The effect of environmental variables on early corrosion of high-strength low-alloy mooring steel immersed in seawater

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Abstract

Traditionally, the designing of mooring lines has been aimed at fulfilling the mechanical strength criteria using standard theoretical models and simulation in wave tunnels. This approach has led to various critical failures since degradation of a mooring line under specific environmental and loading conditions, which depend on the locations of the off-shore platforms, were not properly considered.

The purpose of this paper is to investigate into the effect of three environmental variables – temperature, salinity and dissolved oxygen – on the corrosion behaviour of two steel grades used for mooring chains and to develop an empirical model intended to link these variables with the corrosion rate. A full-factorial experiment was designed on the basis of the statistical analysis of the objective data on the ocean water conditions corresponding to nine regions of Atlantic, Indic and Arctic oceans. A practical uncoupled method to determine the corrosion rate of these steel grades as function of the water conditions was developed.

1. Introduction

In recent years, the offshore industry is showing an increased awareness for the Mooring Integrity Management (MIM) that can significantly lower the risk of mooring failure and environmental pollution by hydrocarbon release. The core tasks of MIM involve analysis of the environmental conditions and loading, integrity assessment, risk and reliability evaluation considering various degradation factors and so on [1-3]. The main focus is usually put on the mechanical strength and fatigue resistance of a mooring line [4, 5]. For corrosion allowances, the offshore standard establishes minimum corrosion rates which shall be used if corrosion data is not available for the actual location [5]. However, depending on the local environmental conditions the actual corrosion rate can significantly vary from the established values that may lead to either reduced endurance or needless oversizing of the mooring chain. Knowledge of the local in-service conditions is necessary to optimize the design of the mooring system (Ad Hoc design), reduce costs and material usage that are the objectives of a circular economy.

Corrosion of low alloy structural steel immersed in actual seawater conditions is a complex phenomenon influenced by the compositional variations of steel [6] and seawater-related issues [6-21]: salinity, pH, water temperature, dissolved oxygen, water velocity, sulphide pollution, bio-fouling and dissolved inorganic nitrogen among others. Melchers proposed a generalized 5-phase probabilistic empirical model for the progression of immersion corrosion of mild and structural steels [21-23]. The model consists of a number of sequential but different rate-controlling processes, and these are influenced in specific ways by the external environment characteristics. Generally, the phases 0, 1 and 2 correspond to abiotic aerobic corrosion processes, while the phases 3 and 4 correspond to suboxic and anoxic corrosion with significant component of Microbiologically Influenced Corrosion (MIC). It should be mentioned that MIC is not a different corrosion mechanism *per se* but rather a particular set of environmental conditions influencing corrosion rates and types [24]. For practical engineering application, the models for deterioration are highly desirable, both to interpret data and to extrapolate any trends the data may have, but the general model should be calibrated against actual data obtained from on site and laboratory experiments with tight control or monitoring of local environmental variables. So, the availability of the actual field data for each new material and specific environmental conditions is crucial for usefulness of the empirical model.

The effect of a number of environmental criteria on chain corrosion in warm sea waters was investigated in Joint Industry Project (JIP) SCORCH [14] using site and laboratory tests. It was found that in temperate and tropical waters with the temperatures of 20 and 25 °C the corrosion rates significantly exceeded the rates specified in existing guides. Intensive pitting corrosion that was observed in the upper water column, 25-30 m below the still water line, was ascribed to MIC. Corrosion behaviour under specific water conditions in the middle and deep water columns, where MIC component is less significant, except on the seabed [25], has been little studied. Generally, corrosion is intensified with the increase of both temperature and dissolved oxygen, although oxygen solubility decreases with increasing temperature [23, 26-28]. The effect of salinity on the corrosion rate of low alloy steel is not straightforward. Some studies showed that corrosion rate initially increases, reaches a maximum at the salt concentration about 0.5 N and then decreases with increasing salinity [26]. Other studies gave evidences that a decrease in salinity from 35 to 15-20 (units of practical salinity scale – pss) increased the corrosion rate on 30-100% [23, 29]. This was attributed to the variation in oxygen and carbonate solubility.

The purpose of this paper is to investigate into the environmental effect on the corrosion behaviour of two steel grades (R4 and R5) using laboratory tests. In this way, the effects of three environmental variables – temperature, salinity and dissolved oxygen – on the early corrosion stage under abiotic conditions were studied. The ranges of the variables studied were chosen to simulate the real seawater conditions in several zones of the world ocean. In addition, to compare the corrosion behaviour of the two grades under various environmental conditions, this study provides the data collection which can be used for calibration of early corrosion phases for the Melchers's model for these two steel grades and given environmental conditions. On the basis of the experimental results, a simple graphical method for estimation of abiotic corrosion rate of R4 steel grade under standard salinity and varying oxygen and temperature was developed. The model can serve as a guideline to structural engineers in new design or analysis situations [30].

