

## INFLUENCE OF SEAWATER SALINITY ON CORROSION OF AUSTENITIC STEEL

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### Abstract

Due to the paramagnetic properties and the ability to passivation, for the production of hulls of some vessels (mainly warships), corrosion-resistant (stainless) steels with austenitic structure are used. This article describes the influence of seawater salinity on selected corrosion properties of high-alloy steel X5CrNi 18-10 (304). The average salinity of the seas is taken as 3.5% content of sodium chloride. Corrosion rate of the tested material was evaluated in an aqueous solution of sodium chloride was evaluated. The NaCl concentration in corrosive solutions was 0.7%, 1.4%, 2.1%, 2.8%, 3.5%, 4.2%. Corrosion tests were performed using the potentiodynamic method. The range of electrochemical potential changes was  $E_{corr} \pm 150$  mV. Corrosion rate was assessed on the basis of corrosion current density measurements. Corrosion potential values against the saturated calomel electrode were also determined. Based on the obtained measurement results and non-parametric significance tests carried out, a significant influence of seawater salinity on the value of corrosion current density and corrosion potential was found. The highest value of corrosion current density ( $j_{corr}$ ), and thus the highest corrosion rate, was recorded for 3.5% NaCl solution. In the concentration range from 0.7 to 3.5% NaCl in solution, the corrosion rate of austenitic steel increases. A further increase in salinity of electrolyte results in the inhibition of corrosion rate of steel. There is almost a full negative, linear correlation between the proportion of sodium chloride in the corrosive solution and the value of corrosion potential. Along with the rise in the salinity of seawater, increase the electrochemical activity, and thus the corrosion susceptibility, thus the corrosion susceptibility, of the austenitic steel X5CrNi 18-10 was observed.

**Keywords:** austenitic steel, corrosion, potentiodynamic test, seawater

### 1. Introduction

Austenitic alloy steels, including steel with a reduced AISI 304 carbon content, have found wide application in various industries, such as: sanitary, catering, food, pharmaceutical, chemical, pulp and paper, paint, architecture, shipbuilding (also as material for the production of hulls of vessels such as minesweepers or submarines) and aviation. These steels owe its wide application to relatively good corrosion resistance and good mechanical properties [3, 6].

Natural corrosion resistance is a feature of precious metals. However, there are many alloys of metals, which do not belong to the group of precious metals; those have high corrosion resistance. Some metals, e.g. aluminum and its alloys, have the ability to produce durable layers under atmospheric conditions, which are their natural corrosion protection. Alloy steels containing a significant amount of chromium in their composition have high corrosion and chemical resistance due to the chromium (III) oxide layer ( $Cr_2O_3$ ) being formed [7].

Corrosion of steel under constant immersion in seawater has electrochemical nature. Due to some of the features of this environment, resulting already from the chemical composition itself and the properties of seawater, this corrosion is characterized by high activity of corrosion cells. This phenomenon results from the significant electrical conductivity of seawater, which is the cause of low inhibition of ohmic cell operation. In this situation, corrosion occurs both because of the work of micro-cells (resulting, for example, because of non-homogeneity of the metal surface),

as well as macro-cells formed by the contact of two metals (e.g. corrosion of the steel hull plating under the influence of a brown propeller). There is a slight role in inhibiting an anodic corrosion process of most structural metals. This is caused by the presence of an extremely aggressive chloride ion, which destroys the protective passive layers. The corrosion rate of steel in seawater is determined by the inhibition of the cathodic process. Corrosion in seawater runs almost entirely with oxygen depolarization. Hence, the velocity of oxygen supply to the corrosive surface is the main controlling factor. Corrosion of steel in seawater is characterized by an increased tendency towards non-uniformity. The maximum depth of corrosion pits can exceed 3 to 4 times the size of the linear corrosion index [2, 4, 5, 9].

## 2. Testing methods

The corrosion test specimens were made of austenitic stainless steel (EN X5CrNi18-10, 1.4301; ANSI 304) with the chemical composition: max 0.05% C, 17.5-19.5% Cr, 8-10.5% Ni, rest Fe. The corrosion properties of X5CrNi 18-10 steel were tested in aqueous NaCl solution (the so-called replacement seawater). The mass fraction of sodium chloride in the corrosive solution was 0.7%, 1.4%, 2.1%, 2.8%, 3.5%, 4.2%.

