

Study of the evolution of a semi-open cooling circuit

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Abstract

Purpose – The evolution of a semi-open cooling circuit of a nuclear reactor was monitored over a two year period. The work aims to provide orientation elements for preventive procedures against localised corrosion.

Design/methodology/approach – The water of the circuit was analysed in stagnation and in circulation, at various sampling points. The rust was analysed by neutron diffraction and the surface quality of the steel was checked by microscopic observations.

Findings – The obtained results did not confirm the presence of rust in iron compounds supported by chlorine, such as the Akaganeite, β -FeOOH. In addition, chemical analysis of water showed that, after two years, the increase of chlorine concentration and water conductivity remained weak. Moreover, the pH was maintained within values favourable rather to the passivation of the steel.

Practical implications – It was deduced through this work that the dosing of the circuit with chlorine was not sufficient that it should require an annual replacement of the water.

Originality/value – The originality of this work resides in the evaluation of a semi-open coolant circuit in service for ten years and located in an area subjected to seasonal sand winds.

Keywords Corrosion, Cooling, Steels

Paper type Research paper

Introduction

For economical considerations, large cooling circuits are generally made of carbon steel. In use, the steel is consumed naturally and in a continuous and uniform way such that there is a need for modification of the metal and/or service environment (Bard and Faulkner, 1980). The generalised corrosion phenomenon is foreseeable and preliminary design engineering allows, amongst other things, the thickness of the steel to be selected to ensure a desired lifetime for the installation (Brown *et al.*, 1995; NACE Technical Committee Report, 1994; Staehle, 2000). When the circuit is in contact with the air, it is not only that aggressive elements contaminate the water. In these conditions, other forms of corrosion appear in addition to the generalised corrosion and can even involve accelerated deteriorations due to synergistic effects. Among these accelerated degradation mechanisms, pitting corrosion remains the most disastrous form because it is not easily predictable, because of the difficulty to detect the initiation of pits at their first step; their fast evolution during subsequent stages; and the complexity of the corrosive environment caused by a great number of parameters that influence the phenomenon at various degrees (Dabosi *et al.*, 1994).

Many works were devoted to the study of separate effects of various parameters on the initiation and the evolution of localised corrosion (Frankel, 1998; Szklarska-Smialowska, 1986; Strehblow, 1995; Natishan *et al.*, 1995; Maurice *et al.*, 2001). It appears that this phenomenon is caused, in the

majority of the cases, by the presence of chlorine in the liquid phase (Yang *et al.*, 2001), or in some cases by other halogens or sulphates (Boucherit *et al.*, 1991). In addition, geometrical discontinuities on the metal surface or the presence of different phases can be worsening factors (Yu *et al.*, 2000; Sato *et al.*, 1996; Suter and Alkire, 2001; Suter *et al.*, 2001) as far as they lead to potential gradients, which generate dissolution and repassivation activities different from one point to another of the solid/liquid interface.

Preventive inspection actions normally include an evaluation of the surface state of the steel and a permanent verification of the water quality, in particular its concentration in corrosive agents. In addition, the analysis of the formed rust can be useful, insofar as the presence of certain forms of iron oxyhydroxides can reveal corrosive situations through which the media has passed. It has been reported that α -FeOOH is thermodynamically the most stable compound to form under slow corrosion conditions (Waychunas, 1991; Majzlan *et al.*, 2001). γ -FeOOH is kinetically the fastest to form, and which is observed in the early stages of atmospheric corrosion (Misawa *et al.*, 1993; Antunes *et al.*, 2003) if the system undergoes abrupt evolutions such as damping/drying cycles. In addition, the β -FeOOH form appears exclusively in the presence of chlorine (Misawa *et al.*, 1971; Gil *et al.*, 2002; Lichti *et al.*, 1999).

