



Article

Optimizing Potentiodynamic Pitting Corrosion Tests for Austenitic Stainless Steel: The Critical Role of Water Flow

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Abstract

Pitting corrosion is particularly dangerous due to its localised nature, which can render materials unusable and cause catastrophic failures. It is important to characterise the material in regard to pitting corrosion resistance in order to improve material selection according to the conditions of the exposed environment. Electrochemical tests were carried out to assess pitting corrosion in austenitic stainless steel EN 1.4301. This study identifies the optimal experimental conditions to ensure reliability and reproducibility in electrochemical tests. The results demonstrate the influence of these parameters in evaluating the resistance of stainless steels to pitting corrosion. To ensure the reproducibility of the breakdown potential (E_b), deaeration was standardised using an N_2 flow rate of 0.6–0.8 L/min for 20 min. Furthermore, mechanical agitation at 280 rpm was established as a necessary condition to homogenise the electrolyte and effectively renew the metal/solution interface. Finally, the water flow rate was set at a critical value of 7 mL/h, statistically identified as the most decisive parameter ($p < 0.05$). This optimisation mitigates crevice corrosion, ensuring that damage nucleation occurs exclusively via a pitting mechanism.

Keywords: pitting corrosion; austenitic; parameters; electrochemical; stainless steel; potentiodynamic

1. Introduction

Corrosion is a critical factor that affects both the economy and the sustainability of industrial processes. NACE International (an acronym for the National Association of Corrosion Engineers) estimates a global cost of 2.5×10^{12} in 2013 associated with the phenomenon of corrosion, which can be reduced by between 15 and 35% with corrosion control measures [1].

Pitting corrosion is a type of localised corrosion in which the passive layer of the material is broken, and the attack spreads into the metal, which could make stainless steel useless and, in the worst-case scenario, could lead to economic, material, and human losses [2]. Therefore, it is essential to conduct research to study and analyse in detail the behaviour of stainless steels in relation to corrosion, to understand how the material responds to specific conditions, and to find solutions to avoid undesirable consequences [3].

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The purpose of this research is to improve electrochemical test conditions in order to obtain more repeatable and reproducible results. It is important to study the factors that can influence the behaviour of stainless steels in potentiodynamic tests, as this is the only way to characterise them correctly in terms of their resistance to pitting corrosion [4,5].

The evaluation of corrosion using electrochemical tests has been studied for years. In 1988, Qvarfort published an article on a cell design that improved the reliability of the data obtained. It took into account the contribution of water to avoid the possibility of crevice corrosion and ensure pitting corrosion in electrochemical tests. It promotes ion recirculation and prevents stagnant areas that are prone to corrosion attack [6–8]. For years, most researchers have agreed that when the current density increases sharply and reaches $100 \mu\text{A}/\text{cm}^2$, it is due to the appearance of the first stable pit in the material. This is generally accepted as standard practice in such electrochemical tests [9,10]. Macdonald (1992) proposes the point-defect model, arguing that the initiation of a pit is due to the accumulation of vacancies, but its activation depends on the distribution of active sites [11]. However, the model developed by Shibata in 1996 demonstrated that pitting corrosion cannot be predicted using a single critical value, but rather on the basis of the survival probability of metastable nucleations [12]. According to this approach, the onset of degradation depends on whether these transient breaches in the passive layer manage to reach a critical phase before being inhibited by the system's intrinsic repassivation capacity. This model highlighted the stochastic nature of pitting corrosion. The exact mechanisms that trigger the initiation of pitting corrosion remain an active subject of investigation.

In 2000, Lena Wegrelius published interlaboratory tests to determine the critical pitting temperature in stainless steels [13]. By 2018, Sun, Wang, Jiang and Li conducted tests on austenitic steels using potentiostatic and potentiodynamic techniques in sodium chloride solutions [14,15], while a nitrogen or argon purging procedure was established as a standard requirement to ensure open-circuit stability [16–18]. Zhang et al. (2019) reviewed the multiple factors that compromise the passive layer's integrity, subsequently leading to pit formation [19]. In that same year, Dastgerdi et al. (2019) [4] advanced the field by utilizing a systematic experimental design to quantify the simultaneous influence of temperature, pH, and chloride concentration on the pitting thresholds of AISI 304L steel. Stirring was recognised as necessary to prevent stagnant areas and ensure the homogeneity of the test solution [20], and Bard & Faulkner (2022) indicated the need to purge the solution with nitrogen before the test to remove oxygen and prevent cathodic oxygen reduction reactions from interfering with anodic measurements [21]. Additionally, Sridhar et al. (2023) recently emphasized that the significant scatter often found in critical temperature data is intimately linked to variations in these very test parameters and the specific chemistry of the electrolyte [5].

However, a critical review of current literature and international standards reveals a significant research gap. While standards such as ASTM G150 [9] and ASTM G61 [16] provide robust frameworks for potentiodynamic polarisation and critical pitting temperature (CPT) measurements, they offer only generalised ranges for auxiliary parameters. For instance, deaeration procedures and stirring rates are established as requirements to ensure open-circuit stability and electrolyte homogeneity; yet, the optimal thresholds to minimise data scattering are rarely defined through systematic statistical analysis. Furthermore, although the “water flush” is recognised as critical for suppressing crevice attack, the recommended flow rates remain broad (typically 1–12 mL/h), and their specific quantitative impact on the breakdown potential is frequently overlooked or taken for granted as a common assumption.

As a model material, AISI 304, according to ASTM A240/240M [22] (EN 1.4301, according to EN 10088 [23]) has long served as the benchmark for evaluating pitting resistance in austenitic stainless steels. Extensive research has characterized its sensitivity to

external and internal variables. For instance, Ezuber et al. (2018) [24] demonstrated that surface roughness and thermal sensitization significantly lower its pitting potential in 3.5% NaCl, while early studies by Leckie and Uhlig (1966) [25] identified its critical temperature thresholds. Furthermore, the classic work of Shibata (1996) [12] utilized Type 304 to frame the stochastic nature of pit initiation, reporting a wide normal distribution of values despite standardized procedures. This study builds upon this extensive material history by shifting the focus to the auxiliary test parameters that underpin these established measurements.

