Harpur Hill, Buxton
Derbyshire, SK17 9JN
T: +44 (0)1298 218000
F: +44 (0)1298 218590
W: www.hsl.gov.uk

HEALTH & SAFETY LABORATORY

A review of performance limits of stainless steels for the offshore industry.

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Project Leader: **E A Geary PhD**

Author(s): **E A Geary PhD**

Science Group: **Engineering Safety**

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CONTENTS

EXECUTIVE SUMMARY

Objectives

To evaluate the critical temperatures for chloride stress corrosion cracking, pitting corrosion and crevice corrosion for the range of stainless alloys currently used in topside operations in the offshore oil & gas industry. This has taken the form of a search of public domain literature and the acquisition of operational limits from a selection of operators.

Main Findings

Owing to the broad remit of the work, and its ongoing nature, it has proved difficult to tabulate simply and concisely all the literature data into useable guidelines on temperature limits. In part, this is because of the large number of variables involved and the relationship between the variables being complex. An added difficulty is that data obtained in the laboratory cannot necessarily provide temperature limits for actual service conditions. Presenting the data in a concise tabular format has not yet been practicable.

In the light of these difficulties, the approach taken has been to extract data regarding critical temperature limits from the literature and incorporate them into a searchable database currently in the form of an Excel Spreadsheet. The spreadsheet can be queried to isolate data of interest. Notes in the last column of each record, in addition to the data, provide the necessary detail from which an assessment of a specific alloy's suitability for use can be made. It is the author's view that the database will provide a valuable repository of corrosion-related service failure data, in addition to laboratory derived data, from which records pertaining to particular alloys, environments, and usages will be extracted. The data will ultimately provide a valuable pan-sector resource that will contain the latest academic data regarding critical temperatures but, possibly of more value to HSE, recent and salient data surrounding individual in-service corrosion failures.

Resource limits have resulted in only 100 of the 210 references obtained from literature in the public domain, which contain critical temperature data, being assessed for inclusion into the ongoing database thus far. Although this has generated over 500 individual records, it is clear that the database is far from complete and certainly less complete than is desirable. As such, this report should be regarded as the first of perhaps several instalments to be issued as the database is updated.

An additional piece of work has been carried out by the author to compare the database with limits currently prescribed by offshore oil and gas operators, as well as International and National Standards: the concern being that these latter data do not reflect the latest findings of corrosion research regarding temperature limits. Where there are discrepancies, these have been highlighted and recommendations for changes to limits have been made as follows:

1. Inconsistencies regarding operational temperature limits within the offshore sector had been identified as long ago as 2003, in that instance, for the use of duplex grades [1]. The present work has indicated that this inconsistency still exists and that it extends across the full range of stainless steels used offshore. There is, therefore, still a need for a review and revision of the temperature limits to reflect the latest developments in corrosion research.

2. The variability of temperature limits used by industry is greatest for chloride stress corrosion cracking (CSCC) and this may be the best initial focus for an exercise to

rationalise and review guidelines. There appears to be greater consistency in the pitting and crevice corrosion limits, with the proviso that there is significantly less data from the operators compared with SCC.

3. Although it is reasonable to assume that a starting point for review might be by focussing on the International Standards, as these provide the mechanism for laying down benchmarks, it has been demonstrated that these are not necessarily up to date and it appears to take many years for advances in research to be adopted. In contrast, industry guidance can be more responsive to changes in technology and the emergence of new data. Therefore, an effort might be made to ensure that industry guidance reflects the most recent developments in corrosion research.

4. Typically, the operator guidelines do not conform with the latest developments (most noticeably for CSCC under evaporative films where temperature limits as low as 70°C and 80°C have been identified for super austenitic, duplex and super duplex steels). Moreover, those that do conform with International Standards (such as Norsok M-001:2004 [2]) may be non-conservative, particularly where an old version of the Standard is used. Again, this is because International Standards do not necessarily reflect the latest developments in corrosion research.

5. Throughout this work it has become apparent that most of the operators do not indicate in their guidance the source of the data on which the basis of their temperature limits have been derived. This constitutes a lack of transparency and makes it difficult to assess independently the validity of the values. This is also true for Norsok Standard M-001, although other International Standards, such as BS EN ISO 15156 and NACE MR0175, MR0176 do provide bibliographies that are better, to varying degrees, in explicitly referencing their source data.

6. The evidence indicates that current advances in corrosion science are being considered and some of the guidelines do now refer specifically to recent work where concentrated chlorides might lead to CSCC at temperatures lower than those currently set in International Standards. Another example, where current advances are being included is the recommendation that ‘ageing’ processes are carried out on components to develop a robust passive film prior to immersion in chlorinated seawaters. [2]

7. In certain operator guidelines and International Standards, the bottom-line for the specification of stainless steel alloys is that where doubt exists then technical expertise must be consulted or specific testing carried out on the alloy in question under the proposed service conditions.

8. There are many fewer data in the operator guidelines regarding temperature limits for localised corrosion (pitting and crevice corrosion), but where stated, they are in slightly better agreement than is the case for CSCC.

9. There is the added complication in that reported temperatures and temperature limits usually reflect the temperature of the environment rather than the all important temperature of the alloy surface.

The operator and standards ‘critical’ temperature data for CSCC, localised (crevice and pitting corrosion) and sour service conditions have been incorporated into a summary table, overleaf, for four main stainless steel types namely: austenitic, super austenitic, duplex and super duplex. The table also presents the ranges of critical temperatures that have been obtained, to date, from the literature incorporated in the database spreadsheet. It is anticipated that the table will be revised as more data becomes incorporated in the spreadsheet.

Although not explicitly addressed in this work, it should be stated that the selection of stainless steels for offshore use should be on the basis of a suitable risk assessment to ensure that risks are kept as low as is reasonably practicable. The data that sit in the database provide a useful resource which can be consulted during this process.

Operator Guideline or Standard	Chloride Environments												Sour Environment °C			
	SCC								Pitting and Crevice Corrosion °C							
	External ° C				Internal ° C											
	A	SA	D	SD	A	SA	D	SD	A	SA	D	SD	A	SA	D	SD
Operator A	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Operator B	60	-	100	110	-	-	-	-	-	-		-	-	-	-	-
Operator C	60	80 - 100[5] | 90 - 110[5]	80 - 100[5]	90 - 110[5]	-	-	-	-	-	-	-	-	60[6]	60,121-171[7]		-
Operator D	50	-	70[1]/112	70[1]/112	-	-	-	-	-	-		-	-	-	150	150
Operator E	60	-	100	120	-	-	-	-	-	30NC/15C		30NC	60[6]	60,121-171[7]	-	-
Operator F	50	120	70	70	-	120	-	-	-	30 NC	-	30NC/20C		-		-
Operator G	30	80	70	80	90[2]	120[2]	110[2]	120[2]	-	-		-	60[6]	60,121-171[7]	-	-
Operator H	50	-	80	110	-	-	-	-	-	-		-	60-120[4], 60-200[3]	200	200[4] | 60 - 200[3]	200
Literature Limits[9]	20 - 30	>50 - 200	70 – 80 ref 13	70 – 80 ref 13					<-2.5 - 35	0 – 20 or 55ref 35	5 - 40	10 - 60[8]				
Norsok M - 001	60,70,85	120	100	110	85					20			120	150	150	150
BS EN ISO 15156-3													60[6]	60, 121-171[7]	232	232
BS EN ISO 21456		100 - 120	80 - 100	90 – 100	60 - 120					20						

Resumé of Temperature Limits for Offshore Operators and Standards

A = Austenitic
SA = Super austenitic
D = Duplex
SD = Super duplex

C = Crevices present
NC = No crevices present

1. 70°C for new plant, 112° for old
2. Hydrocarbon process fluids and produced water (these may constitute sour environment although separate data are given for sour service)
3. Vessels (varies depending on concentration of environmental species)
4. Pipework
5. The lower limit to be used in highly saline atmospheres
6. 60°C where pH_2S is ≤ 100kPa.. Where chloride is < 50mg/l then there is no limit.
7. Temperature varies depending on concentration of environmental species
8. Temperature varies depending on concentration of environmental species, test method and severity of crevices (service data)
9. LITERATURE LIMITS are based on those 100 references whose data have been incorporated into the database to date. In excess of 100 further references remain to be examined and incorporated.

