

## ECONOMIC AND PERFORMANCE EVALUATION OF TWO OXIDISING BIOCIDES IN SEA-WATER COOLING SYSTEMS

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### ABSTRACT

Biofouling of heat exchanger surfaces represents a serious operational problem. Fouling leads to reduced heat transfer efficiency, increased fluid frictional resistance, additional maintenance and operational costs (Bott and Tianqing, 2004). At the present time, legislation is being implemented to restrict the discharge of noxious chemicals with cooling water returned to the environment. Suitable treatment before discharge is likely to be necessary to meet the requirements of the legislation, but a better alternative may be to use alternative biocides. The thrust of the research reported in this paper was to examine the possibility of using peracetic acid (PAA) as an alternative to chlorine, referred to NaClO, in a 550 MW power station, located in Southern Spain. A portable pilot plant, specially designed for this purpose has been used for side-stream fouling monitoring. Circulating sea-water is drawn from the same intake point as the full-scale cooling water system.

### INTRODUCTION

Cooling water systems are used in many industries. In power stations, steam is used to drive the turbine-generators. The pressure drop across the steam turbine is enhanced by condensing the steam at the outlet of the turbine.

Water, used for this purpose, is frequently taken from natural sources, e.g. a river or the sea, and returned to the same source after use. Because of the poor quality of the water, unwanted deposits are often laid down on the condenser surfaces in contact with the water. The deposit restricts heat transfer and thereby reduces the efficiency of the cooling process. A major constituent of the deposits is living matter consisting of microorganisms. In order to maintain the desired performance of the condenser it is necessary to control the accumulation of these deposits. An important consideration in the operation of equipment subject to biofouling is its mitigation. Mitigation techniques broadly fall into (a) mechanical (Bott and Tianqing, 2004; Schmid et al., 2004; Melo and Bott, 1997) and (b) chemical methods (Sohn et al., 2004; Meyer, 2003; Ludensky, 2003; Rajagopal et al., 2003; Ormerod and Lund, 1995). Among these techniques, an effective control technique is to apply a chemical additive, generally referred to as a biocide to kill, reduce or inhibit the activity of the microorganisms.

Because of the detrimental effects on the environment, legislation regulates the discharge of noxious chemicals. Chlorine has been the preferred biocide for many years on account of its effectiveness and relative low cost. Application of biocides against microorganisms is generally practised on a continuous or intermittent mode, depending on the nature of organisms and the severity of the problem. The most important criteria deciding the chlorine dosing frequency are cost and environmental discharge specifications (Mattice and Zittel, 1976). Further, frequency of dosing in relation to biocide concentration can optimize the cost of mitigating the problem (Melo and Bott, 1997). Optimal conditions are likely to be different for different biocides and different operating conditions (Bott and Tianqing, 2004). Chlorine has been used particularly in once-through cooling water systems where large volumes of water are used, in order to minimize the cost of treatment. This results in substantial quantities of chlorine being discharged to the environment, with a serious effect on wild life.

At the present time, legislation is being implemented to restrict the discharge of noxious chemicals with cooling water returned to the environment. Suitable treatment before discharge is likely to be necessary to meet the requirements of the legislation, but a cheaper alternative may be to use alternative biocides. The aim of the research reported in this paper was to examine the possibility of using peracetic acid as an alternative to chlorine in the power station studied. The peracetic acid used is a commercially available product, with a dosage recommended by the manufacturer of 60 mg l<sup>-1</sup> during 15 minutes per day (Schneider, 2000). The residual chlorine concentration at the cooling water discharge from the power station is 0.2 mg l<sup>-1</sup> and has been considered appropriate for the prevention of fouling, because with this concentration approximately 90% reduction in the potential fouling is obtained. Residual chlorine dosages lower than 0.2 mg l<sup>-1</sup> could be effective in controlling fouling development, if mechanical techniques of fouling control are also available.

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

## MATERIAL AND METHODS

### Experimental set-up

Because 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 requiring that the monitoring equipment is suitable for transportation from site to site. In order to fulfill these requirements, the experiments on continuous chlorination and pulsed PAA were carried out using a portable pilot plant, fabricated to fit inside a twenty foot standard container. The design of the pilot plant facilitates the implementation of studies with different tube materials, diameters, biocides and dosage patterns, which 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 test equipment consists of a shell-and-tube heat exchanger 3,100 mm in length, as specially designed to avoid galvanic corrosion, the shell and pipework use PVC pipes (excluding the heat-exchanger tubes). In order to simulate power station condenser conditions, the material of the five tubes was titanium grade 2. These 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 shell of only 0.4 °C, this being achieved by employing a flow rate of 35 m<sup>3</sup> h<sup>-1</sup> through the shell. Cooling sea-water circulated through the tubes with the flow-rate automatically regulated to maintain a prescribed flow velocity (2 m s<sup>-1</sup>). A diagram and exhaustive description of the different components of the pilot plant have been published (Casanueva *et al.*, 2003).

