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In situ experimental study for the optimization of chlorine dosage in seawater cooling systems

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Abstract

The paper details an in situ study for the evaluation of the evolution of fouling heat transfer resistance and to optimize the antifouling chlorine dosage at a 550 MW power station. A portable pilot plant has been designed to simulate the steam surface condenser and used as an accurate fouling monitor that takes the seawater from the same intake point as the power station. This study includes fouling extraction and its characterization for different dosage patterns. The residual chlorine concentration at the cooling-water discharge from the power station is 0.2 mg/l and has been considered appropriate for the prevention of the formation of fouling, because with this concentration approximately 90% reduction in the amount of fouling is obtained. Residual chlorine dosages lower than 0.2 ppm could be effective in controlling fouling development if mechanical techniques of fouling control are also available.

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1. Introduction

1.1. Marine fouling

All the materials exposed to untreated seawater suffer the well-known phenomenon of fouling, consisting of the formation of an unwanted deposit that covers the surfaces in contact with the water.

This fouling can be of a different nature according to the mechanism involved in its genesis. Five types of fouling are usually considered: biological, corrosion, particulate, chemical reaction and precipitation fouling [1]. When seawater is the cooling fluid the phenomenon is enhanced due to the strong corrosive nature of salt water and to its high biological activity [2]. In general, fouling causes important operation and maintenance problems in facilities in contact with seawater, among them, cooling circuits, maritime activity, aquaculture, offshore utilities, etc.

1.2. Problems of fouling in heat exchangers

The formation of fouling in heat exchangers in coastal power stations using seawater for cooling purposes, has special economic significance [3–5]. In this type of facility, fouling is formed inside the condenser tubes, reducing heat transfer between the hot fluid (steam that condenses on the external surface of the tubes) and the cold sink (seawater flowing through the tubes). This fouling has negative consequences in the efficiency of the power station and therefore in its economic balance [6,7].

1.3. Fouling monitoring

For all the above reasons the design and operation of heat exchangers must consider and estimate the fouling resistance to the heat flow. The traditional method is the utilization of published fouling resistance tables [8]. But

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Nomenclature

A_o	outside surface of tube (m^2)	t_{cwi}	cooling water inlet temperature (°C)
C_p	specific heat capacity of seawater at bulk temperature ($J\ kg^{-1}\ K^{-1}$)	t_{hwi}	heating water inlet temperature (°C)
d_i	inside diameter of tube (m)	t_{cwo}	cooling water outlet temperature (°C)
f	friction factor (dimensionless)	t_{hwo}	heating water outlet temperature (°C)
L	tube length (m)	U	overall heat transfer coefficient referred to outside surface ($W\ K^{-1}\ m^{-2}$)
R	overall heat transfer resistance referred to outside surface of tube wall ($m^2\ K\ W^{-1}$)	v	cooling seawater velocity ($m\ s^{-1}$)
R_f	fouling heat transfer resistance ($m^2\ K\ W^{-1}$)	Δp	pressure drop along tube length ($N\ m^{-2}$)
		ρ	seawater density ($kg\ m^{-3}$)

these tables usually show a range of fouling resistance, estimated for very specific conditions that cannot be extrapolated to any other situation. The determination of fouling resistance for heat exchangers in situ therefore, has considerable importance for future design and for efficient operation.

One of the possible strategies for monitoring and detection of fouling is the use of a side-stream, consisting of a device located in parallel with the industrial plant and using the same water source. It allows an estimate of the fouling produced in this side stream to be made, and subsequently to be related to the main stream [7,9]. Although the cost of this type of device is high it offers opportunities for improved heat transfer efficiency and substantial financial saving. In recent years, some side stream monitoring devices have been made (an EPRI report [10] describes and evaluates 18 biofouling detection devices), but few of them are suitable for seawater monitoring, due to the corrosive nature and high biological activity of the seawater.

1.4. Fouling mitigation

In order to minimize this undesirable phenomenon, biocides are usually employed as antifouling agents not for eliminating but rather for reducing deposit accumulation. Chlorine is very common as an antifouling agent due to its low cost (frequently electrolytically generated from seawater) and high effectiveness [11]. Nevertheless, the serious toxic effect of chlorine and of its reaction products in contact with the seawater (chloramines, haloforms, etc.), has to be recognized. For this reason it is important to optimize the amount of chlorine used in once-through cooling systems—typical in coastal power stations- using large water volumes (ranging between 10 and 50 m^3/s) and where chlorine amounts in the outfall need careful consideration [12].

