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# Corrosion of brass in natural and artificial seawater

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## Abstract

The corrosion of brass in artificial seawater, (ASW), and in natural seawater, (NSW), collected at the beach of Ericeira, Portugal, was studied. The weight gains and the corresponding average corrosion rates of brass samples, immersed in both media, during periods of 1 week, 1, 3 and 6 months were determined. The concentrations of $Cu^{2+}$ and $Zn^{2+}$ ions in solution, produced by the corrosion of brass, were determined by atomic absorption spectrometry. The concentration of dissolved oxygen was also determined. The morphology of the corroded surfaces, with and without the corrosion products, was analyzed by visual observation and by scanning electron microscopy. The hydrated basic zinc chloro-sulfate compound, $Zn_{12}(OH)_{15}Cl_3(SO_4)_3 \cdot 5H_2O$, was identified by X-ray powder diffraction as the predominant compound in all the samples, particularly in those with longer exposure to NSW. It was concluded that the corrosion of brass in natural seawater is much higher than in artificial seawater.

## 1. Introduction

It is well known that the aggressivity of seawater is mainly due to its chloride content. However, other factors such as the presence of microorganisms can play an important role, since biofilms are a radically different environment in terms of pH, dissolved oxygen and other species.

Copper and its alloys are widely used in marine environments due to their corrosion resistance, mechanical workability, excellent electrical and thermal conductivities and good resistance to *biofouling* due to the high toxicity of cupric ions. Brass is used extensively in marine applications and in heat exchanger tubes, for example in desalination and power generation, respectively.

The corrosion resistance of copper and copper alloys has been attributed to a protective cuprous oxide layer, $Cu_2O$, formed upon exposure. However, these alloys can deteriorate due to the formation of biofilms, whose polymeric structure allows local gradients of pH and $O_2$ to exist [1]. Although the microbiologically influenced corrosion of carbon and stainless steel has been widely studied, it has been little investigated in copper and copper alloys [2–8]. Mansfeld and Little [3] have concluded that copper alloys exposed to NSW were colonized by bacteria in 3 weeks, and that in all cases the corrosion rates in NSW were higher than those in ASW. For the 70Cu–30Ni alloy they found intergranular corrosion and denickelification after 1 month exposure.

Sequeira and collaborators [6] have postulated, with basis on impedance measurements of admiralty brass in NSW and ASW, a mechanism for the biofilm-related deterioration of brass in NSW.

Kharafi et al. [7] observed a selective dissolution of brass at various potentials and chloride concentrations, and concluded that chloride promotes the dissolution of copper and zinc.

Ravichandaran and Rajendran [9] studied the effect of organic inhibitors on the electrochemical behaviour of brass in ASW.

In this work parallel experiments were carried out with brass coupons exposed to sterilized ASW and to NSW collected from Ericeira Beach, Portugal, transported to the laboratory and kept at 4 °C. The concentration of dissolved $O_2$ was monitored during the various exposure periods. Nagiub and Mansfeld [10] and also Huang et al. [5] have emphasized the importance of performing studies in natural seawater under controlled anaerobic conditions.

## 2. Experimental details

Coupons of brass (63.8% Cu; 36.1% Zn; 0.018% Fe; 0.009% Ni; 0.008% Pb; 0.007 % Sn and 0.001% Al), with dimensions of $1 \times 2.5 \times 0.1$ cm, were used for weight loss studies in natural and artificial seawater, in triplicate for each medium and exposure time. All coupons were polished with emery paper and with alumina powder down to 0.05 $\mu$m, rinsed several times with distilled water, degreased with acetone, washed again with distilled water and dried. All coupons were weighed prior to and after exposure.

McCartney bottles were used. All the material was carefully cleaned and sterilized in an autoclave at 120 °C. The coupons were transferred to the exposure bottles, under aseptic conditions, in a chamber with an inert atmosphere.

