

Electrochemical cell design for *in situ* measurements in condenser tubes

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An electrochemical cell was specifically designed for testing *in situ* the quality of surface films formed on the cooling water side of condenser tubes in various situations of technical interest. Standard electrochemical techniques can be easily carried out even with the plant in operation, just requiring a half-reduction of the output. Rest potentials and polarization resistance results, together with cyclic voltammograms are presented. The results are in good agreement with those previously obtained by destructive sampling, mounting and using conventional electrochemical cells.

1. Introduction

Copper based alloys have proved to be the most widely used materials for the construction of condenser tubes for coastal power stations [1, 2]. Their resistance against corrosion is generally attributed to the existence of a protective film at the internal surface of the tubes. This film is principally composed of Cu_2O and can be modified by the incorporation of alloying elements, which enhance its protectiveness. For this reason, it is of great interest to study the nature of the surface films formed in various particular situations. In fact, such films have been the subject of several studies. To a great extent the characteristic features of the films depend upon the quality of the seawater. Particular attention has been paid to sulfide polluted waters [3–7] and FeSO_4 dosing [8–11].

However, although the operational conditions are very difficult to reproduce, very few studies have been conducted *in situ* [1, 12]. To be performed in plant, the tests should be done in a few hours, as they require a half-reduction of output. Also they should provide quick answers. Thus, a suitable electrochemical test cell was designed, which can be employed to perform a wide variety of standard electrochemical techniques.

In the present work some preliminary laboratory experiments will be described to illustrate several of the potential applications.

2. Experimental details

2.1. General

The seawater used to grow natural passivating films was Atlantic Ocean water, stored in polyethylene drums for not longer than one week, and periodically aerated.

All solutions were prepared from p.a. grade chemicals and doubly distilled water from KMnO_4 . Either 0.1 M borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) or 35 g dm^{-3} NaCl

were employed as electrolyte. When FeSO_4 additions were necessary, the Fe^{2+} concentration in the final solution was determined spectrophotometrically by the orthophenantroline method. Sulfide ions were added from a concentrated Na_2S stock solution.

All potentials were measured and are referred to the $\text{Hg}/\text{Hg}_2\text{Cl}_2$ saturated reference electrode (SCE). The potentiostat employed was a EG&G PAR scanning potentiostat (model 362). The plots were registered on a Houston Instrument X–Y recorder (model 2000).

The experiments were conducted at room temperature, $20 \pm 2^\circ\text{C}$.

2.2. Apparatus

A cell was specifically designed for testing *in situ* the quality of surface films formed on the cooling water side of condenser tubes by means of standard electrochemical techniques. The present design overcomes some of the drawbacks of one previously employed [1].

Figure 1 shows a diagrammatic sketch of the cell. The cell dimensions enable its insertion into the heat-exchanger tubes without making contact with the inner side, so as to avoid disrupting the film. Once the cell is placed inside the tube, one extreme of a lever, A, can be pushed upwards against the tube by means of screw B. When this is done, the cell moves downwards so that pressure is exerted on the rubber seal C, keeping it tightly against the tube to avoid leakage of the electrolyte. The seal is rectangular in shape and purpose molded using any commercial silicone rubber. The dimensions of hole D and those of the rubber seal around it define the electroactive area (working electrode). The area chosen in the present design is 1 cm^2 . A platinum disc (E) placed in one extreme of the chamber acts as counter electrode. The electrical connections from the cell to the potentiostat are made through G. The cell can be filled with any suitable electrolyte through

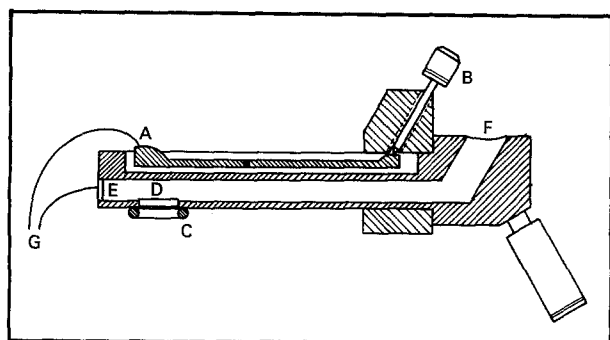


Fig. 1. Scheme of the electrochemical cell employed in the present study. (A) extreme of a lever that moves upwards screwing (B); (C) rubber seal; (D) hole that defines the electroactive area; (E) platinum disc; (F) inlet for reference electrode; (G) electrical contact for counter and working electrodes.

the hole F, at the other end. Once filled, the reference electrode can be placed in this hole. Unscrewing B, the lever A moves down, so that the cell can be inserted and removed without touching the surface films naturally formed.

