

Electrochemical Assessment of the Influence of Temperature on the Pitting Corrosion Resistance of Metallic Materials in Brines

Helmuth Sarmiento Klapper
Baker Hughes
Baker-Hughes-Strasse 1
Celle, 29221
Germany

Sebastian Jesse
Baker Hughes
Baker-Hughes-Strasse 1
Celle, 29221
Germany

ABSTRACT

To assess the influence of temperature on the pitting corrosion susceptibility of metallic materials intended to be used in industrial applications involving corrosive streams several methodologies are followed. The pitting resistance equivalent number (PREN), an empirical relationship purely based on the mass fraction of some alloying elements in the material is commonly used as a general indication for pitting resistance. The critical pitting temperature (CPT) is also frequently used to benchmark the susceptibility to localized corrosion of metallic materials. ASTM G48 and G150 standards describe the test methodologies for determining the CPT of stainless steels and nickel alloys in chloride-bearing solutions. However, standardized electrolytes do not always simulate accurately expected service conditions and have limited thermal stability, therefore, they might lead to conservative values. On the other hand, electrochemical methods can be used for characterizing the pitting susceptibility and repassivation behavior of alloys at expected service conditions, also at high temperatures. In the present study, the pitting corrosion resistance of eight metallic materials typically used in oilfield technology was characterized electrochemically in chloride solutions at temperatures ranking between room temperature and 150 °C and compared to the corresponding reported PREN and CPT-values. The intention is to demonstrate the lack of correlation between the real pitting resistance of most of these materials at elevated temperatures and the conclusions that might be drawn using PREN and CPT-values for predicting pitting susceptibility in service.

Key words: Pitting corrosion, Stainless steel, Nickel alloy, Cyclic potentiodynamic polarization, High temperature

INTRODUCTION

Several industrial applications including the chemical industry and oilfield technology involve frequently halide-containing streams at elevated temperatures, that challenge the pitting corrosion resistance of metallic materials. Pitting susceptibility becomes not only a reject criterion for materials selection during the design stages of engineering components used in these applications. It also constitutes a significant limiting factor to the service life of these components once in service. Therefore, the characterization of the pitting corrosion resistance of metallic materials including the influence that operational factors can have on material's susceptibility is crucial. Temperature is one of these critical factors that influences pitting corrosion of metallic materials.¹ It is well known that the susceptibility to pitting corrosion of metallic materials increases with increasing temperature.^{2,3} The temperature dependence of the pitting resistance changes with the metallurgical properties of the metallic material including its composition as well as with the environmental conditions the material is expected to be subjected to, and these relationships are not always known.

In oilfield technology, corrosion resistant alloys (CRAs) are used in applications where carbon and low alloyed steel will suffer corrosion.⁴ CRAs include a large number of alloys from 13% chromium containing stainless steel all the way to highly alloyed iron (Fe), nickel (Ni), and cobalt based alloys. Austenitic stainless steels, for instance, have been used for many years in components for drilling applications. These stainless steels are intended to meet the demanding requirements in terms of mechanical, magnetic and chemical properties necessary for the latest drilling technologies.⁵ Highly alloyed stainless steels and Ni-alloys are preferred in offshore technology and in applications involving corrosive production environments.⁴ One of the large disadvantages of stainless steels concerns their limited resistance to pitting corrosion in chloride (Cl⁻)-bearing environments at elevated temperatures. Manning and Duquette⁵ and later Wang, et al.⁶ confirmed that the passive film formed on austenitic stainless steels in aqueous environments at high temperature becomes orders of magnitude thicker, more porous, and, consequently, less protective than those formed at atmospheric conditions. Since the Cr₂O₃ protective layer formed on Ni-Fe-Cr-alloys does not considerably differ from the passive film formed on stainless steels, a similar behavior is expectable for these alloys. However, to the knowledge of the authors, this has not been experimentally confirmed.

