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Resistance of stainless steels to crevice corrosion, SCC and corrosion of welded joints

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Abstract

A critical factor in improving the efficiency and longevity of geothermal systems is the careful selection of materials capable of withstanding extreme environmental conditions, including high temperatures, corrosive fluids, and mechanical stresses. This paper aims to provide insights into various grades of stainless steel that are particularly suitable for geothermal energy applications, with a focus on their corrosion resistance in brine.

For well construction it is paramount to assess the influence of design features, such as crevices, bends and weldments, in the corrosion resistance of the materials, reason why we also included those assemblies in our study. The tested grades were S31603, N08904, S32205, S32750, S31254 and N08935.

This study combines historical and new data to obtain an overview of how various stainless steel grades behave in different brines. Recognizing that the risk of corrosion in brines is influenced by various factors, this research evaluates the performance of stainless steels against localized corrosion in chloride concentrations of 20,000, 100,000 and 200,000 ppm, solutions at a temperature of 90°C, pH 4 and 8, with and without aeration.

The findings of this study outline the localized corrosion performance of stainless steel, offering valuable insights for material selection in geothermal applications. Furthermore, the discussion thoroughly explores the factors affecting the corrosion resistance of stainless steel, including chloride content, oxygen levels, and solution pH, thereby contributing to a deeper understanding of the materials best suited to withstand the challenges posed by geothermal environments.

1. Introduction

Corrosion is a common topic in geothermal plants, however, due to the complex and specific chemistry of the geothermal fluids in different sites, there is no single ideal solution when it comes to material selection for the varied plant components. Furthermore, other aspects of the operating conditions such as temperature, flow velocity and scaling add to the system’s complexity, making prediction and mitigation corrosion phenomena even more difficult.

Not only should the corrosion resistance of the construction materials be considered, but also the performance of the components after processing. Therefore, whenever possible, it is also paramount to assess the corrosion resistance of welds, joints, bends, etc. This study compiles our results of tests performed on such design features.

2. Corrosion within the Geothermal Industry

Several works have studied the corrosion resistance of corrosion-resistant alloys (CRAs) and have compared their performance to that of various carbon steels by exposing them to real operating conditions in geothermal plants.

Multiple studies (Veldkamp et al, Wood, Nogara and Zarrouk, Mundhenk) show that several factors affect the corrosion behavior of materials used in geothermal applications, environmental conditions being the most important. Parameters such as chloride levels, temperature, and pH values play a major role in corrosion rates. Higher temperatures typically increase corrosion rates due to enhanced electrochemical reactions, while lower pH values create more acidic and corrosive environments. The corrosion behaviors of carbon steel and corrosion resistant alloys were assessed in several studies of exposure to operational conditions, which are summarized in Table 1 along with a selection of the tested alloys. The alloys marked **bold** exhibited no signs of corrosion, however, several alloys also presented a performance that can be considered acceptable.

Table 1: Summary of studies with exposure tests of carbon steels and CRAs

Site (Country)	T (°C)	Cl- (ppm)	pH	P (bar)	Tested grades (API 5CT or UNS)	time (days)
Soultz-sous-Forêts (France)	80	59,000	4.7	20	P110, N80, **N08031, N06059** S43020 **S31603, N08904** **N06625**	29 34 61 21
		48,507	4.8	18	P110, N80, P235GH, S43020, **S31603, N08904, N06625**	30
Tuscany (Italy)	150	6,900	3.4	5	**S31254, N06625, N08028, N07725, N06022, N07022**	30
(Philippines)	185	5,000 – 6,000	3.5	11	J55, L80, N06059 R53400, **S32750, N08904**	35
(New Zealand)	300	40	6	74	K55, L80, S32205, **S32750, N08367, N06625,** N08825, **N08031,** N06059	120
Salton Sea (USA)	235	152,800 (brine) 90 – 820 (steam)	5.1 – 6.7	23	G10200, G41300, S43020, S31603, 44627, N08367, **S44735, N06007, N06635, N10276, N06625, R53400, Ti-1.5Ni***	30
Geysers (USA)	225	54 (steam)	3.6	-	G10180, L80, S41000, S31603, S32205, S32550, S32750, S44800, N08904, S31254, N08020, N08825, N04400, N06985, **N06022**	210

*Ti-1.5Ni is not included in the UNS

Mundhenk et al exposed carbon steel grades P110, N80 and P235GH and CRAs S43020, S31603, N08904 and N06625 at the Soultz-sous-Forêts geothermal plant, in France. While all carbon steel grades presented uniform corrosion rates higher than 0.1 mm/year (P110 also presented several millimetres of localized corrosion), grades S31603, N08904 and N06625 did not exhibit any signs of corrosion, neither uniform nor localized. Grade S43020 presented a relatively low uniform corrosion rate (0.003 mm/y) and localized corrosion.