1 INTRODUCTION

The Health and Safety Laboratory (HSL) has been commissioned by the Health and Safety Executive (HSE) Offshore Safety Division (OSD) to identify the safe operational temperature limits that are available to offshore oil and gas operators for the types of stainless steel alloys currently utilised in topside facilities. The driving force behind the work has been concern regarding the variability in the critical temperature values defined in the guidelines used by various operators. The work has been carried out in two parts. The first part has involved the generation of an information resource from literature in the public domain. The second part has consisted of a review of the operators' temperature limits with those from the literature and Standards (such as Norsok M-001 [2] and BS EN 21457 [4] on materials' selection, and BS EN ISO 15156 for sour service [3]) and identifying areas of greatest disparity. Together, it is hoped that these will be used to form the basis of operational guidance for inspectors.

In gathering data from the literature, the critical or maximum permissible-use temperature values for three corrosion mechanisms (i.e., pitting corrosion, crevice corrosion, and chloride stress corrosion cracking) have been obtained. These values are described respectively as:

- Critical Pitting Temperature (CPT),
- Critical Crevice Temperature (CCT) and,
- Critical Stress Corrosion Cracking Temperature (SCCT)

In addition, data that relate to more general thresholds have been included in the database. These have often arisen from observations of service failures and the operating temperatures under which the failure occurred, or laboratory-derived investigations examining corrosion behaviour under defined-temperature conditions.

The stainless steel alloy types examined have been:

- Austenitic (e.g., 316L, 304L)
- Super austenitic (e.g., 254SMO or 654SMO)
- Duplex (e.g., 2205 or 22Cr)
- Super duplex (e.g., 25Cr)

While included in the scope of this work, few data have as yet been obtained for martensitic, ferritic and precipitation-hardening alloys.

In addition to evaluating data for chloride environments the author has also attempted to incorporate corrosion-related temperature limits for sour environments and, where available, to include the manufacturing condition and specific service of the alloys.

2 THE APPROACH TAKEN TO FORMAT THE DATA FROM THE LITERATURE

Owing to the broad remit of the work, and its ongoing nature, it has proved difficult to tabulate simply and concisely all the literature data into useable guidelines on temperature limits. In part, this is because of the large number of variables involved and the relationship between the variables being complex. An added difficulty is that data obtained in the laboratory can not necessarily provide temperature limits for actual service conditions. Presenting the data in a concise tabular format has not yet been practicable.

Work has been carried out previously [5] to provide guidelines on the use of stainless steels offshore and in that exercise the authors had primarily to leave the data in the raw state as to tabulate it would have created a construct of great complexity. The work reported here, however, has attempted some tabulation by entering the data into a database, presently in the form of a searchable EXCEL spreadsheet, thus enabling a swift isolation of data of interest. Notes at the end of each record provide the necessary fine detail from which an assessment of temperature limits and suitability for use might be obtained. Appendix 1 lists the field terms used in each record.

Not only does the database contain information regarding steel type and grade, and critical temperatures where available, it also contains information regarding the environment and applications under which, and for which, the data were derived. A large number of these data have come from papers published in scientific journals, but other sources in the public domain have been used and together these are listed in Appendix 2. These data then have provided the foundation for the review of the temperature-limit guidelines for stainless steel alloys currently in use by offshore operators and to assess where differences lie or how closely they reflect the latest limits available in the literature. This information is reported in Section 3 of this report, where recommendations regarding changes to the specified limits and areas for further work have been made. It is anticipated that this information will form part of HSE guidance regarding the appropriate use of stainless steel alloys offshore.

Resource limits have resulted in only 100 of the 210 references obtained from literature in the public domain, which contain critical temperature data, being transposed into the ongoing database thus far. Although this has generated over 500 individual records, it is clear that the database is far from complete and is less complete than is desirable. At this stage the database must be viewed as a working document and as funding permits more data will be entered. The order in which data has been incorporated has simply been on a basis of when it became available to the author. As such, this report should be regarded as the first of perhaps several instalments to be issued as the database is updated.

It is the author’s view that the database will provide a valuable repository of corrosion-related service failure data, in addition to laboratory derived data, from which records pertaining to particular alloys, environments, and usages will be extracted. The data will ultimately provide a valuable pan-sector resource that will contain the latest academic data regarding critical temperatures but, possibly of more value to HSE, recent and salient data surrounding individual in-service corrosion failures.

What has become evident from the data is that it is not possible to prescribe a single critical temperature for each of the three corrosion mechanisms (i.e., CSCC, pitting, and crevice corrosion) for a particular alloy grade in a given service environment. In large part, this is because the traditional ‘critical temperatures’ for a given alloy are generated from accelerated laboratory tests using standard reagents and techniques and are often used as the means of ranking materials' performance. In contrast, service conditions are uniquely diverse in all their variables. Standard laboratory tests, (e.g., ASTM G48, ASTM G150, etc.) have been shown to provide conservative temperatures [6-8, 49]. Under service conditions, however, these data have been shown to be inadequate in describing the operating envelope for the alloy in question. Defined limits, therefore, need to be specific to the environment and the material under consideration.

As advances in corrosion research reveal new mechanisms for corrosion under particular environmental conditions, it will be possible to include these new limiting conditions into materials' selection and use guidance.

A driving force behind the refinement and redefinition of temperature limits is through the accumulation of data from service experience and the subsequent academic work that investigates the mechanisms behind the failure. A notable example of this has been the realisation, in the last 20 years or so, that the traditional view of the CSCC temperature limits for non-sensitised austenitic steels of 60°C is no longer appropriate. This realisation arose following the service failure of stainless steel fasteners in swimming pool environments, in which concentrated solutions developed beneath deposits formed by evaporation at near ambient temperatures. Subsequent academic studies resulted in a revision of the temperature limits for CSCC of austenitic stainless steels under evaporative conditions to temperatures between 20 and 30°C. Following on, similar work examining the performance of higher-alloyed corrosion-resistant alloys, such as super austenitics, duplex and super duplex steels, under conditions of concentrating solutions, has found these alloys to be susceptible to cracking at temperatures lower than originally defined as being the safe operational maxima.

Another example of where unique environmental circumstances have led to CSCC in conditions that were previously considered safe has been corrosion-under-insulation (CUI) where cracking has developed at temperatures below the accepted limit of 50 or 60°C [9, 10] and has been associated with the concentration of trapped salts. Likewise, more recently, the effect of temperature excursions leading to continued propagation of CSCC at low temperatures [11] has demonstrated the importance of the service history of a component and illustrates the challenges of determining a unified temperature below which safe operation can be assumed.

Overall therefore, in order to optimise materials' use and to avoid inappropriate specification, temperature limits need to be defined that are specific to the environment, service and material conditions. It is hoped that the database created in this work might ultimately be used as a resource from which such limits can be defined. Above all, the caveat must be made that the database constitutes a raw data resource which requires the expertise of a corrosion engineer to interpret. It does not constitute an expert system.

The third section of this report presents an initial assessment of the minimum temperature limits available in public domain literature for the four alloy types listed earlier and how they compare with those limits present in the guidelines provided by some offshore operators, and National/International Standards.

2.1 THE RANGE OF LIMITS AVAILABLE FOR AUSTENITIC GRADE 316

An illustration of the complexity associated with determining suitable temperature limits is provided in this section. Using a single grade of austenitic steel, 316 (S31600), as an example, the ranges of CCT, CPT and SCCT values in the literature and more generalised temperature limits have been extracted from the database. It highlights the fact that many variables interact to affect the temperature limit. The values obtained are only from those data that have been entered into the database and therefore only constitute a portion of the data available. They do, however, illustrate the data range within the literature.

Table 2.1 presents stress corrosion cracking data that encompass studies of ambient temperature cracking under evaporative conditions and the traditional higher temperature limits present in current standards and operator guidelines; hence, SCCT values range from room temperature to in excess of 60°C.

Similarly, Table 2.2 illustrates how the CPT data vary widely from sub-ambient through 150°C depending upon the material condition, the environmental chemistry and presence of oxygen. Tests carried out in sodium chloride and seawater tend to provide temperatures that are higher than those derived using ferric chloride in the ASTM G48 test technique. This is not surprising because of the oxidising potential and hence the corrosivity of ferric chloride.

