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Solutions to fouling in power station condensers

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Abstract

The chlorine use was banned in the Italian Lagoon of Venice, as a consequence, alternative antifouling treatments had to be tested, optimised and, finally, adopted. Now, chlorine dioxide is in use in many plants instead of sodium hypochlorite. Peracetic acid (as antislime) and ammonium quaternary salts (as mollusch-icide) are also employed in some cases. The treatments are often combined with in-service mechanical cleaning, reducing significantly their cost. The dosage of the alternative oxidant products, now in use, has been optimised by the electrochemical monitoring system BIOX.

As requested by Italian regulation, toxicity tests were performed and passed successfully before the adoption of each new treatment.

Furthermore, new type of treatments, based on electrochemical low production of oxidant, were also preliminary tested, without significant production of trihalomethanes. The present paper illustrates some detail about the new treatments.

Keywords: Condenser; Biological fouling; Antifouling treatments; Biofilm monitoring; Chlorine dioxide; Mechanical cleaning

1. Introduction

Fouling is a very important problem for condensers and heat exchangers. All industrial circuits cooled with natural fresh and marine water are affected by the phenomenon of biological fouling

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consisting in biofilm growth and settlements of several kinds of living organisms. Biofouling is detrimental to open cooling systems as it causes undesirable effects, such as efficiency loss inside the heat exchanger, clogging of the seawater circuit pipes and reduction in plant reliability over a period of time [1].

Most of the power generation plants efficiently operate by using the basic tools of physical screening, physical cleaning and chemical dosing [2]. A traditional chemical way to control microbial growth and biofouling in power plants remains the use of chlorine, in spite of the fact that chlorination was subjected to the environmental authorities attention for more than 20 years, because of its halomethanes and other organohalogens by-products items [3].

Presently, low level of halogenated by-products is an accepted trade-off ensuring the bacteriological control in drinking waters, waste waters and recycled waters. However, alternative chemical products, as chlorine dioxide and peracetic acid, are replacing chlorine by water supply companies. Now the pressure to reduce chlorine use is particularly focalised on the cooling waters, mainly because of the large quantity of water which can be discharged to different type of water bodies also used for drinking.

European countries have introduced several measures to reduce the discharge of organochlorines into the aquatic environment (such as the new Biocidal Product Directive, 98/8/CE), but the possibility to use controlled chlorination for antifouling treatments of the cooling circuits remains, with some local exceptions only.

High chlorine concentration (1–10 mg/l), used in the past for most effective cooling water biocide treatments causes the development of significant concentration of toxic by-products in the industrial circuits and in the receiving water after the discharge in case of release of free oxidant halogens [4]. Efficient low-level chlorination treatments, suitable for biofilm of the condensers as well as against macrofouling settlement, must be regularly applied avoiding interruption and modifying the treatment in function of the chlorine demand of the water [5].

As a consequence of the difficulty to drive a correct treatment, chlorination is usually supported in several way to physic, mechanical and hydrodynamic cleaning of condenser tubes out of service [6]. The frequency of these cleanings strongly depends on effectiveness of the chemical treatment applied.

Finally, widely applied chlorine discharge restrictions (in the Italian regions the maximum allowed is 0.2 mg/l or less, measured as total residual oxidant) make these requirements a key to achieve clean conditions for cooling circuits and emphasises the important role of treatment monitoring.

Furthermore, in the Italian Venice lagoon, exceptionally, the chlorine use was completely banned since 2000; as a consequence, the plants that were using effective chlorination as antifouling for condensers cooling circuits in that sites had to choose an alternative treatment. Details about the new solutions and the monitoring methods utilised to test and optimise these solutions for power plants have been reported in this paper.

2. Selected alternatives to conventional chlorination

The main trouble of alternative chemicals to chlorination in power plants is basically the cost of products proposed from the market: each one roughly costs one order of magnitude (minimum) more than sodium hypochlorite.

Because of the high cost of continuous dosage, the strategy was to set up new "prescriptions" based on the intermittent chemical dosing. Some chemical products were selected and their use was combined, wherever possible, with the in-service mechanical cleaning, with the aim to minimise the quantity of required biocide.

The steps to reach the new treatments for each plant considered were:

- individuation of the critical biofouling stages in the plant;
- check of the efficiency reachable by different treatments, chemical and mechanical, against the individuated critical biofouling stages;
- define the proper antifouling strategy against the individuated and monitored critical biofouling stages for each plant.