In Tuscany, Italy, Cabrini et al assessed the corrosion performance of 27 stainless steel and nickel alloys over a wide range of Pitting Resistance Equivalent Number (PREN = %Cr + 3.3 x %Mo + 16 x %N), as well as chromium and nickel contents, regarding uniform corrosion, pitting corrosion and stress corrosion cracking (SCC). The grades that exhibited uniform corrosion rate of less than 50 µm/year, no pitting and no cracks, were: S31254, N06625, N08028, N07725, N06022 and N07022.

Other CRAs presented uniform corrosion rates up to 1 mm/year and/or pitting and SCC. Carbon steel samples presented pitting and corrosion rates higher than 1 mm/year.

In the study by Dacillo and Zarrouk, only duplex stainless steel S32750 and super austenitic stainless steel N08904 passed the SCC testing in the geothermal fluid from well XM-02, in the Philippines, while grades J55 and L80-Type 1 presented pitting corrosion and R53400 and N06059 presented cracks.

Nogara et al exposed carbon steel grades K55 and L80, along with several CRAs, to dry steam and observed large uniform and localized corrosion of the carbon steels, and that grades S32750, N08367, N06625 and N08031 did not present visible signs of corrosion.

Carter and McCawley exposed steel grades, nickel super alloys and titanium alloys to the environments of different components of a plant (wellhead, flash unit, scrubber, etc) in the Salton Sea, showing that S31603 presented nearly no uniform corrosion and little localized corrosion in most of the conditions, ferritic stainless steel with high chromium and super austenitic with 6% Mo presented little to no localized corrosion, and nickel, super nickel and titanium alloys suffered no apparent corrosion.

In well environments at the Geysers, Gallup and Farison observed that several CRA's presented no uniform corrosion (S31603 and higher alloyed grades), many of which presented relatively high levels of localized corrosion. Alloys such as super duplex S32750 and S31254 presented localized corrosion levels that can be considered acceptable.

Carbon steels present highest corrosion rates than corrosion resistant alloys, both uniform and localized corrosion. Moreover, fabrication and design choices also play a crucial role in corrosion resistance. Welding techniques can introduce stress concentration, while crevices may trap corrosive agents, leading to localized corrosion. Additionally, applied stress from mechanical loads or thermal expansion can compromise material integrity further. These considerations underscore the necessity for careful material selection and thoughtful engineering design.

This paper is dedicated to an essential objective: comprehensively investigating the corrosion resistance of various stainless steel grades when exposed to chloride solutions. Specifically, the study is conducted in media with different chloride (Cl-) concentrations at controlled pH levels of 4 and 8, with a constant temperature maintained at 90°C. Ultimately, the results of this extensive investigation are expected to provide invaluable guidelines for material selection and design practices in environments characterized by high chloride concentrations, ensuring improved durability and performance of industrial components under hostile conditions.

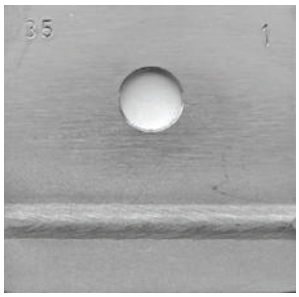
3. Corrosion tests in brine

3.1 Materials and sample preparation

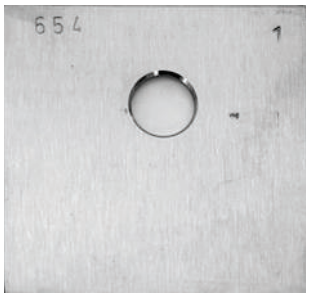
This study comprises relevant stainless steel alloys, summarized in Table 2, detailing their specific designations, surface finishes, and typical chemical compositions. Additionally, the table includes the pitting resistance equivalent number (PREN). To understand the corrosion performance of the tested materials, four different specimen types were prepared: plate, weld, crevice, and stress corrosion, as shown in Figure 1.