In order to carry out a study on the optimization of antifouling treatment it is necessary to consider the factors that influence the formation and development of biofilms. Essentially these factors depend on the physical, chemical and biological characteristics of the water and the design and operation of the heat exchanger (material and roughness of the tubes, flow velocity and temperature) [7,13]. Since these characteristics are very dependent on the location and design of the power station, in situ studies are recommended to take into account, as far as possible the environmental factors and site-specific conditions. The knowledge of the progression and mechanisms of fouling formation will allow the design of an appropriate fouling mitigation strategy to be made.

1.5. Objectives of this study

This investigation deals with an in situ study to optimize the chlorine dosage in "Los Barrios" power station, located in the Bay of Algeciras (Southern tip of Spain).

A portable pilot plant, specially designed for this purpose, has been used for side-stream fouling monitoring. Circulating seawater is drawn from the same intake point as the full scale cooling water system.

2. Materials and methods

2.1. Experimental system

2.1.1. Description of the pilot plant

Taking into account that the type and rate of fouling will be dependent on the specific characteristics of the cooling water, climatology and other operating conditions of the industrial plant, in situ studies are necessary so that the monitor has to be suitable for transportation from site to site. In order to fulfill these requirements, the whole plant has been fabricated to fit inside a twenty foot standard container. The design of the pilot plant makes it easy to carry out studies with different tube materials, diameters, biocides and dosage patterns, that allows optimization of the control procedure to be made. Wireless remote control, monitoring and data transmission from the pilot plant can be carried out via a modem.The pilot plant basically consists of a shell-and-tube heat exchanger 3100 mm in length and specially designed to avoid galvanic corrosion, been the shell and pipework by the use of PVC pipes (excluding the condenser tubes). In order to simulate power station condenser conditions, the five tubes were heated on the shell side by a circulating closed fresh water circuit to maintain a tube surface temperature equal to that in the full scale condenser. The heating water temperature set point was 35 °C with a difference through the shell of only 0.4 °C, this being achieved by employing a flow rate of 35 m^3/h through the shell. Cooling seawater circulates through the tubes, forming a fouling layer on their inside surfaces, and its flow rate is automatically regulated to maintain a prescribed flow velocity (2 m/s).

The variables of operation of the pilot plant, in comparison to the condenser of the full scale power station are given in Table 1.

A diagram of the experimental system is presented in Fig. 1, where the different circuits can be easily recognized.

The complete description and detailed characteristics of the pilot plant are available in previous published work [14].

2.2. Experimental method

2.2.1. Experimental plan

In the course of one year, seasonal experiments over a period of about 90 days have been carried out to evaluate the effect of different chlorine dosages on biofilm development. Each experiment began with commercially clean tubes and increasing chlorine residual doses were employed, from 0 (control tube) to 0.25 ppm (exceeding slightly the permitted quantity of 0.20 ppm in cooling-water discharges). Throughout an experiment, the signals from the sensors were automatically recorded: including cooling water temperature (in and out), flow rate, redox potential and pressure drop, as well as the inlet and outlet temperature in the hot water shell. From all these measured variables on-line instantaneous data of the fouling development were obtained. At the end of the experiments, the fouling deposit was removed from the inner surface of the tubes so that characterization and direct measurements could be made. Simultaneously with these experiments, bi-weekly physico-chemical and biological characterizations of the cooling water were established. Two samples were taken in high and low tide conditions, respectively. Since these analyses began in 2001, a database comprising of data over almost three years, has been obtained.

Table 1
Comparison between the condenser of the real power station and the pilot plant

Variable	Power station	Pilot plant
Tube materials	Aluminium Brass (ASTM-B111,79 Alloy 687)	Aluminium Brass (ASTM-B111,79 Alloy 687)
Tubes dimensions	24/25.4 mm × 12 m	12/15 mm × 3 m
Flow velocity through tubes	2 m/s	2 m/s
Temperature difference through tubes	0.9–1.0 °C/m	1.0–1.2 °C/m
Shell side temperature	34–36 °C	35 ± 0.2 °C
Chlorine concentration (residual)	0.20 ppm	0–0.25 ppm

