The corrosion behaviour of a low carbon steel in natural and synthetic seawaters

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Synopsis

The corrosion behaviour of a low carbon steel was investigated in natural seawater and various synthetic seawaters. It was found that the steel corroded nearly four times faster in a 3.5% NaCl solution than in natural seawater for an exposure time of 21 days. The corrosion rate after immersion in synthetic seawaters (ASTM D1141 and Marine Biological Laboratory seawater) is similar to the corrosion rate after immersion in natural seawater. Calcium carbonate (aragonite) deposits were found on the surface of the steel after immersion in natural seawater and the synthetic seawaters. Some magnesium-containing deposits were also found after immersion in the natural seawater. These deposits act as a barrier against oxygen diffusion and thereby lower the corrosion rate. The morphology of the calcium carbonate deposits that formed during immersion in the natural seawater is different from those formed during immersion in the synthetic seawaters. This may explain the slightly lower corrosion rates obtained in the natural seawater. X-ray diffraction also showed that the oxy-hydroxides formed in the 3.5% NaCl solution differed from those formed in the other solutions.

Keywords: Corrosion, seawater, low carbon steel, 3.5% NaCl, aragonite

Introduction

The major chemical constituents of seawater are consistent worldwide. However, seawater is still a complex chemical system affected by various other factors. These include the concentration and access of dissolved oxygen, salinity, concentration of minor ions, biological activity and pollutants[1]. Samples of natural seawater, when stored, are known to change in corrosivity from the bulk seawater from which they were taken[2]. This is due in part to the fact that the minor constituents, including the living organisms and their dissolved organic nutrients, are in delicate balance in the natural environment. This balance begins to change as soon as a natural seawater sample is isolated from the parent water mass.

Because of its variability, seawater is not easily simulated in the laboratory for corrosion-testing purposes. A 3.5% NaCl solution is used frequently for this purpose and is known to be more aggressive toward carbon steel than natural seawaters[2]. This has been attributed[3] to the presence of other ions occurring in seawater, particularly Ca^{2+} and Mg^{2+}. The cathodic reduction of oxygen produces local alkaline surface conditions, which precipitate $CaCO_3$ and $Mg(OH)_2$ by Equations [1] and [2]:

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow H_2O + CaCO_3 \quad [1]$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \quad [2]$$
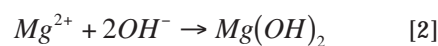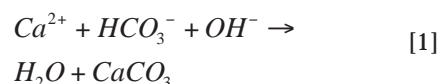
These calcareous deposits[4] are believed to promote a physical barrier against oxygen diffusion and thus decrease the corrosion rate[2,3,5]. Cathodic protection of steel immersed in seawater is known to promote formation of these calcareous deposits[6–8].

Interestingly, a 3.5% NaCl solution is not more aggressive than natural seawater to all alloys. For instance, it has been found that the corrosion rate for aluminium-brass (78.25Cu-14.65Zn-4.5Al-1.5Mg-0.6Mn-0.5Si) is higher in natural seawater than in a 3.5% NaCl solution[9]. In this case the corrosion rate is probably too low to produce the local pH changes needed for the formation of the calcareous deposits.

In order to include the effects of ions other than Na^+ and Cl^- in synthetic seawaters, more elaborate mixtures are available. These include the Marine Biological Laboratory (MBL) synthetic seawater[10] and the ASTM D1141 synthetic seawater[11]. These synthetic seawaters have more complex compositions than the 3.5% NaCl solution and may have less appeal for the quick simulation of seawater behaviour. It must also be remembered that none of these artificial

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seawaters contains organic matter or marine life and therefore do not permit unqualified acceptance of test results as representing performance in natural seawater.

Even though it is stated in literature[2,3] that a 3.5% NaCl solution is more aggressive towards steel than natural seawater, the exact extent for short exposure times is not known that well. It is also not that clear whether the calcareous deposits that form in the synthetic seawaters are similar (in terms of quantity, crystal structure and morphology) to those formed in natural seawaters. Finally, the differences in the oxy-hydroxides that form on low carbon steel when immersed for a few days in 3.5% NaCl solution, synthetic seawaters and natural seawater are not well known. The purpose of this study was therefore to firstly determine how much the corrosion rates of a low carbon steel differ in a 3.5% NaCl solution and in natural and synthetic seawaters. Secondly, the oxy-hydroxides and calcareous deposits that formed in the various solutions were characterized and the differences highlighted and discussed.

Experimental

Seawater

Natural seawater was taken from the Bluff in Durban, South Africa, and stored in closed plastic containers. Again it must be stressed that stored seawater may exhibit different behaviour as a corrosive medium than that of the water mass from which it was taken[1,2].