Table 2: Typical chemical composition and PREN

UNS designation	Outokumpu grade	Surface finish	PREN	Typical chemical composition, %wt					
				C	Ni	Cr	Mo	N	Other
S31603	Supra 316L	2B	24	0.02	10.1	17.2	2.1	-	-
N08904	Ultra 904L	2E Pro	34	0.01	25.0	20	4.3	-	1.5Cu
S32205	Forta DX 2205	2E Pro	35	0.02	5.7	22.0	3.1	0.17	-
S31254	Ultra 254SMO	2E Pro	41	0.01	18.0	20	6.1	0.20	-
S32750	Forta SDX 2507	2E Pro	42	0.02	7.0	25.0	4.0	0.27	Cu
N08935	Sanicro 35®	2E brushed	52	0.02	35.5	27.0	6.4	0.27	Cu



(A) Plate, weld and crevice sample



(B) Plate and crevice sample



(C) Stress corrosion sample

Fig. 2: Specimens before testing

Table 3 details the welding parameters and welding method. The welded specimens were pickled after welding in a mixed acid bath of 3.5 M HNO3 (nitric acid) and 3.0 M HF (hydrofluoric acid) at 60°C. Different stainless-steel materials and weldments require varying pickling times, and these times were adjusted accordingly until the weld oxide and heat tint were removed for each weldment.

Table 3: Typical chemical composition and PREN

UNS designation	Welding method	Shielding gas	Backing gas	Filler material	Voltage (V)	Current (A)
S31603	MAG-pulse	Mison2 He	Formier10	ERS31603 Si	23.1	74.5
N08904	MIG	Mison2 He	N/A	ER385	32.8	172
S32205	MIG	Mison2 He	Formier10	ER2209	35.5	N/A
S31254	MAG	Mison2 He	Formier10	ERNiCrMo-13	32.8	100.0
S32750	TIG-DC	Mison2 He	Formier10	ER2594	25.5	103.0
N08935	TIG-DC	Ar	Formier10	ERNiCrMo-13	10.4	110

Crevice corrosion specimens and welded specimens were sized at 60 x 60 mm, featuring a central hole of 12 mm in diameter. These specimens were mounted on an insulated N10276 or titanium bolt, with PTFE crevice washers placed between each specimen. A torque of 1.58 Nm was applied. Each washer accommodates 20 crevice sites, resulting in a total of 40 crevice sites per specimen. All edge surfaces are finished to a minimum of 320-grit smoothness.

The stress corrosion cracking specimens were subjected to a two-step procedure. These specimens measured 127 x 13 mm and were shaped into U-bends with a radius of 12 mm (or ½ inches). The U-bends were secured using alloy N10276 or titanium bolts and nuts, incorporating polytetrafluoroethylene (PTFE) washers to provide insulation from the test specimens. Additionally,

the edges of the stress corrosion specimens were ground to a minimum of 320 grit. The creviced, welded, and stress corrosion specimens are depicted in Figure 1.

3.2 Long-term immersion test

The testing conditions included variations in pH levels of 4 and 8, specifically in static conditions (without aeration or deaeration). The test solution was prepared using pro-analysis grade sodium chloride (NaCl) and distilled water, achieving the desired chloride ion (Cl-) concentration. The pH of the solution was adjusted to 8 (basic) by adding 0.1 M sodium hydroxide (NaOH). In contrast, a pH of 4 (acidic) was achieved by introducing 5.6 M hydrochloric acid (HCl). Before immersing the specimens, the solution was heated to 40°C and maintained at a stable temperature of 90°C throughout the testing period. The immersion test lasted 56 days, totaling over 1,300 hours. The setup for the long-term immersion test is illustrated in Figure 2. Any signs of corrosion will be documented and categorized as pitting, crevice corrosion, stress corrosion cracking, or edge attack. In instances of crevice corrosion observed beneath the crevice washers, we will record the number of corrosion sites identified under each washer and the maximum depth of corrosion recorded. Edge attacks will not be evaluated as they are typically absent in most applications. In this study, the corrosion rate was not documented because the predominant form of corrosion observed was localized corrosion.

