Experimental design to study the influence of temperature, pH, and chloride concentration on the pitting and crevice corrosion of UNS S30403 stainless steel

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Abstract

Localized corrosion of stainless steel, namely pitting and crevice, affects seriously the performance of these materials in service. In this paper, the design of experiment (DOE) is used to study the influence of temperature, pH and chloride concentration on the pitting and crevice corrosion of AISI 304L (UNS S30403) stainless steel. DOE approach enables to reduce the number of tests (anodic potentiodynamic polarization) necessary to study the effect of several parameters on the passivity breakdown potential. The use of DOE provided a regression equation

that was analyzed by comparison with laboratory and literature results. Among all these parameters, the temperature has the most significant effect on pitting corrosion resistance.

1.   Introduction

Stainless steels are susceptible to localized corrosion, namely pitting and crevice corrosion, in the presence of oxygen and chloride ions, with the local breakdown of the passive film (*corrosion initiation*) and very high corrosion rate due to the macrocell mechanism (*corrosion propagation*) [1–6]. The occurrence of localized corrosion, i.e. when corrosion potential is higher than passivity breakdown potential, depends on several factors related to the metal and the environment, such as metal chemical composition and microstructure, chloride content, temperature, pH, fluid velocity, oxygen content, and so forth. Among all the influencing environmental parameters, chloride concentration, temperature, and pH play a key role in the determination of pitting and crevice corrosion performance of stainless steels [7–17]. It is well known that by increasing chloride concentration, temperature, and acidity of the solution, localized corrosion resistance of stainless steel generally decreases [18–25]. The role of temperature rise is mainly to control the rate of pitting initiation [1] by stabilizing of pits and hindering their re-passivation [26,27]. About the effect of pH, the passivity breakdown potential increases in alkaline conditions, while the passive film is weakened by acidic condition [1,28–30]. In severe acidic condition, the passive film becomes thermodynamic unstable, according to the Pourbaix diagram. Some authors believe that in an acidic medium the reduction in pitting potential derived from decreasing passive film thickness [31–34]. While some others consider the competition between chloride and OH^- ions in which by decreasing pH, the role of chloride become predominant [28,35]. The aggressiveness of chloride ions is attributed to the small size, high diffusivity, and strong anionic nature of these ions [21]. Several studies on the effects of chlorides ions [Cl⁻] on pitting behavior of stainless steels have been shown a logarithmic relationship between passivity breakdown potential and chloride ion concentration [1,3,7,9–11,16,18,28,36,37].

Comprehension and prediction of corrosion behavior of stainless steels in different environmental conditions are of great importance. In this respect, a diagram, called Pedeferri's

Diagram, can be used as a corrosion map that reports the electrochemical potential (E) with respect to the chloride content in the electrolyte (Cl⁻). The diagram has been proposed by Pietro Pedeferri for the application of cathodic protection and prevention of carbon steel in concrete, which shows a passive behavior, like stainless steels, and suffers localized corrosion in the presence of chlorides [38–40]. The diagram is mentioned in ISO 12966 "Cathodic protection of steel in concrete" standard. It reports the corrosion zone, passivity (perfect and imperfect) as defined by Pourbaix [2], and immunity zones. Perfect and imperfect passivity zones are separated by the re-passivation (protection) potential. In a previous paper, the analysis of the electrochemical methods (i.e. potentiodynamic and potentiostatic polarization tests) to determine localized corrosion characteristics (passivity breakdown potential, E_{bd}, re-passivation potential, E_{rep}, and critical chloride concentration) along with the comparison of the two methods were done. Furthermore, the definition of Pedeferri's diagram of UNS S30403 (AISI 304L) stainless steel for chloride containing environments, neutral pH, and the room temperature was discussed [41].