The value of this study lies in addressing this gap by shifting the focus from material characterisation to methodological optimisation. Using AISI 304 austenitic stainless steel as a model material, we present a comprehensive statistical evaluation of four decisive variables: nitrogen flow rate, deaeration time, stirring rate, and water flow rate. By identifying the specific levels required to maximise repeatability and reproducibility, this work transforms empirical laboratory “best practices” into documented, validated technical knowledge, ensuring that measured potentials reflect the material’s intrinsic resistance rather than experimental artefacts.

2. Materials and Methods

Electrochemical tests were performed to evaluate pitting corrosion in EN 1.4301 (type AISI 304) austenitic stainless steel — cold rolled, annealed and pickled —, using square flat samples measuring $40 \times 40 \text{ mm}^2$. Table 1 shows the chemical composition of EN 1.4301 (type AISI 304) steel from Acerinox Europa S.A.U., in accordance with [23]. The chemical composition of the samples was analyzed by X-ray fluorescence and spark optical emission spectrometry (S-OES. Specifically, a Panalytical Axios Fast X-ray fluorescence spectrometer Malvern Panalytical, Malvern, UK, www.malvernpanalytical.com), an OBLFQsn750 (OBLF Spectrometry, Witten, Germany, www.oblf.de), and a Leco CS 600 and TC 600 analyzers (LECO Corporation, St. Joseph, MI, USA, www.leco.com) were used.

Table 1. Chemical composition of EN 1.4301 stainless steel.

Elements (wt.%)								
C	Si	Mn	S	Cr	Ni	P	N	Fe
0.036	0.32	1.46	0.001	18.04	8.2	0.026	0.053	Balance

Electrochemical experiments were performed using a PARSTAT 2273 potentiostat (Princeton Applied Research, AMETEK, Oak Ridge, TN, USA). Using a potentiodynamic electrochemical test, polarisation curves were obtained to evaluate the pitting corrosion resistance. The procedure consisted of a potentiodynamic test, in which an electric variable was controlled and the response of a related variable was registered. In this case, first, the potential was modified by a positive scan with a potentiostat, and the system responded with its conjugate variable, the current, which was measured [16]. According to general convention, the current density is plotted on the abscissa and the potential on the ordinate. Semilogarithmic plots are employed; they are better suited for this type of graphical representation [26]. An indication of the susceptibility to pitting corrosion was given by a sudden increase in the anodic current density, i . The breakdown potential (E_b) was defined as the potential at which a current density increase and the current density of $100 \mu\text{A}/\text{cm}^2$ (i.e., $1 \times 10^{-4} \text{ A}/\text{cm}^2$) was reached. When the corrosion phenomenon that occurs is pitting corrosion, the related potential is considered as the pitting potential [9].

Potentiodynamic tests were conducted in an aqueous sodium chloride solution with a concentration of 35 g/L at a constant temperature of 30 °C. The chloride ions compromise

the stability of the passive layer, causing its localised breakage [27,28]. Before starting the test, dissolved oxygen is removed by purging the solution with a controlled flow of nitrogen gas for a defined period [18]. The nitrogen flow is subsequently maintained throughout the experiment. The working conditions are shown in Table 2.

Table 2. Working conditions used in potentiodynamic tests to evaluate pitting corrosion resistance.

Conditioning Potential	−1.3 V vs. SCE
Conditioning time	180 s
Initial potential	−1.1 V vs. SCE
Final potential	1.6 V vs. SCE
Sweep rate	0.17 mV/s
Test area	1 cm ²

The tests were performed in a flat electrochemical cell designed by Acerinox (Figure 1a) [29], which operates on the same principles as the Avesta cell in ASTM G150. In line with the latter, the corrosion cell employed follows a design based on the flushed-port cell published by R. Qvarfort in 1988 [6]. This configuration incorporates a method for positioning the sample on the exterior of the cell while preventing crevice corrosion by means of a double O-ring system, through which a minor flow of distilled water is continuously circulated. In this case, the sample holder is integrated on the bottom of the cell, as shown in Figure 1b.

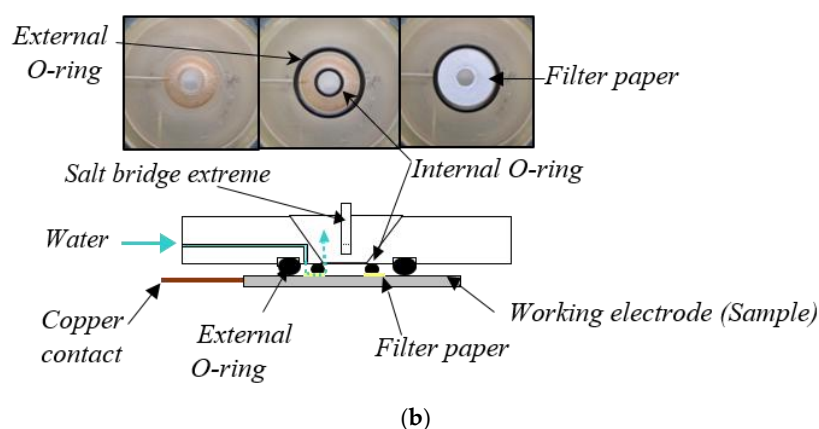
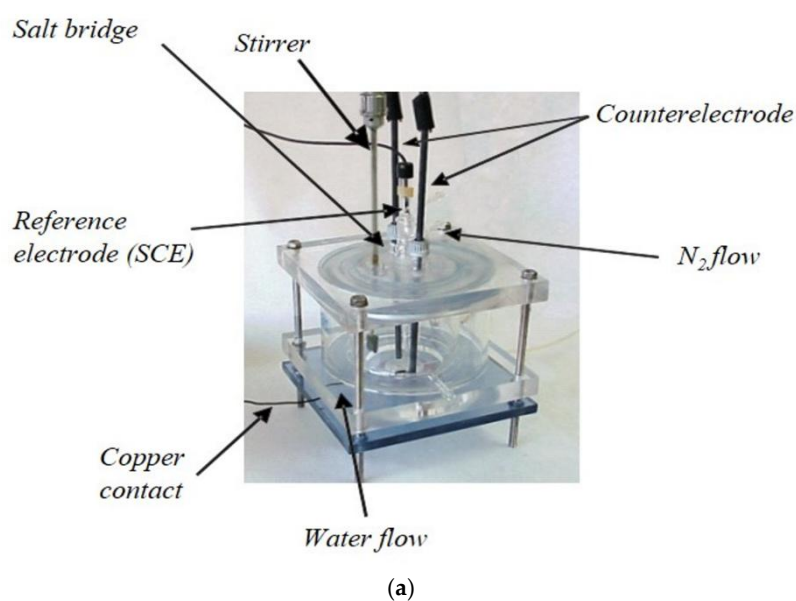


Figure 1. Experimental setup used for electrochemical tests: (a) general view of the flat electrochemical cell assembly; (b) detailed schematic cross-section of the specimen holder and the sealing system highlighting the dual O-ring (internal and external) configuration.