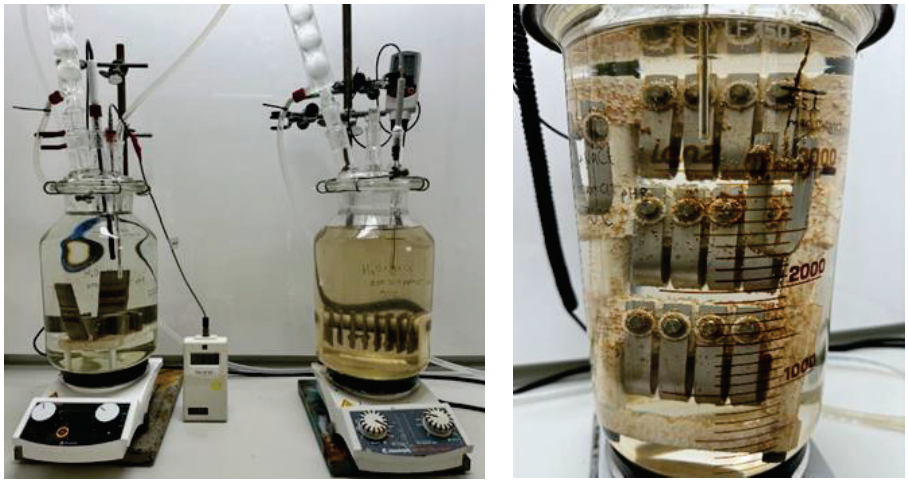


Fig. 2: Long-term immersion test set-up

4. Results

Long-term exposure studies were conducted for 56 days each to evaluate the corrosion performance of materials and the effect of pH in chloride solutions at a temperature of 90°C. The results of these comprehensive tests, conducted with chloride concentrations of 20,000, 100,000 and 200,000 ppm at pH levels of 4 and 8 are demonstrated in Tables 4, 5 and 6, respectively. Additionally, the appearance of the specimens after testing in the 200,000 ppm-chloride solution is documented in Figures 3-6.

Table 4: Results of long-term immersion tests conducted at 20,000 ppm Cl-, pH 4 and pH 8, and 90ºC for plate, weld, crevice and stress corrosion specimens

Steel grade	20000 ppm Cl^-										
	pH 4, aerated					pH 4, N2		pH 8, aerated		pH 8, N2	
	P	C	W	S	E	P	C	P	C	P	C
S31603	X	X	X	O	O	O	X	X	X	O	X
N08904	O	X	O	-	X	O	O	O	O	O	O
S32205	O	X	O	O	O	O	O	O	O	O	O
S31254	O	X	O	-	O	O	O	O	O	O	O
S32750	-	-	-	-	-	O	O	O	O	O	O
N08935	-	-	-	-	-	-	-	-	-	-	-

Table 5: Results of long-term immersion tests conducted at 100,000 ppm Cl-, pH 4 and pH 8, and 90ºC for plate, weld, crevice and stress corrosion specimens

Steel grade	100000 ppm Cl^-																			
	pH 4, aerated					pH 4, N2					pH 8, aerated					pH 8, N2				
	P	C	W	S	E	P	C	W	S	E	P	C	W	S	E	P	C	W	S	E
S31603	X	X	X	O	X	O	X	X	O	O	X	X	O	O	X	X	X	X	O	X
N08904	O	X	X	-	X	O	X	X	-	O	O	X	X	-	X	O	X	X	-	O
S32205	O	X	O	O	X	O	X	O	O	X	O	X	X	O	X	O	X	X	O	O
S31254	O	X	O	-	O	O	O	O	-	O	O	X	O	-	O	O	O	O	O	O
S32750	-	-	-	-	-	-	-	-	-	-	O	O	O	O	O	O	O	O	-	O
N08935	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 6: Results of long-term immersion tests conducted at 200,000 ppm Cl-, pH 4 and pH 8, and 90ºC for plate, weld, crevice and stress corrosion specimens

Steel grade	200000 ppm Cl^-									
	pH 4, no purging					pH 8, no purging				
	P	C	W	S	E	P	C	W	S	E
S31603	O	X	X	O	X	O	X	O	O	X
N08904	O	X	O	O	O	O	X	O	O	X
S32205	O	X	O	O	X	O	X	O	O	X
S31254	O	X	O	O	X	O	X	O	O	X
S32750	O	X	O	O	X	O	X	O	O	X
N08935	O	X	O	O	O	O	X	O	O	O

Note: O = No visible attack, X = Attack, P = Pitting corrosion, C = Crevice corrosion, S = Stress corrosion cracking, E = Attack on cut edges, W = Pitting in weld metal/heat affected zone