The generation of such diagrams for different conditions requires a high number of tests to be performed, if one considers the conventional experiment design approach based on the number of variables and the number of their values. Indeed, such a procedure lets to gain information about one factor in each experimental trial and has to be repeated for all other conditions [42]. According to the fact that localized corrosion initiation of stainless steel is a stochastic phenomenon, statistical approaches can provide appropriate quantitative information for understanding passivity breakdown behavior [43–47]. In the present research, design of experiment (DOE) is used to evaluate the effect of environmental parameters on the pitting and crevice susceptibility of UNS S30403 (AISI 304L) stainless steel. DOE is a statistical technique that allows identifying the best experimental combination by defining the significance of the experimental conditions. This causes an optimization of the experimental condition with a reduced number of tests. Moreover, it is able to develop a mathematical model through a polynomial regression equation in order to obtain information about the relationship between the dependent variable with all the other variables. Design of experiment is used in the field of engineering, especially materials engineering [48,49].

It is worth to note that a high number of the researches focused on the unique contribution of each parameter on the passivity breakdown potential of metals either through mechanistic or

empirical models. The main contribution of the present research is to provide an application of the design of experiment (DOE) approach to the pitting and crevice corrosion. The application of DOE could be interesting in the evaluation of pitting corrosion resistance, providing a method able to define mathematically the effect of different parameters. In this respect, the influence of the environmental parameters (i.e. chloride content, temperature, and pH) on the initiation of pitting or crevice corrosion of 304L stainless steel is evaluated. Eventually, a regression equation is developed by applying DOE to study the effect of these parameters on the passivity breakdown potential of AISI 304L stainless steel.

2. Materials and methods

2.1. Experimental procedure

Laboratory tests were carried out on austenitic stainless steel type UNS S30403 (AISI 304L) bar samples (cross-section of bar stock). Table 1 reports the steel chemical composition (wt. %). In the sample preparation stage, after cutting, specimens were prepared using abrasive papers from 100 to 1200 grits and then the surfaces were cleaned with acetone. After preparation, specimens were kept in free air for one day and then pre-conditioning was performed in free corrosion condition, i.e. by immersing the specimen in the test solution in order to form a stable passive film in that condition. The solution was aerated (exposed to the air) and the oxygen level was considered between 6 and 8 mg·L^{-1} for the range of temperature and chloride used in the present research. Pre-conditioning time was selected based on the chloride concentration and pH of the test solution (Table 2). During the period of pre-conditioning prior to the potentiodynamic test, free corrosion potential was monitored with a frequency of 1 point every minute. For less aggressive conditions (pH > 7 and Cl$^-$ < 10000 mg·L^{-1}), the pre-conditioning time was 24 hours according to the previous experience [41,50]; for more aggressive conditions, it decreased to one hour as reported in ASTM standard [51]. The sample holder configuration was based on ASTM G61 [51] in which the exposed area of the specimen to the test environment was 1 cm^2. Anodic potentiodynamic polarization tests were used to determine the passivity breakdown potential of stainless steel in the presence of chloride. The tests were carried out using potentiostat Metrohm Autolab® Multi Autolab/M204 and the potential scan rate was 0.6 V/h according to standards [51,52]. The potential was measured versus the Ag/AgCl/KCl$_{sat.}$ reference electrode (+0.2 V vs. SHE) placed in a glass Luggin capillary in order to minimize the ohmic

drop contribution in the potential measurement. An inert activated titanium counter electrode with 10 cm^2 surface area was used. The starting potential was set in -0.1 V vs. the free corrosion potential.

Tests were performed in a chloride-containing solution, from 100 to 10,000 mg·L^{-1} concentration. Temperature, T, was in the range from 20°C to 50°C (±1°C), and pH was in the range from 4.0 to 8.0 (±0.1 unit of pH). In all the specimens considered for the statistical analysis, both pitting and crevice corrosions were observed after the test. Therefore, the term passivity breakdown potential (E_{bd}) was selected as the potential in which pitting or crevice can occur. The onset of localized corrosion, namely the passivity breakdown potential, was marked by a rapid increase of the anodic current during polarization and 1 mA/cm^2 is considered as the current at which the potential is reversed.