Artificial seawater, ASW, was prepared by dissolving 40 g of Sea Salts from a Sigma Cell Culture (24.53 g NaCl + 11.10 g $MgCl_2 \cdot 6H_2O$ + 1.54 g $CaCl_2 \cdot 2H_2O$ + 0.70 g KCl + 0.017 g $SrCl_2 \cdot 6H_2O$ + 4.09 g $Na_2SO_4$ + 0.20 g $NaHCO_3$ + 0.10 g KBr + 0.03 g $H_3BO_3$ + 0.003 g NaF) in 1 l of deionized Milli-Q water, from Millipore®.

Natural seawater, NSW, was collected in a sterilized brown flask, at Ericeira beach, Portugal, in March 2004 (winter time), transported and kept in the laboratory at 4 °C. The chemical analysis of the NSW samples was carried out according to standard methods [11].

The concentration of $Cu^{2+}$ and $Zn^{2+}$ in the solutions after the various exposure periods was determined with an atomic absorption spectrometer PyE Unicam model SP9. pH values were measured with a Meterlab portable pH meter, model pHM201. The concentration of $O_2$ was determined, at room temperature, following standard procedures.

The open circuit potentials, (OCP), in duplicate, of brass samples immersed in natural and in artificial seawater in a flask connected to the reference electrode *via* a $KNO_3$ salt bridge were determined with a digital HP® 34 401A multimeter connected through an RS-232 interface to an IBM PC model 80286 which allowed automatic data acquisition during the 18 days of the experiment.

X-ray powder diffractograms were obtained with a Philips PW 1710 diffractometer equipped with a graphite monochromator coupled to a vertical goniometer PW 1820. The X-ray source (Cu-Kα radiation) was operated at 30 mA and 40 kV, with automatic data acquisition (APD Philips (v 3.5 B) software). The diffractograms were obtained in the 2( range of 3–90° at a scan rate of 0.02° $s^{-1}$.

SEM/EDS studies of brass samples after a 6-month exposure, with and without the corrosion products, were performed with a scanning electron microscope JEOL, model JSM-6400.The EDS spectra were recorded with an X-ray diffractometer from Oxford Instruments, model Inca x-sight. The corrosion products were removed by dipping the coupons during 5–10 s in a solution of sulphuric acid and potassium dichromate, according to [12].

The dezincification factor, $z$, was calculated with the equation:

$$z = (Zn/Cu)_{sol}/(Zn/Cu)_{alloy} \qquad (1)$$

where $(Zn/Cu)_{sol}$ is the ratio between $Zn^{2+}$ and $Cu^{2+}$ ions in solution, and $(Zn/Cu)_{alloy}$ is the ratio between the two elements in the alloy. Thus, a dezincification factor higher than one means preferential dissolution of zinc.

## 3. Results and discussion

### 3.1. *Seawater analysis*

The NSW samples were transparent, colourless and without deposits. The following concentrations expressed in g $dm^{-3}$ were obtained: 20.00 $Cl^-$ + 0.179 $HCO_3^-$ + 2.90 $SO_4^{2-}$ + 11.00 $Na^+$ + 1.321 $Mg^{2+}$ + 0.56 $Ca^{2+}$ + 0.339 $K^+$. The alkalinity was 146.5 mg $dm^{-3}$ $CaCO_3$, the pH at 20 °C was 8.14, and the conductivity at 20 °C was 44.6 mS $cm^{-1}$. The concentration of $O_2$ at 20 °C was 13.0 ppm.

### 3.2. *Open circuit potentials, OCP*

The open circuit potentials (free corrosion potentials) of brass coupons immersed in natural and artificial seawater as a function of exposure time is given in Figure 1. The OCP in NSW showed an almost constant value of −0.210 V vs SCE during the first 4 days of exposure, and then decreased abruptly to a plateau at −0.240 V vs SCE with regular oscillations. On the contrary, in sterilized ASW the OCP increased initially (in the noble direction), from −0.150 to −0.120 V vs SCE, during about 1 day, after which it decreased abruptly. A plateau at −0.230 V vs SCE was recorded from the 8th until the 18th day of exposure. The behaviour of the OCP during the first 5 days is similar to that reported by Little et al. [13] for stainless steel in non-sterilized NSW. The negative displacement of the OCP in both media at longer times may be related to the decrease of the $O_2$ levels (see data in Table 1). In a previous study [14], carbon steel specimens immersed for about 2 days in a culture of sulphate-reducing bacteria (SRB) under anaerobic conditions showed a positive shift of the OCP, from −0.600 to −0.300 V vs SCE, leading to a plateau with regular oscillations. The OCP values are in the same range as those reported by Hostis et al. [8].