2. Definition of the variables of ocean environment

Nine zones of the world ocean with the major concentrations of Floating Production, Storage and Offloading (FPSO) units [14] were selected for corrosion simulation. The zones were classified in five geographic areas and their coordinates are given in Table 1.

Table 1. Identification of the geographical zones chosen for this study

Zone	Symbol	Latitude	Longitude
Brazil			
Campos Basin	C	-20...-24	-39...-41
Santos Basin	S	-24...-26	-42...-46
West Africa			
Angola	A	-4 ... -9	11... 12
Nigeria	N	3.5 ... 6	2... 5
Ghana	Gh	3.5 ... 5.5	0...-5
Southeast Asia	SA	6 ... 12	105...119
North Atlantic and Arctic			
North sea	M	53 ... 59	0... 3
Barents sea	B	71 ... 72	20... 24
Gulf of Mexico	GM	18 ... 30	-92...-98

The information on the characteristics of seawater in these zones: temperature (T), salinity (S) and dissolved oxygen (O) was obtained from EN3 v2a database of UK Meteorological Office which compiles data of the World Ocean Database (USA National Oceanic and Atmospheric Administration) [31], Global Temperature and Salinity Profile Project (GTSP) [32-34], a pilot programme “Argo” of the Global Ocean Observing System [35], Arctic Synoptic Basin-wide Observations (ASBO) project [36], etc. as well as from other sources [37-41]. The database EN3 includes a set of in situ measured and objectively analysed data interpolated to 1° grid climatological fields and standard depth levels for annual, seasonal, and monthly compositing periods. It also contains associated statistical fields of observed oceanographic profile data [42].

The number of nodes from the database falling into the selected zones (Table 1) are shown on Table 2.

Table 2. Number of nodes falling in each zone and the depth limits between the top and deep seawater regions

Zone	Number of nodes	Top region (m)	Deep region (m)
A	5	0 – 30	>30
B	4	0 – 30	>30
C	8	0 – 500	>500
Gh	15	0 – 300	>300
GM	72	0 – 800	>800
M	18	0 – 50	>50
N	9	0 – 300	>300
S	8	0 – 500	>500
SA	84	0 – 100	>100

The representative examples of the extracted datasets for two tropical zones of Atlantic Ocean (C and A) are shown in Figure 1. Figure 2 shows the same data for Barents Sea. In all zones both oxygen and temperature significantly varied with depth. However, salinity was quite stable in deep waters varying between 34.5 and 35.2 pss that was close to the standard value (35 pss). In the top seawater layers seasonal and geographical factors such as evaporation, precipitations, ice melting and terrestrial fresh water inflows resulted in significant deviations of salinity from the standard value. The depth level which divides the depth region from the top one at each zone are shown in Table 2. For the development of the design of experiment, the deep and the top seawater regions were considered separately that allowed us to exclude salinity from the predictors in corrosion simulation in the deep regions.

Fig. 1. Representative depth profiles of mean yearly values of objectively analysed variables of ocean water and their standard deviations (*sd*) in various nodes of 1° grid in the zones A and C (Atlantic Ocean): a) temperature (*T*), b) *sd* of *T*, c) salinity (*S*), d) *sd* of *S*, e) dissolved oxygen concentration (*O*), *sd* of *O*. The data were extracted from the database EN3 v2a.

Fig. 2. Representative depth profiles of objectively analysed variables of ocean water and their standard deviations (sd) in various nodes of 1° grid in the zone B (Barents Sea): a) temperature (T), b) sd of T , c) salinity (S), d) sd of S , e) dissolved oxygen concentration (O), sd of O . The data were extracted from the database EN3 v2a.

Figure 3 shows the complete dataset of mean values and confidence intervals for $O - T$ in the deep regions of all zones. Lines show the oxygen solubility limits at S 35 and 31. The following full ranges of the predictor's variation were determined: T [2; 27] and O [1; O_{sat}], where O_{sat} is the solubility at corresponding temperature.

Fig. 3. Distribution of dissolved oxygen concentration in the deep regions of various zones as function of temperature. The tolerance intervals were determined with coverage factor 1.7 (significance level 0.05, degrees of freedom 30). Solid lines show the oxygen concentration in air saturation seawater at salinity levels 35 and 31 pss.

Fig. 4. Distribution of dissolved oxygen concentration in the top regions of various zones as function of temperature. Tolerance intervals were determined with coverage factor 1.7 (significance level 0.05, degrees of freedom 30). Solid lines show the oxygen concentration in air saturation seawater at salinity levels 31, 35 pss and 43 pss.