The effectiveness of each new treatment, as cleaning and good performance of cooling systems, was proved by the following main tools: the response of the electrochemical biofilm monitoring system BIOX; the operational parameters of condensers; inspection of plant components; specific supports for macrofouling.

Following this approach, some combined mechanical/chemical treatments were arranged and, after successful experimentation, finally adopted by different power plants in the Venice lagoon. The treatments and products taken into account have been in-service mechanical cleaning, chlorine dioxide, ammonium quaternary salts, and peracetic acid.

Some acute toxicity tests were performed sampling the water at the discharge during the dosages of the chemical products. The response of commercial "Microtox" system based on luminescent bacterium *Vibrio fischeri* [7] and the high number of survived marine crustacea *Artemia franciscana* (microbiotest Artotoxkit, Creasel) confirmed the absence of acute toxicity on the tested organisms correlated to the new treatments.

3. In-service mechanical cleaning (ISMC)

In-service mechanical cleaning consists in a re-circulation of sponge balls into the condenser tube. Usually, the sponge balls are pushed into the cooling water immediately upstream the inlet condenser shell: after their flow through the tubes, they are captured by special filters inserted after the outlet condenser shell [8]. Some plants use this cleaning system in continuous, whilst many others prefer to use it few times a week or sometimes, particularly if significant corrosion attacks affect the condensers tubes. In these last cases, as well as in all the cases in which the plants have not and cannot be equipped with mechanical cleaning, a chemical solution was necessary to achieve an effective control of biofilm in the condensers and against the biofouling in the cooling canals.

Chlorine dioxide turned out to be the only chemical alternative whose effectiveness, toxicology and environment compatibility of industrial application in marine cooling circuit were well known [9]; for this main reasons it was chosen firstly.

Chlorine dioxide has excellent bactericidal, virucidal, sporicidal and algicidal properties, so that it is used to disinfect water and inhibit the growth of algae too.

In cooling waters characteristic range of pH (6–8.5), chlorine dioxide remains in solution as dissolved gas, unable to react with bromides to form bromine, unlike ozone, chlorine, and hypochlorite.

Furthermore, it does not favour addition and substitution reactions (and, therefore, chlorination reactions) with organic matter and, consequently, it does not form halomethanes by-products. The analytical tests performed at the discharge during some dosages in the cooling circuit of a plant confirmed the absence of this compound in the water under the measurable limit of 0.1 μg/l.

Peracetic acid is a common disinfectant formulated for the control of harmful micro-organisms in raw sewage and sewage effluent [10]. In the commercial formulation, it is an equilibrium mixture of peracetic acid, hydrogen peroxide, acetic acid and water. In surface water, peracetic acid is hydrolysed. The degradation products formed by its hydrolysis are acetic acid and hydrogen peroxide, both of which are easily biodegradable substances and, of course, it does not have halomethanes by-products. This product boasts industrial applications in disinfection of fresh or waste waters, but it was not sufficiently tested in marine water. For this reason, some experimentation was carried out to check its ability against marine biofilm affecting the condensers in plants on the Venetian lagoon and, after the successful experimentation, it was adopted for some specific application.

Ammonium quaternary salts (QUAT) turned out to be a useful molluschicide that can be adopted where the only biofouling problem for the power plant are mussel settlements in the cooling canal. In this case, a successful treatment based on ammonium quaternary salts dosed in concentration of about 3–6 mg/l for few days some time during the year was adopted.

4. Biofouling monitoring

The traditional approach to estimate fouling in condenser tubes consist in calculating the heat exchange by the values of the condenser back-pressure, cooling water flow rate, temperature and other plant parameters; seldom, fouling is measured by using separate instrumentation installed in a by-pass circuit or inside the condensers.

The estimation of biofilm growth in the condenser tubes by plant parameters is not simple, mainly because of the high number of involved variables affecting thermal exchange.

A significant bad condensers back-pressure is often associated to biofouling in the tubes only when the biofilm is stabilised. As a consequence, new methods to monitor the first phase of biofilm growth were set up and experimented during these last years. The electrochemical sensors showed a very high sensitivity to the first stage of biofilm growth [11] and a specific system named BIOX has been implemented for Italian power plants to monitor oxidant treatments of cooling circuits. The BIOX system is presently employed in several Italian power plants to monitor chlorination [12] and it was also used to optimise the alternative antifouling treatments for condensers of power plants in Venice lagoon.