Some authors [3, 6, 8] have attributed the negative shift of the OCP to a reduction of the rate of the cathodic reaction (possibly due to the decrease of the $O_2$ in solution) and/or to an increase of the rate of the anodic reaction.

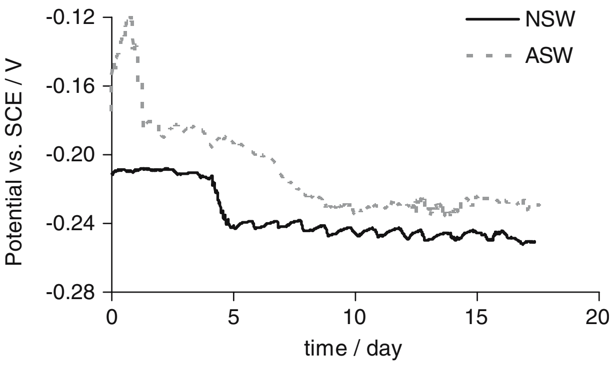

*Fig. 1.* Open Circuit Potential (OCP) of brass coupons in NSW (full line) and in ASW (dashed line).

*Table 1.* Concentrations of $Cu^{2+}$, $Zn^{2+}$, dezincification factor and $[O_2]$, in the solutions in which the brass coupons have been exposed

| Exposure time | $[Cu^{2+}]$ / ppm | | $[Zn^{2+}]$ / ppm | | Dezincification factor | | $[O_2]$ / ppm |
|---|---|---|---|---|---|---|---|
| | ASW | NSW | ASW | NSW | ASW | NSW | NSW |
| 0 | – | – | – | – | – | – | 13.0 |
| 1 week | 0.6 | 1.1 | 0.4 | 4.5 | 1.2 | 7.2 | 6.9 |
| 1 month | 0.7 | 2.3 | 1.1 | 6.3 | 3.0 | 4.8 | 2.3 |
| 3 months | 0.9 | 41.2 | 1.3 | 6.0 | 2.6 | 0.3 | 1.5 |
| 6 months | 1.0 | 48.6 | 2.2 | 20.7 | 3.9 | 0.8 | 0.8 |

The regular oscillations of the OCP curves of brass in natural seawater are indicative of the occurrence of pitting. However, as emphasized by Mansfeld and Little [13], no valid conclusions can be drawn from OCP measurements alone.

### 3.3. *Weight gains and losses*

The evolution of the weight gain with time is plotted in Figure 2. The average weight gain of brass coupons immersed in NSW was much higher than that in ASW, so much so that after 6 months of exposure the respective weight gains were 18 and 2.5 g $m^{-2}$, respectively.

The concentration of $Cu^{2+}$ and $Zn^{2+}$ ions in solution produced by the corrosion of brass, and the levels of dissolved oxygen, are given in Table 1. After 3 months of exposure the $Cu^{2+}$ concentration in NSW was of 41 ppm, while in ASW it was only 1 ppm. The concentration of $Zn^{2+}$ increased only slowly in ASW, while in NSW it increased from 6 to 20 ppm upon increasing the exposure from 3 to 6 months. After 6 months of exposure to NSW the concentration of $Cu^{2+}$ was about twice that of $Zn^{2+}$ (ca. 50 vs 20 ppm).

The dezincification factor of brass samples in NSW was very high during the first week ($z = 7$), but then decreased to 0.3 after 3 months, while in ASW it increased during the whole exposure time, from 1 to about 4. Therefore, in NSW preferential dissolution of Zn occurred only initially, after which the dissolution of Cu predominated. On the contrary, in ASW preferential dissolution of Zn occurred over the whole exposure time.