This cell consists of a double-walled, circular glass chamber to facilitate heating via an external recirculating heat bath, as well as several inlets and connections for temperature measurement, reference and auxiliary electrodes, and gas purging. The counter electrode consisted of high-density graphite rods, and a saturated calomel electrode (SCE) was used as the reference electrode.

Appropriate specimen preparation is essential for ensuring a uniform surface condition and enhancing the reproducibility of the results. For electrical connection to the potentiostat, a copper wire was welded to the specimen, which was thereby used as the working electrode. The specimens were subsequently subjected to sequential mechanical polishing to achieve a fine surface finish using silicon carbide abrasive papers with grit sizes ranging from 120 to 600 [30,31].

This article investigated four selected parameters to assess their influence on electrochemical pitting corrosion tests on stainless steels: nitrogen flow rate, stirring speed, nitrogen deaeration time and water flow rate. Nitrogen purging (flow rate and duration) is essential to ensure complete deoxygenation of the electrolyte, thereby preventing oxygen reduction from interfering with the measurement of the pitting potential. Furthermore, stirring ensures the homogeneity of the solution, and the water supply ensures that only pitting corrosion occurs. While international standards frequently reference these parameters, they often lack precise operational values, particularly regarding the first three [9,16,30]. Consequently, this study underscores the importance of fixing these variables to establish constant experimental conditions, which are essential for ensuring reproducible and comparable results, as they significantly impact the local chemistry at the metal-electrolyte interface. Regarding the water flow rate, the values specified in the ASTM G150 standard proved insufficient in this study to prevent crevice corrosion. Therefore, it was deemed necessary to establish a more optimal flow rate that enables the accurate evaluation of pitting corrosion resistance via potentiodynamic tests, while effectively suppressing the occurrence of crevice corrosion. For each parameter, five levels were applied and five replicates were carried out for each level, as shown in Table 3.

Table 3. The selected parameters and their corresponding test levels employed to investigate their effect on pitting corrosion.

Nitrogen Flow Rate (rpm)	Stirring Rate (L/min)	Nitrogen Deaeration Time (min)	Water Flow Rate (mL/h)
0	0	0	0
0.4	280	10	4
0.6	470	20	5
0.8	660	30	7
1	1050	40	12

The experimental design followed a one-factor-at-a-time (OFAT) approach to evaluate the individual influence of each variable. A baseline condition (representing standard laboratory protocols) was established as a reference, as shown in Table 4. During each test series, the parameters were kept constant at their baseline values while only the variable under study was systematically modified.

Table 4. Baseline conditions for the experimental series.

Parameter	Baseline Value
Nitrogen flow rate (N_2)	0.8 L/min
Deaeration time	20 min
Water flow rate	7 mL/h
Stirring rate	280 rpm

Once the tests are completed, the samples are observed under a digital optical microscope, (DSX1000, Evident/Olympus Corp., Tokyo, Japan) to verify that pitting corrosion has occurred. Data processing and statistical analysis were performed using MATLAB software (version R2023, The MathWorks Inc., Natick, MA, USA) along with the Statistics and Machine Learning Toolbox. Box plots were employed to visualise the statistical distribution of the breakdown potentials (E_b). The statistical significance of the variables was evaluated through ANOVA, considering a p -value of less than 0.05 as statistically significant [32,33].

3. Results and Discussion

3.1. General Polarisation Behaviour

Figure 2 illustrates the influence of the four selected variables on the polarisation behaviour. Specifically, the plots show the effect of (a) nitrogen flow rate, (b) stirring rate, (c) deaeration time, and (d) water flow rate. To facilitate visual comparison, each plot displays a single representative E-i curve, selected from the five replicates performed for each level.