The corrosion resistance of steel was estimated by electrochemical potentiodynamic (polarization) method. Electrochemical polarization studies belong to the classical methods of corrosion testing. It is well understood and relatively frequently used. The rate of measurement is high compared to the gravimetric methods. Electrochemical polarization allows both estimation of the instantaneous rate of corrosion and determination of the nature of the processes involved. The aim of studies of the polarization is to analyse the corrosion current with the aid of the following formula [8]:

$$j = j_{corr} \left[ \left( 1 - \frac{j_a}{j_{da}} \right) \exp \left( \frac{2.3(E - E_{corr})}{b_a} \right) - \left( 1 - \left| \frac{j_c}{j_{dc}} \right| \right) \exp \left( \frac{-2.3(E - E_{corr})}{b_c} \right) \right], \quad (1)$$

where:

$j$  – current density of polarization [mA/cm<sup>2</sup>],

$j_{corr}$  – corrosion current density [mA/cm<sup>2</sup>],

$E$  – polarization potential [mV],

$E_{corr}$  – corrosion potential [mV],

$b_a$  – anodic Tafel constant [mV],

$b_c$  – cathodic Tafel constant [mV].

$j_a$  – partial anodic current density [mA/cm<sup>2</sup>],

$j_c$  – partial cathodic current density [A/cm<sup>2</sup>],

$j_{da}$  – limiting anodic current density [mA/cm<sup>2</sup>],

$j_{dc}$  – limiting cathodic current density [mA/cm<sup>2</sup>].

The polarization measurements in a three-electrode cell were performed. The test sample, platinum counter-electrode (CE), saturated calomel electrode (SCE) were placed in the vessel, in which was 500 ml of NaCl solution at ambient temperature. The samples were exposed to the electrolyte for one hour. During the study, the ATLAS 0531 potentiostat was used. The polarization curves of  $j = f(E)$  in the range of  $E_{corr} \pm 150$  mV were recorded. Rate of change of the potential, in all cases, was 10 mV/min. In order to calculate the value of parameters characterizing the properties of corrosion (corrosion current density, corrosion potential, Tafel constants, limiting current density) of the test material the “Elfit – corrosion polarization data fitting program“ computer program was used. This program calculates the corrosion process parameters of equation (3). To assess the impact of seawater salinity on the corrosion resistance of the normal hull steel, the calculated values of the density of the corrosive current and corrosive potential were used [1, 10].

The 10 repetitions were made measurements of polarization steel, for each NaCl concentration of corrosive solution used.

### 3. Results

In Fig. 1, in the Evans chart, exemplary polarization curves obtained as a result of current density ( $j$ ) measurement as a function of potential change of the electrode being investigated (X5CrNi18-10 steel), in a corrosive environment with variable NaCl concentration are presented. Based on polarization waveforms on Evans charts, on the so-called Anodic curves can be found to have diffusion processes in the electrochemical corrosion process of 5XCrNi-18-10 steel in a sea water replacement environment. The value of the limiting anodic current density increases with the increasing proportion of sodium chloride in the corrosive solution.

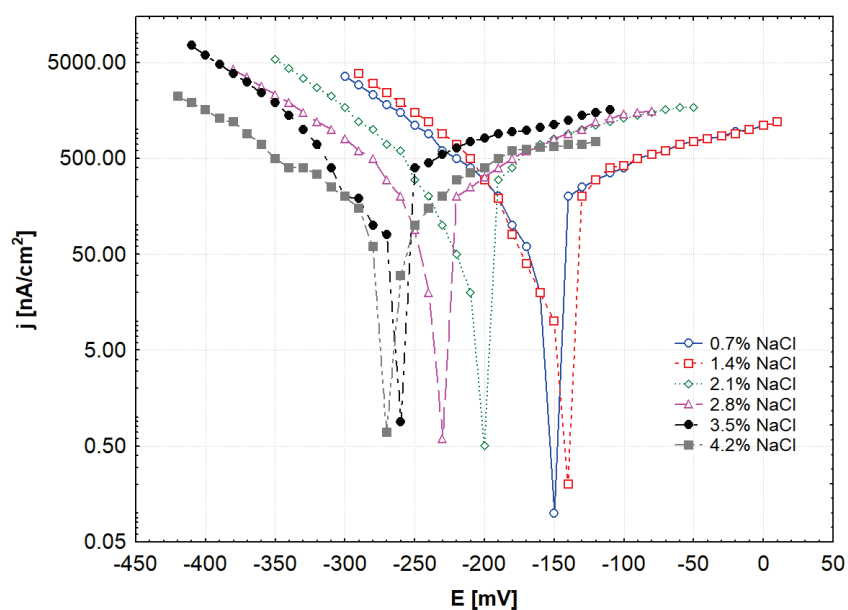


Fig. 1. Exemplary polarization plots  $j = f(E)$  for X5CrNi 18-10 steel in aqueous environment with various degree of NaCl mass fraction