Table 2.3 shows how relatively few CCT data have been obtained for crevice corrosion. The temperature limits vary between calculated sub-zero values to 5°C in acidic ferric chloride solution.

The non-specific temperature thresholds presented in Table 2.4 tend to be operating temperatures for service situations where failures have occurred or prescribed limits in operator guidelines and Standards where the corrosion mechanism is not explicit. Thus, temperature limits vary from ambient through in excess of 500°C.

This demonstration for a single grade of austenitic stainless steel indicates how complex the interaction is between the variables that determine the temperature limits for a corrosion mechanism, and how standard laboratory tests provide limits that do not mirror service limits. It also demonstrates that values for many of the variables are often not provided in a reference making comparison difficult. It is evident that expert analysis is required when selecting a stainless steel for service. To compile similar tables for all grades of stainless steel would be unwieldy and beyond the current scope of this report. Consequently the data have been left in spreadsheet format for consultation.

Reference	Laboratory Environment	Laboratory Environment – Detail	Service Environment	Service Environment - Detail	Product	Application	Condition	SCC°C	Notes
50	chloride deposit	chloride containing droplets in differing relative humidities	not known	not known	not known	not known	not known	ambient	At ambient temperature there is a criticial Relative Humidity around which SCC will occur in 304 and 316, (~10 - 40%RH) and this corresponds with the concentration of solution in a droplet to an optimum level for SCC to occur, and the type of chloride. Higher than this there is too much water around and solution is too dilute, lower than this and there is too little water around for chloride to reach critical concentration.
32	chloride solution	neutral oxygenated (8ppm), chlorides >.1ppm	Not known	Not known	Not known	Not known	Not known	53	Data extracted off graph for worst case environment (high chloride in neutral oxygenated solutions)
51	not known	not known	chloride atmosphere	not known	bellows	valve unit in liquid sodium coolant system in fsat breeder reactor	not known	ambient	Stored for 3 years at ambient in hot humid coastal climate prior to service. Sensitisation found in HAZ and SCC had occurred. Material was specified as 316L, but actually was 316. Interestingly authors had recommended that components be sealed in PVC bags with dehumidifier to prevent recurrence. No observation made regarding possibility of degradation of PVC contributing chloride ions.
25	chloride deposit	U-ring samples with droplets of various chloride content. Differing RH	not known	not known	components in atmosphere in swimming pool	not known	as received strip	30 - 40	When relative humidity is in the range 12 – 40% and Chloride concentration (>12mol Cl^-/kg H_2O. (30 °C (experimental minimum) when calcium chloride was present,)
22	chloride atmosphere	not known	not known	not known	not known	not known	annealed cold rolled strip	30	Stress corrosion cracking at ambient temperature under evaporative conditions. This datum is not definitive but was the minimum temperature examined.
22	chloride solution	MgCl2 and LiCl	not known	not known	not known	not known	annealed cold rolled strip	30	Stress corrosion cracking at ambient temperature under immersion conditions. This datum is not definitive but was the minimum temperature examined. For this to occur the solution was close to saturation, certainly far greater, by magnitudes, than the ppm limits defined in many standards and guidance.
BS EN ISO 21457:2010 [4]	not known	not known	chloride atmosphere	external marine atmospheric environments	not known	not known	not known	50 - 60	50 - 60°C. Uncoated steels in external marine environment. Lower limit represents worse case scenario where high tensile stresses and concentrated chloride (continuously evaporated). This ref indicates that pitting and crevice corrosion temperatures are lower than this and that coatings may be applied to prevent although coatings to prevent SCC should be applied with caution. Also coating longevity may be lower than plant life and may therefore need maintenance.
Operator E	not known	not known	chloride environments	not known	pipework	not known	not known	60	Where operating temperatures are above these limits then sprayed aluminium coating should be applied.

Table 2.1 Critical Stress Corrosion Cracking Temperatures for Grade 316 (UNS S31600)

Reference	Laboratory Environment	Laboratory Environment - Detail	Service Environment	product	condition	CPT°C	Notes
30	chloride solution	1M NaCl ,deaerated	not known	not known	1mm strip	5.0	This paper examines effect of temperatures above CPT on the pitting potential, but contains some actual CPT data.
47	chloride solution	1M NaCl	not known	not known	not known	7.0 – 17.0	7 - 17°C. These laboratory data have originated from a source (ref 14in this ref) deriving CPTs using the Avesta Cell in 1M Na Cl solution
52	$FeCl_3$	6%$FeCl_3$ ASTM G48	not known	plate	welded	9.0	Extracted from Graph sourced from ASM International
Shreir,2010 [53]	$FeCl_3$	1M NaCl, ASTM G 150	Not known	not known	not known	18	From ASTM G150 test
Shreir,2010 [53]	$FeCl_3$	6%$FeCl_3$ ASTM G48E	Not known	not known	not known	20	From ASTM G48E test
52	$FeCl_3$	6%$FeCl_3$ ASTM G48	Not known	plate	not known	14.0	Extracted from Graph sourced from ASM International
45	chloride solution	NaCl 1M acidified (HCl) solution	not known	test pieces	cold rolled, surface finish 2B according to EN10088	15.5	This paper, whilst precise in deriving a CPT, was rather inexact on the CCT as the data gave a range of temperatures over which crevice corrosion was initiated.
7	$FeCl_3$	6%$FeCl_3$+1%HCl solution, ASTM G48	not known	not known	not known	18.0	These CPT temperatures were lower than expected due to significant defects in the microstructure (segregation and inclusions). Tests ASTM G48 and G150 give differing CPTs which this paper attributes to differing temperature ramping rates, G150 is 200 x faster than G48. Therefore equilibrium conditions tend not to be attained in G150. They explicitly state that these tests should not be used as definitive values for service operation, but instead should be simply used to rank materials.
54	chloride solution	0.1%$Fe(SO_4)_3$, 4% NaCl, 0.01M HCl	not known	seamless tube and pipe	not known	20.0	manufacturer data
55	not known	not known	not known	not known	not known	25.0	
54	chloride solution	1%$FeCl_3$, 1%$CuCl_3$,11%H_2SO_4 + 1.2%HCl	not known	seamless tube and pipe	not known	25.0	<25°C manufacturer data
56	seawater	unchlorinated	not known	not known	not known	30.0	Actual range was 28-33°C. A round Robin exercise examining differences in sea water corrosivity. Found little discernible difference in critical pitting temperature for 316 between laboratories.
57	seawater	not known	not known	not known	sheet	31.0	28 - 34°C was the actual temperature range. Tested in a range of European sea waters using the Avesta Cell. Indicated that sea water salinity in the range 4.8% - 37.7% is not a relevant parameter in determining the pitting temperature.
7	chloride solution	1M NaCl, ASTM G150	not known	not known	not known	68.0	Tests ASTM G 48 and G150 give rather different CPTs which this paper attributes to differing temperature ramping rates, 150 is 200 x faster than 48. Therefore equilibrium conditions tend not to be attained in G150. They explicitly state that these tests should not be used as definitive values for service operation, but instead should be simply used to rank materials.
49	$FeCl_3$	ASTM $G48_2$	O_2 free CO_2 containing brines	not known	welded	150.0	Service limit for pitting >150°C in oxygen free CO_2 brines for even common grades such as 316. They are quite immune to pitting attack, and a CPT of >50°C derived in $FeCl_3$ will give a very conservative estimate of the limits of application in service environment . However where O_2 is present the critical temperature reduces dramatically and the laboratory derived CPT can then mirror service limits.