The object of this study was a cooling circuit that had been in service for ten years. It was constructed of carbon steel and contained approximately 1,200 m³ of water. The water was circulated intermittently and its initial conductivity was 50 μ S. With time, the volume of water reduced by evaporation and overflowed at weir in a settling pool, which was the place of the heat transfer with the air. To maintain the water quantity required, demineralised water was added according to requirements. The contact of water with air, under severe climatic conditions characterised particularly by seasonal sand winds, could cause an increase in its

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Anti-Corrosion Methods and Materials
53/4 (2006) 212–217
© Emerald Group Publishing Limited [ISSN 0003-5599]
[DOI 10.1108/00035590610678901]

corrosiveness, due to an elevation of the concentration of chlorine or other pitting promoters. For that reason, the circuit was drained, cleaned, and filled with demineralised water once per annum. However, the replacement of water containing iron already in equilibrium with the steel with demineralised water would undoubtedly entail additional dissolution of iron, and thus a consumption of the steel, which would reduce the lifetime of the installation, especially if pitting agents were retained in the circuit.

The aim of the present work was to review the necessity of draining water, or at least, to reconsider the frequency of that procedure. The chemical properties of water were monitored over a 22-month period. It was hoped that an understanding could be obtained of whether the increase in the chlorine concentration was significant, and if the conductivity tended towards a stable value after several months of service. To conclude definitively about the presence and the influence of chlorine, neutron diffraction analysis was carried out on the rust removed from the interior of the circuit during a maintenance period, to check if it contained the Akaganeite β -FeOOH. Microscopic observations of the surface of steel were carried out in parallel, in order to evaluate the contributions of inclusions and the metallurgical phases in the steel.

Experimental

The monitoring of the water properties of the circuit was carried out over a 22-month period. The samples were taken from four distinct points of the circuit: at surface of the settling pool just after water came into contact with air, and at three other points in the circuit at reasonable distance from one another. Chlorine concentration was measured according to the volumetric method of Mohr (Rodier, 1969). This method is valid for a concentration range between 1 and 100 ppm. Iron was measured by the spectrometric absorption of a complex formed by adding 1,10-phenantroline to the sample (Christian, 1994). This method is valid for a concentration range between 0.054 and 5 ppm. The pH and the conductivity were measured by a conductimeter Consort 835 equipped with auto correction functions which take into account the temperature during the analysis.

The rust intended for the analysis by neutron diffraction was extracted from the internal surface of a canal connected to the settling pool, just after a draining operation. Subsequently, the sample was dried, reduced into powder, and maintained in a vanadium capsule for one week, the time needed to put in operation the installation. The complete description of the neutron diffraction installation has been presented in a detailed communication (Zidi *et al.*, 2001).

Before carrying out microscopic observations, the samples were subjected to mechanical polishing with abrasive paper 600 and put in an ultrasonic cleaning bath. After this, they were polished with alumina powder of 0.05 μm granulometry. To reveal the grain structure of steel, the surface was etched using 3 per cent Nital solution: 3 ml of nitric acid and 97 ml of ethanol. The samples were immersed in the solution for 10 s, then rinsed and dried. The structural characterization was carried out by an optical microscope with $\times 500$ magnification.

Results

Water analysis

The evolution over the time of the conductivity, the chlorine and the iron concentrations is shown in Figure 1. Presented in the same figure are the quantities of demineralised water added to the circuit during the investigation period. The average conductivity of the water, at the moment of its addition, was 50 μS . The water quantity added over one year is comparable with the total volume of the circuit. All results refer to samples taken 1 h after the beginning of the water circulation.

The pH of the demineralised water at the moment of its production varied between 9 and 9.5. However, the contact with air allowed carbon dioxide to dissolve in water to form bicarbonate ions. Consequently, the pH should reduce. This was observed during all the monitoring periods. An average pH of 8.3 ± 0.4 was measured at any point, independent of the water movement. The stability of the pH in situations of low alkalinity is in fact advantageous because under these conditions steel is passivated and tartar formation is inhibited.