The plot of $O - T$ dependencies in top regions of all selected zones is shown in Fig. 4. In all cases the dissolved oxygen concentration was close to saturation with exception of the data marked by a dashed ellipse, which correspond to the tropical zones, at which oxygen levels in seawater were depleted due to biological activity. This latter case was excluded from the analysis, which was focused only on abiotic corrosion. Then, the following ranges of predictor's variation were assigned in the top regions: $T [3; 32]$, $S [31; 43]$ and $O = O_{sat}$.

Combining the ranges for the top and deep regions the following overall ranges were obtained: $T [2; 32]$, $S [31; 43]$ and $O [1; O_{sat}]$.

3. Materials and procedure

3.1. Materials

The present work is focused on the high-strength steel grades R4 and R5 approved by the current Classification Societies [43] for chains and accessories of the mooring lines. These steel grades belong to the class of low and medium alloy steel (Cr, Ni, Mo, V, etc.) in which chemical composition was optimized pursuing to enhance hardenability (mass effect) and the specific mechanical characteristics. The chains were manufactured by flash butt welding (FBW) of rolled steel bars followed by a Double Quenching and Tempering heat treatment.

Simulated tests of steel corrosion were carried out in fully formulated synthetic seawater with addition of heavy metals prepared following the standard procedure [44]. Salinity of synthetic seawater different from the standard value was adjusted either by adding distilled water or by vaporizing the excess of water. Salinity was determined from the measurements of electrical conductivity using the formula described in [45].

3.2. Procedure of simulated corrosion tests

Factorial experiments were designed to study the effect of three environmental variables at the deep and top seawater regions:

- For simulation of the top regions, aerated seawater was used. Dissolved oxygen concentration was kept at saturation level which spontaneously varied with temperature and salinity. Three levels of temperature and salinity were chosen: 2°, 17° and 32° C, and 31, 35 and 43 pss, correspondingly.
- For simulation of the deep seawater regions, two levels of temperature: 2° and 32 °C were used, whereas salinity was set at 35 pss, and oxygen concentration was kept at 1 ± 0.2 mg/l using an automatically controlled nitrogen gas purging system.

This yielded 11 tests summarized in Table 3.

Additionally, to contrast the possible difference between R4 and R5, four tests were carried out with R5 at S35 and two temperature and oxygen levels: 2° and 32° C, and O_{sat} and 1 ± 0.2 mg/l, correspondingly.

It should be mentioned that on site, deep water corrosion could be more intensive than in the tests carried out in this experimentation due to higher hydrostatic pressure [16-18].

Table 3. Experimental design

Test	Grade	T (C)	S (pss)	O (mg/l)
1	R4	2	35	Sat.
2	R4	17	35	Sat.
3	R4	32	35	Sat.
4	R4	2	31	Sat.
5	R4	17	31	Sat.
6	R4	32	31	Sat.
7	R4	2	43	Sat.
8	R4	17	43	Sat.
9	R4	32	43	Sat.
10	R4	2	35	1 ± 0.2
11	R4	32	35	1 ± 0.2
12	R5	2	35	Sat.
13	R5	32	35	Sat.
14	R5	2	35	1 ± 0.2
15	R5	32	35	1 ± 0.2

Steel coupons with dimensions $80\times13\times4$ mm³ were cut from newly fabricated links of a mooring chain (Fig. 5). After grinding, the sample surfaces were degreased using acetone and isopropanol.

Fig. 5. The image of the sample showing an opening in the protective coating and a wire welded at one end.

A steel wire was welded to one end of the samples for electrochemical measurements. The samples were dip coated with two or three layers of protective polymer resin. After polymerization, the coating was removed on one side of the samples leaving a rectangular opening with the area 2 ± 0.2 cm². The sides of the opening were additionally sealed with liquid resin to avoid leaking the electrolyte behind the coating and possible crevice corrosion.

3.3. Electrochemical methods

In the present paper, three electrochemical techniques were used: measurement of the open circuit potential (OCP); determination of the corrosion rate (CR) by the linear polarization resistance (LPR), determination of the Tafel slopes (β_a and β_c) and electrochemical impedance spectroscopy (EIS).

Electrochemical measurements were carried out in a three-electrode configuration. Cylindrical graphite electrode, 6 mm in diameter and 150 mm long, was used as a counter-electrode. The electrical potential of the steel samples (which act as working electrode) were measured against a calibrated Ag/AgCl 3M KCl reference electrode.