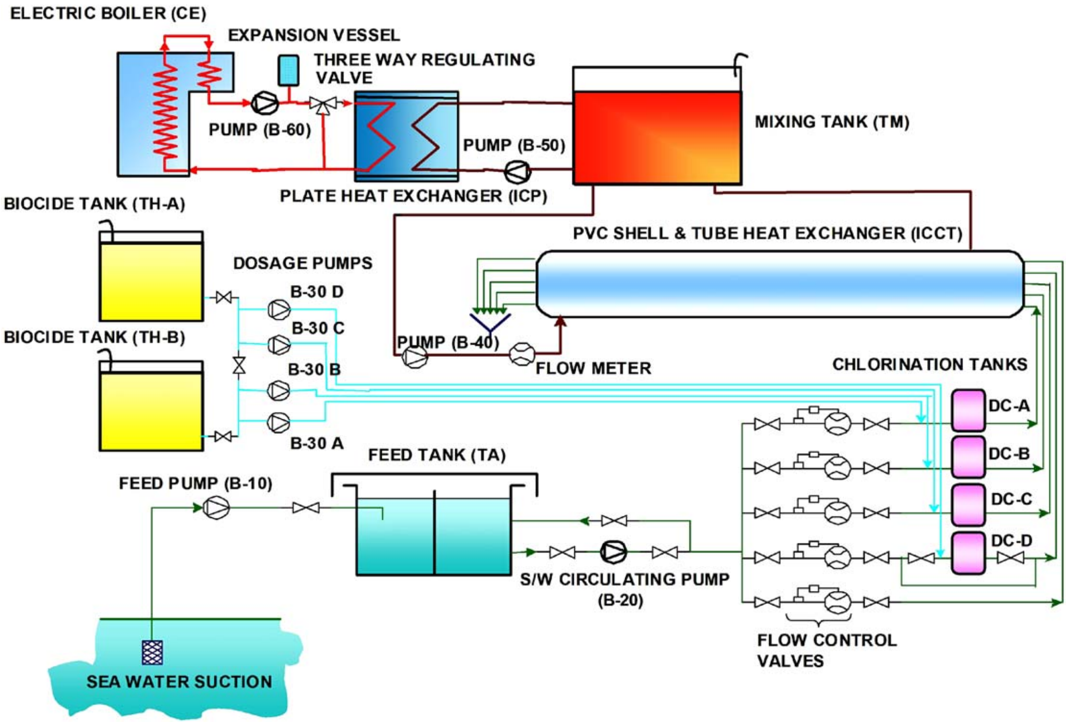

Fig. 1. Diagram of the experimental system.

2.3. Analytical methodology

2.3.1. Residual chlorine measurement

Chlorine residual concentration was maintained at the set point automatically by means of a redox sensor that activates the corresponding dosage pump. The sensors were regularly cleaned and calibrated, by measuring the actual chlorine concentration in the outlet of each tube using the spectrophotometric method of DPD (method no. 4500-Cl G, "Standard Methods for the Examination of Water and Wastewater" [15]). Since the experimentally measured concentration presented slight deviations, at the conclusion of the experiments an average concentration of chlorine for each tube was calculated.

2.3.2. Extraction and direct characterization of fouling

By means of a double rubber piston that fitted perfectly into the inside of the tubes, they were completely cleaned along their 3.2 m length. Details of the device and procedure have been published [14]. The subsequent laboratory measurements, including:

- Fouling wet volume, measured after 4 h settling of the collected fouling in an Imhoff cone.
- Fouling mass of total volatile and inert solids (gravimetric analysis).
- Layer thickness, calculated as the ratio between the wet volume and the inner surface area of the tube. Although this is a simple method of measurement, a good correlation between film mass and thickness was obtained.
- Fouling metallic composition: Fe, Al, Ca, Mg, Cu and Zn.