Rust analysis

The main reason for undertaking the diffraction analysis of the rust was to confirm the existence of Akaganeite β -FeOOH, since the formation of this oxyhydroxide is supported by chlorine. The Akaganeite has been represented in some bibliographical references by the empirical formula $\text{Fe}_{7.6}^{3+}\text{Ni}_{0.4}\text{O}_{6.4}(\text{OH})_{9.7}\text{Cl}_{1.3}$ (*American Mineralogist*, 1991), or x FeOOH, FeOCl (Misawa *et al.*, 1971). In the upper part of Figure 2, the neutron diffraction spectrum obtained from the rust sampled from the cooling circuit can be observed. The diffraction intensity is brought to a random scale. Shown in the lower part of the figure are the positions of the diffraction angles calculated according to the Bragg formula of iron compounds which are most likely to appear (Dobrzynski and Blinowski, 1994). For the sake of clarity, for the majority of the compounds, the three most probable values were selected. This probability is indicated by the height of the associated vertical segments.

Surface steel examination

Localized corrosion is a particularly insidious and not an easily predictable phenomenon. In addition, a microscopic analysis of a small surface of steel and the conclusions drawn from it cannot be extrapolated to the circuit as a whole because of the influence of factors related to geometric and hydraulic conditions. From the surface observations, the intrinsic factors of the steel are retained entirely. The chemical analysis of the steel used on the circuit was carried out by X-ray fluorescence. The composition of the percentage mass is presented in Table I.

Figure 3 shows two micrographic observations obtained on the surface of a steel, of the same nature as that of the circuit, after it had spent one year immersed in the swimming pool of the cooling circuit. The first micrograph was obtained after the elimination of a uniform layer of rust by a simple polishing with 600-emery paper. The observation indicates the presence of dark phases, which correspond to MnS inclusions with an extended form. Although significant studies showed that MnS inclusions constitute preferred locations for pit initiation (Suter and Alkire, 2001; Suter *et al.*, 2001), no microscopic pits were evident around inclusions, or

Figure 1 Evolution of: (a) conductivity; (b) iron concentration; (c) chlorine concentration of a semi-open cooling circuit; and (d) water added to the circuit