In each corrosion experiment, three steel samples were tested in parallel. The samples were fixed vertically with their openings completely immersed in a tank filled with 4 l of synthetic seawater. The counter-electrode and the reference electrode were placed at approximately same distance from each sample. The tank was placed inside a thermostat bath that controlled temperature in the range from 2 to 32 °C with uncertainty less, than 0.5 °C. In order to investigate the repeatability of measurements, about 50% of the experiments at various combinations of *T-S-O* were repeated once or twice under identical conditions using different samples of the same grade and different seawater lots. In most cases test-retest variability determined from these experiments was comparable with the variability in parallel measurements.

3.3.1. Open Circuit Potential

Open circuit potential (OCP), is the electrical potential that a sample (steel coupon) acquired spontaneously while immersed in a corrosive environment (seawater). The OCP was measured with respect to the reference electrode, when no current passed through the cell and no additional polarization was applied. The OCP provided a qualitative information on the risk of corrosion, but not on its instantaneous rate.

3.3.2. Corrosion Rate

The corrosion rate, I_{corr} , was determined using the method of Linear Polarisation Resistance (LPR) measurement which was introduced by Stern and Geary [46] and further developed into an ASTM standard [47] for quantification of the material loss due to corrosion. The sweep rate for the potential variation applied was 10 mV/min. The polarization resistance, R_p , was determined from the slope of the linear region of the experimentally measured polarisation plot *i-E* at the OCP:

$$R_p = \left(\frac{\Delta E}{\Delta i} \right)_{\Delta E \rightarrow 0} - R_e, \quad (1)$$

where R_e is the resistance of the electrolyte.

Then, the corrosion rate is inversely proportional to R_p [47, 48], as is expressed in the Stern-Geary equation:

$$I_{corr} = \frac{B}{R_p}. \quad (2)$$

Stern and Geary method requires that the value of the Stern-Geary constant, B , is previously determined under similar experimental conditions using a destructive test. B is related to the anodic and cathodic Tafel slopes, β_a and β_c , correspondingly [47, 48]:

$$B = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)}. \quad (3)$$

The Tafel slopes were determined using potentiodynamic polarization experiments. Prior to these experiments, the samples were kept immersed in seawater until establishing a steady corrosion regime that was monitored by the OCP. A single polarization cycle with ascending and descending phases and two vertices at -0.9 V and +1.6 V was employed. Portions of these curves are shown in Fig. 9. The polarization rate was 10 mV/min. The electrolyte resistance was determined by EIS and compensated during the experiment.

Various researchers reported that the B slightly varies depending on the metal/electrolyte system and the immersion time, due to the amount of corrosion [48-51]. McCafferty [50] argued that the only way to quantify the instantaneous corrosion rate is through measurement of the Tafel slopes in each experiment that implies destructive large-amplitude potentiodynamic polarization. However, in many cases the range of variation of B is relatively small in comparison with the uncertainties of the experimental variables and measuring system. For corrosion of mild and high-strength low-alloy steel grades in various environments the B typically ranges between 13 and 52 mV [49].

The corrosion rate, CR , was calculated from the I_{corr} considering the Faraday's law:

$$CR = 11.6 I_{corr}, \quad (4)$$

where the CR is in $\mu\text{m}/\text{year}$ and I_{corr} is in $\mu\text{A}/\text{cm}^2$.

The agreement between gravimetrically determined weight loss and the electrochemical measurements has been largely demonstrated for different metal/electrolyte systems [51, 52],

including carbon steel in seawater, for which both values fit exactly for short and mid-term immersion (up to 100 days) [53].

3.3.3. EIS spectroscopy

A sinusoidal signal (alternating current) of a small amplitude (10 mV) with respect to the OCP was applied to the steel sample acting as a working electrode. The frequency ranged from 10 kHz to 1 mHz. The electrical current between the working and counter electrodes was measured at a rate of 5 points per frequency decade. The corresponding impedance was calculated and analysed using NOVA software.

The analysis of the obtained spectra was done by fitting the measured data to an equivalent circuit which is shown in Fig 6. In the equivalent circuit R_e is the electrolyte resistance; CPE_r and R_r are the constant-phase element and resistance of the rust layer, respectively; CPE_{dl} is the constant-phase element of the double layer and R_{ct} is the resistance of charge transfer at metal surface (directly related with the R_p measured by LPR). A constant-phase element was used instead of an ideal capacitor to simulate distorted semicircles on the Nyquist plots.

Several authors [54, 55] demonstrated that at infinitely low frequencies the impedance approaches R_p , so EIS can be used for estimation of R_p , although less accurately, than by LPR method.

Fig. 6. Equivalent electrical circuit for a steel/corrosion products/water interphase. R_e is the electrolyte resistance; CPE_r and R_r are the constant-phase element and resistance of the rust layer, respectively; CPE_{dl} is the constant-phase element of the double layer and R_{ct} is the resistance of charge transfer at the metal surface.