Table 2.2 Critical Pitting Temperatures for Grade 316 (UNS S31600)

Reference	Laboratory Environment	Laboratory Environment - Detail	Condition	CCT°C	Notes
33	$FeCl_3$	ASTM G48	not known	-14.0	The calculated CCT for a 316 grade with a PRET of 24.4 was –14°C. In this review the authors looked at relationship between PRE number (Cr+3.3Mo+16N) and ASTMG 48 CCT. They showed that a relationship existed for austenitic steels: CCT = -81+2.7 (PRE). For the initiation of crevice corrosion in sea water at 30°C - 32.5°C, the lab derived calculated CCT (ASTM G48) = 35C based on the above formula, irrespective of whether the alloy is austenitic, ferritic or duplex.
36	$FeCl_3$	$FeCl_3$ 10%,pH =1, 24Hr exposure	not known	-2.5	These data are extracted from table derived from paper by Redmond JD, in Chemical Engineering, vol 93, No 20 and 22, 1986
45	chloride solution	NaCl 1M acidified (HCl) solution	cold rolled, surface finish 2B according to EN10088	5.0	This paper, whilst precise in deriving a CPT, was rather inexact on the CCT as the data gave a range of temperatures over which crevice corrosion was initiated.
7	$FeCl_3$	6%$FeCl_3$+1%HCl solution, ASTM G48	not known	5.0	

Table 2.3 Critical Crevice Temperatures for Grade 316. (UNS 31600)

Reference	Laboratory Environment	Laboratory Environment - Detail	Service Environment	External Service Environment - Detail	Internal Service Environment - Detail	Product	Application	Condition	Threshold Temperature, °C	Notes
58	NA	NA	road tunnel atmosphere	not known	not known	test pieces	not known	not known	8.0 – 25.0	Actual range was 8 - 25°C. Pitting and crevice corrosion appeared on all samples after 11 months in this environment, however, they did not suffer SCC.
59	NA	NA	chloride atmosphere	swimming pool atmospheres	not known	fasteners	swimming pool	cold formed	27.5	Actually 25 - 30°C. Does not expand on theories, simply states observations and case histories and suggests alternative materials
51	NA	NA	chloride atmosphere	Not known		bellows	Valve unit in liquid sodium coolant system of fast breeder reactor	Not known	ambient	Stored for 3 years at ambient in hot humid coastal climate prior to service. Sensitisation found in HAZ and SCC had occurred. Material was specified as 316L, but actually was 316. Interestingly authors had recommended that components be sealed in PVC bags with dehumidifier to prevent recurrence. No observation made regarding possibility of degradation of PVC contributing chloride ions.
29	$MgCl_3$	30% $MgCl_2$ at 40°C at 35 and 75% relative humidity	chloride atmosphere	not known	not known	not known	not known	not known	40.0	Assessment of SCC following the swimming pool failure in Switzerland
Operator B	NA	NA	not known	not known	not known	piping systems and pressure vessels	not known	not known	60.0	These do not refer to what application and environment these steels are exposed to; whether internal or external etc. They generally refer to NORSOK M-001 for selection of materials
Operator B	NA	NA	not known	not known	not known	piping systems and pressure vessels	not known	not known	60.0	
NORSOK M-001 (2004)	NA	NA	chloride atmosphere	marine environment	not known	bolting for pressure equipment and structural use	not known	not known	60.0	this temperature limit for if the bolting is to be exposed to wet marine atmosphere
NORSOK M-001 (2004)	NA	NA	chloride atmosphere	dry marine air	not known	bolting for pressure equipment and structural use	not known	not known	540.0	this temperature limit presumably for non wet marine atmosphere

Table 2.4 Non-specific Service Environments and Experimental Thresholds for Grade 316 (UNS S31600)

Reference	Laboratory Environment	Laboratory Environment - Detail	Service Environment	External Service Environment - Detail	Internal Service Environment - Detail	Product	Application	Condition	Threshold Temperature, °C	Notes
Norsok M-001 (2004)	NA	NA	chloride environments	not known	not known	materials for pressure retaining purposes	not known	not known	60.0	May be used at higher temperatures if full heating and ventilation and air conditioning or oxygen free environment or sub-sea with cathodic protection
4	NA	NA	not known	not known	not known	piping, valves, heat exchangers and tanks	fresh water systems	not known	60.0	60 - 120°C. Maximum internal temperature limits. Where temperatures higher than 60°C are used then lower chloride concentrations should be used. Also, where external environment is marine then a limit of 60°C should be used to prevent external SCC.
Norsok M-001 (2004)	NA	NA	not known	not known	not known	lubrication and seal oil, hydraulic fluid, instrument air, tubing (process and utility use).	not known	not known	70.0	provided application is indoor or in sheltered area and not insulated.
Norsok M-001 (2004)	NA	NA	chloride atmosphere	not known	not known	pipework	not known	not known	85.0	for un-insulated instrument piping down-stream of a shut off valve provided there is no flow in the piping and process medium temperature is less than 85°C. Under clamps, where tubing is externally in offshore and at onshore plants there could be risk of crevice corrosion, in which case alternative CC resistant tubing must be evaluated.
Operator G	NA	NA	not known	not known	Hydrocarbon process fluids	not known	hydrocarbon process fluids	not known	90.0	These are the current limits used by Operator G for internal environments
Operator G	NA	NA	not known	not known	Hydrocarbon process fluids	not known	produced water	not known	90.0	These are the current limits used by Operator G for internal environments
Norsok M-001 (2004)	NA	NA	Sour environment	not known	- H_2S partial pressure 0.1 bar, 1% max chloride and min allowed pH 3.5 - H_2S partial pressure 0.01 bar, 5% max chloride and min allowed pH 3.5 - H_2S partial pressure 0.1 bar, 5% max chloride and min allowed pH 5. These assume an oxygen free environment	materials for pressure retaining purposes	not known	not known	120.0	Sour environments. If any parameter exceeds these limits then testing is required to ISO 15156-3. The temperature limit may be increased based on field data and previous experience - testing may be required.
4	NA	NA	not known	not known	not known	piping, valves, heat exchangers and tanks	fresh water systems	not known	120.0	60 - 120°C. Maximum internal temperature limits. Where temperatures higher than 60°C are used then lower chloride concentrations should be used. Also, where external environment is marine then a limit of 60°C should be used to prevent external SCC.

Table 2.4 Ctd…..Non-specific Service Environments and Experimental Thresholds for Grade 316 (UNS S31600)

3 A COMPARISON OF TEMPERATURE LIMITS WITHIN OFFSHORE OPERATOR GUIDELINES WITH THOSE AVAILABLE FROM THE LITERATURE

This section describes an exercise carried out to compare those temperature limits prescribed by eight offshore operators in their materials' specification and use guidelines with those data limits found in the literature and currently incorporated into the database spreadsheet. On the basis of the information supplied to HSE by the operators, the guidelines vary between brief to very comprehensive. Several operators extract data directly from Norsok M-001 [2] and BS EN ISO 15156-3:2003 [3], as well as NACE standard MR0175 [12] as the basis of their materials' selection.

It should be noted, however, that even where operator guidelines do refer to National or International Standards, it is evident that these Standards do not always reflect the most recent developments in knowledge. For example, Norsok M-001 has not yet incorporated the work by Hind and Turnbull [13] that has demonstrated, where evaporative conditions occur in chloride containing environments, the stress corrosion cracking thresholds in duplex and super duplex steels are lower than those under full-immersion conditions. This issue is particularly important where new data indicate that original temperature limits are no longer sufficiently conservative under certain conditions.

Just one of the operators' guidelines refers explicitly to current developments in corrosion research, namely developments relating to low temperature cracking associated with evaporated films in humid environments for both austenitic and duplex steels [13,25] that have emerged in the last 10 years or so.

In terms of caveats and qualifiers, most operators refer to the need to take specialist advice on candidate materials where they do not fall into defined operating ranges. Other operators refer to the need for laboratory-based qualification testing where necessary.

3.1 THE APPROACH TAKEN BY THE OPERATORS.

The offshore operators vary in how the temperature limits are specified. These have been grouped variously in terms of:

- Application: (i.e., pipe work or vessels, pressure containing, structural, etc.)
- Corrosion mechanism: (e.g. stress corrosion cracking, pitting, or crevice corrosion),
- Environment: (e.g., external chloride atmosphere, internal seawater, hydrocarbon envelope, etc.)

As a consequence it has been difficult to create a comparable overview of the operator guidelines as they all have different starting points to defining their limits, as follows:

- **Operator A** has an inspection report. No guidelines but limits have been included.
- **Operator B** provides no rationale behind their choice of temperature limits.
- **Operator C** defines limits on the basis of the corrosion mechanisms and environments.
- **Operator D** provides guidelines that refer solely to CSCC management and are defined on the basis of external and internal environments.
- **Operator E** base their guidelines on 'documented industry experience' and their recommendations are defined in terms of pipework, and thence to what process activity

is being used (i.e., hydrocarbon production systems, seawater systems, utilities and external corrosion). Within some of these there are sub-divisions based on environment: sour, CO_2, or external corrosion.