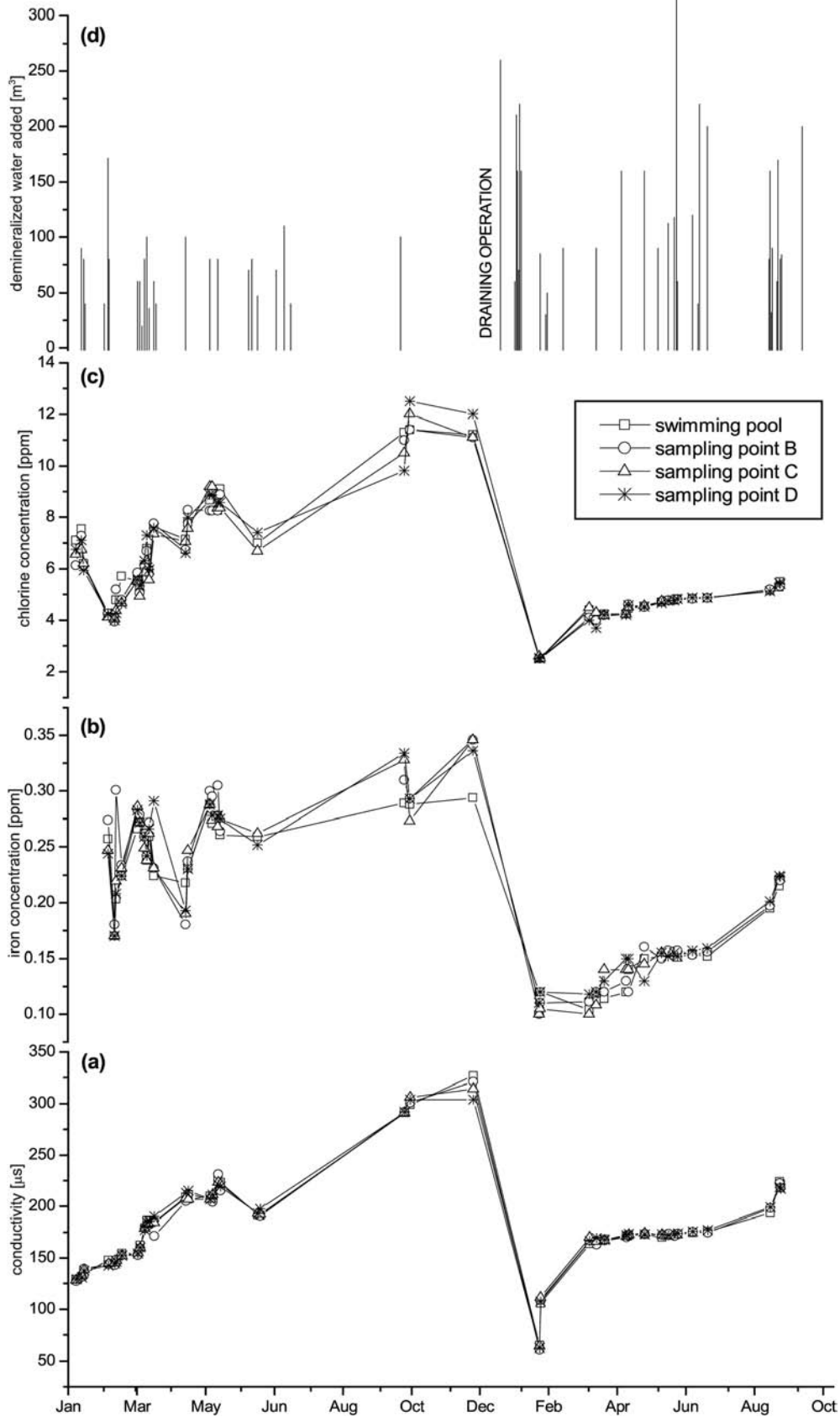
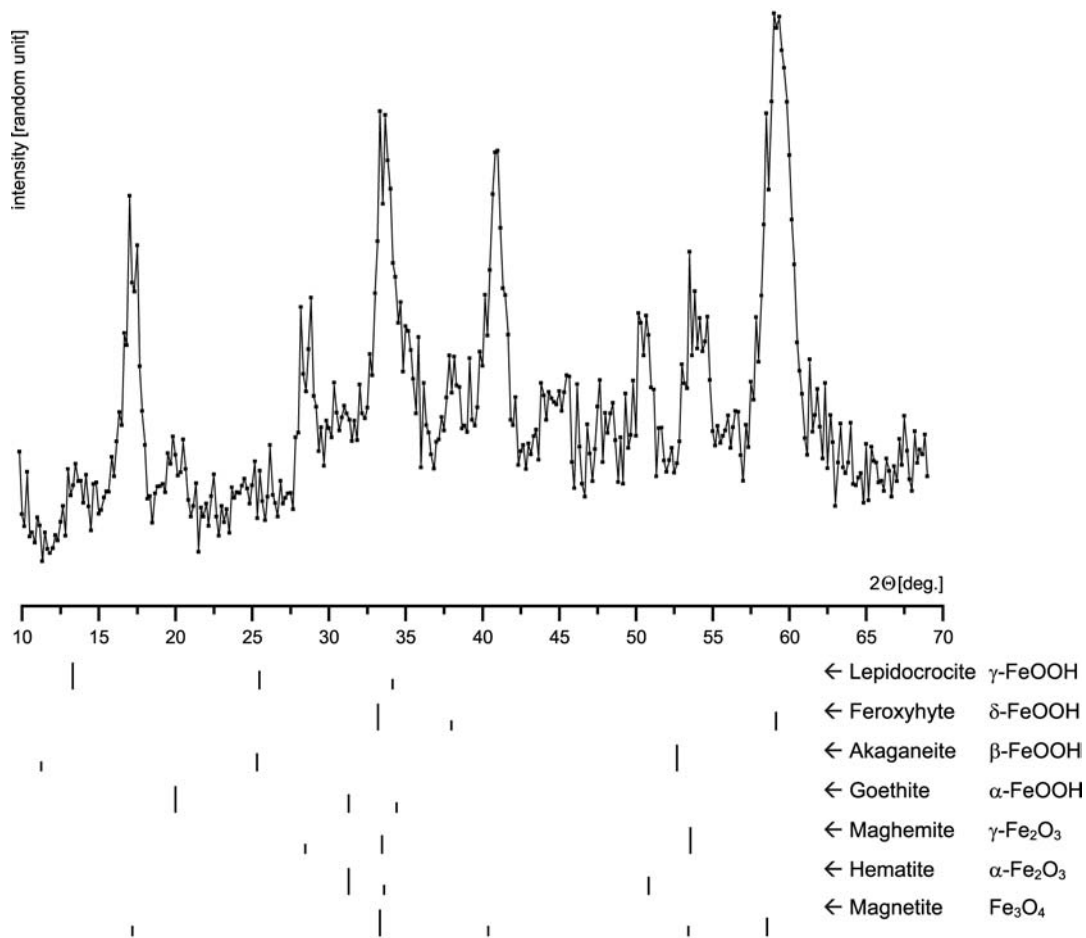