2.2. Statistical approach

By a traditional approach, the number of potentiodynamic tests required to study the effect of three parameters (T, pH and chloride content) on the passivity breakdown potential of AISI 304L stainless steel can be very high. Let us assume five values for each parameter: the total number of tests (with one repeatability) is $5^3 = 125$. A statistical approach based on DOE can be very helpful in order to minimize the number of significant tests. In the statistical approach, the three variables considered were chloride content (log Cl$^-$), temperature and pH.

DOE techniques are divided into two categories including screening and optimization methods. Screening techniques, such as factorial method, apply when it is needed to discover which parameters are effective in the process of interest and to what extent [53]. This is typically done by applying two levels (high and low) for each parameter. Screening methods use the first-order regression model to define the relationship among parameters. Optimization methods are more comprehensive since they are not only able to determine the influential factors but also find the best model for the studied phenomenon [54,55]. One of the most important optimization methods is the Response Surface Methodology (RSM) that are able to develop both first and second-order models. Among the RSM methods Central composite design or CCD has been selected: this method benefits from a five-level design by introducing a coefficient (α) to extrapolate from maximum and minimum levels. [56–58].

For each variable, a range is defined, with a maximum and minimum value, based on the operating condition in which this austenitic stainless steel is used. The numerical values are transformed in a way that the minimum corresponds to -1 and the maximum corresponds to +1, these are called factorial points; the average between the maximum and the minimum is 0 and is called the center point: all these values are coded values. In CCD method, the software considers other points (star points) by applying an alpha coefficient, that leads to generating five levels for each factor: -α, -1, 0, +1, +α (Table 3). Figure 1 shows a schematic representation of CCD design in which "F" is the factorial points, "c" is the center point, and "S" is the star point. The alpha coefficient, that in our case is 1.633, is calculated according to the theory of DOE [54]. Center points have a great role since they help to reduce the amount of error in the model as well as the determination of the true path of the curve through the range (curvature) [53,54].

In this research, blocking is used to reduce or eliminate the variability originated from nuisance (not controlled) factors. Each block provides a relatively homogeneous set of conditions within which different conditions of the variables are compared. The selection of α and the number of center points are of great importance. When blocking the CCD, factorial points and star points will be in different blocks and in all blocks, center points are present. In blocking, the alpha coefficient can be obtained from Equation 1 [54] where n_f and n_A are the number of factorial points and star points, respectively. The terms n_{CA} and n_{CF} are the number of center points in star and factorial blocks, respectively. Factorial block contains 4 center points (n_{CF}) while star block has 2 center points (n_{CA}). In this way the number of center n_c is equal to 6 and the total number of test with one repetition is 20 [53,54].

$$\alpha = \sqrt{\frac{n_f(n_A + n_{CA})}{2(n_f + n_{CF})}} \qquad (1)$$

The total number of experiments (runs) for CCD is calculated with Equation 2 [53] in which 2^k, 2k, and n_c are the numbers of factorial points, star points, and center points, respectively.

$$Run = 2^k + 2k + n_c \qquad (2)$$

Based on Equation 2 and the number of repetition selected (2), the total number of tests is 40 that shows a considerable reduction in number in comparison with the traditional approach where for two repetitions the number of tests is 125*2= 250.

Table 4 reports all the experimental conditions (chloride content, temperature, and pH) considered by DOE design as well as the measured passivity breakdown potential (E_{bd}) and repassivation potentials (E_{rep}). The tests in the factorial block (block 1) include 8 tests in the center (log (Cl^-_{ppm}) = 3, T= 35ºC, and pH= 6) and 16 tests from the combination of maximum and minimum levels for all the parameters. The second block, star block, consists of 4 center points and 12 star points. In star points always two parameters are in their zero levels while the other is in +1.633 or -1.633 as shown in Table 4. After performing tests based on the conditions provided in Table 4, the passivity breakdown potentials obtained from the polarization curves were introduced to the software. In this way, the software was able to elaborate the results to generate a second-order regression equation along with the analysis for the significance of parameters and coefficients. Minitab® [59] was the software by which the planning of the DOE and the analysis of the responses were achieved.