Figure 2 presents the results of the basic statistical analysis (mean value, standard error standard deviation) for the values of corrosion current density ( $j_{corr}$ ) calculated from the formula 1. The average values of corrosion current density ranged from  $74 \text{ nA/cm}^2$  to  $154 \text{ nA/cm}^2$ . The smallest  $j_{corr}$  value in the case of X5CrNi18-10 steel exposed in 0.7% NaCl environment was observed. The highest value of the corrosion current density was found for the material immersed in an aqueous corrosion solution containing 3.5% NaCl. There is a very high positive linear correlation between the density of the corrosive current and the mass fraction of sodium chloride in the corrosive solution. The value of the Pearson coefficient was  $r = 0.81$ . In the range from 0.7% to 3.5% of changes in the concentration of sodium chloride in the aqueous solution corrosion rate of austenitic steel increases with NaCl concentration. In this case, the rate of corrosion processes is related to the increase of ionic conductivity in the solution along with the degree of salinity of seawater because of the decrease in the ohmic resistance value. Chlorine ions contained in a corrosive solution cause local damage to the passive layer located on the surface of the steel being tested. Therefore, depolarization of the working electrode occurs and the polarization resistance of the corrosion cell decreases.

The increase in the value of corrosion current density occurred in aqueous solutions containing a mass fraction of NaCl in the range from 0.7% to 3.5%. In a solution, containing 4.2% NaCl there was a decrease in the value of the corrosion current density compared to the  $j_{corr}$  value for the environment containing 3.5% sodium chloride. The observed decrease in the value of the corrosion current density is related to the phenomenon occurring in solutions of neutral salts. In aqueous solutions, the solubility of gases, including oxygen, decreases with increasing concentration of

neutral salts. In seawater, the pH of which is alkaline ( $\text{pH} = 7.2\text{--}8.4$ ), oxygen is required for corrosion during the reduction reaction. Thus, the electrode reaction occurring on the cathode of the corrosion cell is inhibited. These results are, among other things, in a decrease in corrosive potential (Fig. 3).

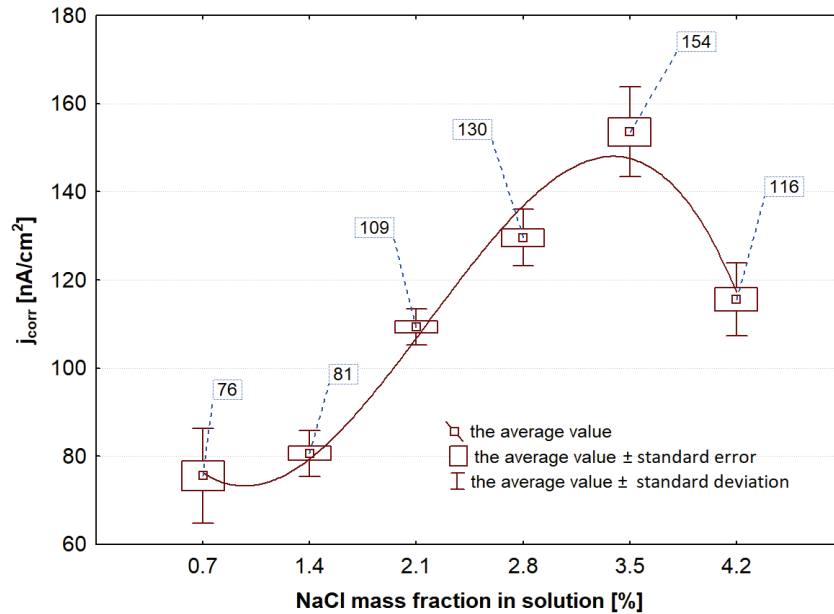


Fig. 2. Effect of NaCl concentration on the corrosion current density value of X5CrNi18-10 steel in seawater environment