The system BIOX is a monitoring equipment capable to control biofilm growth and oxidant antifouling treatments of cooling waters [13]. It consists of a tubular electrochemical probe associated with a specific hardware/software to a computer. In power plant the system is normally installed close to the condenser.

The probe is suitable for the on-line monitoring of several kinds of oxidant treatments of condenser cooling waters (as treatments with peracetic acid, hydrogen peroxide, chlorination, brominations and so on). A temperature sensor and a flow-meter completed the framework of the information achieving by the system. The electrochemical BIOX probe is sensitive to the changes of the cathodic electrochemical processes occurring at the interface between the water and its working electrode. The main cathodic process being the acceleration of cathodic reaction of oxygen discharge due to the aerobic bacteria of the biofilm growing on the probe surface and the cathodic discharge of the oxidant species (biocides) present in the water. System baseline value varies as a function of water characteristics and probe setting; in sea waters it is typically 500–700 mV.

The presence of oxidant species produces an almost linear probe output variation of about 500 mV from the baseline, in a range of concentration depending of the chemical species. Its sensitivity was verified in the range of 0.2–2 mg/l for chlorine, 0.1–1 mg/l for chlorine dioxide and 1–10 mg/l for peracetic acid.

Oxidant detection is fast, while biofilm growth response time is quite long. The latter is due to the time required for bacteria to colonise the complete surface of the electrodes. Therefore, under

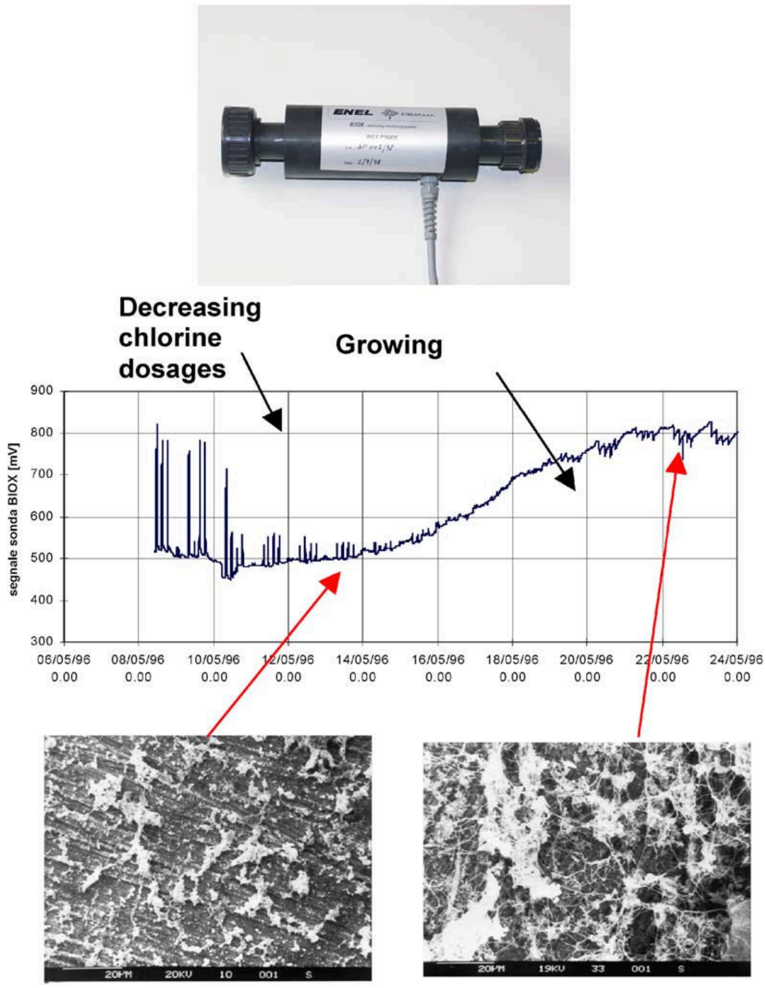

Fig. 1. BIOX probe (upon) and BIOX system output corresponding to chlorine dosages (peaks) decreasing in concentration proportionally with the high of the peaks and two different stage of biofilm growth documented by two SEM microscopy micrographs (in [13,6]).

regular operational conditions, it is possible to distinguish the contribution of both phenomena when viewing the probe output responses with respect to time (Fig. 1).