- **Operator F** provides temperature limits which are defined with respect to the mechanism; either localised corrosion, or CSCC. In the former the materials data limits are defined for particular equipment, for example instrument impulse tubing and fittings, and the latter to whether the exposure is an external or internal environment.
- **Operator G** defines its limits for each alloy initially on the basis of environment: internal or external. For internal environments, limits are set for sour service per BS EN ISO 15156, or hydrocarbon/process fluids. For external environments, limits are utilised to determine whether there is a need to paint or not. Where close insulation is present, all alloys are to be painted regardless of temperature. Operator G does not refer explicitly to corrosion mechanisms and neither does it refer to seawater systems.
- **Operator H** has two-part guidelines: Firstly, a strategy to reduce external CSCC with temperatures varying between new and current facilities; and, secondly, a separate set of guidelines for internal environments in piping and vessels.

It is apparent that the approach taken by the operators varies considerably and that even within an operator's own guidelines a different approach has been taken depending on which corrosion mechanism is being considered. For example, in the case of Operator F, pitting and crevice corrosion temperature limits are defined for equipment type, whereas CSCC is defined in terms of whether the exposure is in an internal or external environment. In this section, the author has taken the information provided by the operators and assessed its agreement with published temperature limits in the literature on the basis of steel type. The author has, where possible, also compared the operator data with Norsok M-001, BS EN ISO 15156 and BS EN ISO 21457 'Petroleum, petrochemical and natural gas industries – Materials selection and corrosion control for oil and gas production systems.' Other standards have also been considered where temperature limits are provided.

3.2 TYPICAL CHEMISTRIES FOR STAINLESS STEEL ALLOYS.

Table 3.1 overleaf provides a list of typical chemistries for the main alloys covered in this report. They are taken from the British Stainless Steel Association's Guide to Stainless Steel Specifications [14] and the Outo Kumpu stainless steel manufacturer's website. [42]

Stainless Type	**Common or ASTM name**	**EN**	**UNS**	**C wt%**	**Cr wt%**	**Ni wt%**	**Mo wt%**	**N wt%**	**Others wt%**
Austenitic	304	1.4301	S30400	≤0.07	17.0 – 19.5	8.0 – 10.5		≤0.11	
	316	1.4401	S31600	≤0.08	16.5 – 18.5	10.0 – 13.0	2.0 – 3.0	≤0.11	
	316L	1.4404	S31603	≤0.03	16.5 – 18.5	10.0 – 14.0		≤0.11	
Super austenitic	6Mo[1]	1.4529	N08926	0.02	19.0 – 21.0	24.0 – 26.0	6.0 – 7.0	0.15	Cu
	254SMO	1.4547	S31254	≤0.02	19.5 – 20.5	17.5 – 18.5	6.0 – 7.0	0.18 – 0.25	Cu
	904L	1.4539	N08904	≤0.02	19.0 – 23.0	23.0 – 28.0	4.0 – 5.0	≤0.15	Cu
	654SMO	1.4652	S32654	≤0.02	24.0 – 25.0	21.0 – 23.0	7.0 – 8.0	0.45 – 0.55	Cu, Mn
Martensitic	420	1.4028	S42000	0.35max	12.0 – 14.0				
Ferritic	430	1.4016	S43400	<0.08	16.0 – 18.0				
Precipitation hardening	17-4 PH	1.4542	S17400	0.07	15.0 – 17.5	3.0 – 5.0			Nb, Ta, 3.0 – 5.0 Cu
Duplex	22Cr	1.4462	S31803	≤0.03	21.0 – 23.0	4.5 – 6.5	2.5 – 3.5	0.10 – 0.22	
Super duplex	25Cr	1.4410	S32750	≤0.03	24.0 – 26.0	6.0 – 8.0	3.0 – 5.0	0.20 – 0.35	

Table 3.1 Typical chemistries for the common stainless grades

3.3 AUSTENITIC STEELS

3.3.1 Chloride environments

In those operator data where the guidelines are brief, the specified limits do not explicitly indicate which corrosion mechanism is being referred to. For example, Operator G states the maximum operating limit for Type 316L as 30°C in un-insulated and un-painted external marine environments, but provides no indication of the rationale. Although the adoption of a low temperature limit is justifiable if it produces a conservative result under all circumstances, it may put unnecessary restrictions on the use of 316.

Stress corrosion cracking

Where chloride SCC is explicitly stated as the corrosion mechanism, the range of temperature thresholds for external use that have been suggested by operators vary between 50°C and 60°C. In most cases, the rationale behind the choice of limit is not explicitly given. The threshold of 60°C is specified by Norsok M-001 for austenitic steels under pressure vessel applications .

Lower temperatures have been associated with sensitised materials in the heat affected zones of welds [26,51], with free machining steels[20] and where iron contamination has occurred [51]. However, regardless of the above circumstances, stress corrosion cracking has also been observed in austenitic steels in both service and laboratory tests, under environmental conditions involving evaporative chloride films, at ambient temperatures [15 - 25]. Yet, with the exception of one operator, these observations have not been referred to and have not been taken into account by an accompanying reduction in the temperature limit under evaporative conditions for austenitic steels.

This appears to be an inconsistent approach as other more recent developments in CSCC research, under evaporative conditions, for duplex and super duplex steels [13, 1] appear to have been incorporated into the temperature-limit guidelines of some operators. Although conjectural it is possible that operator’s have considered CSCC under evaporative conditions for austenitic steels and have concluded that the likelihood of this mechanism at ambient temperature is low in UK offshore environments and applications. Nowhere is a rationale stated, however.

Pitting and Crevice corrosion

The literature [36, 43-45] variously indicates crevice corrosion temperature limits derived using standard test solutions between less than 2.5°C (calculated) and 28°C. The lower temperatures pertain, where information is available, to cold rolled and welded stainless steels, as well as to the higher carbon and lower alloy content steels.

As expected, pitting corrosion temperature limits obtained in seawater and standard test solutions tend to be higher than those for crevice corrosion, in general between 5°C and 35°C, the higher limit generally being obtained for alloy 317LNM. [44]. Temperatures as high as 150°C have been given for grade 316 in oxygen free CO_2 brines [49].

Among the operator data, there are no temperature limits specifically prescribed for pitting and crevice attack for austentic steel in offshore applications and it is likely that due to the lower resistance of austenitic grades such as 304 to localised attack compared with other grades, their use has been excluded. Instead, higher alloys are prescribed. Some operator data make reference to current developments in corrosion science, for example, the need to age components in intermittently or unchlorinated seawater environments and at lower operating temperatures prior to full service use in chlorinated seawater solutions in order to develop the passive film for improved localised corrosion resistance. They do not provide support for this pre-service ageing. Others imply the need to pre-age components through reference to the Norsok Standard (section 5.5.3) which mentions this type of procedure.

3.3.2 Sour Environments

Operator temperature thresholds vary between 60°C and 200°C depending on the precise environmental and service application conditions: many mirror limits prescribed in the current Norsok M-001 and BS EN ISO 15156 standards.

None of the operator guidelines or the Norsok M-001 Standard provide direct evidence for their choice of temperature. The literature that has been reviewed so far does not contain sour service data for austenitic steels.

3.3.3 Summary

In terms of CSCC, for the majority of environments involving full immersion in seawater, and in the absence of other corrosion mechanisms, such as pitting and crevice corrosion, the limit for austenitic steels of between 50 and 60°C has been adopted by the operators. Norsok M-001:2004 states 60°C as the operating limit for austenitic steels. Neither the operators nor Norsok provide source information behind this choice, although 60°C has been the generally held consensus [26] in corrosion science. These temperatures, however, are non-conservative where evaporative conditions are likely to occur in sheltered offshore locations, where there is no likelihood of regular washing, and where the atmosphere falls within a specific range. The lower temperature threshold of 20°C or 30°C should be adopted, bearing in mind that these temperature thresholds apply, strictly speaking, to the metal surface.

The literature gives CPT, CCT and general thresholds for localised corrosion in the approximate range 2.5°C to 35°C. For austenitic steels, however, there are no operator temperature-limit data for pitting and crevice corrosion in chloride environments. Instead, higher alloys such as the Super austenitics and Super duplexes are prescribed.

Operator temperature thresholds vary between 60°C and 200°C in sour service, depending on the precise environmental and service conditions. Other than the Standards, the literature that have been reviewed so far does not contain sour service data for austenitic steels.