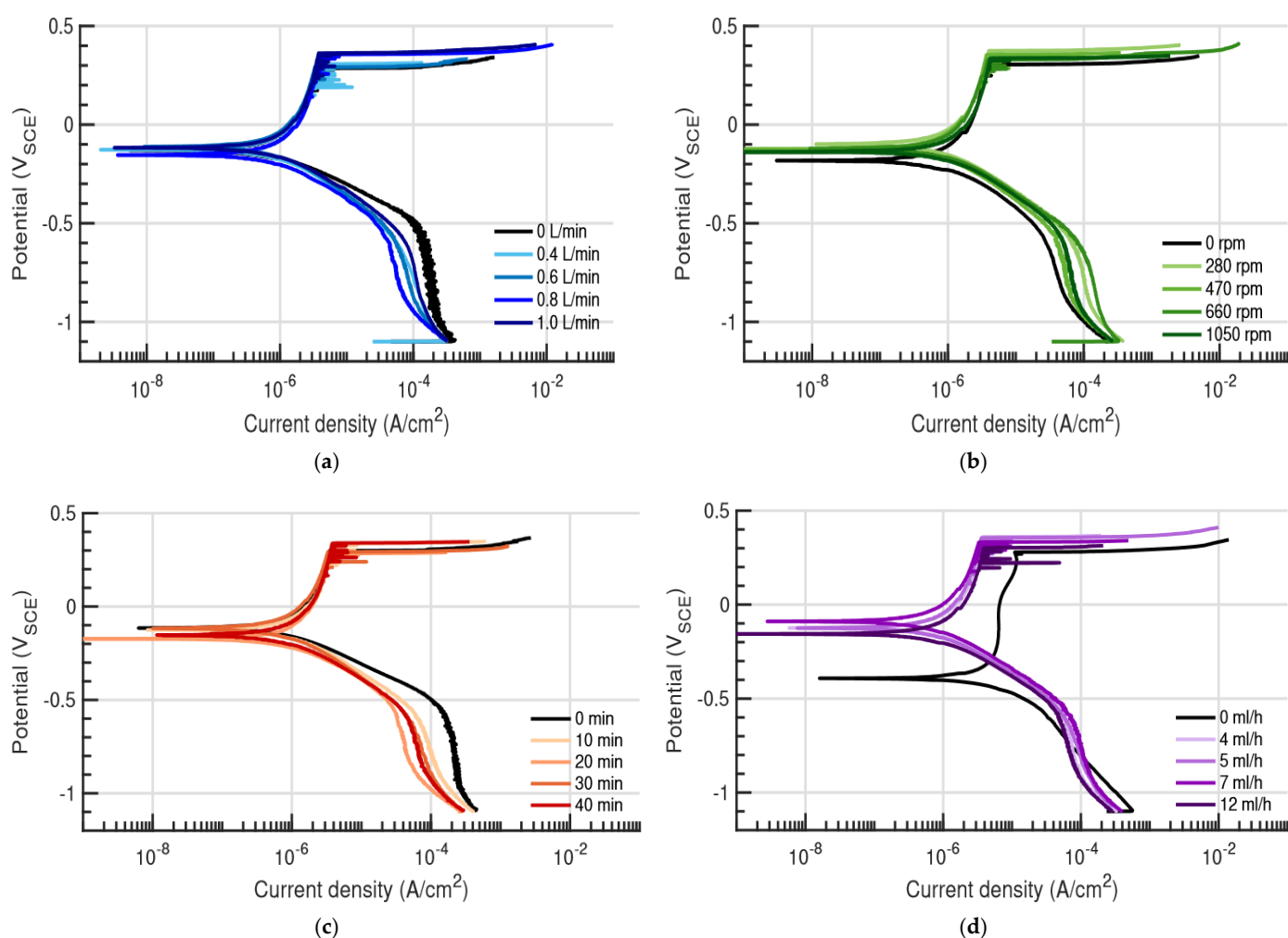


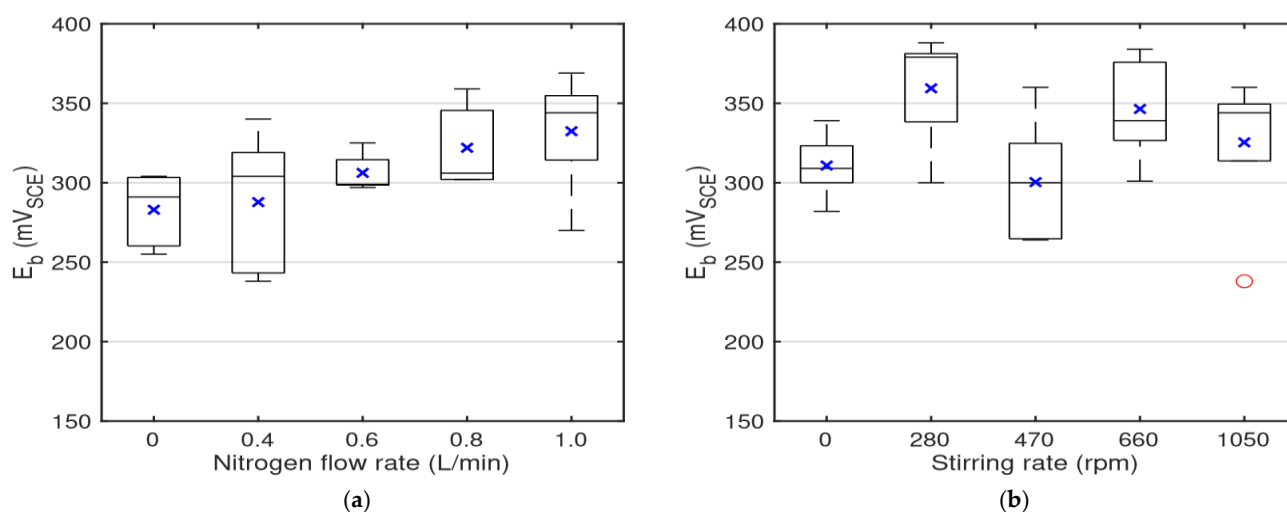
Figure 2. Polarisation curves obtained under different experimental conditions: (a) Nitrogen flow rate, (b) stirring rate, (c) deaeration time, and (d) water flow rate.

The graphical representation of the curves obtained confirms a localised corrosion mechanism, typical of materials with self-passivation capacity in chloride-containing media [7]. During the anodic potential scan, once the corrosion potential has been exceeded, the system presents a region of passive stability in which the current density remains at constant values. The breakdown of passivity occurs abruptly when the breakdown potential is reached, at which point the current density increases sharply due to the onset of stable localised corrosion [10].

The analysis of the polarisation curve morphology reveals several distinctive features that characterise the electrochemical process before proceeding to the statistical evaluation. First, the cathodic branch exhibits a clear dependence on the deaeration parameters; the evident shift of the curves toward lower current densities when nitrogen flow rate and purge time are used confirms the efficient removal of dissolved oxygen, which in turn restricts the cathodic reduction reaction [17]. There exists a pronounced variation in the equilibrium potential (E_{corr}) regarding the water supply (Figure 2d). In tests conducted without water flow, the equilibrium potential dropped to approximately -0.4 V, whereas normal values under baseline conditions ranged between -0.1 V and -0.2 V. This shift suggests that the absence of water promotes a more aggressive environment typical of crevice corrosion, where the equilibrium potential of the cathodic reaction decreases, making the corrosion process thermodynamically favourable at a lower overall potential [8,34,35].

3.2. Statistical Analysis of Breakdown Potentials

The quantitative evaluation of the experimental variables was performed through the analysis of the breakdown potentials (E_b) extracted from the polarisation curves. The statistical distribution of these values across the different levels of each parameter is summarised in the box-and-whisker plots in Figure 3. The corresponding numerical descriptors—including mean values, standard deviations, and the analysis of variance (ANOVA) significance (p -values) are detailed in Table 5 [32,33].