Three different synthetic seawaters were used in this study. The first solution used was a 3.5% NaCl solution. The more complex solutions studied were the MBL synthetic seawater and the ASTM D1141 synthetic seawater. The chemical compositions of these synthetic seawaters are shown in Table I (note that only compounds with a concentration equal to or larger than 0.1 g/L were included when preparing the artificial seawaters). The main difference between the MBL and ASTM D1141 synthetic seawaters is that SO_4^{2-} is added as Na_2SO_4 in ASTM D1141 seawater and as $MgSO_4$ in MBL seawater. In order to get similar Mg^{2+} concentrations, the $MgCl_2$ content of the ASTM D1141 seawater is much higher than in the MBL seawater. The $CaCl_2$, KCl and $NaHCO_3$ concentrations are slightly higher in the ASTM D1141 solution. A final difference is that the MBL seawater does not contain KBr, whereas ASTM D1141 seawater contains 0.1 g/L KBr.

The conductivities of the solutions were measured for comparison and are shown in Table II.

It is seen that the conductivity of the ASTM D1141 seawater is very similar to that of the natural seawater, with the conductivities of the MBL and 3.5% NaCl solutions slightly lower and higher respectively. The conductivities of the four different solutions are in general rather similar.

Material

Low carbon steel (SAE 1006 [UNS G10060]) was used for the experiments. The chemical composition of this steel is given in Table III.

The steel was cut into 50 x 25 x 2 mm samples. The surfaces of the samples were ground clean using silicon carbide grinding paper starting with grit P180 and finishing with grit P800. The samples were then rinsed in distilled water and dried with ethanol to remove residual water. The cleaning procedure was performed quickly to avoid premature corrosion. The samples were weighed accurately (to an accuracy of 3 decimals) before the immersion tests in order to conduct weight loss experiments.

Immersion

Immersion tests were performed in continuously aerated solutions using two samples per solution. The volume of the solution was 1 000 ml. Aeration was achieved by using a small air pump, which also contributed to uniform experimental conditions by stirring. All experiments were conducted at room temperature (25°C). The samples were immersed in the various solutions for 3, 10 or 21 days. The water in the test cells was refreshed every 5 days for the longer exposure times. Before examination in a scanning electron microscope (SEM), the samples were coated with a sputtered layer of gold in order to reduce charging effects.

The corrosion products on the samples used for the weight loss experiments were removed with Clarke's solution[5] prior to weighing. A scale-free sample was also tested in Clarke's solution to verify that minimal metal loss occurred during this treatment.

Table I

Chemical composition (in g/L) of the synthetic seawaters used in this study

Compound	MBL	ASTM D1141
NaCl	24.72	24.53
$MgCl_2$	2.18	5.20
$CaCl_2$	1.03	1.16
KCl	0.67	0.70
Na_2SO_4	-	4.09
$MgSO_4$	3.07	-
$NaHCO_3$	0.18	0.20
KBr	-	0.10

Table II

Conductivities of the various solutions used in this study

	Natural	ASTM D1141	MBL	3.5% NaCl
Conductivity (mS/cm)	53.2	52.7	49.8	55.4

Table III

Chemical composition (in wt%) of SAE 1006 (UNS G10060) steel

C	Mn	Si	Al	Cr	Ni	V	Fe
0.038	0.25	0.02	0.045	0.008	0.001	0.007	Balance

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Electrochemical measurements

Electrochemical measurements were performed on samples after corrosion in the various solutions for 21 days. Freshly prepared aerated solutions at room temperature were used as electrolytes for the potentiodynamic measurements with a Solartron 1287 Electrochemical Interface. A standard three-electrode electrochemical cell was employed with two graphite rods used as counter electrodes. All potentials quoted are with respect to the silver/silver chloride reference electrode (SSC). The cathodic polarization curves were obtained by scanning the electrode potential from -0.8 V to the corrosion potential at a scan rate of 1 mV/s.

X-ray diffraction

A real rust layer is very complex. Corrosion products of steel usually consist of ferric oxy-hydroxides (α-, β- and/or γ-FeOOH), magnetite (Fe_3O_4) and amorphous iron oxide[12]. Adding to the complexity of corrosion product, calcareous deposits ($CaCO_3$ and $Mg(OH)_2$) are also known to form on steel surfaces when immersed in seawater[2-4]. It was therefore decided to study the corrosion products that formed after 21 days' immersion in the various solutions by means of X-ray diffraction (XRD).

Results and discussion

Immersion tests

Three days' immersion

Samples immersed in a 3.5% NaCl solution for three days had a brown homogeneous corrosion layer covering most of the surface. This layer chipped off from the surface easily, revealing a black layer (magnetite—see XRD results) underneath. A secondary electron image of the corrosion product is shown in Figure 1.

This corrosion product is porous and two different morphologies can be observed—needles and a coarser oxy-hydroxide. Obviously no calcium carbonate or magnesium hydroxide precipitates could be formed in this solution.

Samples immersed in the ASTM D1141 and MBL seawaters for three days did not have a homogeneous layer covering the whole surface. Instead, areas were found where a relatively thick brown layer was formed (anodic sites) as well as areas where little corrosion seemed to have occurred (cathodic sites). A secondary electron image of the latter area is shown in Figure 2.

It can be seen from this figure that small precipitates are present. EDX analysis indicated that these precipitates contain calcium, carbon and oxygen. XRD confirmed that these precipitates are calcium carbonate (aragonite). A secondary electron image of the thicker corrosion product (Figure 3) also shows that its morphology is very different from that of the corrosion product that formed in the 3.5% NaCl solution (Figure 1).