4. Experimental results

4.1. Aerated conditions

Figure 7 a) shows the representative graphs of the OCP variation with the immersion time for nine samples of R4 steel grade tested in aerated synthetic seawater with salinity 31 at three temperatures.

Fig. 7. Experimental results for nine samples of R4 steel grade immersed in aerated synthetic seawater at S 31 and three temperatures: a) the evolution of the OCP; b) the evolution of the R_p obtained from LPR.

At the beginning of immersion OCP showed transitional decrease towards more negative values. The duration of the transition phase increased from approximately 1 day at 32 °C to 5 days at 2 °C suggesting that thermally activated processes were involved. Although the transition behaviour significantly varied between the samples, the steady OCP were reproducible both for the samples measured during one test as well as for the samples from different tests.

For the grade R4, the dependences of the mean value and standard error of OCP on S and T are plotted in Fig. 8. The OCP shifted towards more negative values with the increasing temperature for all S . At S 43, the OCP was considerably more positive, than at both S 31 and S 35 that is usually associated with the relative increase of the rate of cathodic reactions such as O_2 reduction [56]. The differences in the OCP at S 31 and S 35 were small or statistically insignificant that indicates that the kinetics of both anodic and cathodic reactions was unchanged or slightly reduced [57] (see also Table 4).

The OCP for the grades R5 and R4 were very similar (Fig. 8 b).

Fig. 8. a) The dependence of mean values and standard error of the steady OCP of grade R4 steel samples immersed in synthetic seawater on temperature and salinity. b) Mean values and standard error of steady OCP for R4 and R5 immersed in synthetic seawater at S 35 as function of temperature.

The representative graphs of the R_p (from the LPR measurements) evolution with the immersion time for R4 steel grade samples in seawater at S 31 and various temperatures are shown in Fig. 7 b). For all samples and seawater conditions R_p was below $2 \text{ k}\Omega \text{ cm}^2$. The R_p decreased with increasing temperature.

Figure 9 shows portions of potentiodynamic polarization curves for R4 and R5 steel grades at various S and T . With increasing temperature the corrosion potential shifted to more negative values that is associated with the relative increase of the anodic reactions rates, and the corrosion current, which is inversely proportional to R_p , increased. The cathodic and anodic slopes (see Table 4) were determined from the linear fits of the data in the Tafel region, which are shown by dashed lines in Fig. 9. In order to investigate the reproducibility seven out of fifteen experiments were repeated ones or twice under identical conditions using different samples of the same grade and different seawater lots. The slopes obtained in repeated experiments were averaged using harmonic means, while the standard errors were calculated according to Norris [58] including the data of repeated and parallel experiments.

Figure 9. The representative potentiodynamic polarization curves in aerated seawater: a) grades R4 and R5, S 35, T 2 and 32°C ; b) grade R4, S 31, T 2, 17 and 32°C ; c) grade R4, S 43, T 2, 17 and 32°C . The graphs show portions of the curves near OCP. Anodic and cathodic slopes were determined using linear fits (dashed lines) of the data in the Tafel regions.

The anodic and cathodic slopes were within the admitted intervals: from 60 to 120 mV/decade for the anodic slope, and ≥ 120 mV/decade for the cathodic one. At S 31 both slopes decreased with increasing T , but their behaviour was non-monotonic at S 35 and 43. The B calculated using (3) laid in the interval from 20.5 to 34.3. The obtained values are consistent with the data of Zou et al. [51] and with literature for similar steel grades in aerated seawater [49, 59, 60]. An independent sample T-test was carried out to compare the observed means of B for R4 and R5 under identical conditions. For all combinations of T and O the calculated P -values were greater, than 0.187. This evidence indicates that for significance level $\alpha=0.05$ the data are consistent with the null-hypothesis ($H_0: B(R4)=B(R5)$), i.e. the differences in B for the two steel grades are statistically not significant.

Table 4. Means of the constant B (mV) and Tafel slopes (β_a and β_c) for the two steel grades determined from potentiodynamic measurements at various combinations of S , T and O . The corresponding standard errors are shown in parenthesis.