A NaClO average initial concentration of 0.5 mg l<sup>-1</sup> of active chlorine was obtained using a variable stroke pump (Milton Roy Ltd). This dosage mode ensured that the whole tube received chlorinated water using NaClO. The untreated tube served as a control. Chlorine residual concentration of 0.2 was maintained at the set point automatically by means of a redox sensor that regulated the pulse frequency of the corresponding dosage pump. The sensors were regularly cleaned and calibrated by using 98% quinhydrone. The actual chlorine concentration at the outlet of each tube was measured using the spectrophotometric method of DPD (method n° 4500-Cl G, "Standard Methods for the Examination of Water and Wastewater" APHA-AWWA-WPCF, 1992). The chlorine demand of the water was calculated and dosing adjusted to achieve the required residuals. The residuals were checked once a week and the dosing pulse frequency and stroke length were adjusted accordingly.

The biocidal solution of PAA (a concentration of 60 mg l<sup>-1</sup> maintained over 15 minutes per day) was injected automatically, using another variable stroke pump (Milton Roy Ltd), by a timer device. Its concentration was checked using (Merck RQflex plus) a reflectometric method and a peracetic acid test (1.16975.0001 Merck) with a range of measurement of 1.0-22.5 mg l<sup>-1</sup>.

### Biofouling characterization

Biofouling characterization was done by direct and indirect measurements (Characklis, 1990).

### Extraction and direct characterization of fouling

The tubes were completely cleaned along their 3.1 m length, by means of a double-rubber piston which perfectly fit inside. Details of the device and procedure have been published (Casanueva *et al.*, 2003). The subsequent laboratory measurements, including:

Fouling wet volume, measured after 4 h settling of the collected fouling in an Imhoff cone.

Fouling total mass (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.

### Indirect measurements of fouling

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

Frictional resistance (f): biofouling increases the frictional resistance since the reduction in the tube effective diameter results in an increase in pressure drop through the tube. Frictional resistance is estimated by the Darcy dimensionless friction factor:

$$f = \frac{2 \cdot d_i \cdot \Delta P}{L \cdot \rho \cdot v^2}$$

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 can be easily determined for each tube in accordance with the following equation:

$$R = U^{-1} = \frac{A_o \cdot [(t_{hwo} - t_{cwi}) + (t_{cwo} - t_{cwi})]}{\frac{\pi \cdot d_i^2 \cdot v \cdot \rho \cdot C_p \cdot (t_{cwo} - t_{cwi}) \cdot \ln \frac{t_{hwo} - t_{cwi}}{t_{hwi} - t_{cwo}}}{4}}$$

By calculating the difference in  $R$  between fouled and clean conditions, the fouling resistance 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.

### Costs of the treatments

The calculations are made supposing 365 days of treatment per year. From the results of Table 3 the viability between the two oxidising biocides in economic terms will be discussed.

### Continuous chlorination

Experiments on optimizing the biocidal dose required for fouling control were carried out using different chlorine residuals of 0.05, 0.10, 0.15 and 0.20  $\text{mg l}^{-1}$  measured at the cooling water discharge. After evaluating the results, 0.20  $\text{mg l}^{-1}$  was considered appropriate for the prevention of fouling because with this concentration approximately 90% reduction in the potential fouling is obtained compared to the control tube (Nebot *et al.*, 2005). Residual chlorine dosages lower than 0.2  $\text{mg l}^{-1}$  could be effective in controlling fouling development if mechanical techniques of fouling control are also available.

The experimental run was for a period of 78 days in the course of the spring season of 2003. Spring and summer show bigger effects of fouling, so this period could be considered as the most adverse operational conditions. The deposit was removed from the chlorinated tube at the end of this period, so that direct measurements could be made. While the experiment was running the indirect measurements were recorded.

### Pulsed peracetic acid

Experiment with pulses of PAA were carried out in the same conditions of NaClO. The PAA injected dosage was 60  $\text{mg l}^{-1}$  during 15 minutes per day.

## RESULTS

In this section are shown the results that allow performance and economic evaluation: a) Thickness ( $\delta$ ) and total solids ( $W$ ) per  $\text{cm}^2$  were used as direct measurements (Table 1), b) the increment in frictional resistance and heat transfer resistance as indirect measurements (Table 2). These measurements assessed the effectiveness of NaClO continuous dosing *versus* pulsed PAA dosing c) The total cost of the two oxidising biocides for a period of a year,

considering 365 days of use, to provide data on the viability of the alternative biocide (Table 3).