5. Monitoring of combined mechanical and chemical treatments

In one of the plant in the Venice lagoon having the mechanical in-service cleaning system, but suffering for biofouling growth in the condensers, a combined mechanical ISMC and chemical treatment, based on chlorine dioxide dosages, was set up and monitored by the electrochemical

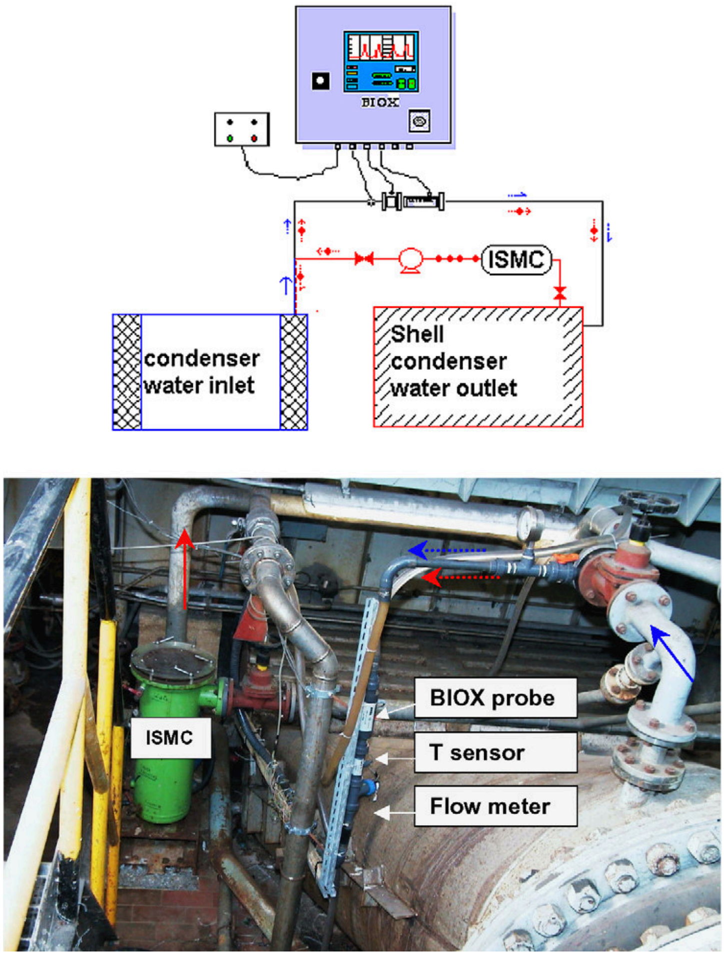

Fig. 2. By-pass of condenser cooling water circuit adopted in a power plant for the monitoring of combined chemical and mechanical antifouling treatments. The test line is equipped with the probes of BIOX system (electrochemical probe, temperature sensor and flow-meter). Normally, a "cold" water coming from the inlet circuit before the condenser (black arrows) flowed through the monitoring circuit. The pump of the mechanical in-service cleaning (ISMC), when it was working, pushed into the monitoring circuit a "warm" water flow (white arrows) coming from the outlet condenser shell mixed with few sponge balls. A schematic of the monitoring circuit is reported upon the picture.

monitoring system BIOX. The monitoring system was inserted in a by-pass of the condenser cooling water in a special configuration involving the mechanical cleaning water circuit, as shown in Fig. 2. When the pump of the mechanical ISMC was working, a ''warm'' water flow coming from the outlet condenser shell was pushed into the monitoring circuit mixed with few sponge balls; when the mechanical cleaning system and its pump was out of service (typical condition), ''cold'' water from the inlet condenser flowed through the monitoring circuit because of the pressure of the cooling circuit. The monitoring circuit built in this special way, and equipped with a temperature sensor and a flow-meter, allowed to control both the mechanical cleaning effect by sponge balls (emphasised in the graphic of Fig. 3) and the biocide effect of chlorine dioxide dosage on several stages of biofilm growth in the tubes (Figs. 4 and 5).