2.3. Description of the specimens

To illustrate the general capabilities of the cell only laboratory tests will be described in the present report. The specimens under study were aluminium-brass cylinders (2.29 cm ext. diam. \times 0.11 cm wall thickness \times 10 cm long) cut from condenser tubes. The aluminium-brass composition (CDA 687) is shown in Table 1.

Prior to starting any of the treatments described below, the internal surface of the tubes was abraded with 600 grit emery paper, after which the tubes were kept in contact with seawater for three days (except for condition I).

2.4. Experimental conditions

Five different pretreatments were tested on the tubes in order to grow surface films of different qualities.

Condition I: The internal surface of the tubes was smoothed with 600 grit emery paper and electrochemically tested immediately afterwards. This will be referred later as the 'polished condition'.

Condition II: The tubes were kept in contact with seawater for two weeks. This condition will represent the behaviour of the surface films formed in unpolluted seawater ('aged situation').

Condition III: 1 ppm $S^{=}$ was added to the seawater three times per day for two weeks. This condition simulates the effect of polluted seawater.

Condition IV: The tubes were treated with $FeSO_4$. Four treatments were performed each day for two

Table 1. Chemical composition of aluminium-brass (% by mass)

Cu	Al	Zn	Fe	P	Sn
77.5	2.4	19.8	0.04	0.01	0.01

weeks. Each treatment consisted of the following sequence of steps:

- seawater was aerated for 10 min.
- 3 ppm Fe^{2+} were added each 20 min for 1 h.

As the $FeSO_4$ solution is an acidic one, seawater pH was kept at its normal value (8 ± 0.2) adding diluted NaOH solution when necessary.

This condition simulates the ferrous sulfate dosing to condenser tubes, which constitutes a common practice in most thermal power stations where seawater is used as refrigerant.

Condition V: The tubes were alternately treated with $S^{=}$ and Fe^{2+} solutions, as described in conditions III and IV. The treatments followed the sequence $Fe^{2+} - S^{=} - Fe^{2+} - S^{=} - Fe^{2+} - S^{=} - Fe^{2+}$, which is the reason why three $S^{=}$ additions were performed in condition III and four Fe^{2+} additions in condition IV. This sequence was repeated every day for two weeks.

This pretreatment was devised to study the effectiveness of the $FeSO_4$ dosing in polluted seawater.

The tubes were kept in clean seawater during the night (except for condition I). During all the treatments the tubes were kept in a horizontal position and during conditions III, IV and V, the seawater was stirred by means of a magnetic stirrer. Results are shown as average values over more than 20 samples.

2.5. Description of the electrochemical techniques

Rest potentials (E_r) were measured in 0.1 M borax solutions, and 35 g dm^{-3} NaCl solutions, using a high impedance multimeter.

Polarization resistance measurements were performed employing 35 g dm^{-3} NaCl as electrolyte. The first step consisted of determining the stability value for the rest potential. This demanded between 5 and 15 min, depending on the pretreatment to which the electrode had been subjected (as described above). Then the electrode was polarized to a potential value 0.015 V negative to E_r . After stabilization, the current was recorded (Δi). Then the E_r was measured again. The same value was usually obtained, although in some occasions a slightly different value resulted, the difference being within 5%. The

Table 2. E_r values measured in deaerated 0.1 M borax solution (electrolyte A) and 35 g dm^{-3} NaCl (electrolyte B)

Condition, electrolyte	E_r /V vs SCE
I, A	-0.120 ± 0.005
II, A	-0.201 ± 0.011
III, A	0.030 ± 0.030
IV, A	-0.175 ± 0.025
V, A	-0.135 ± 0.013
I, B	-0.255 ± 0.019
II, B	-0.292 ± 0.024
III, B	-0.120 ± 0.060
IV, B	-0.327 ± 0.049
V, B	-0.269 ± 0.016

Table 3. R_p values calculated using Equation 1
Results obtained in 35 g dm⁻³ NaCl

Condition	$R_{p+}/k\Omega\text{ cm}^{-2}$	$R_{p-}/k\Omega\text{ cm}^{-2}$
I	7 ± 2	5 ± 1
II	170 ± 131	70 ± 15
III	14 ± 5	5 ± 3

procedure was then repeated. The new potential value was 0.015 V positive to E_r and the anodic current was registered ($\Delta i+$).