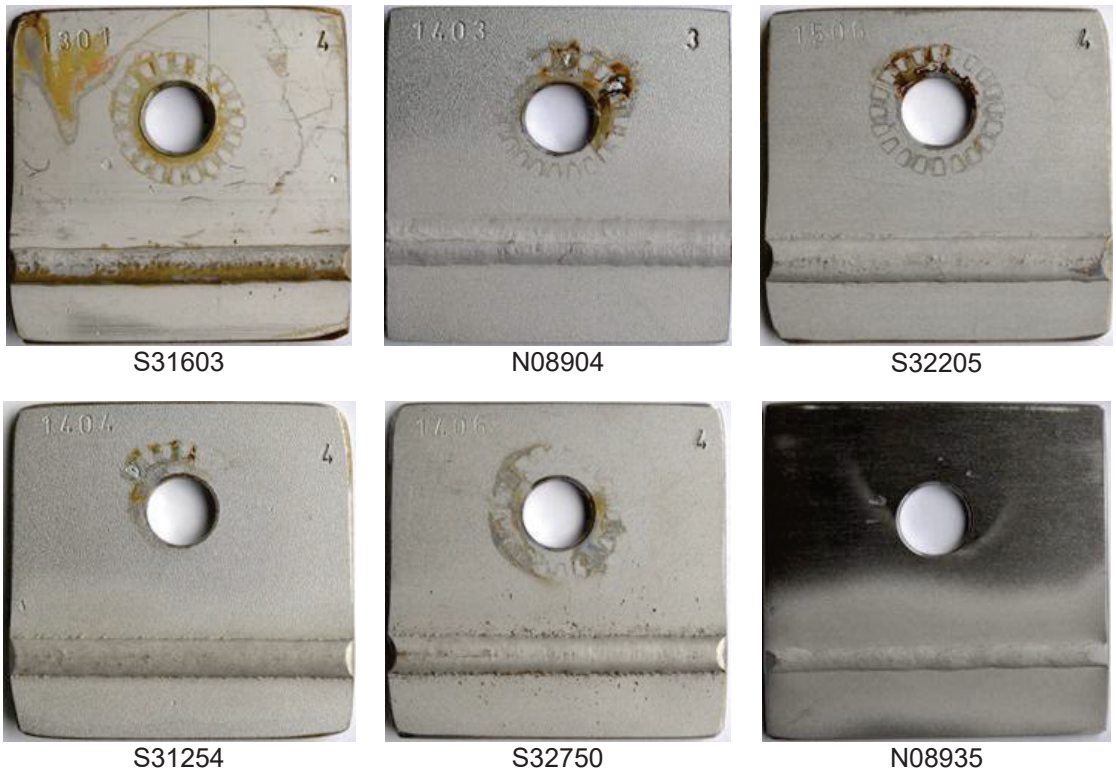


Figure 3. Photos after test of plate/weld/crevice specimens tested in 200000 ppm Cl^-, pH 4 at 90ºC



Figure 4. Photos after test of stress corrosion specimens tested in 200000 ppm Cl-, pH 4 at 90ºC

