DOI 10.36146/2026_02_18

Validation of pitting engineering diagrams for stainless steel used in water applications: some recent case studies

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Pitting engineering diagrams have been developed for various grades of stainless steel, informed by extensive long-term electrochemical testing, to assist in the selection of appropriate materials for a range of water applications. Key factors affecting pitting resistance of stainless steel include alloy composition, chloride ion concentration, temperature, and the oxidizing potential of the water, which can differ across contexts, such as sterile tap water versus slightly chlorinated environments.

This paper introduces pitting resistance engineering diagrams as stainless steel selection tools for water applications. The diagrams assist in the selection process of stainless steel and are further supported by relevant case studies that showcase its practical utility and applicability in real-world scenarios. The engineering diagrams provide a visual reference to define the pitting resistance of various stainless steel grades, while case studies demonstrate the performance of these materials in water-related environments. Overall, this selection tool aims to improve decision-making for engineers and designers involved in aquatic applications, ensuring the longevity and reliability of stainless steel components in challenging conditions.

KEYWORDS: PITTING ENGINEERING DIAGRAM; WATER APPLICATION; STAINLESS STEEL; PITTING CORROSION; CHLORIDE ION; TEMPERATURE; OXIDIZING POTENTIAL OF WATER SYSTEM;

INTRODUCTION

Localized corrosion (e.g., pitting and crevice corrosion) is one of the most critical degradation mechanisms in stainless steel, as it can initiate locally, grow rapidly, and ultimately compromise structural integrity. The resistance of stainless steel to localized corrosion depends upon both the material's characteristics, such as alloying elements and surface conditions, and the environment it is exposed to. In aquatic environments, factors such as chloride ion concentration, temperature, and solution pH are crucial factors to consider when determining the appropriate grade of stainless steel for a particular application [1-21]. However, the corrosivity is also significantly influenced by the oxidizing potential of the system. For instance, the open-circuit potential (OCP) in a sterile tap water system can vary widely, typically between 100 and 200 mV vs saturated calomel electrode (SCE), whereas in chlorinated water systems, the open-circuit potential increases with chlorine concentration, reaching approximately 700 mV vs SCE [2-11]. In natural water environments, the OCP may also rise, attributed

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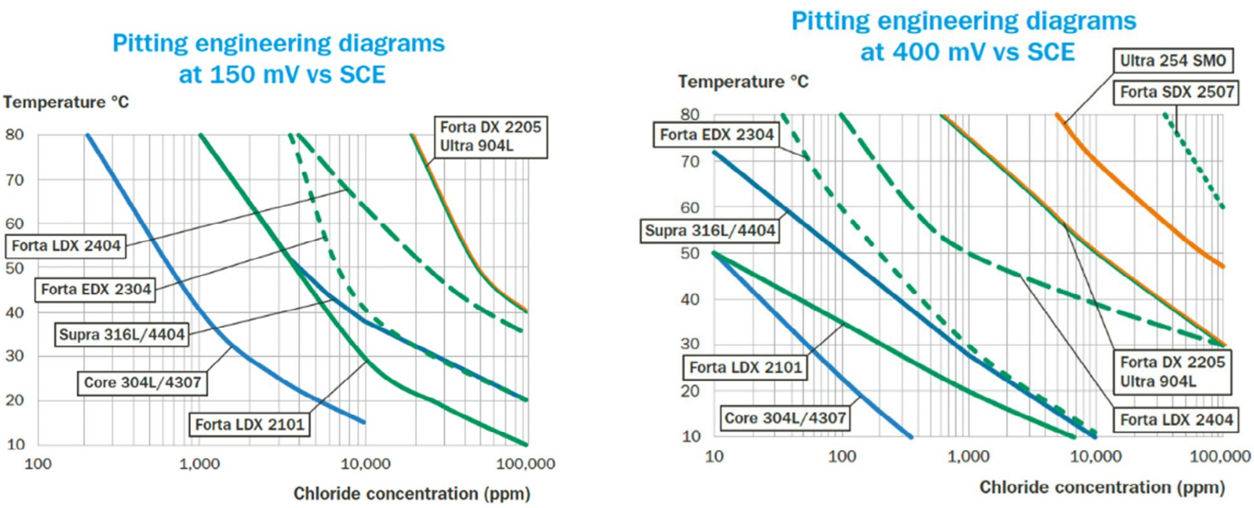
to more efficient cathodic reactions, and can reach levels around 400 mV vs SCE, depending on the water quality [2-5]. In this regard, pitting engineering diagrams serve as valuable tools that facilitate the selection of appropriate materials for specific environments and applications [1, 22-25].