O (mg/l)	S	T (°C)				
		2		17	32	
		R4	R5	R4	R4	R5
sat.	31	B	28.5 (4.26)	-	26.3 (3.19)	20.5 (1.63)
		β_a	83.9 (16.0)	-	77.3 (12.0)	57.9 (5.68)
		β_c	301 (18.6)	-	279 (2.20)	254 (1.89)
	35	B	30.2 (1.80)	24.9 (2.10)	34.3 (2.09)	20.7 (1.94)
		β_a	85.2 (3.03)	72.1 (7.63)	122 (5.97)	63.1 (1.33)
		β_c	380 (108)	279 (1.63)	226 (13.6)	197 (74.9)
	43	B	26.3 (3.40)	-	22.3 (0.70)	27.2 (3.97)
		β_a	64.9 (8.99)	-	72.0 (2.86)	72.8 (12.4)
		β_c	888 (159)	-	178 (5.80)	449 (5.68)
	1	B	27.4 (1.62)	27.2 (1.60)	-	22.5 (1.33)
		β_a	94.1 (5.59)	87.7 (0.35)	-	111 (6.55)
		β_c	193 (11.9)	220 (13.0)	-	97.7 (5.76)

Mean corrosion rates of R4 and standard errors calculated from the LPR experiments using equations (2) and (4) at various S and T are shown in Fig. 10 a). Generally, for all S , the corrosion rate (CR) increased with increasing temperature. This is in line with the model of corrosion rate controlled by chemical reactions and oxygen diffusion (Melchers's phases 0 and 1) [61]. In addition, it was found that the CR at non-standard salinity levels was considerably higher, than at S 35. The increase in severity of corrosion of various low alloy steel grades at $S > 35$ as well as at $S < 35$ has been previously reported [11, 62]. This complex behaviour was associated with the simultaneous acting of several factors, which have either positive or negative response to the salinity increase. On the one hand, there is an understandable tendency to assume that increases in seawater salinity represent more aggressive environments [63]. On the other hand, oxygen and carbonate solubility decreases with increasing salinity [30]. Higher Cl^- concentrations are known to promote formation of β -FeOOH instead of γ -FeOOH [56]. However, the limiting Cl^- concentration at which switch from γ -FeOOH to β -FeOOH occurs is not clear. It can be suggested that in the range of salinity 31-35 the higher CR at S 31 might be attributed to higher oxygen solubility.

The effect of temperature is not straightforward as well. Both the diffusion coefficient for oxygen through a film of corrosion products and the corrosion rate increase with increase of temperature. However, oxygen solubility decreases from nearly 11 mg/l at 2 °C to below 6 at 32 °C. Considering that in short-term experiments corresponding to the Melchers's phases 0 and 1 the build-up of the film of the corrosion products was not finished, the temperature dependence of the corrosion rate should be controlled mainly by the kinetic factors (oxygen concentration and rate). This assumption is in line with the observed OCP behaviour. Gradual shift of the OCP towards more negative values with the increasing temperature indicates the increase of the rates of anodic reactions. The discussion continues further in the next section.

The range of the CR between 0.2 and 0.5 mm/year obtained in this study is consistent with the available literature data [57, 64-66]. For instance, Refait et al. [64] reported the average CR of carbon steel after 6 years immersion 150 ± 40 μ m/year, whereas during the first year the CR was notably higher, than the average. They observed that on local anodic zones the corrosion rate reached very high values, up to 500 μ m/year. Matsushima [66] summarized overall corrosion rates of steel continuously immersed in quiescent seawater at many locations throughout the

world. He found that during the first year the corrosion rate scattered between 90 and 380 $\mu\text{m}/\text{year}$ and the average of the corrosion rates in the first five years was 140 $\mu\text{m}/\text{year}$.

For the grade R5, the CR was slightly lower, than for the grade R4, but showed very similar dependence on temperature (Fig. 10 b).

Fig. 10. Corrosion rates of the steel grades in synthetic seawater calculated from LPR: a) grade R4 at various T and S ; b) comparison of grades R4 and R5 at $S35$ and various temperatures. Vertical bars show standard errors.

4.2. Oxygen starvation conditions

The OCP behaviour notably changed in comparison with Fig. 6 when oxygen concentration in seawater was set at 1 mg/l. The OCP suffered two transitions (Fig. 11 a). At 2 °C the OCP first shifted to more negative values, and after 20 to 30 days, a second transition to more positive values occurred. At 32 °C the OCP behaviour was opposite. The transient periods were longer and more pronounced, than under aerated conditions. The R_p was much higher, than in aerated seawater, and reached 20 $\text{k}\Omega\text{ cm}^2$ at 2 °C.

Fig. 11. Evolution of the OCP (a) and R_p (LPR) (b) for steel samples grade R4 immersed in synthetic seawater with $S\ 35$, $T\ 2\ ^\circ\text{C}$ and $O\ 1\ \text{mg/l}$. Three samples were tested at each temperature.