2.3.3. Indirect measurements of fouling

Another way to confirm tube fouling is to compare actual and design or expected values of some transport parameters affected by the fouling. Those consequently represent indirect measurements for estimating the accumulation of deposits:

Frictional resistance (f): biofouling increases the frictional resistance as the effective diameter of the tube diminishes and roughness increases. This will result in an increase in pressure drop through the tubes. Frictional resistance is estimated by the Darcy dimensionless friction factor:

$$f = \frac{2 \cdot d_\mathrm{i} \cdot \Delta p}{L \cdot \rho \cdot v^2}$$

Heat transfer resistance (R): The overall heat transfer resistance (sum of conductive and convective resistances) is expressed by the reciprocal of the overall heat transfer coefficient and will be easily determined for every tube in accordance with the following equation:

$$R = U^{-1} = \frac{A_\mathrm{o} \cdot [(t_\mathrm{hwo} - t_\mathrm{cwi}) + (t_\mathrm{cwo} - t_\mathrm{cwi})]}{\frac{\pi}{4} \cdot d_\mathrm{i}^2 \cdot v \cdot \rho \cdot C_p \cdot (t_\mathrm{cwo} - t_\mathrm{cwi}) \cdot \ln \frac{t_\mathrm{hwo} - t_\mathrm{cwi}}{t_\mathrm{hwi} - t_\mathrm{cwo}}} \ (\mathrm{m^2\,K/W})$$

Table 2
Identified taxons of zooplankton

Potentially fouling-forming taxons	Other taxons
Anthozoa (larva)	Amphipods
Ascidian (larva)	Appendicularians
Bivalves	Cladocera
Bryozoan (larvae)	Copepods
Cirripedes (nauplius and cipris)	Decapods (larvae)
Hidrozoan	Echinoderms
Polychaeta (larvae)	Euphausiacea
	Foraminifers
	Gastropods (veliger)
	Isopods
	Ostracods
	Fish (larvae)
	Chaetognaths
	Siphonophores
	Thaliacea

By calculating the difference in R between fouled and clean conditions the fouling resistance, R_f can be determined.

These transport properties are computed and monitored from the pilot plant through suitable software (SCADA) for each tube using the values of the on-line measured variables (pressure drops, flow rates and temperatures).

The decreasing heat-transfer coefficient as fouling progresses, is thereby assessed.

2.3.4. Seawater characterization

Physico-chemical parameters were analyzed bi-weekly: Conductivity, phosphates, nitrates, nitrites, ammonium, silicates and dissolved organic Carbon using the methods that appear in Standard Methods for the Examination of Water and Wastewater [15].

Biological parameters: The zooplanktonic density of 22 different taxons in plankton was identified and measured, within which, 7 taxons corresponded to groups whose species have a major tendency to develop biofouling (Table 2).

3. Results and discussion

3.1. Seasonal variation of the characteristics of the cooling water

3.1.1. Nutrients and physico-chemical parameters

From January 2001 cooling seawater at the inlet point of the power and pilot plants was analyzed bi-weekly. The recorded data allowed the seasonal variation of the characteristics of the cooling water, from the point of view of the physico-chemical and biological parameters to be determinated. A typical coastal water tendency was observed, where concentrations of nutrients in winter suffer a decrease in spring and summer due to their consumption by the greater phytoplanktonic activity in the warm seasons.

3.1.2. Plankton

Zooplankton abundance also shows a typical tendency which is the opposite of that stated for the nutrients: i.e.

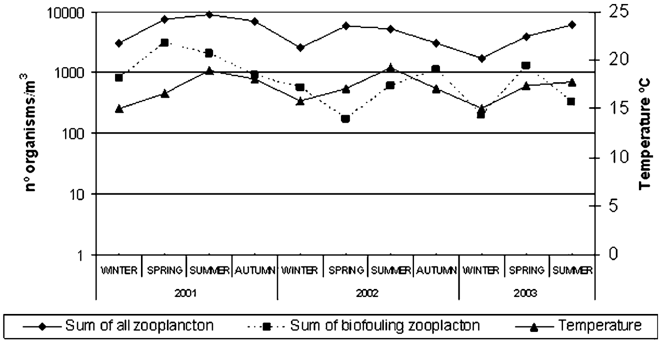

Fig. 2. Seasonal variation of zooplankton abundance versus temperature.

