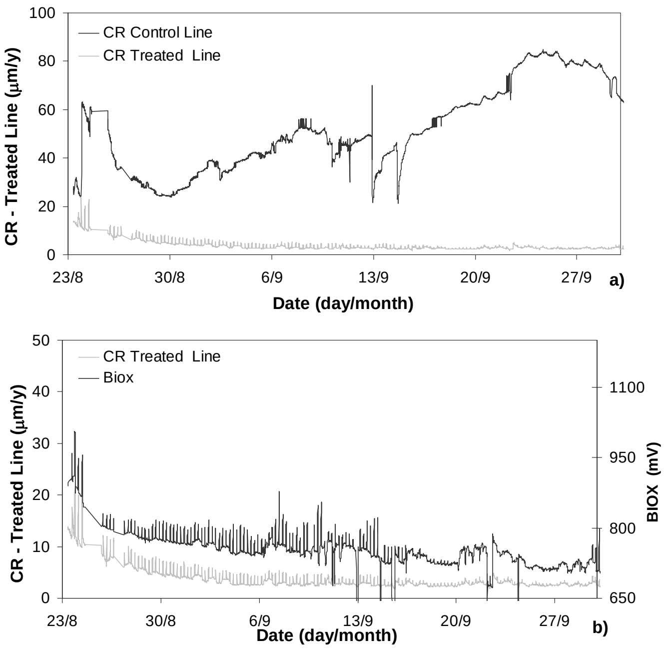

Figure 6: a) Corrosion Rate (CR) of CuNi 70/30 exposed to the chlorination treatment (Treated Line) and non-chlorinated (control Line) in the period August-September b) BIOX signal (right side scale) and corrosion rate (left side scale).

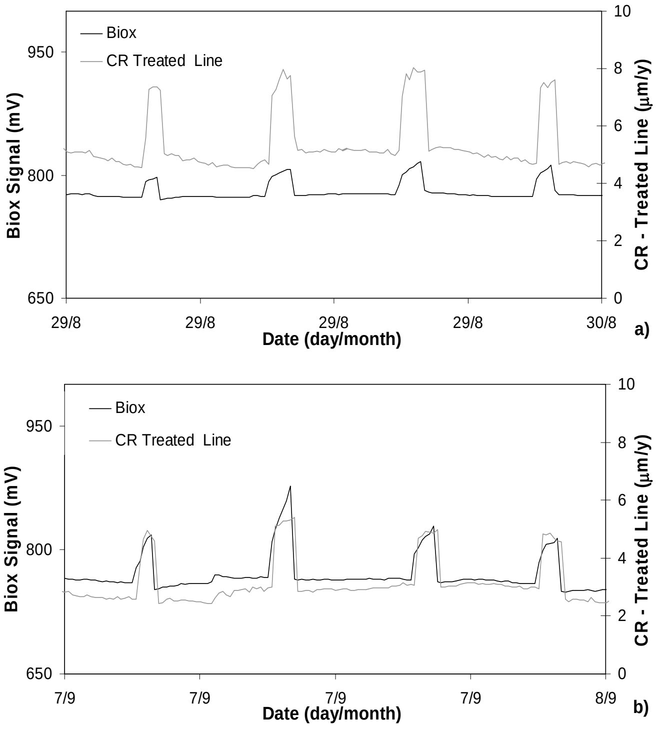

Figure 7: BIOX signal and Corrosion Rate (CR) of CuNi 70/30 during daily chlorination treatments for a) August, b) September.

In Fig. 9 is exposed the corrosion behavior during the first weeks of March. It shows a significantly and quickly increase of the corrosion rate, above 10 µm/y base line, besides the antifouling treatment in the treated line. Gravimetric determinations confirmed the electrochemical data.

In coincidence with this phenomenon, the test line became fouled, and the BIOX probe indicated biofilm growth.