3.   Results

3.1.   Potentiodynamic polarization tests

Figure 2 (a-d) shows the results of potentiodynamic polarization tests in some of the test conditions reported in Table 4, varying chloride content, temperature, and pH. The repeatability in each condition is two, except the center points (i.e. $Cl^- = 1000$ mg·L⁻¹, T = 35°C, and pH = 6) which are 12 (Figure 3). In Figure 2(a-d), the anodic potentiodynamic curves at two temperatures (i.e., 20°C and 50°C) are compared, while chloride concentration and pH are fixed. As can be seen, by increasing temperature, polarization curves move to the higher current densities in the passivity range and passivity breakdown potentials drop, as expected. In the case of 100 mg·L⁻¹ chloride concentration and pH 4 (Figure 2a), the passive potential range is strongly reduced at 50°C compared to 20°C. At pH 8, the passive region is more stable for both temperatures and less oscillation can be observed (Figure 2b). This is due to the beneficial effect of alkalinity on the passivity of steel alloys. Similar behavior is observed for 10,000 mg·L⁻¹ chloride concentration as well (Figure 2c and 2d). Figure 3 shows the effect of pH in a fixed temperature and chloride content ($Cl^- = 1000$ mg·L⁻¹, T = 35°C). It shows that increasing pH shifts the

passivity breakdown potential to higher values. Moreover, in highly acidic conditions (pH = 2.7), the metal shows active behavior and passive range of the polarization curve disappears (Figure 3).

3.2. Data elaboration by DOE

The passivity breakdown potentials collected from potentiodynamic polarization curves (Table 4) were used by the software to generate the regression equation. Equation 3 represents the regression equation created by the CCD method in which the dependent variable, i.e. passivity breakdown potential (E_{bd}) depends on the independent variables of the equation, i.e. Cl⁻, T, and pH, and their interactions.

$$E_{bd}(V \text{ vs. Ag/AgCl/KCl}_{sat.}) = \left(8 - 8A - 12B + 8C + A^2 + 4B^2 + 4C^2 - 3AC\right) \cdot \frac{1}{100} \tag{3}$$

$$A = \log\left(Cl^-_{mg \cdot L^{-1}}\right) - 3$$

$$B = \frac{T(°C) - 35}{15}$$

$$C = \frac{pH - 6}{2}$$

As can be seen, the equation includes an intercept, three linear terms, three quadratic terms, and one interaction term. The parameters A, B, and C are the functions of chloride, temperature, and pH, respectively. The only interaction term recognized as significant by the software is the interaction of chloride with pH (AC); either chloride-temperature (AB) or temperature-pH (BC) interactions were insignificant, therefore removed from the equation. This is related to the confidence level (95%) used for the analysis of variance (ANOVA). The level of confidence is the degree of the statistical reliability of the model and it allows determining the uncertainty or risk degree, which is the difference between 1 and the confidence level (5% in this case). For every independent variable, if the P-value is lower or equal to the risk degree (0.05) there is a significant correlation between the dependent variable (in this case the E_{bd}) and the independent one, while P-value higher than 0.05, shows that the dependent variable is not correlated to the independent one.

Based on the application of the DOE, the temperature has the highest effect on the passivity breakdown potential of AISI 304L stainless steel then chloride and pH. This is reflected in the coefficients of Eq. 3 where the absolute value of temperature coefficient is the highest (0.12) among the others. As expected, by increasing chloride concentration and temperature, passivity breakdown potential drops and shifts to lower potentials, while an increase of pH shifts the passivity breakdown potential to more noble values, in agreement with the mechanism of pitting and crevice corrosion and the experience gained from the laboratory and field.