A method for generating pitting engineering diagrams has been proposed based on electrochemical laboratory testing [12, 15, 19-25]. The various electrochemical approaches utilized in prior research have effectively established pitting diagrams that delineate the boundaries between pitting and non-pitting conditions with respect to chloride concentration, temperature, and the oxidizing potential of the system. Previous studies indicate that the electrochemical procedure can also be used for ranking different grades of stainless steel based on their resistance to localized corrosion. Long-term potentiostatic laboratory testing over 30 days yields the most conservative data, as the extended duration allows for a prolonged incubation period, making it the most representative method for simulating real-world applications. It was found that the incubation time for pitting initiation is a crucial factor to consider [12, 15]. Generally, lower temperatures correspond to longer incubation times before a pit can initiate and begin to grow. To thoroughly account for both the incubation time and the oxidative power of the system, the engineering diagrams in figure 2 were developed based on extensive laboratory testing conducted over a 30-day period at two distinct potentials: 150 mV and 400 mV vs SCE. These oxidising potentials correspond to sterile tap water and slightly chlorinated water (or water with some bacterial activity), respectively [1, 2, 4, 5, 12, 16, 17]. Further details regarding the testing methodology can be found in references [12, 16, 17].

Briefly, after determining the open-circuit potential (OCP) in the corresponding electrolyte, the potential is swept from EOCP to the target potential (E_{app}) of 150 mV or 400 mV vs SCE, while maintaining a constant electrolyte temperature throughout the test duration (i.e., 30 days). All other parameters, such as material geometry (30 x 60 mm), exposed area (40 cm^2), and surface condition (#320 mesh ground), are kept constant for better comparison. To establish such pitting engineering diagrams, the chloride concentration and temperature were varied to assess the boundary between pitting and non-pitting conditions. As shown in figure 1, an increase in potential enhances the aggressiveness of the water, leading to a downward shift in the pitting corrosion boundary on the diagrams. Figure 1 presents all the studied grades, where each diagram represents only one potential. Notably, the grades Ultra 254 SMO (EN 1.4547) and Forta SDX 2507 (EN 1.4410) are exclusively included in figure 1B, as they exhibit adequate pitting resistance in all tested conditions at the lower potential of 150 mV vs SCE (see figure 1A) [1, 12, 15, 17]. Table 1 presents details of the chemical composition and the pitting resistance equivalent number (PREN = %Cr + 3.3%Mo + 16%N).[1].

Tab.1 - Typical chemical compositions of the stainless steels investigated (wt%). The alloys are given in order of increasing PREN within each group.

Stainless steel	EN designation	Grade	Typical chemical composition, wt%						PREN
			C	Ni	Cr	Mo	N	Other	
Austenitic	1.4307	Core 4307	0.02	8.1	18.1	-	-	-	18
	1.4404	Supra 4404	0.02	10.1	17.2	2.1	-	-	24
	1.4539	Ultra 904L	0.01	24.2	19.8	4.3	-	1.4 Cu	34
	1.4547	Ultra 254 SMO	0.01	18.0	20.0	6.1	0.20	Cu	43
Duplex	1.4162	Forta LDX 2101	0.03	1.5	21.5	0.3	0.22	5Mn, Cu	26
	1.4362	Forta EDX 2304	0.02	4.3	23.8	0.5	0.18	Cu	28
	1.4662	Forta LDX 2404	0.02	3.6	24.0	1.6	0.27	3Mn, Cu	34
	1.4462	Forta DX 2205	0.02	5.7	22.0	3.1	0.17	-	35
	1.4410	Forta SDX 2507	0.02	7.0	25.0	4.0	0.27	-	43



(1A) 150 mV vs SCE (1B) 400 mV vs SCE

Fig.1 - Pitting engineering diagrams indicating the pitting resistance boundaries for various stainless steels in two different water systems. a) 150 mV vs SCE simulating sterile tap water, and b) 400 mV vs SCE representing slightly chlorinated water or water with some biological activity [1, 15].

Please be aware that these diagrams provide only approximate guidance regarding the resistance of the respective grades. The final selection will depend on several additional factors, many of which are discussed in this section. It is essential to recognise that actual service conditions may vary significantly from those used to create the diagram. For instance, the presence of crevices or weld oxides in the construction can impact the performance of stainless steel. Crevice corrosion typically initiates more readily than pitting corrosion, which is why the lines in the diagram are set to more conservative values in such cases [1, 4, 5, 22, 24]. Additionally, if present in the water, certain contaminants or substances may facilitate or inhibit the corrosion process, further influencing outcomes.

In the following sections, case studies are presented to demonstrate the consistency between the results of the pitting engineering diagram and the materials' performance in real applications or field tests.