Table 1. Direct measurements for Control, NaClO and PAA dosed tubes from the pilot plant (spring 2003).

	Control	PAA	NaClO
Dosage $\text{mg l}^{-1}$	0	60	0.50
$W \text{ mg/cm}^2$	1.36	0.43	0.16
$\delta \text{ } \mu\text{m}$	434	119	60
$W \text{ \% reduction}$	0	73	86
$\delta \text{ \% reduction}$	0	68	88

Fig. 1 Development of the Darcy factor for Control, NaClO and PAA dosed tubes (spring 2003).

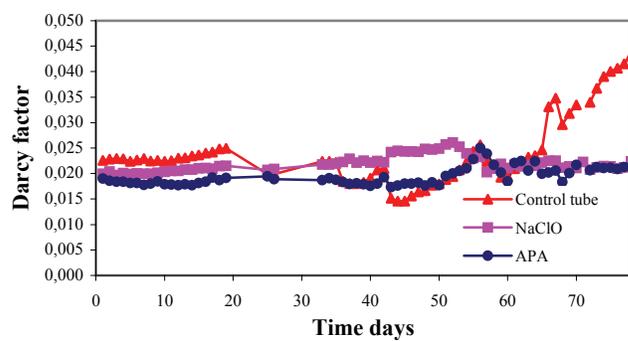


Fig. 2 Development of heat transfer resistance for Control, NaClO and PAA dosed tubes (spring 2003).

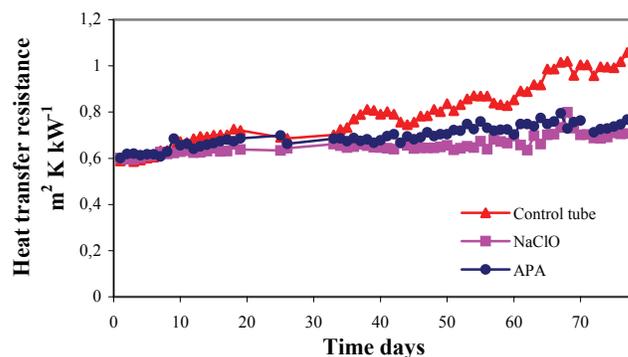


Table 2. Indirect measurements, showing the results for Control, NaClO and PAA dosed tubes, obtained from the pilot plant during (spring 2003).

	Control	PAA	NaClO
$\Delta f$	0.0199	0.0030	0.0024
$\Delta R, \text{m}^2 \text{ K kW}^{-1}$	0.5821	0.1902	0.1103
$f \text{ \% reduction}$		85	88
$R \text{ \% reduction}$		67	81

Table 3. Cost of the NaClO<sub>e</sub>, NaClO<sub>c</sub> and PAA in the power station

	NaClO <sub>e</sub>	NaClO <sub>c</sub>	PAA
Water Volume, m <sup>3</sup> h <sup>-1</sup>	53574	53574	53574
Dosage Concentration, mg l <sup>-1</sup>	0.5 chlorine <sub>a</sub>	0.5 chlorine <sub>a</sub>	60
Duration per day, min	continuous	continuous	15
Time per year, d	365	365	365
Cost, € ton <sup>-1</sup>	198	72	1500
Quantity, ton y <sup>-1</sup>	235	2347	293
Cost electrodes € y <sup>-1</sup>	16000		
Total Penalty CO <sub>2</sub> € y <sup>-1</sup>	13613		
Total Cost, € y <sup>-1</sup>	76075	168951	439976

\*The tonnage of NaClO<sub>e</sub> is ten times higher than NaClO<sub>c</sub> because NaClO commercially available form is at 10%.

## DISCUSSION

### Effect of residual chlorine concentration and peracetic acid in fouling deposition

#### Effect on the amount of fouling

The effect of chlorine and peracetic acid dosage on the accumulation of fouling is presented in Table 1. It can be seen that a reduction in the amount of fouling of 86 and 73 percent, respectively, and a biofilm thickness reduction of 88 and 68 percent, respectively, are given by the different doses. It is clear that the effectiveness of the peracetic acid dose is less than the chlorine dose employed. If this dosing regime of the peracetic acid was to be used, then some additional treatment would be necessary to bring the effectiveness to the same level as the chlorine addition.