The mean steady OCP and standard errors as function of temperature and dissolved oxygen concentrations are shown in Fig. 12 a) and b) for the grades R4 and R5, correspondingly. At 2 °C the OCP was more negative, than under oxygen saturation, and shifted to more positive values with increasing temperature. This tendency was opposite to the OCP behaviour in aerated seawater. It can be inferred that under oxygen starvation the increase of the temperature led to the increase of the rates of cathodic reactions due to higher availability of oxygen at the higher temperature. This is not surprising considering that relative oxygen concentrations at 2°C and 32 °C were 9.3% and 17% of corresponding saturation levels, respectively. So, the effect of oxygen concentration on the rate of the cathodic processes was larger, than the effect of temperature on the kinetics of anodic processes.

The corrosion rates for steel grades R4 and R5 at two levels of dissolved oxygen and temperatures are shown in Fig. 13. The decrease in dissolved oxygen concentration led to notable reduction in the CR at both temperatures as expected. However, the decrease in the CR was not directly proportional to the decrease in the oxygen concentration as it is predicted by a kinetically

controlled corrosion model (Melchers's phase 0). At $T 2^{\circ}\text{C}$ the absolute oxygen concentration (at 1 bar atmospheric pressure) decreased from 10.7 down to 1 mg/l, while the CR decreased 9.1 times. At 32°C the decrease from 5.9 mg/l to 1 mg/l in oxygen concentration led to the decrease of the CR 3.2 times. The lack of direct proportionality between the CR and the oxygen concentration can be related with the build-up of the film at the end of the immersion time and initiation of Melchers's phase 1, which is controlled by oxygen diffusion from the environment. The differences between corrosion rates for R4 and R5 under similar environmental conditions were statistically insignificant.

Fig. 12. a) The OCP as function of T and O for the grade R4 in synthetic seawater at $S 35$. b) The OCP as function of T and O for the grade R5 at $S 35$.

Fig. 13. a) The CR as function of T and O for the grade R4 in synthetic seawater at $S 35$. b) The CR as function of T for the two grades in synthetic seawater at $S 35$ and $O 1 \text{ mg/l}$.

4.3. Electrochemical impedance spectrometry (EIS)

Figure 14 shows some examples of representative EIS results for the samples of steel grade R4 immersed in synthetic seawater at $S 35$ as a function of temperature and dissolved oxygen concentration. With exception of oxygen starvation at 2°C the Nyquist plots were notably affected by the immersion time. This means that the charge transfer resistance of the steel samples considerably varied with the immersion time. The asymmetric shape of the peaks on the Bode phase-frequency diagrams reveals the existence of one dominating and another secondary time constants. The maximum phase angle reached values between 50° and 75° . At the end of immersion, the frequency at which the phase angle reached its maximum shifted to lower frequencies one to two orders of magnitude. These results agree with the findings of Liu et. al [53] for high strength low alloy steel. The observed spectra are typical for corrosion of active metal in a corrosive media. The two time constants can be attributed to the charge transfer processes at the steel surface (the dominant component) and the rust layer (secondary component). Under the oxygen starvation conditions, the second time constant had larger contribution, than for aerated seawater that can be conceivably related with formation and following oxidation of

iron hydroxides. The dense blackish rust layer was typically observed on the samples subjected to corrosion at low oxygen concentration that supports this hypothesis. The spectra didn't provide any evidence for diffusion related process in the rust layer, so, the corrosion processes can be classified as Melchers's Phase 1 corrosion controlled by oxygen diffusion through surrounding water [12].

Fig. 14. Representative Nyquist plots (a, d, g and j) and Bode plots (b, c, e, f, h, i, k and l) for grade R4 steel sample immersed in synthetic seawater at S 35 saturated with oxygen (a–f), and at O 1 mg/l (g–l). The temperature was T 2 °C (a–c and g–i) and 32 °C (d–f and j–l). Dots – experimental data, lines – fitted graphs. The graphs shown in blue correspond to the beginning of the immersion period while those shown in green were obtained at steady corrosion.

The parameters of the equivalent circuit shown in Fig. 6 were determined by fitting this circuit to the electrochemical impedance data. Although the fitting quality was in general satisfactory with χ^2 typically below 0.02, statistically significant estimations of the parameters defining the CPEs could not be obtained for all spectra. Therefore, the analysis was focused on the resistance components.

Considering that the impedance at low frequencies: $R_{tot} = R_r + R_{ct}$ asymptotically approaches the polarization resistance, R_p , obtained in linear polarization tests (LPR at a rate of 10 mV/min), R_{tot} and R_p should be correlated. The correlation between the R_p and the impedance at low frequencies, around 100 mHz, at the same immersion times was studied using linear regression. As an example, Figure 15) shows the graph of R_p (measured by LPR) vs. R_{tot} (obtained by EIS) for steel grade R4 in aerated seawater at S 35 and various temperatures. The data were fitted by a linear function yielding values of R_{adj}^2 0.9800 and 0.9110 for aerated and oxygen starvation conditions, correspondingly (Table 5). Under aerated conditions the slope R_p / R_{tot} was 15 to 20% higher than unity, and this difference was statistically significant at the significance level $\alpha=0.05$. Under oxygen starvation the slope was close to unity. These findings gave evidences of reliability of the measured data. Under aerated conditions EIS gives slightly lower values of the extrapolated polarization resistance.