CASE STUDIES IN DIFFERENT WATER APPLICATIONS

Case 1: Long-term immersion test for domestic water heater application

Stainless steels are widely used in domestic water heaters due to their natural corrosion resistance in potable water, eliminating the need for linings or cathodic protection. This study involved long-term corrosion tests conducted over a period of one year in water containing 250 ppm chlorides at a temperature of 75 °C. The materials evaluated included welded specimens of standard austenitic grades (Core 304L/4307 and Supra 316L/4404) as well as duplex grades (Forta LDX 2101, DX 2304, LDX 2404, and DX 2205). The focus of the assessment was specifically on pitting corrosion [26].

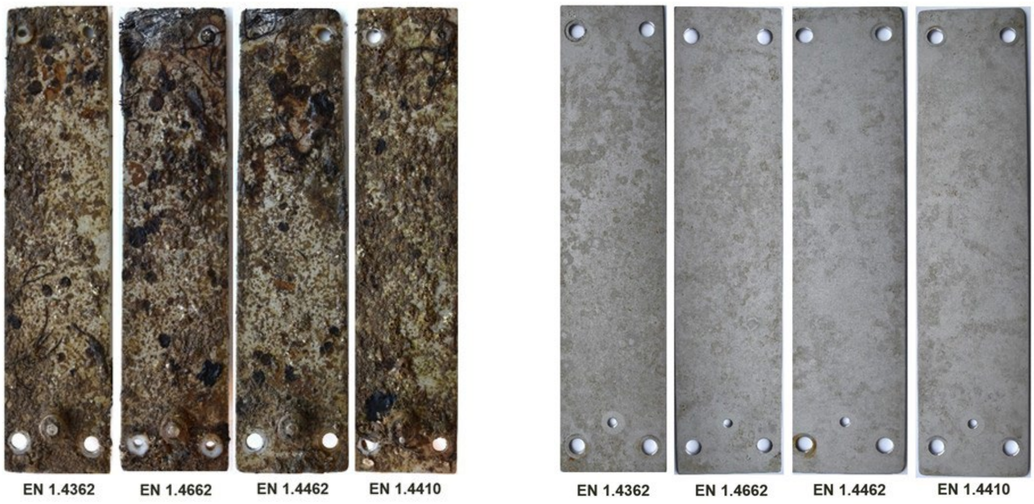
The long-term laboratory results were compared with pitting engineering diagrams and real-world experiences involving stainless steel in domestic water heaters. A summary of the observations for the various specimens involved in this study can be found in figure 3. After one year of exposure, it was concluded that pitting corrosion is unlikely to occur on the tested grades in a 250 ppm Cl- environment at 75 °C, except for Core 304L/4307 (EN 1.4307). Over the one year, no significant weight loss was observed in any of the specimens; however, some discolouration was observed, as illustrated in figure 2. Overall, the results for this environment correlate well with the pitting engineering diagram at 150 mV vs. SCE, unless the potential is raised, e.g., through chlorination.

(2A)	(2B)	(2C)	(2D)	(2E)	(2F)
Core 304/4307 Pitting corrosion (Red circle)	Supra 316L/4404 No corrosion	Forta LDX 2101 No corrosion	Forta DX 2304 No corrosion	Forta LDX 2404 No corrosion	Forta 2205 No corrosion

Fig.2 - The results and appearance from testing various welded specimens at a 250-ppm chloride ion concentration at 75°C over the course of one year. The red circle shows the area with the most severe pitting corrosion.

Case 2: Field testing in North Sea seawater for the marine structural application

Field testing in North Sea seawater (near Helgoland) has been conducted, focusing on four grades of duplex stainless steel: Forta EDX 2304 (EN 1.4362), Forta LDX 2404 (EN 1.4662), Forta DX 2205 (EN 1.4462), and Forta SDX 2507 (EN 1.4410). These materials were subjected to immersion tests in the seawater over a span of two years [27]. During the testing period, the average chloride concentration in the seawater was found to be 18.5 g/L. Additionally, documented annual fluctuations in sea temperature, particularly near Helgoland, ranged from 5 °C to 20 °C. At the end of the 24-month study, all grades demonstrated significant biofouling on their surfaces, as illustrated in figure 3A. The magnitude of biofouling, which often induces microbiologically influenced corrosion (MIC), increased steadily throughout the testing duration. Literature indicates that the OCP rises by approximately 300-400 mV vs. SCE after an initial incubation period in seawater under varying climatic conditions [1, 28]. After cleaning and the removal of the biofilm and marine organisms, only staining remained, with no pitting observed (see figure 3B). This finding aligns well with the pitting engineering diagram, indicating that a 400-mV vs SCE increase in potential is not sufficient to cause pitting on such grades according to the pitting engineering diagram. The pitting - no pitting borderline in figure 1B for grade Forta EDX 2304 (EN 1.4362) is very close to the seawater chloride concentration and the mean temperature of 10 °C. The lack of pitting corrosion on this grade in the field exposure is related to the conservative approach in generating the pitting engineering diagrams and uncertainty in the boundary between pitting susceptibility and resistance (see figure 1).