None of the operator guidelines, nor the Norsok Standard, provide direct evidence for their choice of temperature.

3.4 SUPER AUSTENITIC STEELS

3.4.1 Chloride environments

Stress Corrosion Cracking

Operator specified CSCC limits vary between 80°C and 120°C depending on the application and environment and on the alloy content of the steel as indicated by the Pitting Resistance

Number (PREN)[2]. The lower ranges are for leaner alloys such as 904L, the higher ranges for richer alloys such as 6Mo. The operator guidance is not clear at times.

Norsok recommends 120°C for chloride atmospheres, whilst BS EN ISO 21457 indicates that in external chloride atmospheres a temperature limit of 100°C to 120°C may be used. No source data behind these choices of temperature are given.

Presently, the database incorporates little information on the CSCC of super austenitic steels. However, under non-evaporative conditions in artificial seawater the SCCT of 6Mo has been given as 120°C [27, 28] rising to greater than or equal to 200°C in the absence of air [26]. However, data from work examining the effect of evaporative films have indicated that the super austenitic steels such as 904L and 254SMO are not as susceptible, compared with the austenitic grades, under these conditions even at temperatures as high as 50°C [25, 29].

Pitting and Crevice corrosion

In chlorinated seawater applications where crevices are present a limit of 15°C is prescribed for the 6Mo grade by some operators. This rises to 30°C where crevices are absent. However, both BS EN ISO 21457 and Norsok M-001 recommend that 20°C is the limiting temperature and that crevice geometries should be avoided in all instances. Both Standards indicate that sufficient consideration should be given to start-up conditions (ageing and discontinuous chlorination to mature the passive film).

Examining the literature, crevice corrosion temperature limits range between 15°C [30 - 32] for 904L to in excess of 60°C [33] for 654SMO.

Pitting temperatures vary between 30°C for 904L and 254SMO [52], to 110°C for the more highly alloyed Uranus 66 and 654SMO [47,60], with a spectrum of data between, covering both grades that varies depending on the precise environmental conditions under which the data were derived.

The NACE technical committee report on the use of corrosion resistant alloys in oil field environments [34] give localised corrosion limits for grade 254SMO between 0°C and 40°C; the lower temperatures for untreated seawater, while the higher temperatures for chlorinated seawater.

3.4.2 Sour environments

In sour environments operator limits vary between 60°C, 121°C to 171°C and 200°C depending on hydrogen sulphide and chloride ion concentrations. The first two temperature limits are those set down in the NACE MR0175 and ISO 15156 Standards. The Norsok standard prescribes a limit of 150°C.

ISO 15156 cites the European Federation of Corrosion, Publications 16 and 17, as the source of their data. None of the operators, nor Norsok, have provided source data behind their choices of temperature.

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[2] PREN or pitting resistance number is a value based on the alloy content of the steel. The commonly used expression for it is $PREN = Cr + 3.3(Mo + 0.5W) + 16N$

3.4.3 Summary

There appears not to be a consensus for CSCC for the super austenitic steels. For CSCC in external marine atmospheres, where evaporative conditions could lead to concentrated chloride, the limits appear to be set non-conservatively by Operator F at 120°C and Norsok because guidance has not been kept up to date with developments. The more conservative limit of 80°C adopted by Operator G, and the range 80°C to 110°C adopted by Operator C, and that within BS EN ISO 21457 would appear more appropriate. In this regard the Norsok standard may be viewed as out of date.

Operators E, H, B and D give no information on external CSCC limits for super austenitics.

For internal seawater systems, where localised corrosion is the likely mechanism, then a limit of 30°C is used by Operator E and Operator F where no crevices are present. This value reduces to 15°C in the presence of crevices. In contrast, the current version of Norsok M-001 and BS EN ISO 21457 [4] recommend 20°C and that crevices are not tolerated under any circumstance. Within the literature there is evidence that the more highly alloyed 654SMO can sustain a crevice corrosion limit of 45°C or 55°C [35] but the leaner alloys may have limits in the range 0°C to 15°C [31, 34]. Overall it would seem that the few operator data that are available are relatively non-conservative compared with the current standards but that this is probably an appropriately cautious response.

Neither the operator data nor the National Standards provide any data to support their choice of temperature.

In sour environments the limits vary between 60°C, 150°C, 121°C to 171°C and 200°C depending on who is prescribing the limit and the hydrogen sulphide and chloride concentration.

3.5 DUPLEX STEELS

3.5.1 Chloride Environments

Stress Corrosion Cracking.

The stress corrosion cracking thresholds for these steel types vary between 70°C and 112°C across the operators depending on the application and whether research into CSCC [13, 28] under evaporative conditions has been taken into account.

The Norsok guidelines currently state that 100°C is the limit for duplex steels in chloride atmospheres and BS EN ISO 21457 gives the range 80°C to 100°C.

Service failure data have been obtained for components in an HP separator and a hydrocyclone at temperatures of 100°C (weld zone) and 120°C for 22Cr Duplex steel [28]. The most recent developments in CSCC in duplex alloys indicate that low temperature cracking can be associated with evaporated films in humid environments [13] and gives temperature limits for 22Cr as low as 70°C to 80°C. It is these data that are the evidence on which a move to lower operating limits has been made by several operators.

3

Pitting and Crevice corrosion.

None of the operators provide temperature limits for pitting and crevice corrosion resistance for duplex steels.

The Standard BS EN ISO 21457 indicates that chlorinated seawater, pipework and vessels made of duplex 25Cr[4] containing crevices should not be used at temperatures in excess of 20°C. Norsok does not appear to provide guidance on the duplex steels for pitting and crevice resistance.

The literature indicates critical pitting temperatures in the range 20°C to 40°C for duplex grades such as 22Cr in both $FeCl_3$ and chloride solutions [46 – 48]. Critical crevice temperatures are lower than critical pitting temperatures, being in the ranges 5°C in $FeCl_3$ to 40°C in both $FeCl_3$ and chloride solutions [36, 33] with outliers at 100°C in de-aerated weak chloride solution [37, 40].

Sour Environments

Operators' limits vary depending on the application. In sour environments the limit for duplex steel pipe-work is 200°C; however, for vessels in the same environment the limit varies between 200°C at low chloride and hydrogen sulphide levels to 60°C for a specific and higher combination of chloride and sulphide. Other operators' limit are based on the 150°C threshold recommended in Norsok. The Norsok standard gives no indication of the basis for this choice of temperature.

The Standard BS EN ISO 15156 - 3 gives 232°C as the limit for duplex steels. Again, little direct data are given to support these temperatures.

The literature examined to date provide no numeric data regarding sour service limits for duplex steels, this may be for a range of reasons, a significant one being that the duplex steels largely do not appear to be prescribed for sour service conditions.

3.5.2 Summary

CSCC limits based on temperatures in excess of 100°C may now be deemed non-conservative in the light of the recent developments [13] regarding cracking under evaporative seawater conditions where temperatures above 70°C to 80°C have resulted in CSCC in both duplex and super duplex grades. Some operators have adjusted their external limits downwards in response. The Standards such as Norsok remain to be changed although BS EN ISO 21457 has incorporated a lower range, possibly indicating that practice can be adapted quickly to reflect changes in science.

There are no operator limits for pitting and crevice corrosion of duplex steels. The literature [46 – 48] gives values for CPT between 20°C and 40°C whereas values for CCT [33, 36, 37, 40] vary between 5°C and 40°C, and even as high as 100°C.

Only Operator H and Operator D give sour service limits, these being between 60°C and 200°C, and 100°C, respectively, depending on the precise combination of H_2S, chloride and pH. These values vary either side of the Norsok Standard's 150°C limit and below the 232°C stipulated in

[4] *This alloy is more widely referred to in the super duplex bracket.*

BS EN ISO 15156. Neither Standard nor operator indicate the source data from which these values are derived but clearly the data in the Standards may be non-conservative.

3.6 SUPER DUPLEX STEELS

3.6.1 Chloride Environments

External Stress Corrosion Cracking.

Operator limits vary between 110°C and 120°C for external CSCC. The present limit prescribed by Norsok for pressure retaining applications is 110 °C.

Several operators, C, D, F, and G, have taken into account the latest developments on CSCC under evaporative films [13,38] and their limits have been reduced accordingly to values between 70°C and 90°C, for conditions where concentrated chloride environments are likely to occur.