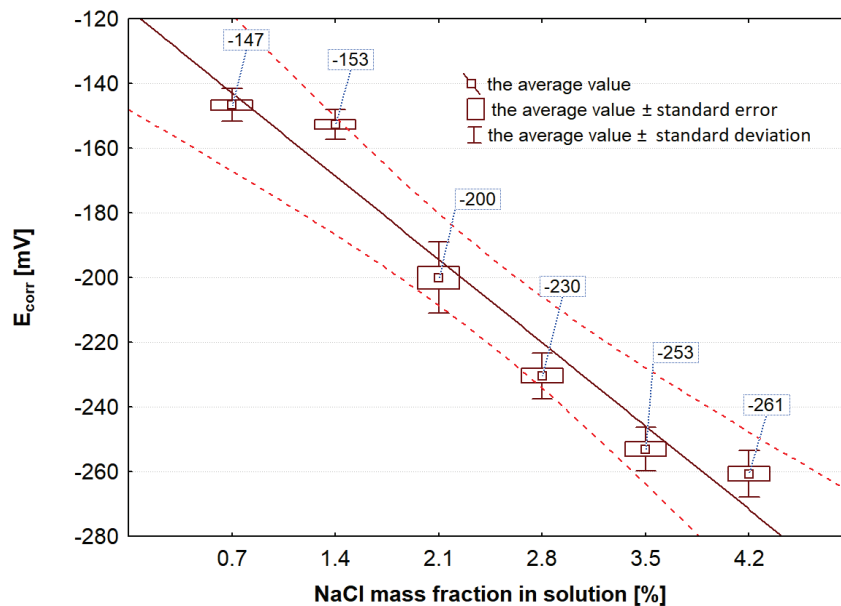


Fig. 3. Effect of NaCl concentration on the potential corrosion current density value of X5CrNi18-10 steel in seawater environment

During corrosion tests, a relatively large spread of the determined values of the corrosion current density was observed. In the case of corrosive solutions with a concentration of 0.7 and 1.2% as well as 2.1, 2.8 and 4.2% NaCl, similar ranges of the corrosion current density values obtained from individual measurements were found (Tab. 1). In order to check whether the obtained average values of  $j_{\text{corr}}$  in individual corrosion solutions significantly differ from each other, statistical non-parametric significance tests were performed for many groups of independent

variables (Kruskal-Wallis and median tests). The null hypothesis was formulated as follows: the value of  $j_{corr}$  does not depend on the concentration of NaCl in the corrosive solution. The results of non-parametric significance tests for the  $j_{corr}$  variable are presented in Tab. 2. The obtained values of the Kruskal-Wallis test  $H = 53.69$  and the median test  $X^2 = 45.18$ , at the assumed significance level of  $\alpha = 0.05$  allow to reject the null hypothesis. Thus, with a 95% probability, it can be concluded that the corrosion rate of the steel tested depends on the salinity of seawater. The prediction of the corrosion current density values for X5CrNi 18-10 steel can be made using the regression equation (4) (value of the determination coefficient for the equation  $R^2 = 0.98$ ):

$$j_{corr} = 10.33(\%NaCl)^3 + 67.77(\%NaCl)^2 + 102.11(\%NaCl) + 118.1, \quad (2)$$

where:

$j_{corr}$  – corrosion current density [nA/cm<sup>2</sup>],

%NaCl – mass fraction of sodium chloride in a corrosive solution [%].

Tab. 1. The values of the range of intermediate measurements of the corrosion current density  $j_{corr}$  (nA/cm<sup>2</sup>) in seawater with various contents of sodium chloride

%NaCl	Number of measurements	Minimum value	Maximum value	Range
0.7	10	58	95	37
1.4		75	90	15
2.1		103	116	13
2.8		117	139	22
3.5		131	167	36
4.2		102	132	30

Tab. 2. Results of significance non-parametric tests for independent variables: corrosion current density ( $j_{corr}$ ) and corrosion potential ( $E_{corr}$ ) of X5CrNi 18-101 steel in solutions with variable concentration of NaCl (p level – calculated level of significance)

Variable	The values of the tests			
	Kruskal-Wallis test		median test	
	$H$	$p$ level	$X^2$	$p$ level
$j_{corr}$ [nA/cm <sup>2</sup> ]	53.69	<0.01	45.18	<0.01
$E_{corr}$ [mV]	55.25	<0.01	56.4	<0.01

Figure 4 presents the histograms of the results of the measurement of corrosion potential of X5CrNi 18-10 steel in a seawater replacement environment with various sodium chloride content. Based on the histograms of the  $E_{corr}$  variable, it can be stated that for some corrosive environments (e.g. with a NaCl mass fraction of 2.8%, 3.5%, 4.2%) similar corrosion potentials were obtained for individual measurements. In order to check whether the obtained average values of  $E_{corr}$  (Fig. 3) in individual corrosion solutions significantly differ from each other, statistical non-parametric significance tests were performed (Kruskal-Wallis and median tests). The results of non-parametric significance tests for the  $E_{corr}$  variable are presented in Tab. 3. The obtained values of the Kruskal-Wallis test  $H = 55.25$  and the  $X^2$  median test = 56.4 showed that the  $E_{corr}$  changes are statistically significantly at the assumed level of  $\alpha = 0.05$ .