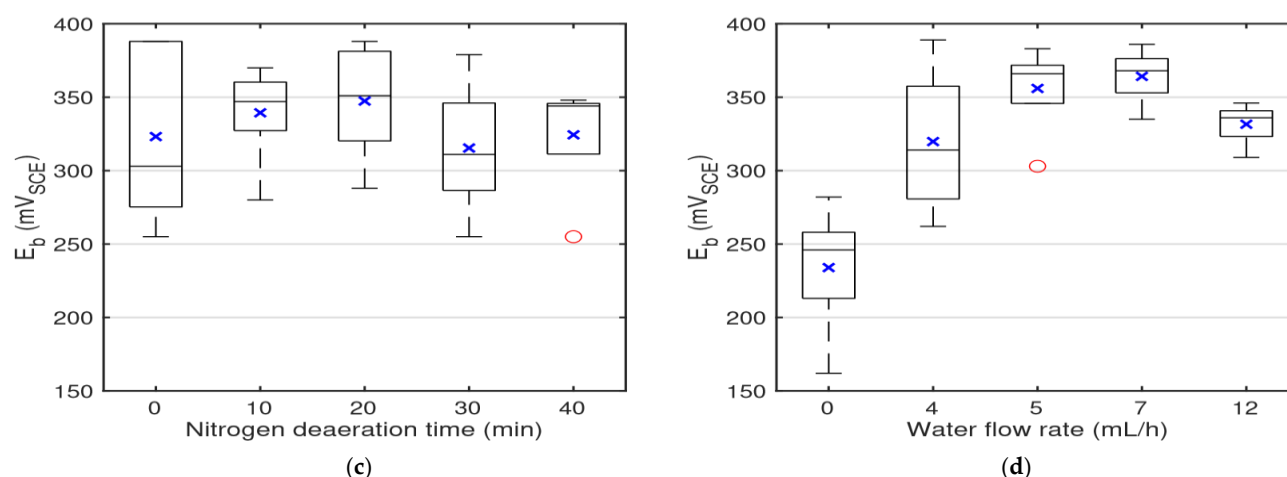


Figure 3. Variation in breakdown potential for EN 1.4301 steel in relation to the different variables studied: (a) nitrogen flow rate, (b) stirring rate, (c) deaeration time, and (d) water flow rate. These diagrams allow for a clear identification of data variability, representing the mean (cross), the median (horizontal line), the interquartile range (IQR) (box) and the presence of potential outliers (identified with red circles) across the different experimental conditions.

Table 5. Statistical analysis of the obtained data.

Variable	Level	Mean Value (Eb)	Std. Dev.	<i>p</i> -Value
Nitrogen flow rate	0.00	283.00	23.07	0.08
	0.40	287.80	44.39	
	0.60	306.20	11.88	
	0.80	322.00	26.39	
	1.00	332.40	37.71	
Stirring rate	0	310.80	20.63	0.10
	280	359.40	36.00	
	470	300.40	39.65	
	660	346.40	33.04	
	1050	325.40	49.47	
Deaeration time	0	323.20	61.55	0.08
	10	268.80	34.85	
	20	339.40	34.80	
	30	347.40	40.18	
	40	315.40	45.92	
Water flow rate	0	195.00	103.47	0.00006
	4	267.17	136.44	
	5	297.50	145.92	
	7	304.66	146.82	
	12	278.33	131.09	

A global assessment of the data revealed that the water flow rate was the only variable exhibiting a statistically significant difference at a 95% confidence level ($p < 0.05$) [32]. In contrast, parameters such as nitrogen flow rate and deaeration time yielded p -values of approximately 0.08 [36,37]. This outcome is largely attributed to the inherent stochastic nature of pitting corrosion and the associated standard deviations, which were particularly high in certain series. Despite this, the results clearly demonstrate that the systematic standardization of these parameters is critical to ensuring the reliability and repeatability of the electrochemical evaluation [33].

3.2.1. Effects of Oxygen Removal: Nitrogen Flow and Deaeration Time

The influence of deaeration parameters on the breakdown potential is illustrated in Figure 3a,c. Regarding the nitrogen flow rate, a progressive increase in the mean values of E_b is observed as the flow rate rises from 0.4 L/min to 0.8 L/min. This trend aligns with the qualitative observations of the polarisation curves, where higher flow rates effectively displaced dissolved oxygen [17,18,38], thereby increasing the nobility of the material's response. However, the highest flow rate (1.0 L/min) did not yield a proportional increase in E_b , suggesting a saturation effect in the deaeration efficiency under the current electrochemical cell geometry. The intermediate values (0.6 L/min and 0.8 L/min) provided the most consistent results with reduced standard deviations.

Similarly, the deaeration time (Figure 3c) proved to be a critical factor for reproducibility. The tests conducted without prior deaeration (0 min) exhibited the highest data scattering and the lowest average breakdown potentials. This behaviour is expected, as the presence of fluctuating amounts of dissolved oxygen interferes with the stability of the passive film and the kinetics of the incipient pits [10,17].

As the deaeration time increased from 10 to 20 min, the E_b values stabilised and the dispersion was significantly reduced, whilst the mean and median increased. For times of 30–40 min, the potential decreases slightly; although the variance decreases, the outlier and the slight decrease in the mean suggest that excessive times do not provide additional benefits and could lead to experimental errors. These results justify the selection of 20 min as the optimal reference condition because it maximises electrochemical stability, ensuring that the cathodic reaction is sufficiently limited to allow a reliable assessment of the material's inherent resistance to pitting corrosion.

3.2.2. Solution Homogeneity: Stirring Rate

The effect of the stirring rate on the breakdown potential is illustrated in Figure 3b. Interestingly, the tests performed without stirring (0 rpm) exhibited the lowest statistical dispersion. However, as previously discussed, this experimental condition should be avoided in standardised electrochemical testing for stainless steels. The absence of forced convection leads to the formation of localised concentration gradients and stagnant areas, particularly at the interface between the sample and the O-ring seal. These conditions can artificially influence the pitting process by allowing the accumulation of aggressive species.

As the stirring rate increases to 280 rpm, a slight increase in the median E_b is observed, suggesting that moderate electrolyte renewal contributes to a more uniform environment at the metal-solution interface, effectively preventing the stabilisation of stagnant corrosive micro-environments [20]. Nevertheless, at the highest stirring rate (1050 rpm), the emergence of several outliers at lower potential values indicates that excessive turbulence may introduce instabilities. Consequently, 280 rpm is confirmed as the optimal baseline condition, as it provides the necessary solution homogeneity without compromising the stability of the electrochemical measurement.