It is apparent that some operators' limits are now non-conservative, as is the Norsok limit. BS EN ISO 21457 has included a lower range that incorporates a lower value for those conditions where high concentration of chloride may occur.

Internal Stress Corrosion Cracking.

Operator G has provided a temperature limit of 120°C for hydrocarbon fluids and process water. It is unclear, however, whether this refers to sour environments, chloride based fluids or both.

Other than the references to the NPL work on CSCC under evaporative films, made by the two operators C and F, none of the guidelines and Standards provide direct evidence to support their temperatures for CSCC.

Pitting and Crevice corrosion

For raw seawater applications, where residual chlorine and crevices are present, operator temperature limits vary between 15°C and 20°C, rising to 30°C where residual chlorine and crevices are absent. The lower 15°C limit appears to be based on the 1997 version of Norsok M-001. The 2004 version of the Norsok Standard and BS EN ISO 21457 are more cautious and indicate that 20°C should be the limit under all conditions and that no threaded connections (i.e., no crevice formers) are used.

Operators H and E suggests that high PREN super duplex can be used in the presence of crevices at temperatures as high 30°C. This is non-conservative with respect to limits set by both operators and Standards.

Literature values vary. Field experiments using 25Cr super duplex, butt welded tubes [39] in natural, but chlorinated seawater have identified a localised corrosion resistance limit of 60°C, when crevices are absent. This limit falls to 40°C when crevices are present in both chlorinated and unchlorinated seawater and down to between 25°C and 30°C in the presence of severe crevices, such as threads.. Laboratory data on super duplex steels have indicated crevice temperature limits of between 10°C and 15°C in $FeCl_3$ [36] up to as high as 100°C in chloride solutions[40] depending on alloy content and environment. The adoption of limits between 20°C and 30°C by the two operators who have provided pitting and crevice temperature maxima appear to be pitched between the values found in the literature. There are no indications regarding what source data was used to set these limits.

3.6.2 Sour environments

Few operator limit data for sour service have been obtained. Values of the Norsok limit of 150°C or 200°C have been prescribed.

Norsok currently prescribes 150°C as the limit for super duplex steels in sour service whilst BS EN ISO 15156-3 recommends a higher limit of 232°C. There are no supporting references for these values.

3.6.3 Summary

Although operator limits of temperatures of 120°C, are in line with the current Norsok standard, these are now non-conservative in the light of developments regarding CSCC under evaporative chloride films and field experience of failures in service. Lower temperatures of 70°C and 80°C are now the accepted limit where evaporative films may occur.

Localised corrosion temperature limits for super duplex steel vary between 15°C where free chlorine is present in seawater and crevices are present, to 30°C when crevices are absent. Norsok and BS EN ISO 21457 currently state that the limit is 20°C and that crevices are not tolerated. Operator data are therefore a little non-conservative with respect to Norsok regarding localised corrosion in the presence of crevices. Literature values vary between 10 to 15°C from laboratory derived data [36] to 60°C where crevices are absent [49].

Sour service limits of 150°C and 200°C have been prescribed by operators.

3.7 OTHER STAINLESS TYPES

The author has seen no operator recommendations for the use of ferritic, superferritic and only one reference to martensitic stainless steels for offshore use. Operator C has explicitly prohibited the use of martensitic and precipitation-hardened stainless steels in sour or alkaline sour environments.

The Norsok guidelines give a limit of 90°C for 13Cr 4Ni martensitic valve steel 420 in sour environments.

3.8 SUMMARY OF DATA

It has been difficult to develop a clear picture of the guidelines supplied by the eight operators because they define their limits using differing criteria. This has been discussed in Section 2. Some use only the corrosion mechanism to define the operational temperature limits for each stainless steel type and grade. Others, in contrast, use a mixed approach, for example, referring to product type when defining limits for pitting and crevice corrosion, but then adopting environmental criteria for stress corrosion cracking limits.

However, having extracted the temperature limits, where they are stated, the variability between operators becomes clearer as does where their values sit relative to the temperature minima that exist in the literature[5] that have been incorporated to date in the database spreadsheet. Table 3.2 presents this information. It must be noted that this table is a distillation of the data and it is not accompanied by the very large number of caveats and qualifiers regarding their application that accompany some of the data; to have included this accompanying information would have produced a matrix as complex as the original uncombined data. Once again, this highlights the fact that critical temperatures are specific to environment and material conditions and cannot be generalised.

The evidence displayed in Table 3.2 suggests that many operators limits are a reflection of those currently stated in the Standards such as Norsok M-001[2].

[5] *It must be noted that the literature values have been obtained, to date, from only 100 of the 200+s total references that have been acquired for examination, as only this number have been incorporated into the database spreadsheet. It is anticipated that once the remaining data are examined and included a revised table would be created.*

Operator Guideline or Standard	Chloride Environments												Sour Environment °C			
	SCC								Pitting and Crevice Corrosion °C							
	External ° C				Internal ° C											
	A	SA	D	SD	A	SA	D	SD	A	SA	D	SD	A	SA	D	SD
Operator A	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Operator B	60	-	100	110	-	-	-	-	-	-		-	-	-	-	-
Operator C	60	80 - 100[5] | 90 - 110[5]	80 - 100[5]	90 - 110[5]	-	-	-	-	-	-	-	-	60[6]	60,121-171[7]		-
Operator D	50	-	70[1]/112	70[1]/112	-	-	-	-	-	-		-	-	-	150	150
Operator E	60	-	100	120	-	-	-	-	-	30NC/15C		30NC	60[6]	60,121-171[7]	-	-
Operator F	50	120	70	70	-	120	-	-	-	30 NC	-	30NC/20C		-		-
Operator G	30	80	70	80	90[2]	120[2]	110[2]	120[2]	-	-		-	60[6]	60,121-171[7]	-	-
Operator H	50	-	80	110	-	-	-	-	-	-		-	60-120[4], 60-200[3]	200	200[4] | 60 - 200[3]	200
Literature Limits[9]	20 - 30	>50 - 200	70 – 80 ref 13	70 – 80 ref 13					<-2.5 - 35	0 – 20 or 55ref 35	5 - 40	10 - 60[8]				
Norsok M - 001	60,70,85	120	100	110	85					20			120	150	150	150
BS EN ISO 15156-3													60[6]	60, 121-171[7]	232	232
BS EN ISO 21456		100 - 120	80 - 100	90 – 100	60 - 120					20						

A = Austenitic
SA = Super austenitic
D = Duplex
SD = Super duplex

Table 3.2. Resumé of Temperature Limits for Offshore Operators and Standards

C = Crevices present
NC = No crevices present

1. 70°C for new plant, 112° for old
2. Hydrocarbon process fluids and produced water (these may constitute sour environment although separate data are given for sour service)
3. Vessels (varies depending on concentration of environmental species)
4. Pipework
5. The lower limit to be used in highly saline atmospheres
6. 60°C where pH_2S is ≤ 100kPa. Where chloride is < 50mg/l then there is no limit.
7. Temperature varies depending on concentration of environmental species
8. Temperature varies depending on concentration of environmental species, test method and severity of crevices (service data)
9. LITERATURE LIMITS are based on those 100 references whose data have been incorporated into the database to date. In excess of 100 further references remain to be examined and incorporated.

To provide further clarification, the separate summaries for the steel types have been brought together under the corrosion mechanism headings:

3.8.1 Stress Corrosion Cracking

As is evident from Table 3.2 the limits vary considerably between operators and alloy groups.

The variation is smallest for the austenitic grades, with the temperature limits being set at either the current Norsok M-001 level of 60 °C or 10 degrees lower at 50°C. None of the operators or Norsok have provided source data to support the adoption of the lower value although 60°C appears to have been the 'common consensus' [26] in corrosion science for some time. Little mention has been made of the literature regarding ambient temperature CSCC in austenitic steels under evaporative conditions. In sheltered offshore locations, where there is no likelihood of regular washing and where the atmosphere falls within a specific range (such as the humid Far East), it is possible that a figure of 50°C is still not sufficiently conservative and that a move to a lower threshold such as 20 or 30 °C could be justified.

The super austenitic steels do not appear to have as broad a range of use in offshore environments as the austenitic and duplex steels and data have only been supplied by three operators. The lower limit of 80°C has been adopted by two of the operators leaving the other operator, along with the Norsok standard, with the appearance of being potentially non-conservative with a limit of 120°C and in need of review.