Samples immersed in natural seawater for three days also contained these two different regions. A secondary electron image of the corrosion product that formed on this sample is shown in Figure 4.
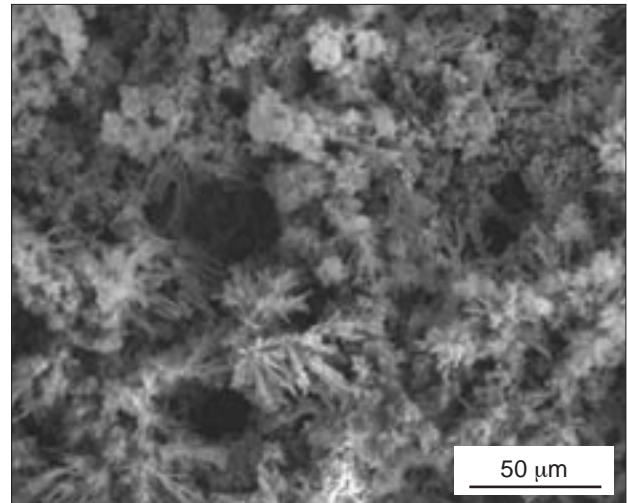

Figure 1—Secondary electron image of the corrosion product formed on SAE 1006 steel after immersion for three days in 3.5% NaCl
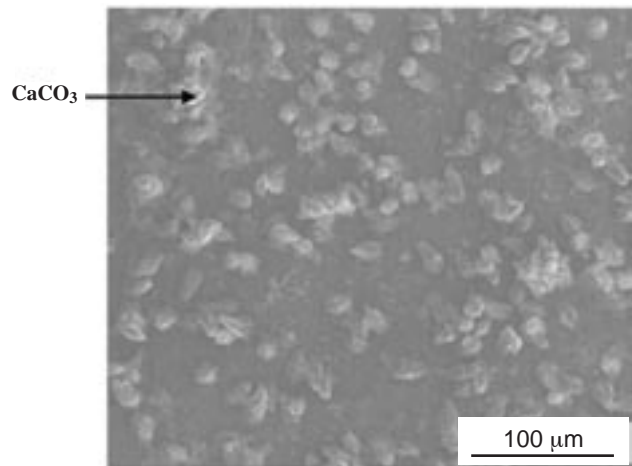

Figure 2—Secondary electron image showing small calcium carbonate precipitates that formed at cathodic sites during immersion for three days in ASTM D1141 artificial seawater
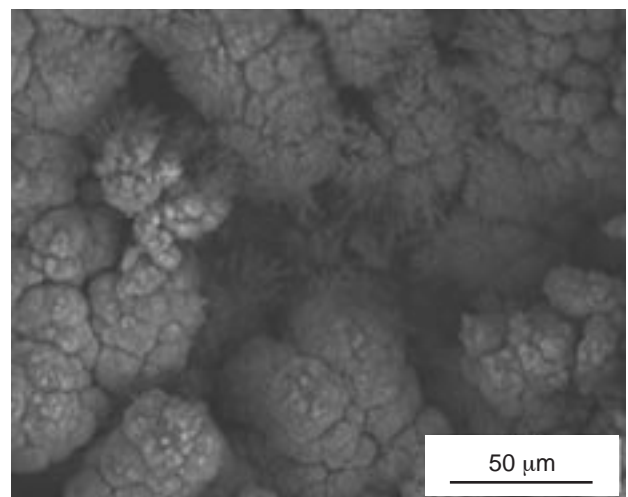

Figure 3—Secondary electron image of the corrosion product that formed during immersion for three days in ASTM D1141 artificial seawater

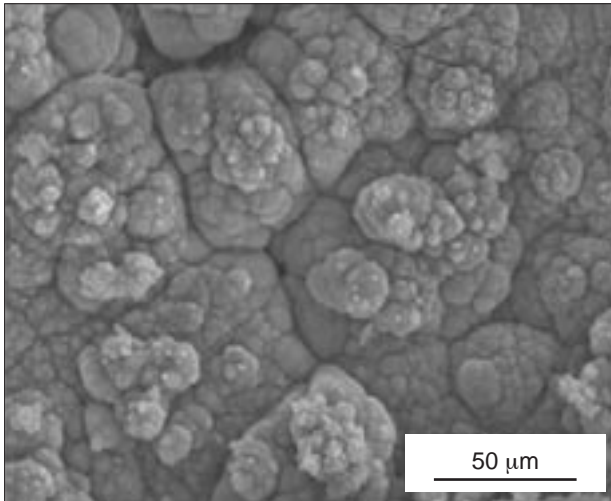Figure 4—Secondary electron image of the corrosion product that formed during immersion for three days in natural seawater
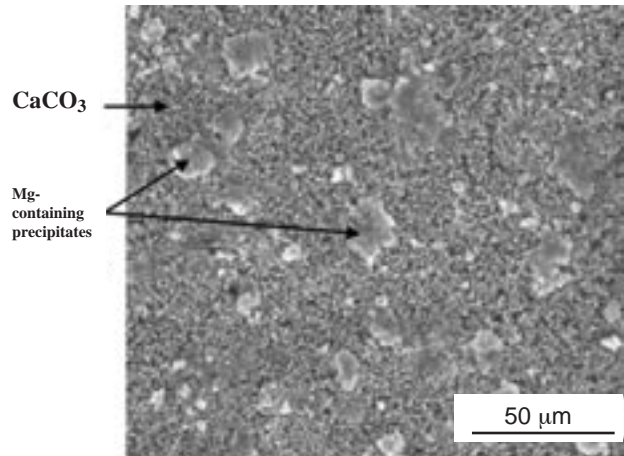