Figure 4 (a-b) and Figure 5 (a-b) show the effect of pH and temperature on the passivity breakdown potential of AISI 304L stainless steel predicted by the model (Eq. 3). The figures report the passivity breakdown potential vs. chloride content (semi-logarithmic axis): dashed curves were originated from the equation and the experimental points are the ones that have been introduced to the software to generate the regression equation. At a fixed temperature, by increasing pH from 4 to 8, passivity breakdown potential increases; however, this effect is reduced for higher chloride concentrations (10,000 mg·L^{-1}). Moreover, change in pH cause changing the slope of the curves in a way that at higher pH, the slope of the curves is steeper rather than that of the lower pH (Fig. 4). Influence of temperature is shown in Fig. 5 by fixing the pH and changing the temperature from 20°C to 50°C. An increase of temperature reduces passivity breakdown potential without any changes in the slope of the curves.

In order to find out if the equation presents a proper prediction of the corrosion behavior, some additional potentiodynamic polarization tests have been done in the conditions of pH, chloride concentrations and temperatures different from those considered for DOE elaboration (but in the range reported in Table 3). These results are reported in the form of mean value and standard deviation; for each condition, minimum 5 tests were done (Figures 6 and 7). The match with DOE prediction (dashed curve) is good: at pH = 6 and T = 20, 40, and 50°C, the results depict a good overlapping with the regression equation. The same consideration can be extended also for pH = 4 and T = 20°C. Hence, it can be deduced that the regression equation provides a good estimation of the stainless steel's passivity breakdown potential in the environmental conditions considered.

4. Discussion

Pitting corrosion occurs if the free corrosion potential (E_{corr}) is higher than the passivity breakdown potential ($E_{corr} > E_{bd}$). It follows that one of the characteristics that account for the tendency of the metal to pitting initiation is the difference between passivity breakdown potential and corrosion potential. The higher is this difference, the lower is the tendency for pits initiation [19]. In this respect, the aforementioned differences were calculated for different pH (4, 6, 8, and 10), temperatures (10-60°C), and a fixed chloride content (1000 mg·L^{-1}) from the potentiodynamic polarisation results reported in Tables 5 and 6. Then their mean value and standard deviations are reported in Figure 8 and Figure 9. The results show that the propensity to pitting is reduced by moving from pH 4 to 6 while staying in the same range from 6 to 8 (Figure 8) in a fixed temperature and chloride content. For higher pH (i.e. 10), the difference between E_{bd} and E_{corr} increased. This is because of the enhancement of passive layer performance in terms of localized corrosion resistance in the strong alkaline environment [28,31,60].

The observation of passivity breakdown potentials (Figure 4) showed that in low chloride content (100 mg·L^{-1}), the effect of pH is more pronounced in comparison to higher contents. It is stated in some references that in this range of pH (4-8), pitting potential exhibits small variations [1,30,61]. In highly acidic media, general corrosion occurs, while corrosion resistance improves for basic solutions (Figure 3) [1].

Figure 9 shows that, by increasing temperature from 10 to 40°C, the difference between passivity breakdown potential and corrosion potential decrease and the tendency to initiation of stable pits is increased. However, the slope of the curve is reduced with rising temperature more than 40°C and experiences a shallow slope as predicted by the model in which temperatures 40°C and 50°C are closer to each other (Figure 6). This is in agreement with the results obtained by Tousek (reported in [1]) and Leckie and Uhlig [28].

Actually, it is not easy to find a physical meaning for the effect of parameters and their interactions through the regression equation (Eq. 3) mainly due to the quadratic terms included. For example, one can see that the effect of chloride and pH through the linear term is to reduce and increase E_{bd} (-0.08A and 0.08C), respectively. While all the quadratic terms are positive and have an increasing effect on E_{bd} (0.01A^2 and 0.04C^2).