(3A) Before cleaning (3B) After cleaning

Fig.3 - An overview of the assembly of the samples after 24 months of field exposure, before (A) and after (B) cleaning. Samples from left to right in each panel are: Forta EDX 2304 (EN 1.4362), Forta LDX 2404 (EN 1.4662), Forta DX 2205 (EN 1.4462), and Forta SDX 2507 (EN 1.4410).

Case 3: Long-term immersion test for brine handling applications

As desalination technologies advance and the concentration of corrosive chlorides in rejected brine increases, a critical inquiry arises regarding the corrosivity limits of commonly utilized stainless steel grades, specifically duplex Forta SDX 2507 (EN 1.4410). This investigation aimed to assess the applicability of grade 2507 for brine environments characterized by high chloride levels.

In this study, welded tube samples of duplex Forta SDX 2507 (EN 1.4410) were exposed to sodium chloride solutions at 50,000 and 70,000 ppm chloride ion concentration at 40 °C for one month. Measurements of open-circuit potential were recorded, yielding values ranging from 250 to 400 mV versus SCE (see figure 4) [4]. These findings are in alignment with the recognized threshold of 400 mV vs. SCE, as illustrated in figure 1B. Furthermore, the potential measurements were corroborated by visual inspections utilizing a light optical microscope, which revealed no traces of pitting corrosion across all tested specimens. The results indicate that grade Forta SDX 2507 is a promising option for applications in environments with elevated chloride concentrations, meeting the established 400 mV vs. SCE criteria.

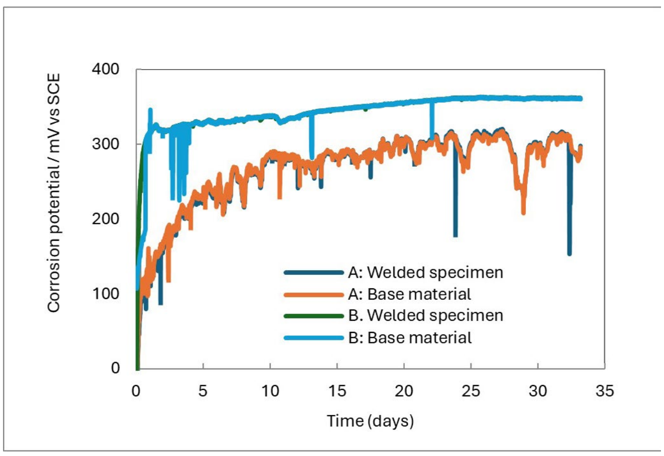


Fig.4 - Corrosion potentials of specimens in Forta SDX 2507 (EN 1.4410) in the experiment with 50000 mg/L of chlorides at 40 °C. [4]

Case 4: Failure of heat exchanger tubes in the food industry

The failure case of heat exchanger tubes made from austenitic stainless steel grade Supra 316L/4404 within the food industry underscores critical concerns regarding material performance under specific environmental conditions. Notably, these tubes exhibited failure within a mere four weeks of operation, predominantly manifesting as red spots and localized pitting on the outer walls, as depicted in figure 5.

During this operational period, the tubes were cooled with cooling water containing 100 mg/L (ppm) chloride ions, which had been treated with chlorine dioxide. The tube wall temperatures ranged from 60 °C to 65 °C. Initial corrosion assessments indicated a low open-circuit potential in the tube heater system, which would indicate that the 150-mV vs SCE line (Dark blue) in figure 1A could be used. This suggested that the likelihood of pitting corrosion was minimal at that time. However, an alarming development occurred after four weeks of service: the open-circuit potential increased, attributed to the oxidative effects of the chlorination process, in which case the 400-mV vs SCE line (Dark blue, figure 1B) would be more applicable, which would indicate a shift towards conditions conducive to pitting corrosion on Supra 316L/4404. In this system, figure 1B (400 mV vs SCE diagram) could be used to select a more appropriate material.