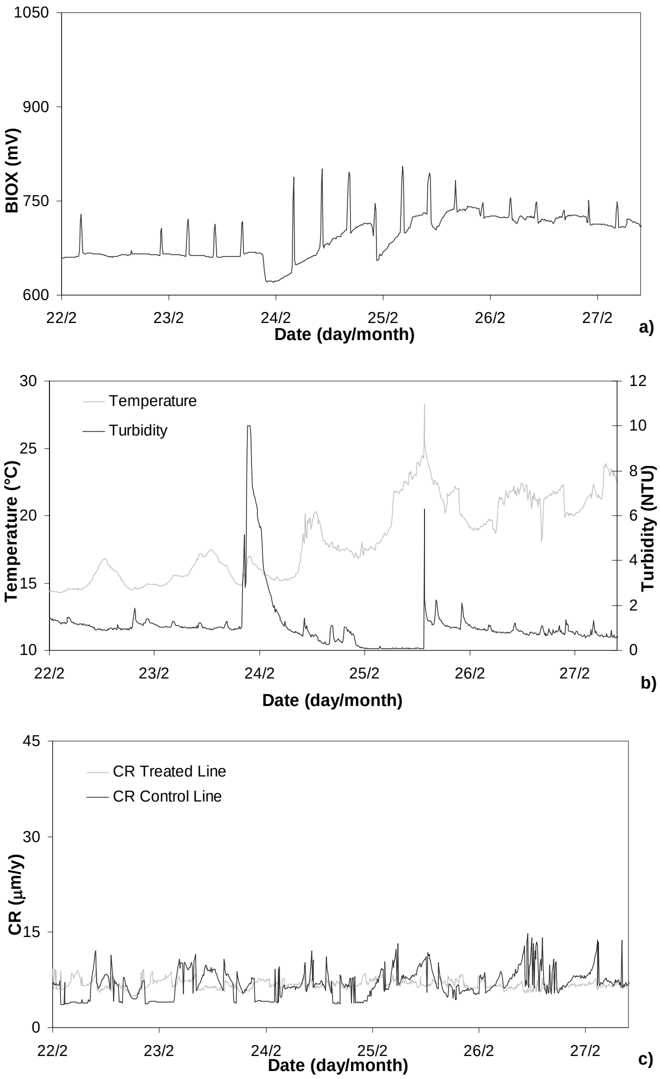

Figure 8: CuNi 70/30 samples: a) BIOX signal, b) temperature and turbidity, c) Corrosion Rate in the two test lines: chlorinated line (treated line) and non-chlorinated (control line).

This phenomenon can be explained by the inspected and drastic decay of the seawater velocity from 1.8 ms^{-1} to 0.08 ms^{-1}. The biofilm is particularly aggressive and grows very rapidly in so low flow conditions. In stagnant waters or at very low flows, the oxygen could be quickly consumed by biofilm and anoxic conditions (partial or total absence of oxygen) occur. The pH lowers and local conditions become particularly aggressive, which can bring more quickly, puncture the tubes.

The BIOX signal is not showing anymore the chlorination treatments, because, with the low and/or absent flow the treatment is not adequate and there is no enough contact time between seawater and the metal tube.

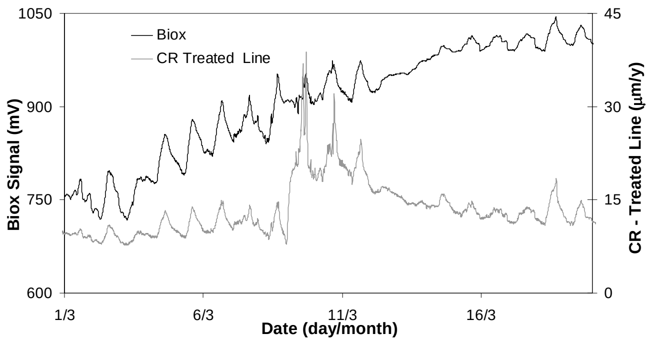

Figure 9: Effect of the decrease of flow velocity (1,8 ms^{-1} to 0,08 ms^{-1}) on the BIOX signal and Corrosion Rate (compare these values with Fig. 8a and 8c).

5. CONCLUSIONS

The study conducted underlined the importance of to perform a correct chlorination treatment of seawater operating with CuNi 70/30 copper alloys condenser tubes, in order to prevent corrosion.

An integrated, on-line system based on few electrochemical probes (BIOX + corrosimeter based on LPR technique) demonstrated to be sufficient to monitor in real time: corrosion, biofilm growth and chlorination treatment, helping the plant operators of industrial cooling circuits to guarantee the efficiency and availability of the condenser.

6. ACKNOWLEDGEMENTS

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