In both media the concentration of dissolved $O_2$ decreased with time, reaching values as low as 0.8 ppm after 6 months. It is worthwhile mentioning that while in NSW $[Zn^{2+}]$ increased from the 3 to the 6 months exposure, the intensities of the main peaks at $2\theta = 6.5°$ and $2\theta = 13.65°$ in the X-ray powder diffractograms, assigned to Zn corrosion products, decreased from 100 to 33.8 % and from 14.1 to 8.6 %, respectively (see data in Figure 3), in a clear indication that the $Zn^{2+}$ in solution was produced by dissolution of the zinc corrosion compounds.

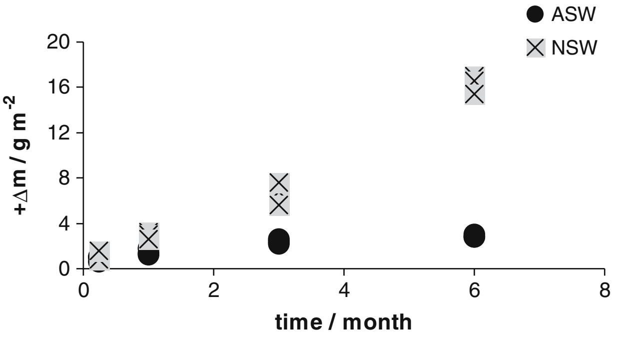

*Fig. 2.* Plots of weight gains of brass coupons as a function of exposure time to NSW (filled squares) and to ASW (filled diamonds).

The average corrosion rates estimated from weight losses after removal of the corrosion products are given in Table 2. In both media the average corrosion rate decreased significantly with time, and was higher in NSW, although after 6 months it was about the same in NSW and ASW, 1.4 and 1.3 mg $dm^{-2}$ $day^{-1}$, respectively ($0.60 \times 10^{-2}$ and $0.56 \times 10^{-2}$ mm/year), an excellent resistance when generalized corrosion is considered. Corrosion rates after 1 week are of the same order as those recently reported by Ravichandran and Rajendran [9] for brass after 5 days in ASW ($\approx 10 \times 10^{-2}$ mm/y). Since the corrosion rates are so low after a 6-month exposure, one may conclude that a protecting film is almost completely formed after 3 months by reaction of the main anions of the seawater ($Cl^-$, $SO_4^{2-}$ and $HCO_3^-$) with copper and zinc, as follows:

$$Cu + Cl^- \rightarrow CuCl\ (\text{nantokite}) + e \tag{2}$$

$$4CuCl + 1/2O_2 \rightarrow Cu_2O\ (\text{cuprite}) + 2CuCl_2 \tag{3}$$

$$CuCl + Cl^- \rightarrow CuCl_2^- \tag{4}$$

$$2CuCl_2^- + 2OH^- \rightarrow Cu_2O\ (\text{cuprite}) + H_2O + 4Cl^- \tag{5}$$

$$Cu_2O + 1/2O_2 + Cl^- + 2H_2O \\ \rightarrow Cu_2(OH)_3Cl\ (\text{atacamite/paratacamite}) + OH^- \tag{6}$$

$$4Cu + SO_4^{2-} + 6H_2O \rightarrow CuSO_4 \cdot 3Cu(OH)_2 \\ (\text{brochantite/antlerite}) + 6H^+ + 8e \tag{7}$$