With these data, the anodic and cathodic polarization resistance parameters, R_{p+} and R_{p-} , respectively, were calculated as

$$R_{p+} = 15/\Delta i+ \quad \text{and} \quad R_{p-} = 15/\Delta i- \quad (1)$$

where if $\Delta i+$ is measured in $\mu\text{A cm}^{-2}$, R_p is in $k\Omega\text{ cm}^2$. These values can be tested using the 'pass or fail' criteria originally proposed by Effertz and Fichte for α -brass [8] and used later by Parker and Roscow for brass and cupronickel [12]. Syrett and Macdonald [13] have shown the validity of polarization resistance to evaluate the corrosion rate of copper-nickel alloys in seawater.

Prior to recording cyclic voltammograms the specimens were kept for 5 min at E_r . The voltammograms were then registered at 0.02 V s⁻¹ in deaerated 0.1 M borax solution starting at E_r , between the potential limits of hydrogen evolution (-0.8 V) and E_r . In the first half cycle from E_r to -0.8 V, the reduction of the surface species formed during the corresponding treatment was measured. Then another complete cycle was registered for comparison.

3. Results and discussion

3.1. Rest potential

Typical values for the rest potentials, E_r , measured under various experimental conditions are shown in Table 2.

With reference to the E_r value for the polished specimens (condition I), the E_r value moves in the negative direction as the pretreatment changes from polished to Fe²⁺ treated or aged samples. This can be interpreted in terms of the mixed potential theory assuming that corrosion processes on copper alloys are cathodically controlled, so that it is the rate of oxygen reduction which is reduced in the presence of a passivating film.

This interpretation has been proposed earlier in the literature [4, 7, 14]. If the effect of the passivating film is to reduce the rate of the anodic dissolution, the E_r values should move towards more positive values for conditions II and IV, which is opposite to the observed direction.

The most positive E_r value is obtained when the passivating film is formed in sulfide containing seawater (condition III). In the case of copper-nickel alloys, a similar effect was described before by other

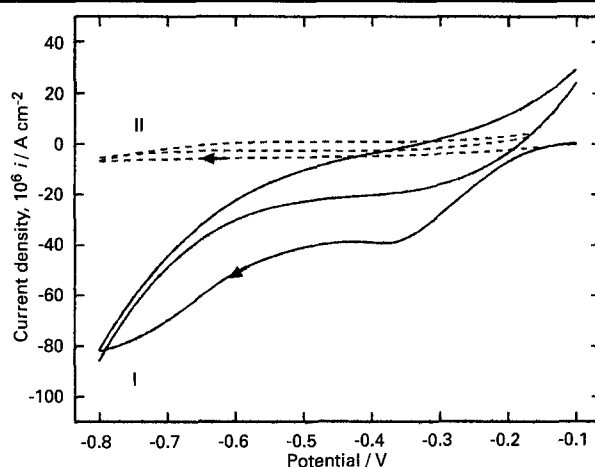


Fig. 2. Cyclic voltammograms in deaerated 0.1 M borax solution at 0.02 V s⁻¹. The potential scan goes from E_r to -0.8 V and then a further complete cycle is shown. Full line: polished specimens (condition I); dashed line: aged specimens (condition II).

authors [5, 6]. Again, this result is in good agreement with that predicted by the mixed potential theory when taking into account that the incorporation of sulfide ions to the passive film enhances the cathodic half-reaction.

Finally, for condition V, the specimens show intermediate values between those of the Fe²⁺ treated samples and the S⁼ treated ones, proving the effectiveness of ferrous dosing in sulfide polluted waters. The results obtained in two different electrolytes show the same tendency.

3.2. Polarization resistance

This kind of test was performed to compare extreme conditions, such as I, when no passive film is present, in contrast to II, where the specimens are aged and a film naturally forms, and IV where a passive film is formed in the presence of Fe²⁺ ions. $R_{p\pm}$ values were calculated by Equation 1. The results are presented in Table 3. These results are in good agreement with the criteria established by Effertz and Fichte [8]. According to these authors, dangerous corrosion does not occur at condenser tubes made of special brass if

$$R_{p-} > 20 k\Omega\text{ cm}^2$$

$$R_{p+} \approx 10 k\Omega\text{ cm}^2$$

These values are said to be independent of the composition of the water.