Figure 3 presents the results of the measurement of corrosive potential in seawater with a different degree of salinity. Depending on the percentage of sodium chloride in the corrosive solution, the average value of corrosion potential was in the range from -261 to -147 mV. Almost full correlation between salt-water salinity and corrosion potential was found. The average value of corrosion potential in the corrosive solution decreases with the increase of NaCl concentration. The decreasing  $E_{corr}$  value is connected on the one hand to the reduction of the reduction reaction

and on the other hand to the faster depolarization of the anode. The rate of the anodic reaction increases because of increasing the electrical conductivity of the electrolyte with increasing NaCl concentration. The prediction of the corrosion potential of steel X5CrNi18-10 in the seawater environment can be made using the following regression equation ( $R^2 = 0.95$ ):

$$E_{corr} = -36.79(\%NaCl) - 117.09, \quad (3)$$

where:

$E_{corr}$  – corrosion potential, [nA/cm<sup>2</sup>],

%NaCl – mass fraction of sodium chloride in a corrosive solution, [%].

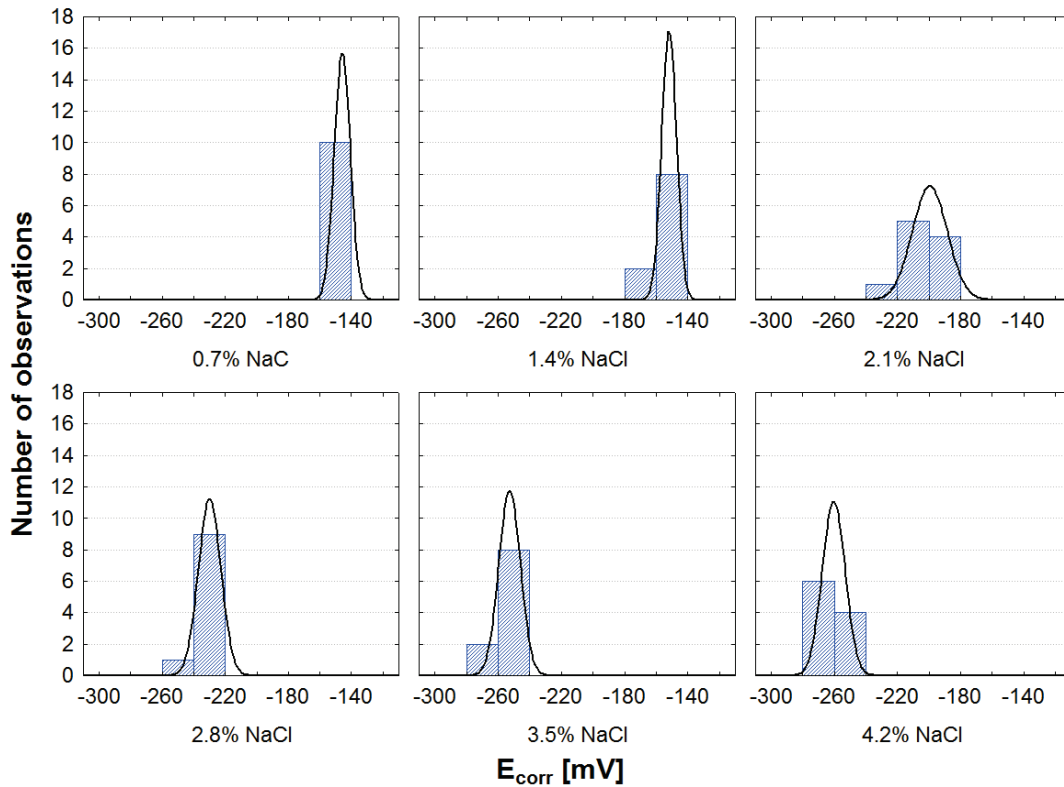


Fig. 4. Categorized histograms for  $E_{corr}$  variable

#### 4. Conclusions

- 1) Statistically significant influence of seawater salinity on corrosion properties of X5CrNi18-10 austenitic steel was found.
- 2) The highest value of the corrosion current density was observed in the solution containing 3.5% NaCl mass fraction.
- 3) In seawater with a sodium chloride content in the range of 0.7 to 3.5%, an increase in the value of the corrosion current density was observed, along with the increasing share of NaCl. In seawater with higher salinity, the corrosion rate was reduced.
- 4) The corrosion potential of X5CrNi18-10 steel, and thus the susceptibility of this material to corrosion, decreased with the NaCl content in the corrosive solution.

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