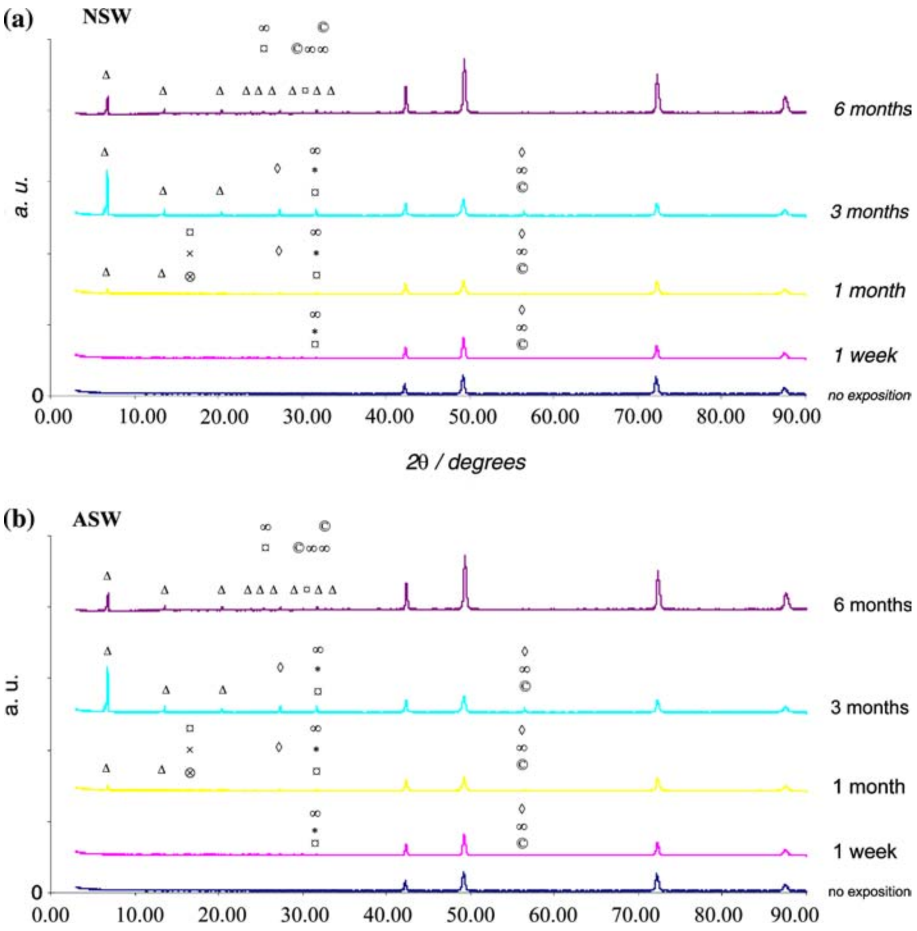

*Fig. 3.* X-ray powder diffractograms of the corrosion products of brass coupons exposed to: (a) NSW; (b) ASW for 1 week, and 1, 3 and 6 months. Symbols: × $Cu_4SO_4$ $(OH)_6$, ◇ NaCl, Δ $Zn_{12}(OH)_{15}Cl_3(SO_4)_3.5H_2O$, ⊗ $Cu_4SO_4(OH)_6.H_2O$, ¤ $Zn_5(OH)_8Cl_2$, * CuS, ∞ $Cu_2Cl$ $(OH)_3$, © $Cu_2(OH)_3Cl$.

Zinc in the alloy may also contribute to the formation of the following corrosion compounds: hydrated zinc basic chloride-sulphates, $Zn_{12}(OH)_{15}Cl_3(SO_4)_3 \cdot 5H_2O$, zinc hydroxide chloride, $Zn_5(OH)_8Cl_2 \cdot H_2O$, s*imonkoleite*, zinc hydroxides, $Zn(OH)_2$, and zinc carbonates, such as $Zn_2CO_3(OH)_6$ (*hidrozincite*), among others. The zinc compounds, in general, are white or pink, while the copper compounds, *i.e.* paratacamite, atacamite, brochantite, antlerite have a greenish colour. Nantokite is white-grey, while azurite is blue.

Brass coupons immersed in NSW for 1 week show a brownish colour, possibly from $CuCl_2$ or $Cu_2O$ mixed with other compounds, small greenish-blue zones, possibly paratacamite/atacamite and/or brochantite/antlerite, and white precipitates of zinc compounds or nantokite. After 1 month the coupons had a heterogeneous patina (brownish, greenish-blue, white and pink). After 3 and 6 months the coupons showed several greenish-blue and white zones with larger areas covered with corrosion products, particularly in NSW. Pink and white corrosion products, possibly the basic zinc chloride-sulphate, $Zn_{12}(OH)_{15}Cl_3(SO_4)_3 \cdot 5H_2O$, were also observed. There were less pink compounds after 6 months than after 3 months. The reddish colour characteristic of cuprous oxide was not observed in the 3 and 6 months exposed samples. In fact, if it forms it is during the first few days only, being then transformed into paratacamite/atacamite.