3.2.3. Critical Factor: Water Flow Rate

The water flow rate (flush) was identified as the most critical variable in this study, being the only parameter with a statistically significant effect on the breakdown potential ($p < 0.05$) according to the ANOVA results (Table 5) [33,39]. As illustrated in Figure 3d, the mean values of E_b show a significant upward trend as the flow rate increases from 0 mL/h to 7 mL/h. This observation is directly linked to the effective prevention of crevice corrosion at the O-ring/sample interface [34,35]. In the absence of an adequate water supply, the confinement and lack of electrolyte renewal promote a highly aggressive local

environment, resulting in low potentials. This transition is clearly evidenced in the micrographs shown in Figure 4, where a shift from localised attack at the seal (crevice) to isolated pits in the central area is observed as the water flow is introduced [6].

Interestingly, the average breakdown potential reached its maximum at 7 mL/h, followed by a surprising decrease when the flow was further increased to 12 mL/h. This non-monotonic behaviour suggests that excessive flow rates might introduce localised turbulence or interfere with the stability of the incipient salt films necessary for pit repassivation [40]. Although the potential flow rates of 5 mL/h showed the lowest standard deviation, surface analysis revealed an interstitial condition, rendering it unsuitable for assessing pitting corrosion resistance. Therefore, 7 mL/h is established as the optimal reference flow rate, as it effectively suppresses crevice corrosion and ensures maximum experimental reproducibility and passive plateau stability.

The critical role of the water flow rate in shifting the corrosion mechanism is further supported by the surface morphologies presented in Figure 4. In the absence of a water supply (Figure 4a), the specimen suffers a severe, extensive, and continuous attack predominantly concentrated in the perimeter of the exposed area, precisely where the O-ring makes contact with the stainless-steel surface. This morphology is characteristic of crevice corrosion, where the stagnant electrolyte and the lack of oxygen renewal within the shielded gap trigger an early breakdown of the passive film. Notably, even when a water purge is introduced at flow rates of 4 mL/h (Figure 4b) and 5 mL/h (Figure 4c), which correspond to the standard volumes recommended by ASTM G150, the specimens continue to exhibit distinct crevice corrosion damage [9]. This indicates that under these specific experimental conditions, the standard flow rates remain insufficient to fully displace the electrolyte from the slit-like contact zone. Under all these lower flow conditions (Figures 4a–c), the measured E_b values are not representative of the material's true pitting resistance, but rather of the cell's sealing limitations. A radical change in the corrosion pattern is observed as the water flow is increased to 7 mL/h (Figure 4d) and beyond (Figure 4e). At this critical threshold, the perimeter remains entirely undamaged, confirming that the continuous renewal and displacement of the electrolyte at the O-ring interface successfully suppresses the crevice mechanism. Instead, the damage appears exclusively as isolated, well-defined pits randomly distributed across the central area of the specimen. These features are the result of a true pitting mechanism, where the breakdown occurs solely at the most susceptible points of the passive film.

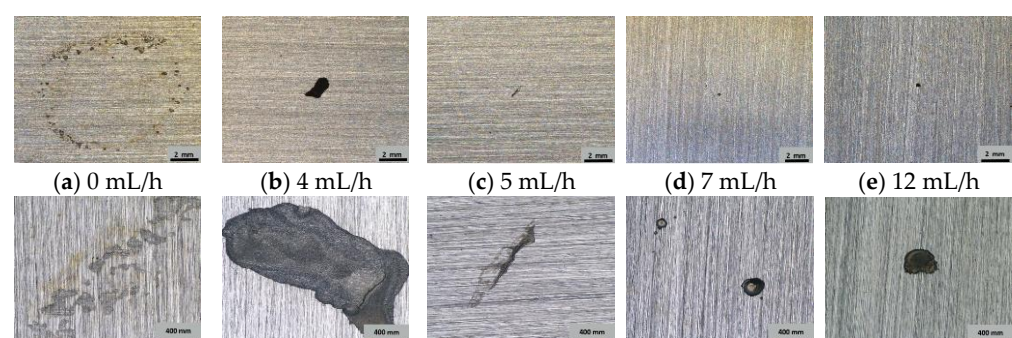


Figure 4. Micrographs of the surfaces obtained for samples tested at different water flow rates using digital optical microscopy. The (**upper**) images were captured at $\times 1$ magnification, whereas the (**lower**) images were acquired at $\times 10$ magnification.

It was determined that an intermediate nitrogen (N_2) flow rate within the range of 0.6–0.8 L/min, combined with a standardised deaeration period of 20 min, constitutes the optimal regime for improving the reproducibility of the breakdown potential (E_b). As the deaeration time increased to 20 min, the E_b values stabilised and the data scattering was

significantly minimised. This improvement is attributed to the removal of dissolved oxygen, which otherwise interferes with the stability of the passive film [38]. However, statistical analysis ($p \approx 0.08$) revealed that extending deaeration beyond this threshold yields no significant gain in efficiency, justifying the selection of 20 min as the optimal baseline for reliable pitting resistance assessment. Mechanical agitation was identified as a necessary condition to ensure electrolyte homogeneity and mitigate the formation of localised concentration gradients. An optimal agitation speed of 280 rpm facilitates adequate renewal of the medium at the metal/solution interface, maintaining a stable diffusion layer without reaching the turbulent flow regimes observed at higher speeds. Conversely, excessive agitation at 1050 rpm introduces significant hydrodynamic instability, leading to the appearance of statistical outliers.

Regarding the configuration of the electrochemical cell, it was identified that the water flow rate (flush) was the most decisive experimental parameter, as it was the only variable with a statistically significant impact on the breakage potential (E_b) at a confidence level of 95% ($p < 0.05$). Optimisation of this parameter is essential to ensure that damage nucleation occurs exclusively as a result of a pitting mechanism on the exposed surface, and not as a result of crevice corrosion. Specifically, a critical flow rate of 7 mL/h. Below this value, the electrolyte stagnating within the confined space promotes the localised accumulation of aggressive species and acidification of the medium, leading to premature breakdown of the passive film at artificially low potentials.