Figure 2 Neutron diffraction spectrum of the rust formed in a semi-open cooling circuit**Table I** Chemical composition of the steel

Elements	C	Mn	Si	P	S	Cu	Al	Ti	Ni	Cr	Mo	Sn
Percentage of mass	0.18	0.52	0.22	0.009	0.008	0.11	0.007	0.003	0.039	0.063	0.015	0.003

away from them. In the second figure, the granular structure of the steel was revealed by the etching procedure. The steel was made up of two phases: the clear phase was the ferrite, which is supposed to contain only iron; and the dark phase called “pearlite” is a layered structure of ferrite and cementite. The cementite contains carbon in the form of Fe_3C (Berranger *et al.*, 1994). In recent studies, it has been shown that pearlite is the most vulnerable phase in relation to pitting (Boucherit and Tebib, 2005). However, under the conditions the steel was subjected to, and at the level of our observation, pits were not evident in any phase.

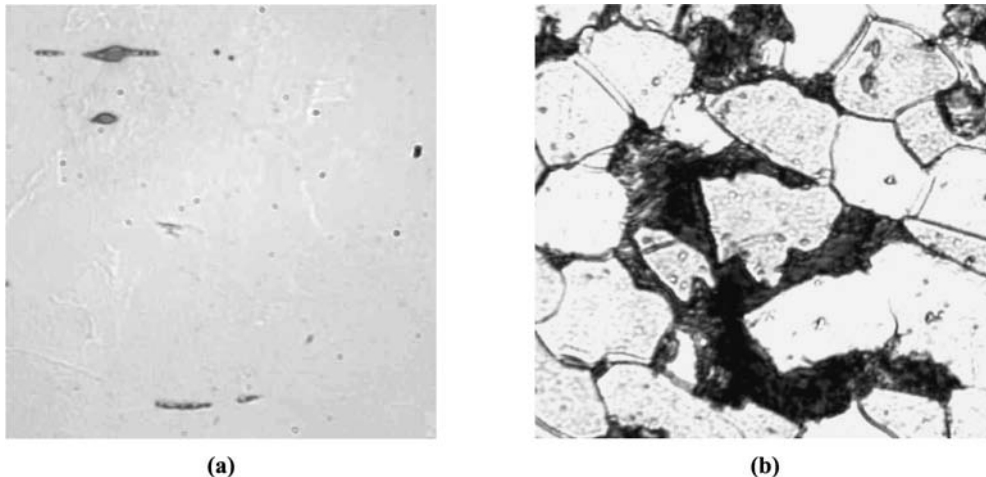
Discussion

It appears in Figure 1(d), that the frequency and the volume of the demineralised water added to the circuit were irregular. Just after a draining, the filling operation requires several days. It depends on the capacity of the demineralised water production and on the water volume necessary to occupy the air compartments formed in the circuit. Except for the filling operation, the water addition was carried out to compensate

for that lost by overflows during operation and evaporation throughout the summer period. Thus, before the draining operation, the installation did not work and it was not necessary to adjust the water quantity, whereas for the same period the following year, significant quantities of water were added due to relatively frequent operation of the plant.