*Table 2.* Average corrosion rates of brass as a function of exposure time

| Exposure time | $v_{corr}$ / mg $dm^{-2}$ $day^{-1}$ | | $10^2\Delta x/t$ / mm $y^{-1}$ | |
|---|---|---|---|---|
| | ASW | NSW | ASW | NSW |
| 1 week | 11.4 | 16.8 | 4.9 | 7.2 |
| 1 month | 3.2 | 5.1 | 1.3 | 2.2 |
| 3 months | 1.3 | 1.9 | 0.6 | 0.8 |
| 6 months | 1.3 | 1.4 | 0.6 | 0.6 |

### 3.4. *Surface morphology and corrosion products*

Figure 3 shows the X-ray powder diffractograms of the corrosion products formed on brass coupons immersed in natural and artificial seawater after the various exposure periods. The main compounds were $Zn_{12}(OH)_{15}Cl_3(SO_4)_3.5H_2O$ and possibly traces of NaCl in all the samples for all the exposure periods (3 and 6 months) and for both media. Atacamite, $Cu_2Cl(OH)_3$,

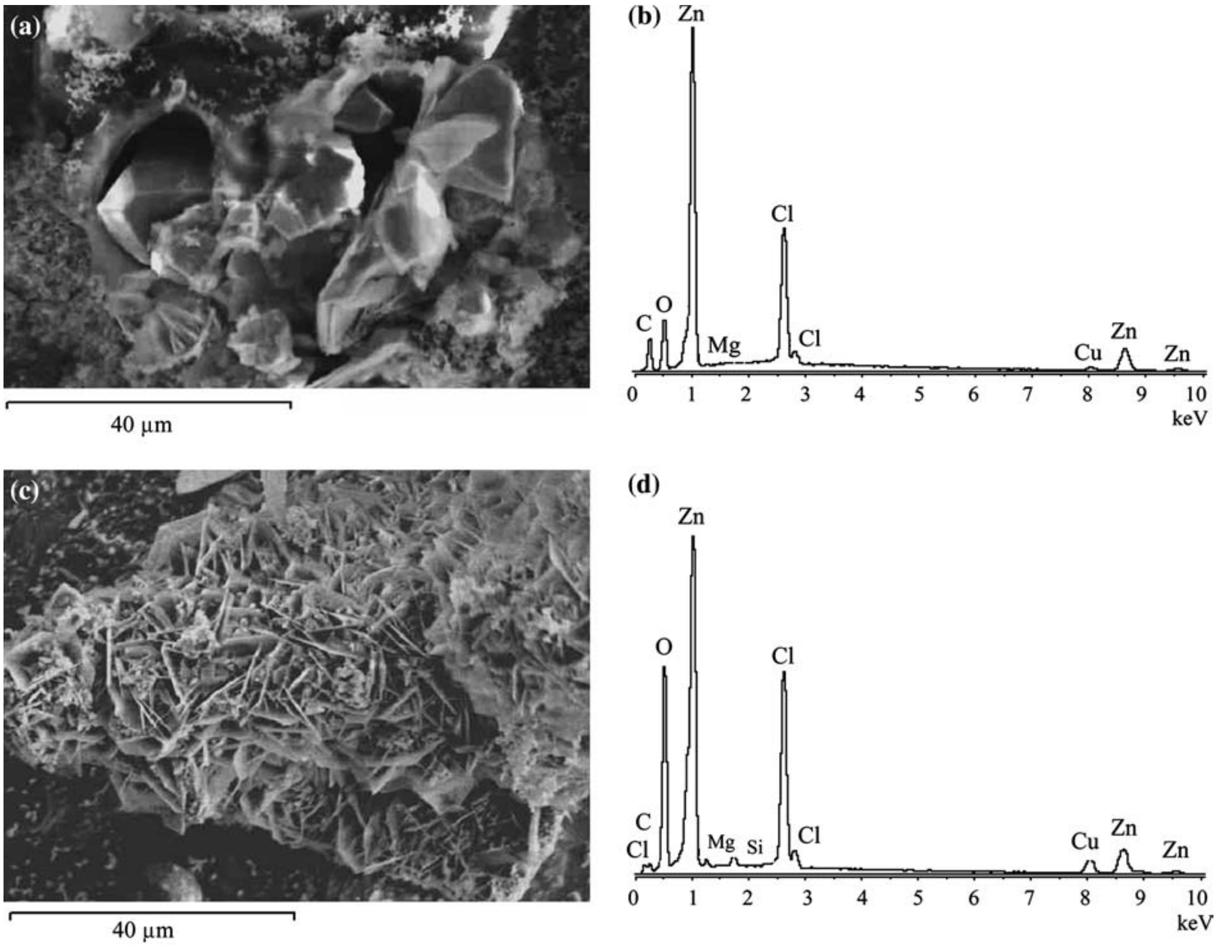

*Fig. 4.* SEM micrographs ($A = \times 100$) of brass coupons with 6 month exposure to: (a) NSW; (c) ASW; (b) and (d) corresponding EDS spectra.

and paratacamite, $Cu_2(OH)_3Cl$, were identified in coupons after longer exposures to NSW and after 1 month in ASW, while brochantite, $Cu_4SO_4(OH)_6$, was detected only after longer exposures (1, 3 and 6 months in ASW and 6 months in NSW). The diffraction lines at $2\theta = 6.85°$ and $2\theta = 13.65°$, attributed to $Zn_{12}(OH)_{15}Cl_3(SO_4)_3.5H_2O$ compound, decreased significantly from the 3 to the 6 month exposure to NSW, indicating that this compound had dissolved during the last 3 months of the 6 month exposure.