4. Conclusions

The study evaluates the influence of nitrogen flow, deaeration time, stirring rate, and water flow rate on the reproducibility of pitting corrosion tests for stainless steel.

- The study identifies water flow rate (flush) as the most decisive experimental parameter, being the only variable with a statistically significant impact ($p < 0.05$) on the breakdown potential (E_b). An optimised water flow of 7 mL/h is essential to effectively suppress crevice corrosion at the O-ring interface, ensuring that the measured potential reflects the material's intrinsic pitting resistance rather than an artificial crevice attack.
- Parameters such as nitrogen flow rate and deaeration time showed no statistically significant difference ($p \approx 0.08$) within the tested ranges. However, the observed trends suggest that a 20 min deaeration at 0.8 L/min provides a stable baseline for oxygen removal, which is necessary to minimise data scattering and restrict interfering cathodic reactions.
- While the stirring rate did not exhibit statistical significance ($p = 0.10$), a moderate speed of 280 rpm is recommended to ensure solution homogeneity. Avoiding stagnant conditions (0 rpm) or excessive turbulence (1050 rpm) is critical to preventing localised concentration gradients and statistical outliers.

In summary, while water flow is the primary driver of test reliability in this cell configuration, the systematic standardisation of stirring, deaeration, and nitrogen flow is recommended to reduce experimental variability and improve the reproducibility of the potentiodynamic evaluation.

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Acquisition, Writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Bowman, E.; Thompson, N.; Gl, D.; Moghissi, O.; Gould, M.; Payer, J. *International Measures of Prevention, Application, and Economics of Corrosion Technologies Study*; Technical Report; Nace International: Houston, TX, USA, 2016. Available online: <http://impact.nace.org/documents/Nace-International-Report.pdf> (accessed on 25 June 2026).
2. Caprio, G.D. *Los Aceros Inoxidables*; Inoxcenter, S.L., Ed.; Grupinox: Barcelona, Spain, 1999.
3. Liu, Y.; Hao, Y.; Hao, H.; Li, H.; Zhou, Y. Dynamic response of concrete beams considering spatial variability of pitting corrosion damages subjected to impact loads. *Eng. Struct.* **2025**, *332*, 120026. <https://doi.org/10.1016/j.engstruct.2025.120026>.
4. Dastgerdi, A.A.; Brenna, A.; Ormellese, M.; Pedferri, M.; Bolzoni, F. Experimental design to study the influence of temperature, pH, and chloride concentration on the pitting and crevice corrosion of UNS S30403 stainless steel. *Corros. Sci.* **2019**, *159*, 108160. <https://doi.org/10.1016/j.corsci.2019.108160>.
5. Sridhar, N.; Anderko, A.; Kung, S. Effects of solution and alloy composition on critical crevice temperature. *J. Electrochem. Soc.* **2023**, *170*, 031502. <https://doi.org/10.1149/1945-7111/ACC13D>.
6. Qvarfort, R. New electrochemical cell for pitting corrosion testing. *Corros. Sci.* **1988**, *28*, 135–140. [https://doi.org/10.1016/0010-938X\(88\)90090-X](https://doi.org/10.1016/0010-938X(88)90090-X).
7. Russell, J.; Covino, B.S.; Bullard, S. Applications of electrochemical methods for investigations of localized corrosion of nitrogenmolybdenum stainless steels. *Corrosion* **2001**, *57*, 360–368. <https://doi.org/10.5006/1.3290360>.
8. Thompson, N.; Syrett, B. Relationship between conventional pitting and protection potentials and a new, unique pitting potential. *Corrosion* **1992**, *48*, 649–659. <https://doi.org/10.5006/1.3315985>.
9. *ASTM G150-18*; Standard Test Method for Electrochemical Critical Pitting Temperature Testing of Stainless Steels and Related Alloys. ASTM International: West Conshohocken, PA, USA. <https://doi.org/10.1520/G0150-18>.
10. Galvele, J. Tafel's law in pitting corrosion and crevice corrosion susceptibility. *Corros. Sci.* **2005**, *47*, 3053–3067. <https://doi.org/10.1016/j.corsci.2005.05.043>.
11. Macdonald, D.D. The point defect model for the passive state. *J. Electrochem. Soc.* **1992**, *139*, 3434–3449. <https://doi.org/10.1149/1.2069096>.
12. Shibata, T. 1996 w r whitney award lecture: Statistical and stochastic approaches to localized corrosion. *Corrosion* **1996**, *52*, 813–830. <https://doi.org/10.5006/1.3292074>.
13. Wegrelius, L. Round robin comparison of critical pitting temperatures determined according to ASTM G 150-97. In *Proceedings of the International Congress Stainless Steel '99, Sardinia, 1999; Properties and Performance*; Associazione Italiana di Metallurgia: Milan, Italy; Volume 3, pp. 91–99.
14. Ebrahimi, N.; Momeni, M.; Kosari, A.; Zakeri, M.; Moayed, M. A comparative study of critical pitting temperature (cpt) of stainless steels by electrochemical impedance spectroscopy (eis), potentiodynamic and potentiostatic techniques. *Corros. Sci.* **2012**, *59*, 96–102. <https://doi.org/10.1016/j.corsci.2012.02.026>.
15. Sun, Y.T.; Wang, J.M.; Jiang, Y.M.; Li, J. A comparative study on potentiodynamic and potentiostatic critical pitting temperature of austenitic stainless steels. *Mater. Corros.* **2018**, *69*, 44–52. <https://doi.org/10.1002/maco.201709641>.
16. *ASTM G61-86*; Standard Test Method for Performing Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron, Nickel, or Cobalt Alloys. ASTM International: West Conshohocken, PA, USA, 2024.