To rate the pitting corrosion resistance of CRAs the pitting resistance equivalent number (PREN) is commonly used, also in the oilfield. ISO 21457⁷, for instance, includes recommendations for materials selection based on PREN, which is a relationship purely based on the mass fraction of the alloying elements chromium (Cr), molybdenum (Mo), tungsten (W) and nitrogen (N) in the material. The PREN concept derives from research work done mainly on stainless steels⁸ but it has been extended to Ni-alloys.⁹ There is consensus that alloys having high PREN own superior resistance to pitting corrosion. However, how PREN correlates with the temperature dependence of pitting susceptibility is still unclear. On the other hand, the critical pitting temperature (CPT) directly considers the influence of temperature on pit growth stability.² In the past, the CPT was understood as the lowest temperature at which stable pitting corrosion occur, and it was assumed to be independent over a wide range of environmental parameters, therefore, it was considered as a measure of the resistance to stable pit propagation.¹ More recently the CPT has been defined as a statistically distributed value that represents the temperature where the first transition of a pit from metastable to stable growth occurs, therefore, it can be influenced by both pit nucleation and stabilization.¹⁰ ASTM⁽¹⁾ G48¹¹ practices C and E describe immersion tests in acidified ferric chloride solution for determining the CPT of Ni-alloys and stainless steels, respectively. Alternatively, ASTM⁽¹⁾ G150¹², which describes a potentiostatic method, can be also used for determining CPT of CRAs in a 1 M NaCl-solution. In general, the higher the CPT, the more resistant is the CRA to pitting corrosion. However, CPT-values obtained in these standardized test solutions have only a limited applicability for assessing pitting corrosion resistance at service conditions that significantly differ chemically from those. Consequently, CPT-values obtained according

⁽¹⁾ ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

© 2022 Association for Materials Protection and Performance (AMPP). All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means (electronic, mechanical, photocopying, recording, or otherwise) without the prior written permission of AMPP.

Positions and opinions advanced in this work are those of the author(s) and not necessarily those of AMPP. Responsibility for the content of the work lies solely with the author(s).

to standard methods are commonly used to benchmark CRAs. To use CPT-values for material selection in real applications, the expected operational conditions must be simulated during the test.

Besides the use of PREN and CPT, electrochemical methods have been extensively used in the laboratory to determine the influence of temperature on pitting corrosion resistance of CRAs in service. This effect can be seen either by changing the temperature at fixed applied potential, like the method described in ASTM G150¹², or by performing a cyclic potentiodynamic measurement as described in ASTM G61¹³ at a constant temperature and comparing the results at different temperatures.^{14,15} Recently, an analogy between both methodologies has been proposed considering similar experimental parameters.¹⁶ During polarization scans at low temperatures, extremely high pitting potentials (E_{pit}) are measured, these correspond to early stages of transpassive dissolution rather than to pitting corrosion. On the other hand, at temperatures above the corresponding CPT, pitting corrosion is expected to occur at a potential that is far below the transpassive potential and close to the open-circuit potential (OCP).

All these previously mentioned methodologies have their assets and drawbacks to predict pitting susceptibility of metallic materials in service. Mameng et al.¹⁷ used several methodologies to determine the pitting corrosion resistance of different stainless steels in sodium chloride solutions at 90 °C. The intention was to use the data for providing recommendations for materials selection. Therefore, the chloride (Cl^-) and oxygen content as well as the pH of the test solutions were varied in their experimental plan. Table 1 summarizes the results obtained on the investigated materials after exposure (1300 h) to a deaerated 100,000 ppm Cl-solution at 90°C. Mameng et al. also reported the CPT-values obtained according to ASTM G150¹² in deaerated brines having the same Cl-content. The CPT-values reported in bold in Table 1 correspond to values below 90 °C, while E_{pit} -values were determined by cyclic potentiodynamic polarization tests. The occurrence of pitting corrosion on the specimens after the polarization test at 90 °C was confirmed for UNS S31603, N08904 and S32205.