Figure 5—Secondary electron image of calcium carbonate and magnesium-containing deposits that formed at cathodic sites during immersion for three days in natural seawater

It is seen that its morphology is similar to that of the oxides formed after immersion in the synthetic seawaters (Figure 3). The cathodic sites (Figure 5) have a very fine distribution of calcium carbonate precipitates (aragonite). EDX analysis revealed that the larger precipitates contain Mg and O.

These are believed to be $Mg(OH)_2$ (H cannot be detected by this technique) and was not observed on the samples immersed in the synthetic seawaters.

Ten days' immersion

A secondary electron image of a sample immersed in a 3.5% NaCl solution for 10 days is shown in Figure 6.

The number of needle-like areas is less than in Figure 1, being replaced with the coarser form of the oxy-hydroxide. A secondary electron image of cathodic sites on a sample immersed in ASTM D1141 seawater for 10 days is shown in Figure 7.

The number of precipitates is clearly much more than after only three days' immersion (Figure 2). EDX analysis at points between the calcium carbonate precipitates in Figure 7 indicated the presence of mainly Fe, O and Mg. Even though no individual Mg-containing precipitates were observed, this result may suggest some kind of gel-like magnesium-containing deposit covering the surface between the calcium carbonate precipitates. A secondary electron image of a sample immersed in natural seawater is shown in Figure 8.

The calcium carbonate precipitates are finer than those that formed in the synthetic seawaters. They are, however, coarser than after three days' immersion in natural seawater (Figure 5). No magnesium-containing deposits were found in this case, in contrast to what was found after three days.

Immersion for 21 days

A secondary electron image of a sample immersed in a 3.5% NaCl solution for 21 days is shown in Figure 9.

Comparing this figure with Figures 1 and 6 shows that all the needle-like areas have been replaced with the coarser form of the oxide.
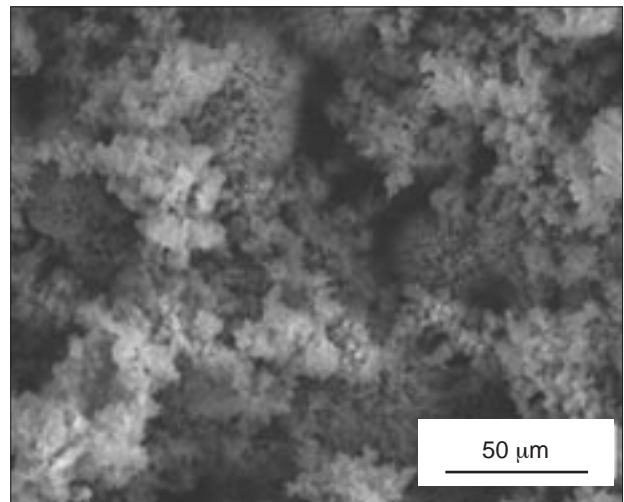

Figure 6—Secondary electron image of the corrosion product formed on SAE 1006 steel after immersion for 10 days in 3.5% NaCl
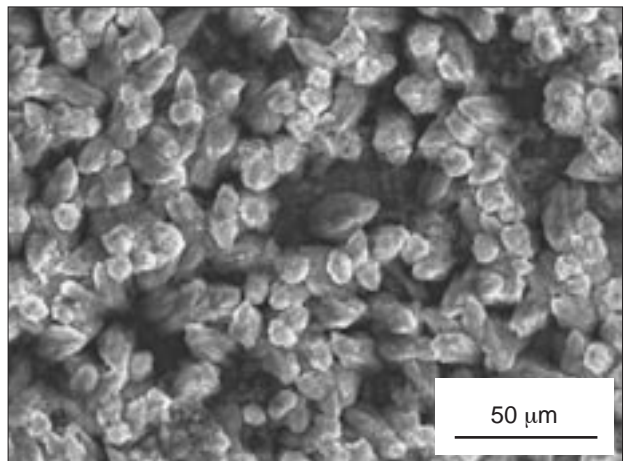