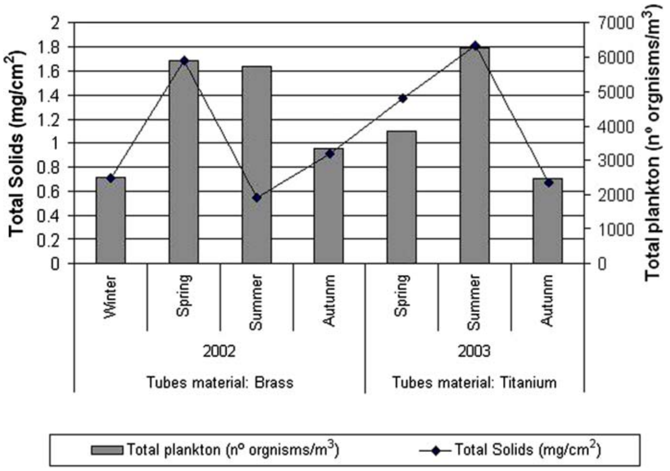

Fig. 3. Accumulation versus zooplankton present in the four seasons.

maximum in spring and minimum in winter. In Fig. 2 it maybe observed that this tendency is verified for both total zooplankton and the sum of those species more prone to form macrofouling. Throughout the study attempts were made to verify the assumption of a greater presence of cirripedes larvae and other organisms detected in spring and summer also corresponding to a greater rate of fouling in these seasons. This fact implies a greater requirement of residual antifouling agent concentration. Although the biofouling is mainly based on bacteria and microorganisms that were not measured, it has been established that there is a correlation between macro and microorganisms in seawater due to seasonal variations.

3.2. Seasonal evolution of fouling formation

3.2.1. Quantity of fouling formed

In order to evaluate the fouling formed in each season, direct and indirect measurements have been made. Since experiments have run for slightly different periods (between 60 and 97 days) results have been normalized to 85 days (assuming that fouling accumulation was roughly proportional to the time of the exposure of the tubes to the seawater). In order to verify the stated seasonal effect, the results of exposure corresponding to no-dosed control tubes are compared.

In relation to the total mass of fouling formed (Table 3), expressed either in total solids attached per cm^2 of tube surface or in film thickness, it can be seen that its maximum value is in spring, in autumn it is visibly lower than in spring and it has a minimum value in winter, and agrees with the water analyses carried out. For the summer an anomalous value, was obtained that was smaller than expected, due to operational problems that led to no water flow for some days that resulted in a certain loss of fouling.

To overcome this fact, results corresponding to subsequent experiments (employing titanium tubes) have shown that the amount of fouling deposited in summer is similar to that found in spring. As seen in Fig. 3 a good correlation between total solids and zooplankton accumulation is obtained for both materials (aluminium brass and titanium) with the same pattern of deposition.

3.2.2. Nature of fouling formed

Regarding the nature of fouling, as shown in Table 3, the organic fouling fraction is less important than the inorganic portion. Approximately 25% of the fouling is organic matter with a content of total carbon ranging between 8% and 10%, this carbon being mainly organic (95%). These data indicate that precipitation, deposition and corrosion phenomena have more quantitative importance than biological growth. A greater proportion of organic matter in the two warmer seasons has been detected: spring and summer, suggesting that the increased biological activity will increase the tendency for fouling of occur, in these seasons.

Fig. 3 illustrates the amount of fouling in the control tubes, as total solids per cm^2, versus the total concentration of organisms present in the cooling seawater for each season. It confirms that both parameters follow a parallel tendency (not taking the case of the summer into consideration for the previously stated reasons) demonstrating that the

Table 3
Quantity and composition of fouling formed in the different seasons

Chlorine dosage (mg Cl_2/l)	Season	Total solids [mg/cm^2]	Organic matter (%)	Inorganic matter (%)	%C	%C organic	Wet volume [cm^3]	Fouling thickness [μm]
0	Winter	0.538	24.30	75.70	9.5	–	19.3	148.3
0	Spring	1.680	27.17	72.83	10.1	95.9	60.4	500.9
0	Summer	0.548	28.05	71.95	–	–	23.4	193.8
0	Autumn	1.008	21.49	78.51	8.1	95.2	21.8	199.8
0	Seasonal average	0.944	25.25	74.75	9.2	95.5	31.2	260.7

biofilm accumulation in condensers—in no chlorination conditions—is clearly dependent on the season of the year.

3.3. Effect of residual chlorine concentration in fouling deposition

3.3.1. Effect on the amount of fouling

The effect of chlorine dosages on accumulated fouling can be observed in Fig. 4 where the changes in the superficial accumulation of fouling, related to the current dosages of chlorine, are shown. It maybe seen that the amount of deposit diminishes in exponential mode as chlorine dosage is increased, in such a way that for a residual concentration of 0.2 mg/l (that used in the power station) a reduction of over 85% in the fouling surface accumulation is obtained. In addition, it can be seen that for the chlorinated tubes, seasonal differences are less significant in comparison to non-chlorinated tubes. The explanation of this phenomenon can be that chlorine greatly reduces the biofouling growth, even while very low residual concentrations are employed (say 0.05 mg/l).