Fig. 3 shows a fast growth of biofilm when water flow is low. In this case, it was found that the biofilm can be easily controlled by mechanical cleaning. If biofilm grew in high flow water (Fig. 4), only a combined chemical and mechanical treatment guaranteed a complete control of it. On the basis of monitoring results, it was prescribed an effective treatment based on a daily dosage of about 1 mg/l of chlorine dioxide for 1.5 h, combined with the weekly use of in-service mechanical system, 1 h working. A biofilm growth corresponding to a BIOX signal value less than 800 mV was considered acceptable for this plant, as no significant loss in condenser performance was associated to values lower than that. Fig. 6 reports the response from a BIOX system installed in another plant and the values of condenser back-pressure measured immediately before and after a chemical cleaning dosage in that cooling circuit. The experimental data collected confirmed that, when BIOX signal rises more than 800 mV, the heat transfer through the monitored condensers gets significantly worse.

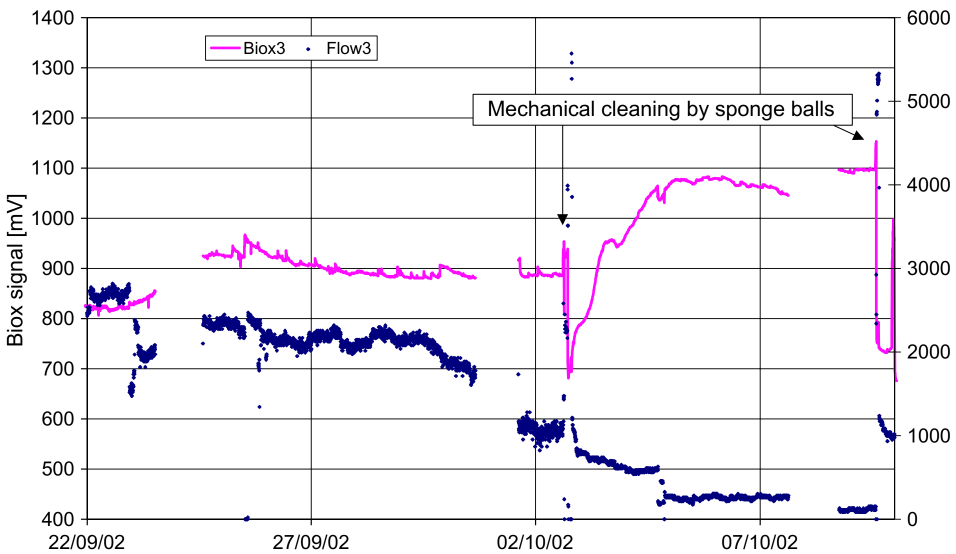

Fig. 3. Monitoring of the mechanical ISMC by BIOX system. The graphic show the effect caused by the treatment with sponge balls on two different stages of biofilm growth on the probe. The BIOX signal of about 900 mV corresponding to a ''moderate'' biofilm growth, fell down after the first passage of balls. Then, it immediately grew again, reaching almost the saturation, because the decrease in the water flow. The second passage of ball was effective enough to destroy the new biofilm stage too.