Figure 7—Secondary electron image showing calcium carbonate precipitates that formed at cathodic sites during immersion for 10 days in ASTM D 1141 artificial seawater
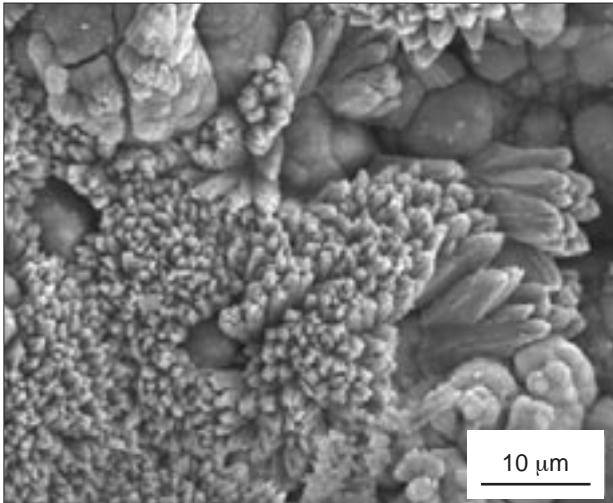
Figure 8—Secondary electron image showing calcium carbonate precipitates that formed at cathodic sites during immersion for 10 days in natural seawater
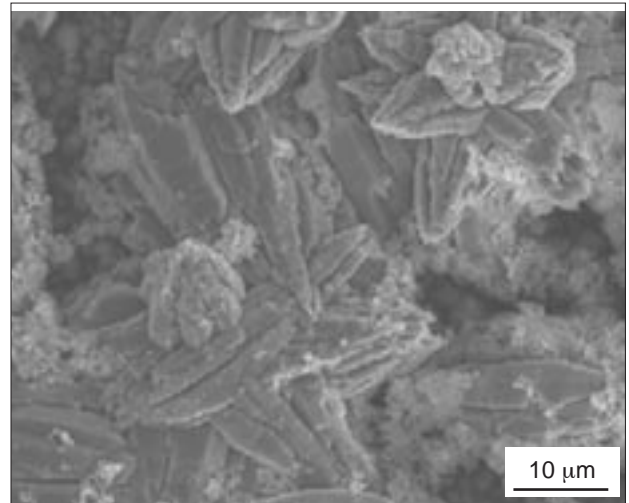

Figure 10—Secondary electron image showing calcium carbonate precipitates that formed at cathodic sites during immersion for 21 days in ASTM D1141 synthetic seawater
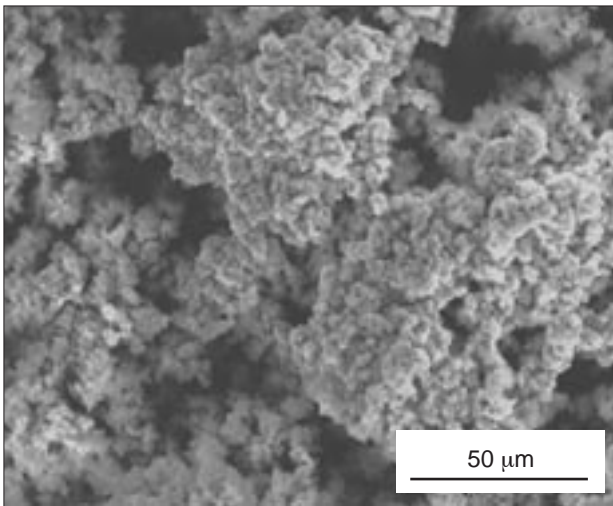

Figure 9—Secondary electron image of the corrosion product formed on SAE 1006 steel after immersion for 21 days in 3.5% NaCl—no needles observed
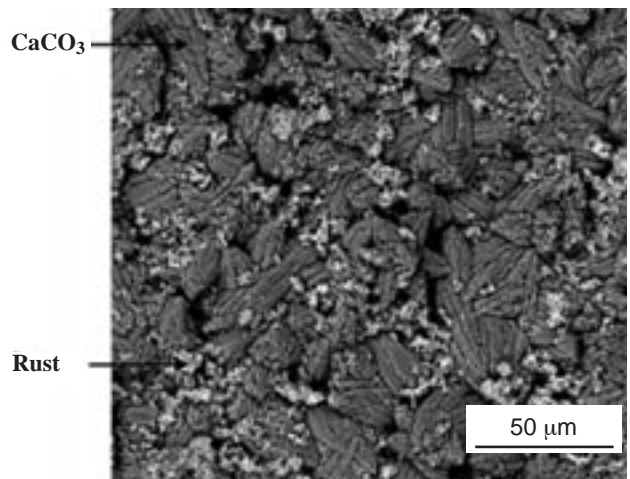

Figure 11(a)—Backscattered electron image of sample immersed for 21 days in ASTM D1141 seawater
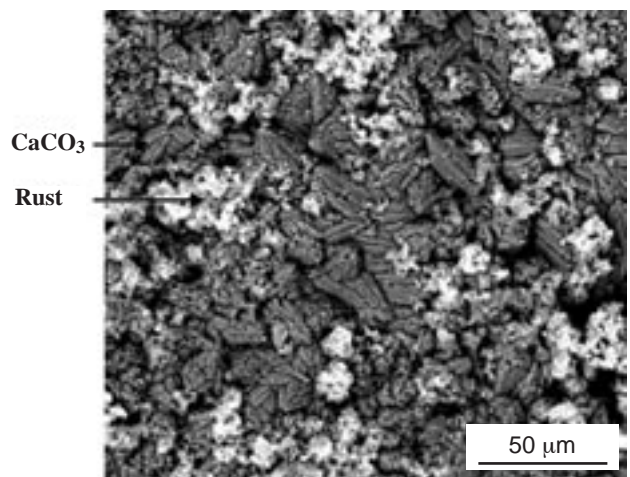
A secondary electron image of cathodic sites on a sample immersed in ASTM D1141 seawater for 21 days is shown in Figure 10.