Table 1
Results from Pitting experiments on different Stainless Steels in 100,000 ppm Cl-solutions¹⁶

Material	PREN	Exposure test	E_{pit} @ 90°C [mV _{SCE}]	CPT [°C]
UNS S31603	28	pitting	80	~ 17
UNS N08904	34	no pitting	350	45
UNS S32205	35		350	55
UNS S31254	41		1100	75
UNS S32750	42		1050	77
UNS S32565	46		900	> 90
UNS S32654	54		1000	> 90

Mameng et al.¹⁷ determined that aeration conditions, i.e. oxygen content, plays a decisive role influencing the susceptibility of the materials to pitting corrosion. Aerated high Cl-containing solutions were the most corrosive environments, while decreasing pH from 8 to 4 increased the corrosiveness of the brines. It was also noted that those materials having a PREN in the range between 34 and 42, for instance UNS N08904 (34), UNS S32205 (35), UNS S31254 (41) and UNS S32750 (42) have shown similar resistance to localized corrosion after the exposure tests. On the other hand, while only one from the seven investigated stainless steels has shown pitting corrosion after the exposure tests, the obtained CPT-values (Table 1) would suggest that only two materials might be suitable for service in the deaerated 100,000 ppm Cl-solution at 90 °C. Even though pitting resistance increased with a higher PREN, no clear correlation between the calculated PREN and the E_{pit} -values as the one reported in the past by Saithala et al.¹⁴ for stainless steels in aerated NaCl-solutions (1,000 ppm Cl^-) at 150 °C could be observed. The CPT-values also suggest a significant difference in the pitting resistance of UNS N08904 and S32205 assumed to have a similar performance based on their almost identical PREN. In consequence, depending upon which methodology is followed and/or which results are considered to

reliably describe the expected service conditions, a different material selection decision can be taken. Mameng et al. concluded that short term electrochemical tests provide more conservative results than long term exposure tests. Therefore, electrochemical tests should not be used to do risk assessment for pitting corrosion in service. However, according to the authors¹⁷ results from electrochemical tests could help to identify risky service conditions leading to pitting i.e. an increase in the electrochemical potential of the alloy by the presence of oxidizing agents, as in fact confirmed in the field¹⁸

Saithala et al.¹⁴ have conducted extensive testing to determine the susceptibility to pitting corrosion of stainless steels in Cl-bearing environments at temperatures up to 170 °C. They investigated the influence of temperature on the pitting resistance by cyclic potentiodynamic polarization measurements. Based on their experimental results regression models were proposed to estimate E_{pit} of stainless steels using the combined effect of temperature, chloride concentration, and material's chemical composition. Even though, these empirical equations are not expressed in terms of PREN, the Authors confirmed that the material with the highest PREN (UNS S32760) showed the highest E_{pit} at all temperatures. Since the equations developed by Saithala et al. are only valid for stainless steels in brines having a maximum chloride content of 10,000 ppm the applicability of these equations for oilfield environments is unfortunately limited.

Recently, Marya¹⁹ reported results on pitting resistance from different stainless steels commonly used in the oilfield. The investigated materials were tested in aerated 3.5 wt.% NaCl solution (approx. 21,000 ppm Cl⁻) also at 35 °C. The corrosion (E_{corr}) and pitting potentials were determined by cyclic potentiodynamic polarization tests using a rather unusual high scan rate of 2 mV/s, while the CPT-values were determined potentiostatically according to ASTM G150 in the mentioned NaCl-solution. As shown in Table 2, the Ni-alloy UNS N07718 with a PREN of 29, almost identical to the PREN calculated for UNS S31603 (Table 1), has shown a similar pitting resistance compared to the alloys having PREN > 40. Furthermore, the alloy UNS S32750, which has shown a CPT-value beyond 70°C in the deaerated highly Cl-concentrated brine (Table 1) exhibited a much lower CPT in the more diluted NaCl-solution. This contrasts with the well-known detrimental effect of the Cl-concentration also confirmed by Mameng et al. in their investigations.¹⁶ It is, therefore, assumed that the presence of oxygen in the 3.5 wt.% NaCl solution is responsible for the significant reduction in the CPT-value of this alloy. It also must be noted from these results that alloys having CPT-values below 35°C (highlighted in bold in Table 2) have shown surprisingly a positive difference $E_{pit} - E_{corr}$, which typically indicates sufficient pitting corrosion resistance in the corresponding environment.²⁰

Table 2
Results from Pitting experiments on different Stainless steels in 3.5 wt.% NaCl solution¹⁹

Material	PREN	$E_{pit} - E_{corr}$ @ 35°C [mV]	CPT [°C]
UNS S41000	14	330	23
UNS S17400	15	170	25
UNS S66286	19	215	32
UNS N07718	29	1140	42
UNS S32750	43	950	39
UNS N08830	45	1002	38
UNS S31010	48	941	51

In an attempt to confirm this lack of correlation between the real pitting resistance of CRAs and the assumptions that might be taken using PREN and CPT-values for predicting pitting susceptibility in service, this paper provides new data regarding the influence of temperature on the pitting corrosion resistance of eight different metallic materials typically used in oilfield technology. The results were obtained electrochemically in chloride solutions at temperatures ranging between room temperature and 150 °C and are compared to the corresponding calculated PREN, and to the CPT-values reported in the literature.