17. Zeng, H.; Yang, Y.; Zeng, M.; Li, M. Effect of dissolved oxygen on electrochemical corrosion behavior of 2205 duplex stainless steel in hot concentrated seawater. *J. Mater. Sci. Technol.* **2021**, *66*, 177–185. <https://doi.org/10.1016/j.jmst.2020.06.030>.
18. Su, H.; Liang, Y.; Wang, Y.; Wang, B.; Tong, H.; Yuan, Y.; Wei, S. Effect of dissolved oxygen on pitting corrosion behavior of low-alloy steel under hydrostatic pressure. *Int. J. Electrochem. Sci.* **2019**, *14*, 4812–4827. <https://doi.org/10.20964/2019.05.49>.
19. Zhang, B.; Ma, X. A review—Pitting corrosion initiation investigated by tem. *J. Mater. Sci. Technol.* **2019**, *35*, 1455–1465. <https://doi.org/10.1016/j.jmst.2019.01.013>.
20. Llongueras, J.G.; Romero, R.D.; Martínez, R.G.; Flores, J.M. Efecto del flujo turbulento sobre la cinetica de corrosion de un acero API X52 en soluciones acuosas que contienen H₂S. *Afinidad* **2005**, *62*, 448–454.
21. Bard, A.; Faulkner, L.; White, H. *Electrochemical Methods: Fundamentals and Applications*; Wiley: Hoboken, NJ, USA, 2022. Available online: <https://books.google.es/books?id=eZ6HDAEACAAJ> (accessed on 25 June 2026).
22. ASTM A240/A240M-24; Standard Specification for Chromium and Chromium-Nickel Stainless Steel Plate, Sheet, and Strip for Pressure Vessels and for General Applications. ASTM International: West Conshohocken, PA, USA, 2024.
23. UNE-EN 10088-1:2024; Stainless Steels—Part 1: List of Stainless Steels. Technical Report. Asociación Española de Normalización: Madrid, Spain, 2024. Available online: <https://www.une.org/encuentra-tu-norma/busca-tu-norma/> (accessed on 25 June 2026).
24. Ezuber, H.; Alshater, A.; Nisar, S.O.; Gonsalvez, A.; Aslam, S. Effect of surface finish on the pitting corrosion behavior of sensitized AISI 304 austenitic stainless steel alloys in 3.5% NaCl solutions. *Surf. Eng. Appl. Electrochem.* **2018**, *54*, 73–80. <https://doi.org/10.3103/S1068375518010039>.
25. Leckie, H.P.; Uhlig, H.H. Environmental Factors Affecting the Critical Potential for Pitting in 18–8 Stainless Steel. *J. Electrochem. Soc.* **1966**, *113*, 1262–1267. <https://doi.org/10.1149/1.2423801>.
26. ASTM G3-14; Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing. Technical Report. ASTM International: West Conshohocken, PA, USA, 2019. Available online: <https://www.astm.org/g0003-14r19.html> (accessed on 25 June 2026).
27. Bernhardsson, S.; Mellström, R.; Brox, B. Limiting chloride contents and temperatures with regard to pitting of stainless steels. In *Proceedings of the CORROSION 1980*; AMPP: Houston, TX, USA, 1980; pp. 1–13. <https://doi.org/10.5006/C1980-80085>.
28. Pardo, A.; Otero, E.; Merino, M.C.; López, M.D.; Utrilla, M.V.; Moreno, F. Influence of pH and chloride concentration on the pitting and crevice corrosion behavior of high-alloy stainless steels. *Corrosion* **2000**, *56*, 411–418. <https://doi.org/10.5006/1.3280545>.
29. Merello, R.; Botana, F.; Botella, J.; Matres, M.; Marcos, M. Influence of chemical composition on the pitting corrosion resistance of non-standard low-Ni high-Mn–N duplex stainless steels. *Corros. Sci.* **2003**, *45*, 909–921. [https://doi.org/10.1016/S0010-938X\(02\)00154-3](https://doi.org/10.1016/S0010-938X(02)00154-3).
30. ASTM G5-14; Standard Reference Test Method for Making Potentiodynamic Anodic Polarization Measurements. Technical Report. ASTM International: West Conshohocken, PA, USA, 2021.
31. Tang, Y.; Dai, N.; Wu, J.; Jiang, Y.; Li, J. Effect of surface roughness on pitting corrosion of 2205 duplex stainless steel investigated by electrochemical noise measurements. *Materials* **2019**, *12*, 738. <https://doi.org/10.3390/ma12050738>.
32. ASTM G16-13; Standard Guide for Applying Statistics to Analysis of Corrosion Data. Technical Report. ASTM International: West Conshohocken, PA, USA, 2019.
33. ISO 5725-1:2023; Accuracy (Trueness and Precision) of Measurement Methods and Results—Part 2: Basic Method for the Determination of Repeatability and Reproducibility of a Standard Measurement Method. Asociación Española de Normalización: Madrid, Spain, 2023.
34. Pettersson, R.; Flyg, J. *Electrochemical Evaluation of Pitting and Crevice Corrosion Resistance of Stainless Steels in NaCl and NaBr*; Technical Report; Outokumpu: Stockholm, Sweden, 2004.
35. Pettersson, R. *Localised Corrosion of Stainless Steels—Limits and Mechanisms*; Technical Report; Outokumpu: Stockholm, Sweden, 2004.
36. Shibata, T.; Takeyama, T. Stochastic theory of pitting corrosion. *Corrosion* **1977**, *33*, 243–251. <https://doi.org/10.5006/0010-9312-33.7.243>.
37. Williams, D.; Westcott, C.; Fleischman, M. Stochastic-models of pitting corrosion of stainless-steels.1. modeling of the initiation and growth of pits at constant potential. *J. Electrochem. Soc.* **1985**, *132*, 1796–1804. <https://doi.org/10.1149/1.2114220>.
38. Coelho, L.B.; Torres, D.; Bernal, M.; Malet, L.; Makogon, A.; Kanoufi, F.; Shkirskiy, V.; Ustarroz, J. Oxygen effects on passive film evolution and metastable pitting in 316L stainless steel using SECCM. *Corros. Sci.* **2026**, *263*, 113708. <https://doi.org/10.1016/j.corsci.2026.113708>.

39. UNE-ISO 3534-3:2014; Statistics. Vocabulary and Symbols. Part 3: Design of Experiments. Asociación Española de Normalización: Madrid, Spain, 2014.
40. Frankel, G.S. Pitting corrosion of metals: A review of the critical factors. *J. Electrochem. Soc.* **1998**, *145*, 2186–2198. <https://doi.org/10.1149/1.1838615>. Correction in *J. Electrochem. Soc.* **1998**, *145*, 2970a.

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