The values presented in Table 3 show a broad dispersion. This is probably mainly related to the non-reproducible formation of surface films and is the reason why over 20 samples were tested for each condition. In spite of this dispersion, the bands are clearly separated suggesting that these simple measurements may be used as a semi-quantitative criterion to help determine whether a protective film is being formed in a condenser tube. The results obtained for condition II show that the quality of the surface films naturally formed in unpolluted seawater is very good. It is worth noting, however, that this

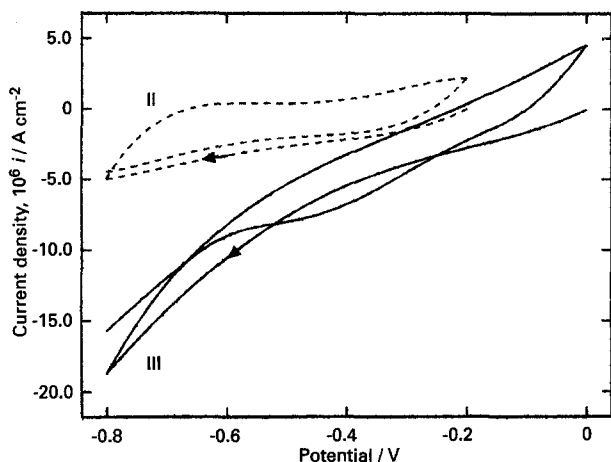


Fig. 3. Cyclic voltammograms in deaerated 0.1 M borax solution at 0.02 V s^{-1} . The potential scan goes from E_r to -0.8 V and then a further complete cycle is shown. Full line: specimens aged in clean seawater (condition II); dashed line: specimens aged in S^{2-} contaminated seawater (condition III).

laboratory test represents a condition seldom attained in plant.

3.3. Cyclic voltammetry

The cyclic voltammograms registered after the different pretreatments are shown in Figs 2 to 4. For the sake of simplicity, they are presented in pairs. It is important to notice the difference in the current scale of the figures. In Fig. 2, the results obtained with the aged and polished specimens are compared. Clearly, in the aged one the currents are comparatively lower. The natural formation of a protective film when keeping the specimen in contact with clean seawater, greatly reduces the cathodic currents. The high currents observed for the polished specimen within the first potential scan from E_r to -0.8 V may possibly reflect the reduction of surface films formed after polishing, as the current is much reduced in further cycles.

The situation of ageing the specimen in clean and polluted seawater is compared in Fig. 3. As can be seen, both the anodic and the cathodic currents increased when the tube was kept in S^{2-} polluted seawater. The disappearance of the so-called 'double-layer' region as an effect of S^{2-} addition has been observed before [6]. This suggests that the repassivation process of this sample is inhibited. This sample also shows a characteristic feature not shown by any of the others. Within the potential range where the reduction of the cuprous species occurs, the currents of the first sweep are lower than those of subsequent ones. This may be due to a difference in the composition of the surface film formed in the presence of sulfide. After the potential is swept in the positive direction, this feature disappears and higher currents are registered.

The voltammograms resulting from samples aged in sulfide contaminated seawater with and without Fe^{2+} dosing (conditions III and V, respectively) are

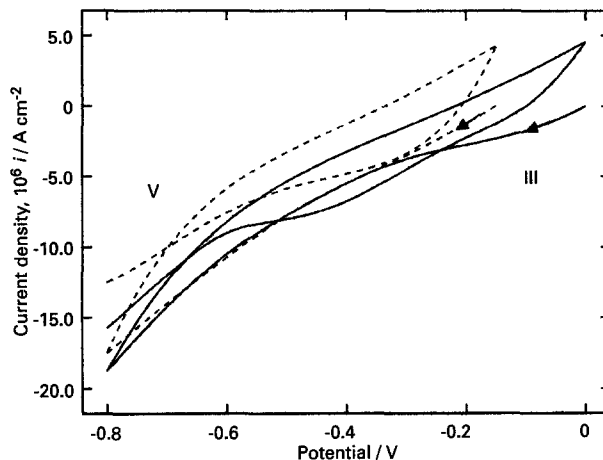


Fig. 4. Cyclic voltammograms in deaerated 0.1 M borax solution at 0.02 V s^{-1} . The potential scan goes from E_r to -0.8 V and then a further complete cycle is shown. Full line: specimens aged in S^{2-} contaminated seawater (condition III); dashed line: specimens subjected alternatively to S^{2-} treatments and FeSO_4 dosing (condition V).

presented in Fig. 4. The Fe^{2+} treated specimens show lower currents in all the potential range investigated.

4. Conclusions

- (i) An electrochemical cell has been designed to be used *in situ* in order to test the cooling water side of condenser tubes.
- (ii) The cell can be easily inserted and removed, so that it can be used even when the condenser is in operation, with a 50% reduction of output.
- (iii) Various electrochemical techniques were applied in order to evaluate the protective character of the passive films grown under five different conditions.
- (iv) The results are in good agreement with those previously obtained by destructive sampling, mounting the specimens and using conventional electrochemical cells.

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