Fig. 15. Correlation of the polarization resistance (R_p) measured by LPR with the total resistance (R_{tot}) measured by EIS for steel grade R4 under seawater corrosion at S35 and O max. Three samples were tested at each temperature.

Table 5. Results of linear fitting the experimental data of polarization resistance (R_p) plotted against the total resistance, R_{tot} , determined from electrochemical impedance spectra: adjusted coefficient of determination (R_{adj}^2), slope (R_p/R_{tot}) and standard error of the slope (se). The experimental data correspond to the grade R4.

O (mg/l)	O_{max}			1
S	31	35	43	35
R_{adj}^2	0.9872	0.9926	0.9874	0.9110
R_p/R_{tot}	1.15	1.16	1.20	0.97
se(R_p/R_{tot})	0.018	0.014	0.019	0.035

4.4. Empirical model

In his fundamental works Melchers noticed that a comprehensive study of steel corrosion in sea environment should be accompanied by a development of guidelines for structural engineers “as to how such information may be transported to new design or analysis situations” [30]. The systematic data obtained in this study may have two practical implications. On the one hand, the dataset can be used for calibration of the corrosion models for short-term immersion (Melchers’s phases 0 and 1). On the other hand, it can serve for estimating the corrosion allowances at higher depths (except the seabed), where oxygen concentration is below the saturation level and where most microorganisms are in so-called “starved” condition, with very slow metabolic rates and relatively inactive microbiological activity [24]. At the deep seawater region salinity is almost constant and can be excluded from the analysis. Therefore, under given assumptions, the corrosion rate is controlled by seawater temperature and oxygen concentration. Figure 16 shows the experimental data (dots) and linear approximation of the CR (lines) as function of O at various T at standard salinity, $CR=f(S35, T, O)$. The blue and red lines correspond to the CR at T 2 °C and 32 °C, respectively. The dashed line between the red and blue lines is the estimation of the linear function $CR=f(S35, T$ 17, $O)$. Although statistical methods could not be applied for deriving the linear equations because of lack of sufficient experimental data, this diagram is useful for rough estimation of the CR in a standard seawater at any temperature T_x in the range 2 °C < T_x < 32 °C and any dissolved oxygen concentration O_x in the range 1 mg/l < O_x < O_{max} . For this purpose a vertical line should be traced through the abscissa $O=O_x$. This vertical line crosses the blue and red lines in points A and C, correspondingly. The segment AC should be now divided by a point D, which ordinate is found from the following equation:

$$\frac{AD}{AC} = \frac{T_x - 2}{30}. \quad (5)$$

The ordinate of the point D corresponds to the sought value of the CR.

Fig. 16. Simplified empirical diagram for determination of the corrosion rate for steel grade R4 as function of oxygen concentration and temperature. The salinity of seawater is $S\ 35$. The dotted line denotes the data measured in aerated seawater.

This method can be further developed and its precision can be enhanced by adding new experimental data measured at different experimental conditions. In surface seawater MIC is a dominant factor for long-term immersion, thus modelling of short-term corrosion is of less practical importance.

5. Conclusions

The influence of temperature, salinity and dissolved oxygen concentration on the rate of short-term abiotic immersion corrosion of steel grades R4 and R5 was studied using factorial experiment and lab-scale simulation. For both steel grades the corrosion rate tended to increase with increasing temperature. Under aerated conditions the corrosion rate was significantly affected by salinity. The corrosion rate was the lowest at a standard salinity (35 pss) and increased at both higher (43 pss) and lower (31 pss) levels of salinity. This could be related with a complex dependence of the corrosion rate on the aggressiveness of seawater, which increases with salinity, and oxygen and carbonic solubility, both of which decrease with increasing salinity. As expected, under oxygen starvation (1 mg/l) the corrosion rate steeply decreased. The decrease in the corrosion rate was more significant at 2 °C. Temperature had a less significant effect on the corrosion rate. The differences in corrosion rates for grades R4 and R5 were statistically insignificant.

A bulk of experimental data obtained in this study allowed developing a simple but useful for engineering practice graphical method for assessing the corrosion rate at various combinations of temperature and salinity under abiotic conditions. This method is valid for short-term immersion of steel grade R4 in seawater under abiotic conditions and for the ranges of temperature 2 °C - 32 °C and dissolved oxygen concentration 1 mg/l - $O_{\max}$.

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