3.3.2. Effect on the fouling composition

In the previous section it was shown that the fouling formed under the particular site conditions is predominantly inorganic. When the proportion of different metals and elements in the fouling is analyzed (Figs. 5 and 6), different behaviour of the particular chemical element is observed. Iron is the predominant metal, and its proportion tends to increase with the residual chlorine concentration. This fact could be explained by supposing that the iron is incorporated into the deposit by a precipitation process from iron II present in seawater, becoming much more insoluble iron III in an oxidizing environment. Aluminium which is the second metal in importance shows the opposite behaviour, diminishing its proportion as biocide concentration increases. This fact could be explained assuming that this metal is incorporated into the fouling through biological adsorption forces, as is ratified by the identical evolution shown for Al (Fig. 6) and C (Fig. 7) versus chlorination. Although Al is present in aluminium brass alloy, its proportion is small (about 2%) and it is suggested that its origin in the fouling is the Al in natural seawater, because similar Al quantities have been found when employing titanium tubes. Consequently, as chlorination increases, the biological processes and aluminium adsorption are reduced. Increase in copper and zinc within the layer is very clear: both of them are constituent metals of brass and their presence in fouling is due to corrosion processes and consequently their presence increases with the oxidant (chlorine) dosage. Finally,

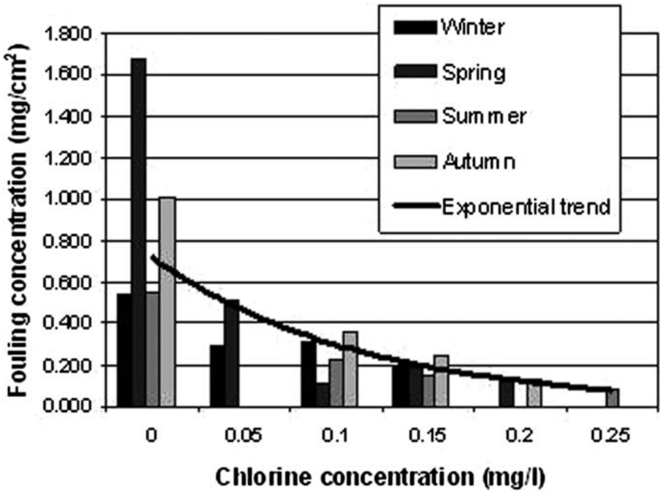

Fig. 4. Chlorine effect over fouling specific concentration.

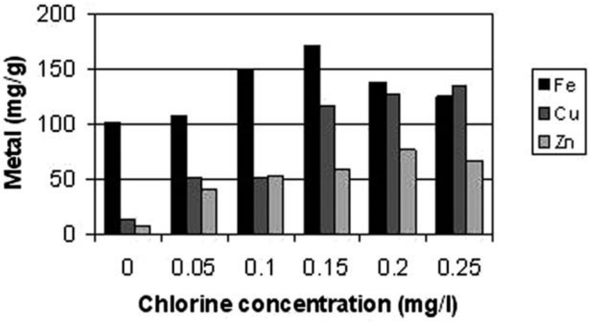

Fig. 5. Fe, Cu and Zn content of biofilm versus chlorine dosage.

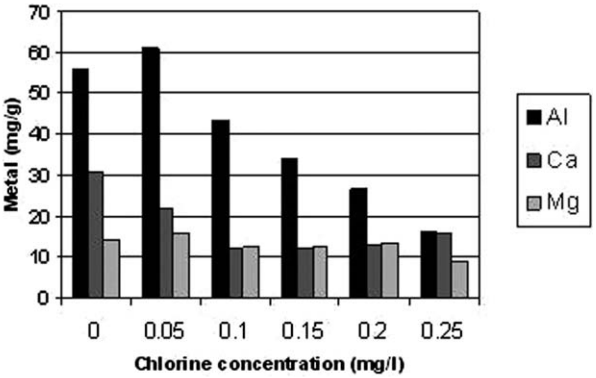

Fig. 6. Al, Ca and Mg content of biofilm versus chlorine dosage.