The calcium carbonate deposits cover most of the surface and only a limited quantity of oxy-hydroxide is found in between the precipitates. Backscattered electron images for the steel sample that was immersed in ASTM D 1141 (Figure 11a) and in MBL seawater (Figure 11b) show that slightly more calcium carbonate precipitates and less corrosion product (oxy-hydroxides) were formed in the ASTM D1141 than in the MBL seawater.

The possible reason for this small, but important, difference will be discussed in the following section.

The morphologies of the calcium carbonate precipitates formed in natural seawater and in the two synthetic seawaters still differ considerably. The precipitates formed in natural seawater are again much finer (Figure 12) than those formed in both the ASTM D 1141 and MBL seawaters.

Figure 11(b)—Backscattered electron image of sample immersed for 21 days in MBL seawater

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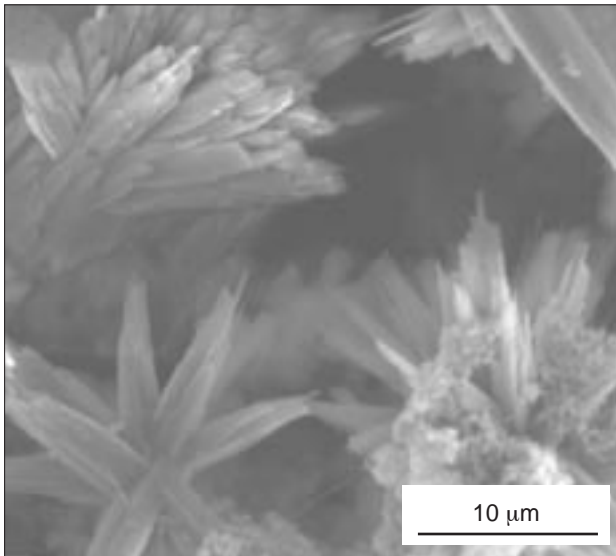

Figure 12—Secondary electron image showing fine calcium carbonate precipitates that formed at cathodic sites during immersion for 21 days in natural seawater

XRD investigation of the deposits that formed after 21 days' immersion

When cathodic protection is used for steel in the absence of Mg^{2+}, the $CaCO_3$ in calcareous deposits precipitates as two well-defined crystalline forms, namely calcite and aragonite[6]. In the presence of Mg^{2+}, $CaCO_3$ is observed exclusively under the form of aragonite[6]. The X-ray diffraction pattern of the deposit that formed at a cathodic site on the sample immersed in ASTM synthetic seawater (Figure 13) confirms that aragonite, and no calcite, precipitated under these conditions. No magnesium-containing precipitates could be detected by means of XRD on any of the samples.

The X-ray diffraction patterns of the deposits that formed at the anodic sites on the samples immersed in 3.5% NaCl (Figure 14), ASTM D1141 synthetic seawater (Figure 15) and natural seawater (Figure 16) show some interesting differences. The oxy-hydroxides formed in 3.5% NaCl consists of both magnetite (Fe_3O_4) and lepidocrocite (γ-FeOOH). For the samples immersed in ASTM D1141 seawater and the natural seawater, lepidocrocite was the main constituent. It is known[13] that γ-FeOOH can react with Fe^{2+} to form Fe_3O_4 according to Equation [3]:

$$Fe^{2+} + 2FeOOH \rightarrow Fe_3O_4 + 2H^+ \qquad [3]$$

The higher corrosion rate of the steel in the 3.5% NaCl solution (which should give a higher Fe^{2+} concentration close to the steel surface) may explain why both magnetite and lepidocrocite are found on this sample (Figure 14), and mainly lepidocrocite on the other two samples (Figures 15 and 16).

Small peaks indicating the presence of aragonite can also be seen for the deposits from the anodic sites at the ASTM D1141 and natural seawater samples. Again, no calcite or magnesium-containing precipitate could be found (Figures 15 and 16).

Corrosion rate of SAE 1006 steel in seawater

The cathodic polarization curves for the steel samples in the different electrolytes are shown in Figure 17.

The corrosion current densities (i_{corr}) were determined by extrapolating the cathodic polarization curves to the corrosion potentials. The results are shown in Table IV.