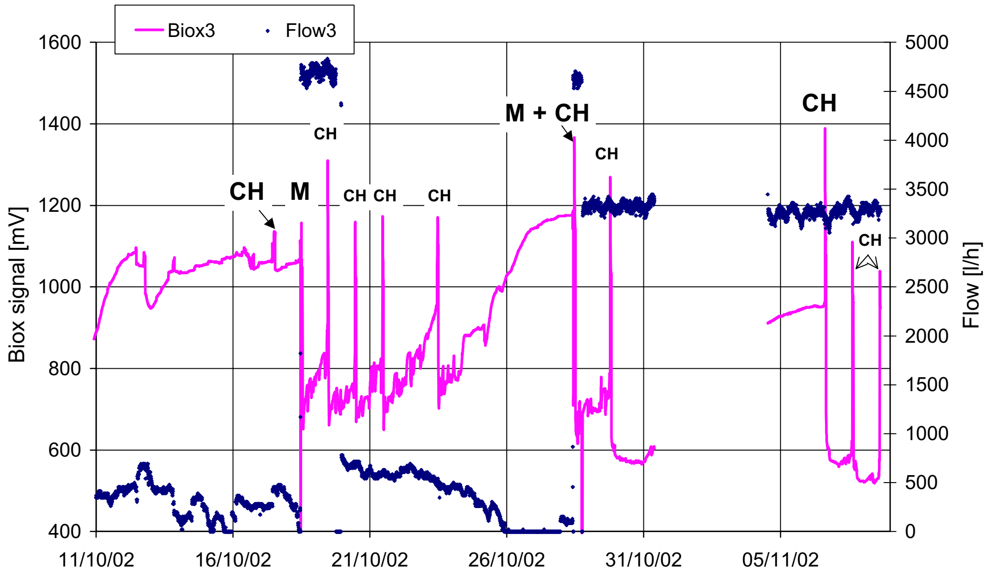

Fig. 4. Monitoring of the combined mechanical and chemical cleaning by BIOX system under variable flow. Chlorine dioxide short dosages (peaks CH) and sponge balls passage (M). Chemical dosage alone (1 mg/l of chlorine dioxide for 1 h) resulted more effective to inhibit biofilm growth under high flow water than low flow; mechanical cleaning gave better results than chemical cleaning in low flow conditions.

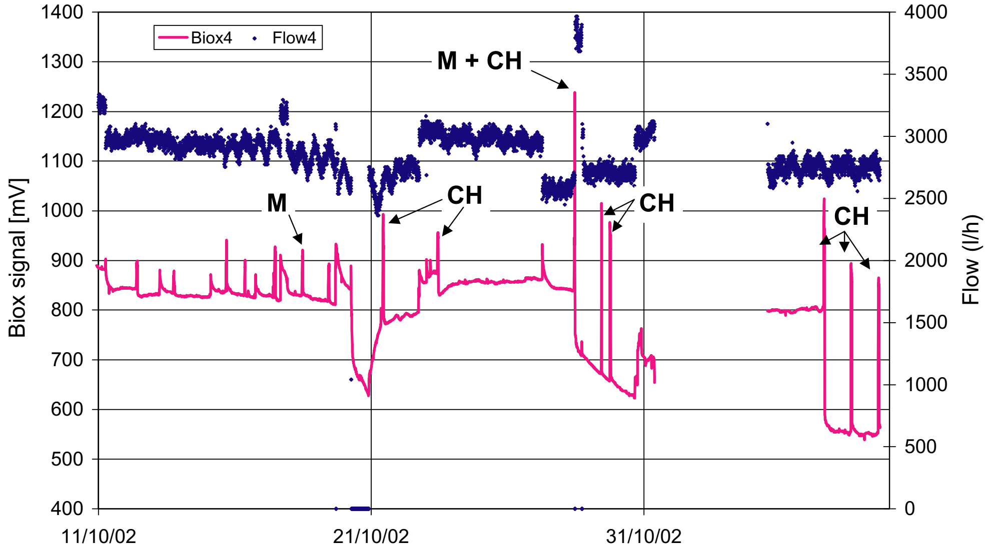

Fig. 5. Monitoring of the cleaning treatments by BIOX system under high flow. The chemical treatments, based on chlorine dioxide short dosages (peaks CH), better than mechanical sponge balls passage (M), was able to control biofilm at the level corresponding to a BIOX signal under 800 mV. A combined treatment resulted necessary against biofilm corresponding to a BIOX signal values more than 800 mV.

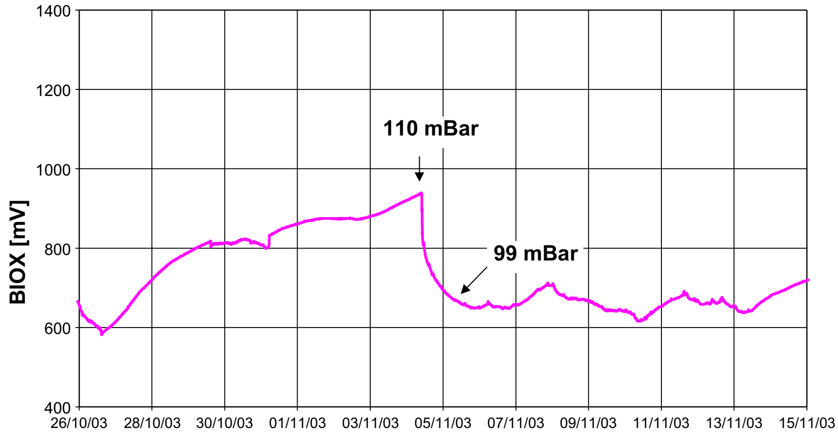

Fig. 6. Monitoring by BIOX system in a power plant. The values of condenser back-pressure get significantly worse when BIOX values rise more than 800 mV.