EXPERIMENTAL PROCEDURE

Materials and Test Solution

The pitting corrosion resistance of several oilfield alloys covering a range of PRENs between 16 and 74 has been assessed electrochemically. The chemical compositions of the investigated materials are included in Table 3. These alloys were in different metallurgical conditions including precipitation hardened (PH), cold-worked (CW) and warm-worked (WW), as indicated in Table 3. Specimens were cut by wire-electrical discharge machining (EDM) in longitudinal direction from bar stock in as-delivered condition.

Table 3
Chemical composition of investigated materials, wt.%

UNS	Condition	Cr	Mn	Ni	Mo	N	Fe	Cu	W	Nb	PREN*
S17400	PH (H1025)	15.3	0.64	4.5	0.15	-	Bal.	3.19	-	0.27	16
N07718	PH (6ACRA 140K)	18.6	0.08	54.4	3.0	-	17.3	-	-	5.0**	28
N09946		20.6	0.07	53.5	3.2	-	14.8	1.95	-	4.0	31
S21000	WW	20.4	4.91	17.8	4.9	0.36	Bal.	-	-	-	42
S32750	CW	25.5	0.49	7.0	3.6	0.25		0.54	0.65	-	43
N08830	WW	21.7	4.39	30.0	5.2	0.38		1.17	0.89	-	47
N07716	PH (6ACRA 140K)	20.9	0.08	61.0	8.1	-	4.2	0.04	-	3.7**	48
N07022	CW	20.2	0.32	61.0	16.4	-	Bal.	-	0.03	-	74

PH: Precipitation hardened, CW: Cold-worked, WW: Warm-worked

* PREN calculated acc. to AMPP NACE MR0175 / ISO 15156-3²¹

** Nb+Ta

The electrochemical examinations were conducted in deaerated 80,000 ppm Cl-containing solutions having a near-neutral pH measured at room temperature (RT). The test solutions were prepared using NaCl and deionized water. The tests were conducted at different temperatures 22°C (RT), 80°C and 150°C. Prior to the electrochemical tests the test solution was purged 30 min with pure nitrogen. The amount of dissolved oxygen (DO) in the solution after deaeration with nitrogen was 1±0.2 ppm, which corresponds to the value measured optically (Visiferm DO Arc 120⁽²⁾) at RT. However, the oxygen concentration in the solution was significantly lower depending upon the test temperature and expected to be the lowest at 150 °C. At 80 °C an oxygen concentration of 0.03±0.01 ppm was determined.

Electrochemical Tests

Cyclic potentiodynamic polarization tests were used to assess the pitting corrosion resistance of the investigated materials. A conventional three-electrode configuration including a KCl-saturated Ag/AgCl reference electrode (199 mV_{SHE}) and a TiO-covered Ti counter electrode was used. Before testing, the surface of the specimen was prepared by mechanical grinding using SiC-paper up to 360 grit, rinsed with deionized water and ethanol, and finally dried with hot air. Immediately after specimen preparation the sample was immersed in the test solution. For tests at RT and 80 °C the test solution was in a glass cell including a condenser. The cell was heated using a thermostat. Electrochemical tests at 150 °C were conducted in an autoclave using an external 3M KCl/Ag/AgCl reference electrode (207 mV_{SHE}) for high temperature applications.²² The same specimen geometry having an effective surface of 845 mm² was used in both experimental arrangements.

Prior to the start of the polarization scan, the OCP was monitored for one hour at the test temperature. For measurements at 150 °C the OCP was measured over a period of two hours whereas the first hour

⁽²⁾ Tradename from Hamilton Company.