The primary factors influencing this corrosion scenario include elevated operational temperatures, the chloride concentration in the cooling water, and chlorination treatment, which collectively augment the risk of pitting. To address these corrosion challenges, it is critical to improve water-quality management within the cooling system. Furthermore, transitioning to a higher-alloy material, such as duplex grade Forta LDX 2404 (EN 1.4662) or Forta DX 2205 (EN 1.4462), is advisable and would offer improved corrosion resistance.

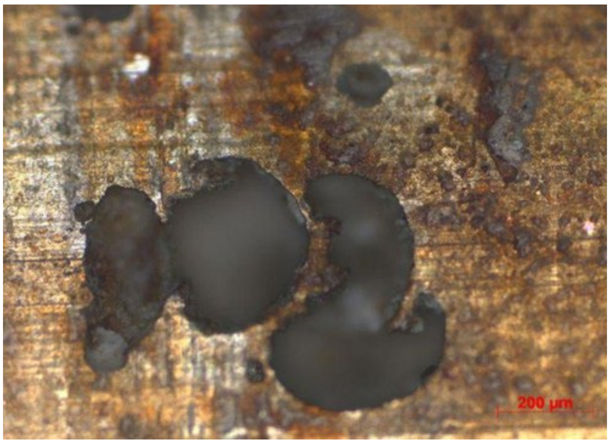
In summary, this case highlights the importance of selecting suitable materials and maintaining optimal environmental conditions to prevent premature failure, e.g., in heat exchangers, particularly in sensitive industries such as food processing.

Fig.5 - Photographs showing pits on the tube wall surface.

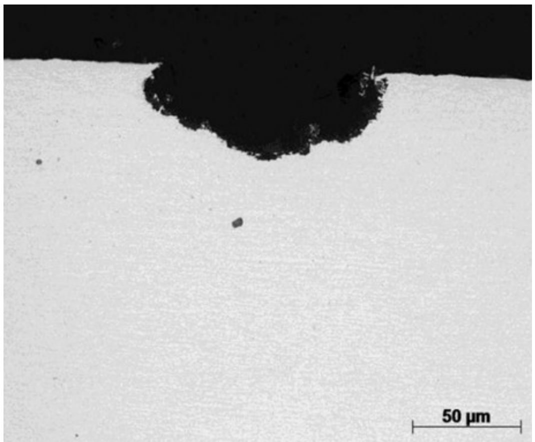
Case 5: Failure of the heat exchanger tube used in wastewater application

A pilot plant for condenser tubes utilizing duplex grade Forta DX 2304 (EN 1.4362) was constructed; however, this material experienced failure after merely nine months of operation within the wastewater system. Corrosion damage was evident on both the interior and exterior surfaces of the outer tube walls, with the most severe deterioration occurring on the exterior surfaces, as depicted in figure 6.

The investigation revealed that the primary cause of the corrosion stemmed from a combination of high temperatures (ranging from 65 °C to 125 °C) and water containing elevated concentrations of corrosive species, particularly chloride ions (ranging from 28,000 ppm to 48,000 ppm). These conditions exceed the corrosion resistance capabilities of Forta DX 2304, as indicated in figure 1A. The engineering diagram in figure 1A further illustrates that the operational conditions—specifically the chloride concentration and temperature—during production surpassed the limiting thresholds beyond which Forta DX 2205 (1.4462) is prone to pitting corrosion. To mitigate the risk of localized corrosion, it may be prudent to consider utilizing a higher-alloyed material, such as Forta SDX 2507 (EN 1.4410) or Ultra 254 SMO (EN 1.4547), for this system.



(6A)



(6B)

Fig.6 - The optical micrographs (A) and cross-section (B) of the pit attack from the outside of the tube wall.

SUMMARY

Key factors influencing pitting resistance of stainless steel in water applications include alloy composition, chloride ion concentration, temperature, and the oxidizing potential of the water. In this regard, pitting engineering diagrams are valuable assets for the selection of the optimum stainless steel in corresponding applications. The accuracy of these diagrams has been validated through various case studies, which support their reliability and performance. These studies encompass investigations into failure analysis and long-term testing conducted in both controlled laboratory settings and real-world environments. The focus is on identifying the factors behind pitting failures and evaluating the applicability and reliability of engineering diagrams over extended periods. Findings from these investigations contribute to improved design practices and the optimization of material selection across diverse applications and support the validation of pitting engineering diagrams for water applications. This selection tool can be a primary tool for facilitating decision-making for engineers and designers involved in water applications, ensuring the longevity and reliability of stainless steel components in challenging conditions. However, it should be noted that while these diagrams highlight factors such as chloride ion concentration, temperature, and oxidizing potential, they do not account for all variables affecting corrosion, including surface conditions, environmental fluctuations, pH and other contaminants.

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