Therefore, it was tried to simplify this equation by some mathematical elaborations; consequently, a semi-logarithmic equation (Eq. 4) was obtained. This is in agreement with the

equation widely reported in several reference books and scientific articles [1,3,7,10,16,18,19,36]. In the equation, coefficient B is the function of pH and constant A is the function of both pH and temperature. Coefficient B determines the slope of the curves as already discussed for Figure 4. The absolute value of the slopes obtained in the range of 100 to 10000 mg·L^{-1} (82 mV/decade and 97 mV/decade for pH 6 and 7, respectively) are consistent with Leckie and Uhlig [28] whose results revealed a decrease of 88 mV for an increase of one order of magnitude in the concentration of chloride ions for neutral condition and room temperature.

$$E_{bd}(V \text{ vs. Ag/AgCl/KCl}_{\text{sat.}}) = A - B \cdot \log\left(Cl^-_{mg \cdot L^{-1}}\right) \tag{4}$$

$$A = -0.0078 \cdot T(°C) + 0.083 \cdot pH + 0.17$$

$$B = 0.015 \cdot pH - 0.0078$$

It has been already explained that in the presence of chloride, the temperature may promote the process of pitting by accelerating pit ==initiation== that occurs as a result of an increase in the transition from metastable to stable condition for pits [19,26,27]. Moreover, the reduction of critical chloride content and the strength of passive film are the consequence of rising temperature, as well [36].

Findings of the present research confirm the accelerating effect of temperature which illustrated a parallel trend (same slope) among different temperatures and fixed pH (Figure 6). This trend is also observed in other research for the range of 20 to 80°C where the slope remained constant [36]. According to the effect of pH and temperature in Equation 4, a change of 10°C in temperature has approximately the same effect of changing one unit of pH.

Figure 10 shows a simulation of the potential-log Cl$^-$ diagram, named Pedeferri's diagram [40], for pH 6 and temperature 20°C. The solid line is generated by the semi-logarithmic equation (4) and points are the experimental points. Since in Pedeferri's diagram, localized corrosion potential is a scattering band [38,41], it is necessary to define maximum and minimum passivity breakdown potentials for different chloride concentrations (pH = 6 and T = 20°C) by which ranges are defined (dotted lines). This is related to the stochastic nature of pitting corrosion that must be analyzed from a statistical point of view to determine potential distribution [43]. As can be seen, the solid line is passing through the results and scattering band, moreover, this is in

accordance with the previous work in which Pedeferri's diagram is determined without using DOE [41]. The scattering of E_{bd} in each chloride concentrations is about 100 mV (±50 mV from the solid line) which is lower than the scattering reported in ASTM G61 [51]. The repassivation potential results are also reported in Figure 10 so that to obtain different regions of Pedeferri diagram. As can be observed, the repassivation potential does not change significantly in different chloride concentrations and its slope is not the same as the passivity breakdown potential slope.

Furthermore, in order to see if Equation 4 presents a good estimation of the occurrence of the passivity breakdown potential in different conditions, some simulations are carried out as reported in Table 7. In the simulation, the solution of different chloride concentrations, temperature, and pH are compared in terms of passivity breakdown potential and the possible range of corrosion potentials. Corrosion potential for freshwater, brackish water, and the acidic condition are considered in the range of $-0.14 \leq E_{corr} \leq 0.14$ V vs. Ag/AgCl/KCl$_{sat}$. This range is selected on the basis of the E_{corr} range obtained in the present research and in the previous paper [41], while the passivity breakdown potentials are derived from Equation 4. In the case of seawater, two conditions were considered, with or without bacterial activity. As known, the presence of oxidizing bacteria in seawater can cause an ennoblement of the corrosion potential of stainless steel. Corrosion potential ranges for seawater without bacteria were mainly between -0.2 V $\leq E_{corr} \leq 0.2$ V vs. Ag/AgCl/KCl$_{sat}$ [62–64]. The presence of bacteria causes to increase corrosion potential by about 200–300 mV compared to that in sterilized seawater [5,6,65–67]. The last column of the table states the possibility of localized corrosion occurrence in which the term "yes" is used if the breakdown of passivity can take place ($E_{corr} > E_{bd}$).