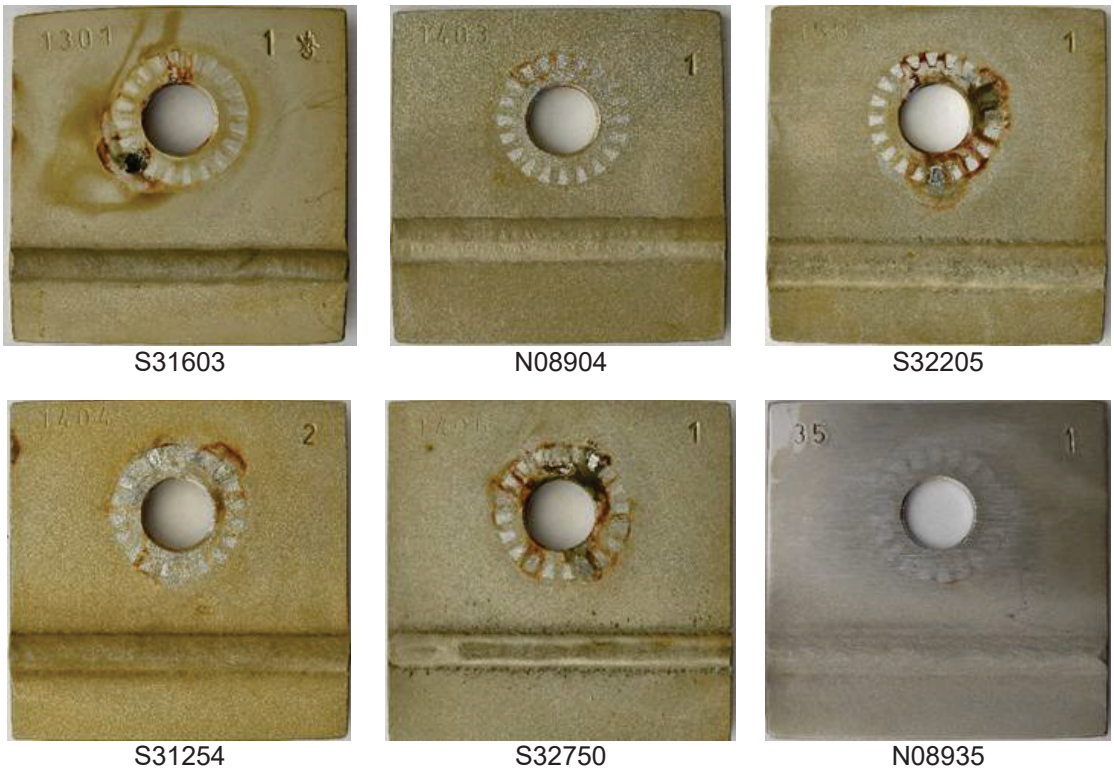


Figure 5. Photos after test of plate/weld/crevice specimens tested in 200000 ppm Cl^-, pH 8 at 90ºC



Figure 6. Photos after test of stress corrosion specimens tested in 200000 ppm Cl^-, pH 8 at 90ºC

5. Discussion

A rough ranking of the corrosion resistance in high chloride concentration environments is thus:

S31603 < N08904, S32205 < S31254, S32750 < N08935

In 100,000 ppm Cl- at pH 4 pitting corrosion in connection with the weld occurs for N08904 under both aerated and de-aerated conditions, while no pitting is observed on S32205. This may be a result of the higher molybdenum content of N08904, which makes it more sensitive to molybdenum segregation in the weld if no heat treatment is performed after welding. No crevice corrosion was found on the specimens of S31603 with crevice former, instead edge attack was present on those specimens as well as pitting, in such a corrosive environment it is possible that pitting corrosion readily occurs, and once pitting has initiated the potential of the specimen decreases, thus crevice corrosion might not initiate. However, crevice corrosion was detected underneath the washer on the U-bend stress corrosion specimens.

The current results indicate that crevice corrosion does not occur at 100,000 ppm Cl- on S32750 at the high temperature of 90°C. Results from previous tests in 50,000 and 70,000 ppm Cl- at 40°C with air saturation showed that S32750 suffered crevice corrosion at both chloride contents while no corrosion occurred on S34565 at 70,000 ppm Cl^- (Halling and Randström). This could be an effect of the higher solubility of oxygen at 40°C than at 90°C. This once again indicates the significance of oxygen content on the corrosiveness of brine solution.

The results obtained in this study indicate that there is no significant difference in corrosiveness conditions between pH 4 and pH 8 in the tested solution of 200,000 ppm Cl-, at 90°C under static conditions. In contrast to previous tests (Mameng), the corrosion performance of stainless steel revealed that oxygen content is a critical factor affecting the corrosiveness of sodium chloride brine solutions at pH 8, even with identical chloride concentrations and temperatures. Prior research showed that pitting corrosion occurred in the welded areas of S31603, N08904, and S32205 under aerated conditions (Mameng). It was determined that oxygen content plays a significant role in influencing the corrosiveness of sodium chloride brine solutions, with the most corrosive environments being those that are aerated. None of the grades were able to resist crevice corrosion in the 200,000 ppm Cl^-.

6. Conclusions

All examined materials demonstrated effective resistance to stress corrosion and, except for S31603, all resisted pitting corrosion in the base material; however, they were unable to withstand crevice corrosion in the tested environments.

When evaluating the corrosion performance of the tested stainless steels at pH levels of 4 and 8, the single significant difference observed when exposed to a chloride concentration of 200,000 ppm at a temperature of 90 °C under static conditions was the pitting in the weld seam of S31603.

The results of this study offer important recommendations for choosing materials that can withstand high chloride concentrations. Nevertheless, it is fundamental to bear in mind that the corrosion resistance of stainless steels in static conditions might be different from operating conditions, especially due to the high flow of the brine.

When designing components and equipment, it is paramount to avoid or minimize crevices and other features that create stagnant conditions.

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