#### Effect on the transport properties

From the data recorded for each tube (temperature, differential pressure, flow rate, etc.), it is possible to observe the change in two indirect variables as a result of the fouling accumulation. These variables are the Darcy friction factor and the resistance to heat transfer.

It may be seen from Fig. 1, that the friction factor (*f*) is sensitive to the effects of the two dosing regimes when the results for the spring season, are compared with the untreated control tube. The reductions in comparison to the control tube were 88 and 73 percent for the chlorine and peracetic acid dosing, respectively. Despite this result it is probably true to say that the use of the friction factor for

fouling assessment is less sensitive than the measurement of heat transfer resistance.

Taking 0.6 m<sup>2</sup> K kW<sup>-1</sup> as initial value for the overall heat transfer resistance for the control tube, it rose throughout the experiment to the values shown on Fig. 2. The reductions in the increment of the heat transfer resistance for chlorine and peracetic acid tubes, respect to the control tube, were 81 and 67, respectively. At the highest level of 0.20 mg l<sup>-1</sup> chlorine allowed in the discharge, a loss of 15.4 percent in the overall heat transfer coefficient of the power station condensers could be anticipated after 78 days operation. These data are close to an assumed cleanliness factor of 85 percent often used for design purposes. If a greater thermal efficiency is required then it would be necessary to employ some additional mechanical technique to supplement the chlorine dosing, such as the circulation of sponge rubber balls (the Taprogge system). Results from the side-stream device would be useful to assess the combined use of biocide and physical removal method, indicating the period between mechanical cleanings that would be required to maintain the thermal efficiency at the desired level.

### Cost of NaClO and PAA

In case of chlorine produced on site by seawater electrolysis, we also have to consider the cost of electrodes replacement and CO<sub>2</sub> emission penalty due to the power consumption of the sea-water electrolysis. According to Kyoto protocol the present value of additional emission could be 20 € per ton of CO<sub>2</sub>. Taking into account data showed on Table 3., the cost of using industrial sodium hypochlorite and PAA resulted 2.2 and 5.8 times more expensive than chlorine electrolytically generated, respectively. So, after considering the economic and performance evaluation, the use of an alternative biocide as PAA is of doubtful implementation in power stations with open sea-water cooling systems. Unless the chlorine discharge regulations become more and more stringent, chlorine will be the preferred biocide for shore once-through cooling systems.

## CONCLUSIONS

The European Union has introduced legislation to reduce the risks associated with the discharge of hazardous substances including chlorine into the environment (e.g. Water Framework Directive 60/2000/EC). Although the use of controlled chlorine strategy for antifouling treatment of cooling water remains as an option, it is very likely that its use will be further restricted in the future. It is vital therefore to investigate the use of alternative biocides, such as peracetic acid tested in this study, in case it becomes impractical to continue to use chlorine. The cost of alternative chemicals for water treatment such as offered by peracetic acid, will be higher than the use of sodium

hypochlorite and so it will be necessary to devise dosing strategies that minimise the cost of application. The adoption of new treatments will depend on a number of factors that will need to be carefully considered. These include the operating conditions of the power plant, geographical location (Strauus, 1989; Sasikumar et al., 1992), quality of abstracted water (Corpe, 1977), the tolerance ranges of the biofouling species encountered (Jenner, 1980; Sasikumar et al. 1992; Rajagopal et al., 1995) the life stages and size classes of biofouling organisms when exposed to treatment (Rajagopal et al., 1995), and future legislation with respect to water treatment and discharge.

#### NOMENCLATURE

$A$	Outside surface of tube wall, $m^2$
$C_p$	Specific heat capacity of seawater, $J\ kg^{-1}\ K^{-1}$
$d$	Diameter of tube, $m$
$f$	Darcy factor, dimensionless
$L$	Tube length, $m$
$R$	Overall heat transfer resistance referred to outside surface of tube wall, $m^2\ K\ kW^{-1}$
$t$	Temperature, $K$
$U$	Overall heat transfer coefficient referred to outside surface, $kW\ m^{-2}\ K^{-1}$
$v$	Cooling water velocity, $m\ s^{-1}$
$W$	Mass per unit area, $mg\ cm^{-2}$
$\Delta P$	Pressure drop along the tube length, $N\ m^{-2}$
$\delta$	Thickness, $\mu m$
$\rho$	Density of seawater, $kg\ m^{-3}$

#### Subscript

$a$	→ active
$c$	→ commercially available
$cwo$	→ cooling water outlet
$cwi$	→ cooling water inlet
$e$	→ generated on site by electrolysis
$hwi$	→ heating water inlet
$hwo$	→ heating water outlet
$i$	→ inside
$o$	→ outside

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