It seems that in most conditions, DOE presents a good agreement with the experience regarding the occurrence of localized corrosion. However, in some conditions where typically AISI 304L stainless steel does not resist to corrosion (according to literature and practical experience [68]), the results of the DOE model give very high passivity breakdown potential. For instance, in the chloride range of 1000 to 5000 mg.L^{-1}, localized corrosion on AISI 304/304L stainless steel in water systems at room temperatures (20°C, pH = 7) occurs, because the critical chloride content is in the order of a few hundreds of mg·L^{-1} [68]. In this condition, the DOE result seems to overestimate the pitting corrosion resistance. A possible reason for this difference is the different surface area and finishing or the presence of more severe crevices in real applications.

The DOE approach applied to 304L stainless steel can be extended to other materials, provided that the environment is able to promote pitting corrosion.

5.   Conclusions

In this research, design of experiment (DOE) is used as a method to evaluate the effects of environmental parameters (chloride, temperature, and pH) on the pitting corrosion of AISI 304L stainless steels.

Passivity breakdown potential is strongly influenced by pH, temperature and chloride concentration, as expected. Among all these parameters, the temperature has the most significant effect, especially in the range 20°C to 40°C.

The equation obtained by DOE model has been simplified in a linear trend between E_{bd} and log [Cl^-]. The slope of the line depends on the pH while the intercept depends on pH and temperature.

The results of this research have been compared with the susceptibility to pitting and crevice corrosion of AISI 304 L in some practical conditions, like seawater, brackish water, fresh water and acidic conditions with a fair agreement in most cases.

Data Availability

The data cannot be shared at this time because:

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

6.   References

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Figure 1 - Schematic representation of CCD design with the position of different points (adapted from [53])

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Table 1

Grade	Cr	Ni	Mn	Si	Cu	Mo	N	P	C	S	Fe
UNS S30403	17.27	8.42	1.46	0.37	0.36	0.08	0.06	0.033	0.018	0.003	Balance

Table 2

pH	Chloride (mg.L^{-1})	Pre-conditioning time (h)
pH ≤ 4	Without considering chloride concentration	1
4 < pH ≤ 7	> 1000	1
	≤ 1000	24
7 < pH ≤ 9	≥ 10,000	1
	< 10,000	24

Table 3

	Levels				
	-α	**Min**	**Center**	**Max**	**α**
Factors (k)	**-1.633**	**-1**	**0**	**1**	**1.633**
log chloride (mg.L^{-1})	1.367	2	3	4	4.633
Temperature (°C)	10.5	20	35	50	59.5
pH	2.7	4	6	8	9.3

Table 4

Condition	N° of tests	Block	log (Cl$^-_{ppm}$)	T (°C)	pH	E_{bd} vs. Ag/AgCl/KCl$_{sat.}$ (V)	E_{rep} vs. Ag/AgCl/KCl$_{sat.}$ (V)
1	2	1	2	20	4	0.233, 0.266	-0.062, ND
2	2	1	2	20	8	0.468, 0.510	-0.084, -0.053
3	2	1	2	50	4	0.070, 0.060	-0.148, -0.106
4	2	1	2	50	8	0.239, 0.285	-0.208, -0.166
5	8	1	3	35	6	0.050, 0.056, 0.123, 0.112, 0.088, 0.142, 0.057, 0.075	-0.167, -0.074, -0.142, -0.132, -0.166, -0.075, -0.148, -0.148
6	2	1	4	20	4	0.240, 0.240	-0.178, -0.157
7	2	1	4	20	8	0.235, 0.289	-0.145, -0.132
8	2	1	4	50	4	-0.063, -0.076	-0.15, -0.139
9	2	1	4	50	8	0.023, 0.049	-0.225, 0.16
10	4	2	3	35	6	0.096, 0.075, 0.034, 0.062	-0.149, -0.148, -0.154, -0.162
11	2	2	3	35	2.7	Active corrosion	-
12	2	2	3	35	9	0.306, 0.298	-0.178, -0.2
13	2	2	3	60	6	-0.012, 0.011	-0.121, -0.177
14	2	2	4.633	35	6	-0.025, -0.035	-0.185, ND
15	2	2	1.367	35	6	0.282, 0.190	-0.105, -0,128
16	2	2	3	10	6	0.382, 0.386	-0.097, ND