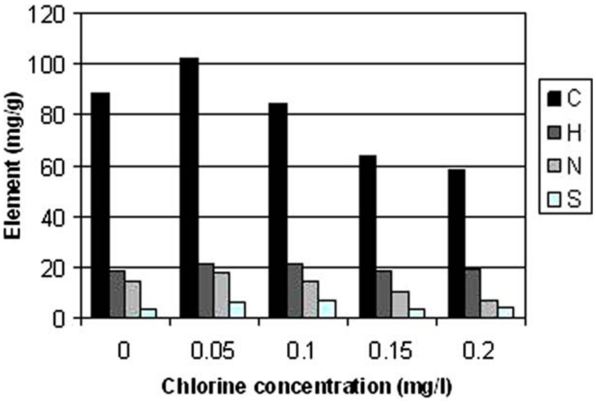

Fig. 7. C, H, N and S content of biofilm versus chlorine dosage.

calcium and magnesium are present in deposits due to biological and precipitation processes, with a prevalence of biological phenomena for calcium which suffers a strong reduction as chlorination increases, while magnesium content remains more or less invariable throughout all the experiments.

H and S are present in much smaller concentrations (see Fig. 7) and no chlorination dependence was found. For N, similar behaviour to C is shown, although its proportion is under 2%.

3.3.3. *Effect on the transport properties*

From data automatically monitored, controlled and recorded for each tube (temperatures, differential pressure, flow rate, etc.), it has been possible to follow the change of two parameters related to the transport properties representing indirect measures of fouling. These properties were: the friction factor and the heat transfer resistance.

The *friction factor* (*f*) shows, in this study, insufficient sensitivity—only for the control tube in spring an acceptable signal increment was obtained—as can be seen in Fig. 8 where the evolution of *f* versus time for different residual chlorine concentration is plotted for that season. Therefore, this parameter is not considered helpful for monitoring seawater fouling development, under the conditions of the study and within the practical operational limits in full scale power stations.

The *heat transfer resistance* (see Fig. 9) due to fouling (R_f) was, on the other hand, a suitable indirect parameter to monitor fouling development. It is more reliable than *f* because, in the measured conditions, the effect of fouling over heat transfer is greater than its hydraulic effect. Fig. 9 shows the increase of this parameter for the experiment carried out in spring, it can be seen that the R_f increment is highly dependent on chlorination. In Table 4, the seasonal average of the *R* is registered, showing a clear increasing tendency of the final heat transfer resistance as chlorination is reduced. Taking 0.60 m^2 K/kW as initial value for the overall heat transfer resistance corresponding to clean tubes, *R* increased throughout the experiments up to the values shown in Table 4. It can be seen that for a non-chlorinated tube, final *R* value doubles its initial value causing the heat rate to drop by 50%. For 0.2 ppm (the highest dose permitted by the environmental authorities) a loss of a near 15% of heat transfer capacity is reached after 85 days of operation. These data coincide with a generally accepted cleanliness factor of 85% for design purposes. If greater thermal efficiency or lower residual chlorine concentration in the effluent is required combined chemical and mechanical techniques (e.g. Taprogge system) must be employed. In this case also, the information given from the side-stream device can be useful, indicating the time between mechanical cleaning in accordance with the R_f value reached in the tubes of the pilot plant.

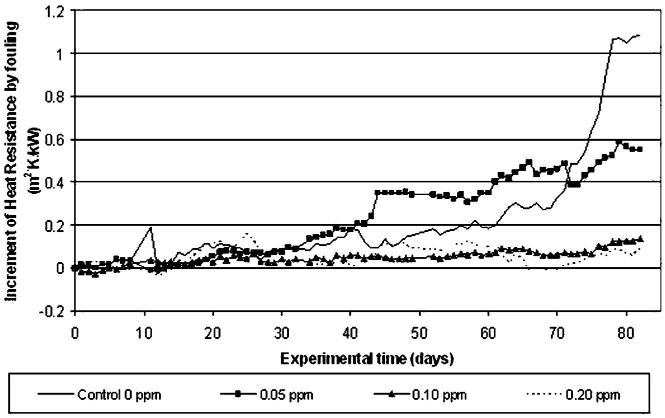

Fig. 9. Evolution of fouling heat transfer resistance in aluminium brass tubes (spring season).