The corrosion rates of the samples were also calculated by using average weight loss measurements after immersion for 21 days in the different solutions. These results are also shown in Table IV. It can be seen from Table IV that the corrosion rate calculated by means of electrochemical methods is close to but slightly higher than when it is calculated by loss in weight. The corrosion rate of this steel is nearly four times higher in the 3.5% NaCl solution than in the natural seawater. This can mainly be attributed to the precipitation of calcium carbonate, which acts as a physical barrier against oxygen diffusion and thus decreases the corrosion rate by a lowering of the cathodic current densities
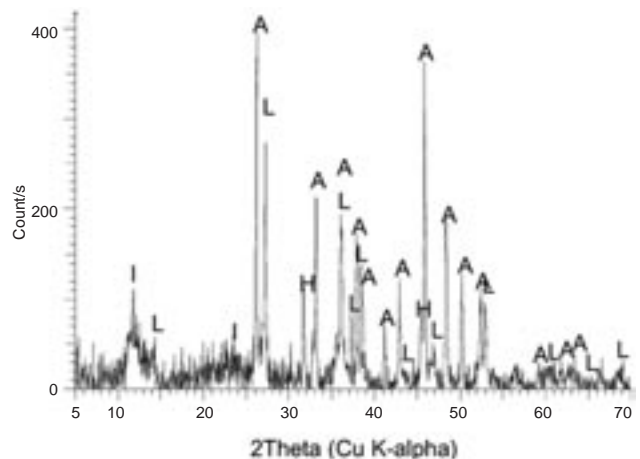

Figure 13—X-ray diffraction patterns of a cathodic site on a sample immersed in ASTM D1141 seawater for 21 days. A—Aragonite ($CaCO_3$), I—Iron carbonate hydroxide ($Fe_6(OH)_{12}CO_3$), L—Lepidocrocite (γ-FeOOH), H—Halite (NaCl)
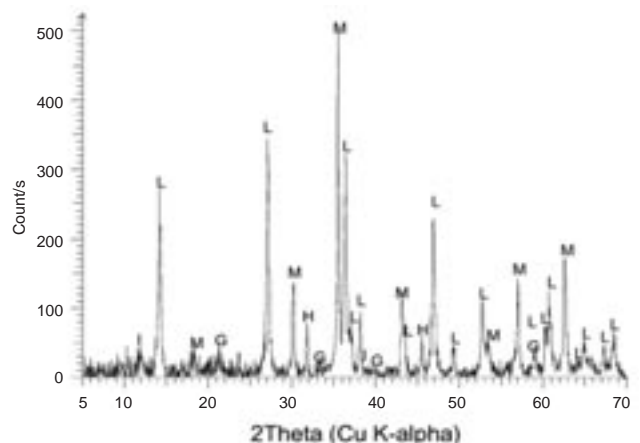

Figure 14—X-ray diffraction patterns of the deposit that formed on a sample immersed in 3.5% NaCl for 21 days. M—Magnetite (Fe_3O_4), L—Lepidocrocite (γ-FeOOH), H—Halite (NaCl), I—Iron carbonate hydroxide ($Fe_6(OH)_{12}CO_3$), G—Goethite (α-FeOOH)
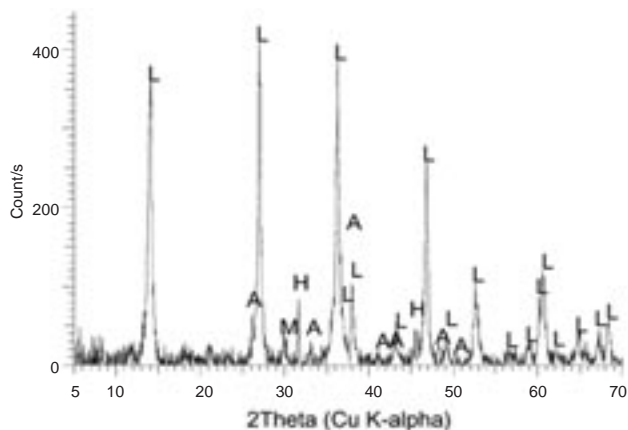
Figure 15—X-ray diffraction patterns of an anodic site on a sample immersed in ASTM D1141 seawater for 21 days. M—Magnetite (Fe_3O_4), L—Lepidocrocite (γ-FeOOH), H—-Halite (NaCl), A—Aragonite ($CaCO_3$)
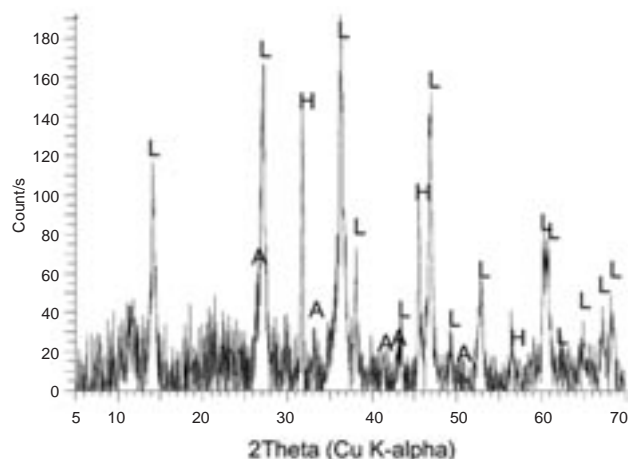