ND = Not defined

Table 5

T= 10°C		T= 20°C		T= 35°C		T= 40°C		T= 50°C		T= 60°C	
E_{bd}	E_{corr}	E_{bd}	E_{corr}	E_{bd}	E_{corr}	E_{bd}	E_{corr}	E_{bd}	E_{corr}	E_{bd}	E_{corr}
0,382	-0,034	0,218	-0,036	0,050	-0,081	0,039	-0,060	-0,022	-0,074	0,011	-0,044
0,386	-0,070	0,29	-0,049	0,123	-0,058	0,040	-0,055	-0,014	-0,078	-0,012	-0,083
0,394	-0,050	0,262	-0,116	0,112	-0,074	0,028	-0,074	0,003	-0,082	-0,012	-0,050
0,395	-0,050	0,296	-0,026	0,089	-0,080	0,045	-0,050	0,027	-0,076	0,016	-0,070
0,380	-0,080	0,255	-0,061	0,142	-0,066	0,048	-0,064	-0,003	-0,084	0,018	-0,050
		0,291	-0,052	0,057	-0,063						
		0,276	-0,088	0,075	-0,060						
		0,224	-0,099	0,096	-0,063						
		0,237	-0,06	0,075	-0,060						
		0,317	-0,047	0,062	-0,076						

Table 6

pH= 4		pH= 8		pH= 10	
E_{bd}	E_{corr}	E_{bd}	E_{corr}	E_{bd}	E_{corr}
0,283	0,002	0,320	-0,067	0,410	-0,140
0,290	-0,009	0,255	-0,062	0,411	-0,135
0,273	0,012	0,250	-0,074	0,435	-0,170
0,145	0,011	0,220	-0,056	0,394	-0,140
0,200	-0,022	0,224	-0,045	0,437	-0,185

Table 7

Conditions	Cl^- $(mg \cdot L^{-1})$	T (°C)	pH	E_{bd} (V vs. Ag/AgCl/KCl$_{sat.}$)	Corrosion ($E_{corr} > E_{bd}$)
Fresh water ($-0.14 \leq E_{corr} \leq 0.14$ V vs. Ag/AgCl/KCl$_{sat}$)	50	20	7	0.43	No
	250	60	7	0.05	Yes
Brackish water ($-0.14 \leq E_{corr} \leq 0.14$ V vs. Ag/AgCl/KCl$_{sat}$)	1000	20	7	0.30	No
	5000	20	7	0.24	No
	1000	50	7	0.07	Yes
	5000	40	7	0.08	Yes
Aerated acidic solution ($-0.14 \leq E_{corr} \leq 0.14$ V vs. Ag/AgCl/KCl$_{sat}$)	10,000	20	4	0.14	Yes
Sea water ($-0.2 \leq E_{corr} \leq 0.2$ V vs. Ag/AgCl/KCl$_{sat}$)	20,000	20	7	0.18	Yes
Sea water (Bacteria) ($E_{corr} = +0.3$ V vs. Ag/AgCl/KCl$_{sat}$)	20,000	20	8	0.20	Yes