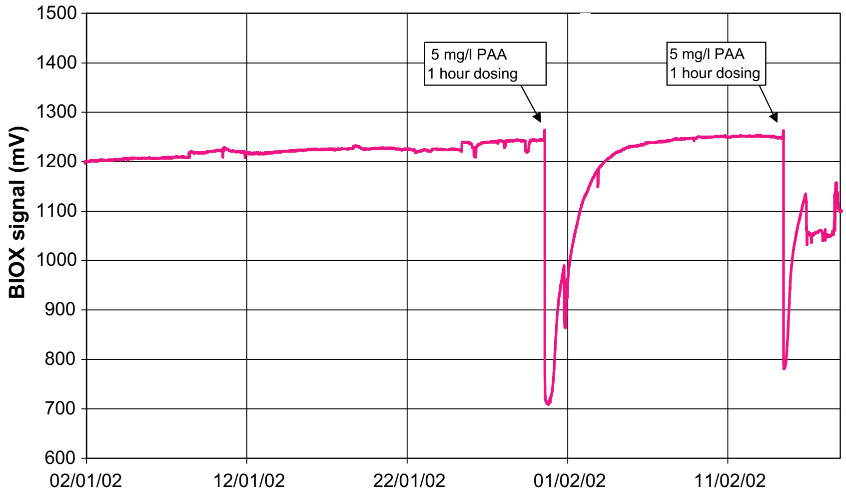

Fig. 7. Effects of short dosages of peracetic acid (PAA) on biofilm monitored by BIOX system in a power plant cooling circuit. The high BIOX signal, corresponding to a probe full covered by biofilm, fell down to the level indicating the deactivation of bacteria in the biofilm in coincidence with the PAA dosage of 5 mg/l dosed for 1 h inlet the cooling circuit of the power plant.

Lastly, the effect of short dosage of peracetic acid was also monitored by the BIOX system, as shown in Fig. 7. During the experimentation, the BIOX signal decreased in coincidence with the addition of 5 mg/l of peracetic acid, conducted for 1 h in the cooling circuit of the power plant. The biocide effect on the "mature biofilm" grew on the BIOX probe, documented by the fall of signal, was similar to that obtained by mechanical cleaning shown in Fig. 3. This last experimentation confirmed preliminarily the possibility to use peracetic acid dosages in support to the other qualified treatments.

6. Innovative solutions for heater exchangers

Many other tests were carried out in the plants of Venice lagoon including the use of other chemical products different from that treated in this paper and antifouling coatings.

One of the promising technique consists of the structures in titanium anodically polarised by a current of some tens of mA/m^2. The current applied to the titanium causes a low production of oxidant species (chlorine and bromine) at the metal–sea water interface. The current is low but is enough to inhibit the growth of biofilm on the tubes. Preliminary tests performed with polarised titanium panels immersed in the sea water of the Venetian lagoon demonstrated that it is also possible to control the settlement of macro-organisms and algae with a polarisation of about 100–200 mA/m^2. Considering the effect of the pH decrease in the water close to the anodic polarised surface of titanium, this technique could be particularly interesting for application on heater exchanger because it could allow both the control of biofouling and the scale on the tubes [14].

At present, an experimentation by pilot cooling circuit is setting up employing standard heat exchangers equipped with polarised titanium tubes with the aim to verify their antifouling and antiscale performances.

7. Conclusion

The ban of chlorine gas and sodium hypochlorite for antifouling treatments in the Venice lagoon forced the industrial plants to adopt another solution and the site become a "full scale" laboratory for experiences and experimentation of innovative alternative to traditional chlorination and innovative equipment, as polarised titanium heat exchangers.

The new treatments already adopted successful by the plants extend the number of the valid solutions to the problems of biofouling affecting cooling marine circuits of industrial plant, particularly the power station condensers.

The best rate cost/condenser performances was reached by combining mechanical in-service cleaning and chemical short dosages. The monitoring of these treatments by the electrochemical BIOX system allowed to reduce the frequency of dosages to that strictly necessary to guarantee acceptable level of cleaning.

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