Figure 16—X-ray diffraction patterns of an anodic site on a sample immersed in natural seawater for 21 days. M—Magnetite (Fe_3O_4), L—Lepidocrocite (γ-FeOOH), H—Halite (NaCl), A—Aragonite ($CaCO_3$)
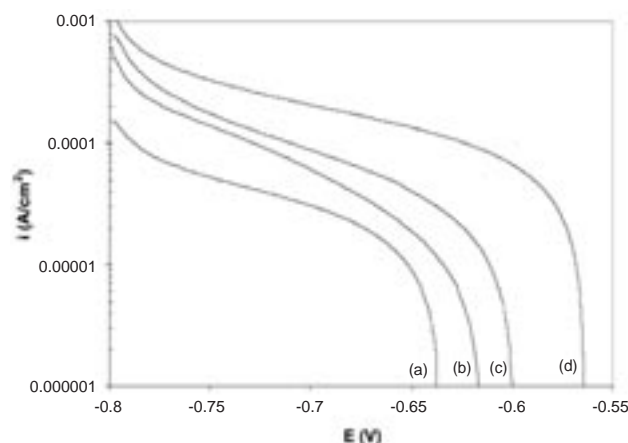

Figure 17—Cathodic polarization curves on steel for samples after 21 days' corrosion. (a) Natural, (b) ASTM D1141, (c) MBL, (d) 3.5%NaCl

Table IV

Corrosion current densities and corrosion rates obtained for the corrosion of SAE 1006 steel in seawater (W = Weight loss and E = Electrochemical)

	Natural		ASTM D1141		MBL		3.5% NaCl	
	W	E	W	E	W	E	W	E
i_{corr} (μA/cm^2)	14.8	17	16.7	19	21.9	24	54.8	62
Rate (mm/y)	0.17	0.20	0.19	0.22	0.25	0.28	0.63	0.72

(Figure 17). According to literature[2,5], the deposition of both $CaCO_3$ and $Mg(OH)_2$ should be able to cause a decrease in the corrosion rate. In this study, the deposition of only a few individual Mg-containing precipitates was observed only after three days immersion in natural seawater (Figure 5). Elbeik *et al.*[3] also found deposition of $CaCO_3$ and no $Mg(OH)_2$ after immersion of a mild steel sample in BDH artificial seawater (supplied by BDH Chemicals Ltd, Poole, England). According to Barciche *et al.*[6], an unstable porous layer on cathodically protected steel could be detected only by *in situ* impedance methods. This film formed in the absence of Ca^{2+} and was favoured by an increase of the Mg^{2+} concentration. The authors concluded that this gel-like film was due to Mg^{2+} and might be the precursor of the solid crystallized $Mg(OH)_2$ brucite deposit, which was obtained only at more cathodic potentials. Moreover, when brucite was formed at cathodic potentials, the $CaCO_3$ layer developed on the brucite layer and not directly on the steel. It must be remembered that in this study no cathodic protection was provided. These factors may explain why $Mg(OH)_2$ deposits were difficult to detect by means of *ex situ* SEM and XRD analyses.

Despite the fact that the morphologies of the calcareous deposits differ significantly for the natural and synthetic seawaters, the calculated corrosion rates are still similar. However, the corrosion rate is marginally lower in the natural seawater than in the synthetic solutions. The finer calcium carbonate precipitates observed after immersion in the natural seawater probably cover the surface more effectively and may therefore be a better barrier against oxygen diffusion than the coarse precipitates formed in the two synthetic seawaters.

The corrosion rate of the steel is marginally higher in the MBL seawater than in the natural seawater and ASTM D1141 seawater. This may be attributed to the differences in composition (Table I). The MBL seawater has slightly lower concentrations of Ca^{2+} and HCO_3^- than the ASTM D1141 seawater. From Figures 11(a) and (b) it can be seen that less of the surface is covered by $CaCO_3$ after immersion in the MBL seawater. These small differences in concentration probably lead to the slight difference in corrosion rates (Table IV).

Conclusions

The conclusions of this study are:

➤ The corrosion rate of SAE 1006 steel is nearly four times higher in 3.5% NaCl solution than in natural seawater (for an immersion time of 21 days)
➤ The corrosion rate of SAE 1006 steel after immersion in synthetic seawaters is similar to the corrosion rate after immersion in natural seawater

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➤ Calcium carbonate deposits (as aragonite) were formed on the steel during immersion in natural seawater and the more elaborate synthetic seawaters. Magnesium-containing deposits were more difficult to detect

➤ The aragonite deposits that formed during immersion in the natural seawater have a finer morphology than those that formed during immersion in the more elaborate synthetic seawaters. This may explain the slightly lower corrosion rates obtained in the natural seawater

➤ X-ray diffraction indicated that the oxy-hydroxides that formed on the steel immersed in the 3.5% NaCl solution for 21 days are different from those formed in the other solutions. The oxy-hydroxides that formed in 3.5% NaCl consisted of both magnetite (Fe_3O_4) and lepidocrocite (γ-FeOOH). However, for the samples immersed in ASTM D1141 seawater and the natural seawater, lepidocrocite was the main constituent.

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