SEM micrographs and EDS spectra of brass coupons after a 6-month exposure to both media, before the removal of the corrosion products, are given in Figure 4. The coupons immersed in ASW showed a more compact film, whose main constituents were chlorine, oxygen, zinc and copper, with smaller peaks attributed to carbon and magnesium. The same elements were identified in coupons exposed to NSW.

SEM images showed, already at lower amplifications, a significant influence of the medium on the morphology of the film (Figure 5). A porous layer was most probably produced by selective dissolution of zinc, leaving almost pure copper (see Figure 5(a)), as reported by other authors. Tubercles above pits are also visible in the SEM images of Figure 5(b).

After the removal of the corrosion products the coupons exposed for 6 months to NSW showed well-defined large round pits, while those exposed to ASW showed only very small pits without a well-defined shape (black spots in Figure 6). Some remaining corrosion products are still visible in Figure 6(b) (white zones).

## 4. Conclusions

Higher corrosion rates and higher amounts of corrosion products were observed on brass samples immersed in NSW as compared with ASW, this being necessarily due either to the organic matter and/or to the microorganisms of NSW.

Dezincification was much higher in NSW, particularly during shorter exposure periods (dezincification factor of 7 after 1 week), while decuprification predominated upon longer exposures (3 and 6 months). On the other hand, in ASW dezincification occurred for all exposure periods, although its maximum value, 4, was about half of the corresponding value in NSW.

The nature of the medium strongly influenced the morphology of the corrosion layer as well as the size and morphology of the pits underneath the corrosion