Table 4
Thermal resistance increment and heat transfer reduction versus chlorine concentration after 85 days

mg Cl_2/l	*R*	% *R* Increment (respect clean tube)	% Heat transfer reduction (respect clean tube)
0	1.213	102.2	50.54
0.05	1.011	68.5	40.66
0.1	0.753	25.5	20.32
0.15	0.797	32.8	24.69
0.2	0.701	16.8	14.36
0.25	0.600	0.0	0

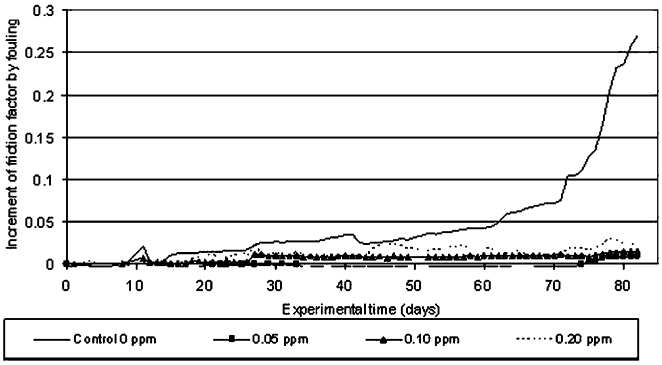

Fig. 8. Friction factor evolution (spring experiment).

4. Conclusions

4.1. *Seasonal variation of main cooling water characteristics in Algeciras Bay*

- A typical behaviour pattern of coastal waters has been observed over three years, showing maximum concentrations of nutrients in winter and a reduction in spring and summer resulting from their consumption by the greater planktonic activity in the warmer seasons.
- Zooplankton concentration also follows a typical but inverse, tendency to that for the nutrients: greater amounts in spring and lesser in winter.

4.2. *Seasonal evolution of fouling formation*

- In general, a good correlation between the total fouling formed under no-chlorination conditions, and an abundance of zooplankton in cooling seawater is observed. It has been shown that spring is the most favourable season for fouling accumulation.
- The organic fraction of fouling is lower than expected for a temperate latitude (25% approximately), indicating the major significance of precipitation and corrosion phenomena compared to biological growth. A slightly greater fraction of organic matter in the two warmer seasons of spring and summer has been detected. This fact demonstrates that in these seasons biological processes are relatively of greater importance.

4.3. *Effect of residual chlorine concentration in fouling formation in aluminium–brass tubes*

- Chlorination of cooling water affected the fouling development, the fouling quantity, its composition and its transport properties. The response to the chlorination is very similar in the four seasons of the year when chlorine dosage is controlled by the required residual value. For this reason, it is not recommended that a lower chlorine residual should be used at the test site in the colder season. This is in contrast to the cooling water systems in higher latitudes where such high concentrations of chlorine would be not required in winter.
- The different behaviour of metals in relation to chlorination provides an explanation for the adhesion phenomena for each metal. Iron is incorporated into the fouling layer by means of a precipitation process from iron II present in a natural form in the seawater. In an oxidizing environment iron II becomes much more insoluble than iron III. Aluminium is integrated in the deposit through biological adsorption. The presence of copper and zinc in the foulant layer, attributed to corrosion processes, was due to the use of brass tubes in the experiments. Finally, calcium and magnesium are present in the fouling due to biological and precipitation processes, dominated by microbiological activity for calcium which suffers a strong reduction as chlorination increases, while the magnesium content is virtually invariable throughout all the experiments.
- The residual chlorine concentration applied in the full scale power station, 0.2 mg/l, has been found appropriate for fouling prevention in the steam condenser tubes. With that dosage, around a 90% reduction in the quantity of fouling formed is achieved, corresponding to a reduction of only 14.3% in the efficiency of heat transfer after 85 days.
- It should be possible to employ a lower residual chlorine concentration than 0.2 mg/l, without operational problems in efficiency, using a combined (chemical–mechanical) fouling control strategy. With an appropriate schedule, environmental chlorine discharges and tube erosion can be minimized.
- In situ studies using a pilot plant are a useful and reliable tool for fouling monitoring, for a better understanding of its evolution and for optimizing condenser cleaning schedules. By taking into account the full scale operating conditions the results are directly related to the potential fouling.

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