It was noticed that the ionic conductivity was the property that had less disparity from one sampling point to another. Moreover, it was not affected at all by the water circulation. It evolved in a nearly parabolic way with time. Initially, water was introduced at $50 \mu\text{S}$. After one year, it did not exceed $350 \mu\text{S}$. On the basis that the domestic water at the site had a conductivity which reached $1000 \mu\text{S}$, and when the almost-parabolic increase in conductivity with time is taken into account, it could be concluded that the increase in the ionic population in the circuit was not significant.

The minimum concentration of chlorine was 2.5 ppm. This reading was obtained just after a renewal of water. The chlorine concentration increased continuously at about 1 ppm/month. This increase was observed at all of the sampling points. The maximum value reached after one year

Figure 3 Microscopic observation of the surface of the steel: (a) before; and (b) after exposition to Nital solution

was approximately 13 ppm. Considering that the domestic water at the plant site contained 99 ppm and demineralised water 2.5 ppm, it can be concluded that the quantity of chlorine, as well as its evolution over the time were not of concern. For this reason, it is assumed that chlorine, taken separately, should not be considered as a risk for localised corrosion in this circuit. It is, however, important to keep in mind that localised corrosion is an event that arises from a great number of parameters, and in many circumstances they may act in a synergistic way (Frankel, 1998; Szklarska-Smialowska, 1986; Strehblow, 1995).

The values of iron concentration present some disparities, not only with time but also with the sampling points. The measured maximum value was 0.35 ppm. It was obtained just before the draining of the circuit. The iron quantity in the analysed samples did not reflect the material lost by the circuit. Indeed, the dissolved iron ions will contribute to the passivation of the surface, but at the same time, they will form insoluble deposits of hydroxides and iron oxyhydroxides due to the slightly basic character of the water. A fraction of iron remained nevertheless in the water and it was only this quantity, which was sampled and analysed. This is well illustrated by the rapid increase in the iron concentration observed just after the draining. In fact, iron present in these samples would come from the ferric deposits, which were not eliminated by the removal of the water.

The analysis of the neutron diffraction spectrum of the rust shows that no peak corresponded to the Akaganeite values. In addition, the presence of Fe_3O_4 magnetite is obvious because of the existence of all the peaks corresponding to the diffraction angles of this oxide. The attribution of these peaks to magnetite is supported by the fact that this iron oxide, recognizable during the sampling by its black colour and its intermediate position between the steel and the external red layer of hydrated oxide, is the most stable oxide form, which appears during thermal or wet oxidation (Boucherit *et al.*, 1989). The presence of the two other oxide forms: the hematite $\alpha\text{-Fe}_2\text{O}_3$ and the maghemite $\gamma\text{-Fe}_2\text{O}_3$ is justified, principally, by the presence of peaks at 28.5 and 50.2°.

The complexity in the analysis of this spectrum is due, from one side to the importance of the background noise, which reduces the conviction about the existence of weak peaks, and from another side, to the proximity between the values of

diffraction angles of the species likely to appear. In the light of these results, it was accepted that there was only a weak chance that any oxyhydroxides would be observed. These would have certainly undergone dehydration after the sampling, drying, crushing into powder and the delay of a week before performing the analysis. Dehydration would lead to the oxide formation according to the reaction $2\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$. It can be deduced that, at the time of the analysis, rust was made up of magnetite and a mixture of maghemite and hematite but there was absolutely no trace of Akaganeite $\beta\text{-FeOOH}$.

Conclusion

From this study, it can be stated that after two years exposure, and under the particular environmental conditions of the cooling circuit, observable pits were not evident on the surface of the steel; compounds favoured by chlorine did not exist in the rust formed on the circuit; and the increase in chlorine concentration over one year remained low. However, during the procedure of water replacement, the risk was inevitably increased. The emptying and refilling actions caused deterioration in the passive film which tends to protect the steel and caused additional consumption of the construction material as it equilibrated with the fresh deionised water. Without doubt, each renewal of water reduced the thickness of the steel and, inevitably, its service life. It is recommended, therefore, that under conditions such as these of no localised corrosion, the period before water renewal should be extended to more than one year.

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