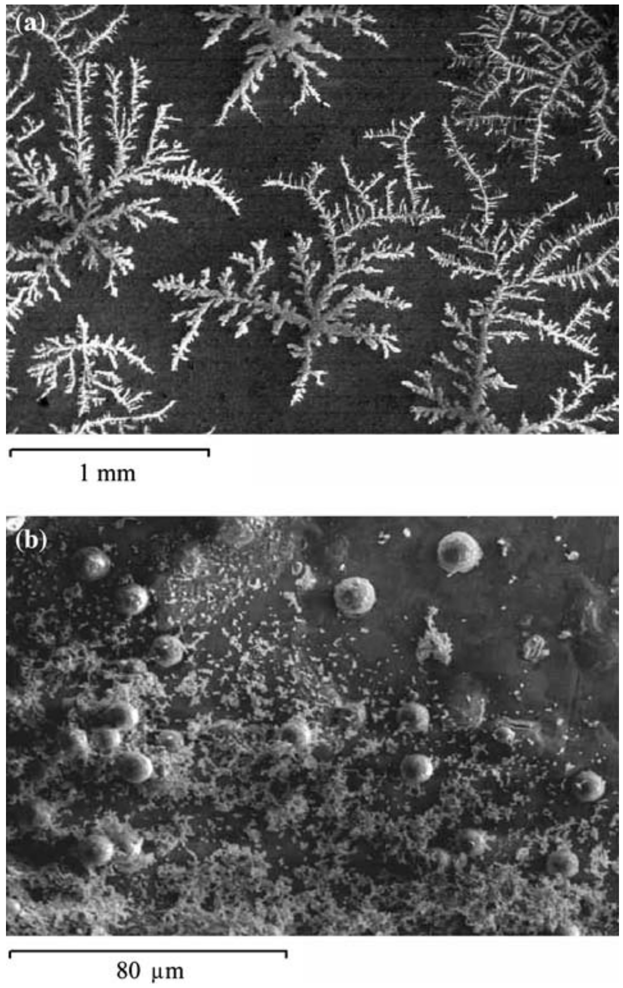

*Fig. 5.* SEM micrographs of brass coupons with 6 month exposure to (a) NSW ($A = \times 40$); and (b) ASW ($A = \times 700$).

products. So, while coupons exposed for 6 months to NSW showed a more open film with well-defined and large pits, those exposed to ASW showed a more compact and uniform film with only a few small pits.

The medium does not significantly affect the nature of the corrosion products, which were mainly hydrated zinc basic chloride-sulphates, $Zn_{12}(OH)_{15}Cl_3(SO_4)_3.5H_2O$ and zinc hydroxide-chloride, $Zn_5(OH)_{18}Cl_2.H_2O$. Copper compounds such as atacamite, $Cu_2Cl(OH)_3$, and paratacamite, $Cu_2(OH)_3Cl$ were also identified after longer exposures to NSW and after 1 month exposure to ASW.

Studies on the corrosion of brass in non-sterilized NSW, under anaerobic conditions, are in progress. We also recognize that it would be important to perform XPS analysis of the corroded bronze surfaces in order to reach conclusions about dezincification.

## Acknowledgements

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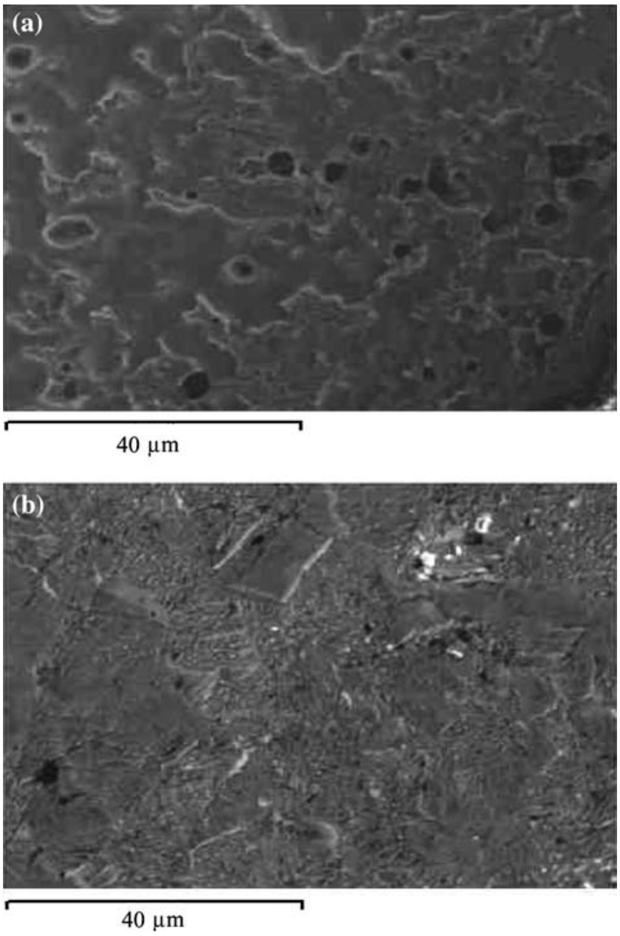

*Fig. 6.* SEM micrographs, after the removal of the corrosion products, of brass coupons after 6 months exposure to: (a) NSW; and (b) ASW.

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