A similar observation may be expressed for the duplex and super duplex steels in the light of the recent developments regarding cracking under evaporative seawater conditions and service experience of failures [13, 38]. CSCC temperature limits based on temperatures in excess of 100°C may now be deemed non-conservative and many operator guidelines and the Norsok standard should be amended to include the lower values of 70° and 80°C that have been identified under evaporative conditions.

Only Operator B and Operator H give references to support their choice of temperatures.

3.8.2 Localised Corrosion

For austenitic steels the literature [36, 43-45] variously indicates crevice corrosion temperature limits between less than 2.5°C and 28°C. The lower temperatures pertain, where information is available, to cold rolled and welded stainless steels, as well as to the higher carbon and lower alloy content steels. As expected, pitting corrosion temperature limits tend to be higher than those for crevice corrosion, between 5°C and 35°C, the higher limit generally being obtained for alloy 317LNM. [44]

For superaustenitic steels the literature examined to date give crevice corrosion temperature limits range between 15°C [30 - 32] for 904L to in excess of 60°C [33] for 654SMO. Pitting temperatures vary between 30°C for 904L and 254SMO, to 110°C for the more highly alloyed Uranus 66 and 654SMO, with a spectrum of data between covering both grades that varies depending on the precise environmental conditions under which the data were derived.

The literature for duplex steels indicates critical pitting temperatures in the range 20°C to 40°C for duplex grades such as 22Cr in both $FeCl_3$ and chloride solutions [46 – 48]. Critical crevice temperatures are lower than critical pitting temperatures, being in the ranges 5°C in $FeCl_3$ to

40°C in both $FeCl_3$ and chloride solutions [36, 33] with outliers at 100°C in de-aerated weak chloride solution [37, 40].

For Super duplex steels the literature values vary. Field experiments using 25Cr super duplex, butt welded tubes [39] in natural, but chlorinated seawater have identified a localised corrosion resistance limit of 60°C, when crevices are absent. This limit falls to 40°C when crevices are present in both chlorinated and unchlorinated seawater and down to between 25°C and 30°C in the presence of severe crevices, such as threads.. Laboratory data on super duplex steels have indicated crevice temperature limits of between 10°C and 15°C in $FeCl_3$ [36] up to as high as 100°C in chloride solutions[40] depending on alloy content and environment.

There are no operator temperature limits defined for either austenitic or duplex steels specifically in terms of pitting and crevice corrosion resistance. Likewise, Norsok M-001and the BS EN ISO 21457 provide no guidelines in this regard for these alloy types.

Only two operators, Operator E and F, have provided temperature limits for the more highly alloyed super austenitic and super duplex stainless steels for internal seawater systems where localised corrosion is the likely degradation mechanism. The limits adopted by these two operators (i.e., 15°C to 30°C) are broadly in agreement with the Norsok M-001 and the BS EN ISO 21457 Standards (i.e. 20°C for super austenitic steels).

Neither the operators nor the Standards provide any data to support their choice of temperature maxima for crevice and pitting. A demonstration that more recent developments in corrosion science are being adopted is indicated explicitly by Operator E by reference to the Norsok Standard, which suggests that 'ageing' is carried out on products to be used in environments where there is a risk of localised corrosion in order to generate a robust passive film.

3.8.3 Sour Service

In general the austenitic and super austenitic stainless steels are more widely recommended for sour service than the duplex grades, possibly because of their superior resistance to sulphide stress cracking and hydrogen cracking. For austenitic grades the threshold temperatures are set primarily at 60°C this being for environments where the partial pressure of H_2S is less than or equal to 100kPa. One Operator provides a range between 60°C and 200°C depending on application and environment. The super austenitic stainless steels have limits between 60°C and 121 – 171°C again depending on application and environment. These values tend to reflect the limits set in BS EN ISO 15156-3

Sour service temperature limits for duplex or super duplex stainless steels have only been provided by Operators D and H. Their values fall within the range specified by Norsok (i.e., 150°C and BS EN ISO 15156-3 (i.e., 232°C). Neither Standards nor operator directly indicate the source data from which these values are derived.

Overall therefore, the limits for sour service amongst the operators are more uniform than for SCC, particularly for the austenitic grades. The limits appear to be founded mainly on the data provided in BS EN ISO 15156-3, although the Norsok limits are used by one operator.

3.9 OBSERVATIONS

The complexity of the issues governing the use of stainless alloys in the offshore environment, where a wide range of operating conditions exist, are demonstrated within both the operator guidelines and the National Standards. This is seen not only in the diverse approaches taken in defining for which environmental conditions or products the temperature limits are set, but also in the observation that qualification testing, or the need to take specialist advice, is often advocated for materials and environments where there exists uncertainty.

Overall, there is considerable variability in the critical temperatures designated by the different operators. As there is a general lack of supporting literature accompanying the guidelines it is difficult to establish their validity. This general lack of transparency is one of the principal issues emerging from this exercise. Indeed, it is only for external CSCC of duplex and super duplex steels under evaporative chloride environments, that any of the operators have explicitly referred to the original work by Hind and Turnbull at NPL [13, 41].

The operators' data indicate that current trends in corrosion science are being considered and incorporated into some of the guidelines[6], but there is a delay adopting them uniformly across the industry or defining precisely what the values should be.

Few operators' guideline data were available for pitting and crevice corrosion. The majority of the data provided were associated with the prevention of CSCC and it is with CSCC that the variability between operators appears greatest. CSCC may therefore be the best initial focus for a review of guidelines. Recent developments in corrosion science, regarding the generation of CSCC under evaporative films, have begun to be incorporated into operator guidelines and the standard BS EN ISO 21457. However, the Norsok Standard, and other operator guidelines remain unchanged.

Guidance and Standards need to be more responsive to scientific developments, particularly when these indicate that current limits may be non-conservative under certain environmental conditions. Norsok M-001 includes temperature limits for CSCC, for super austenitic, duplex and super duplex steels, that are up to 40°C higher than those set by some of the operators.

Despite the complexity regarding the specification of temperature limits for stainless alloys in offshore environments it is hoped that this section has provided an assessment of the current status of operators' guidelines relative to the latest temperature limits in the literature, and that it has highlighted those areas where additional investigation is required. Standards, developed on the basis of industry guidance, tend to lag behind scientific research by several years and therefore might not provide the best starting point on which to base operating limits.

3.10 CONCLUDING REMARKS

1. Inconsistencies regarding operational temperature limits within the offshore sector had been identified as long ago as 2003, in that instance for the use of duplex grades,[1]. The present work has indicated that these inconsistencies still exist and that they extend across the full range of stainless steels used offshore. There is therefore still a need for a review and revision of the temperature limits to reflect the latest developments in corrosion science.

2. The variability in temperature limits used by industry is greatest for CSCC and this may be the best initial focus for an exercise to rationalise and review guidelines. There appears to be greater consistency in the pitting and crevice corrosion limits, with the proviso that there is significantly less data from operators.

[6] *As in the case of SCC under evaporative conditions. Likewise, for improved resistance to pitting attack some operators such as Operator G make direct reference, and others by reference to Norsok, indicate that ageing is carried out on components prior to full service operation in order to generate a robust passive film.*

3. Although it is reasonable to assume that a starting point for review might be by focussing on the International Standards, as these provide the mechanism for laying down benchmarks, it has been demonstrated that these are not necessarily up to date and it appears to take several years for advances to become incorporated into them. In contrast, industry guidance can be more responsive to changes in technology and the emergence of new data. Therefore, an effort should be made to ensure that industry guidance documents reflect the most recent developments in corrosion science.

4. Typically, the operator guidelines do not conform with the latest developments, most noticeably for CSCC under evaporative films where temperature limits as low as 70° and 80°C have been identified for super austenitic, duplex and super duplex stainless steels. Moreover, those that do conform with International Standards such as Norsok M-001 may also be non-conservative (particularly where an old version of the Standard is used). Again, this is because the International Standards do not necessarily reflect the very latest developments in corrosion science.

5. Throughout this work it has become apparent that most of the operators do not indicate in their guidance the source data on which the basis of their temperature limits have been derived. This constitutes a lack of transparency and makes it difficult to assess independently the validity of the values. This is also true for the Norsok Standard although other Standards, such as BS EN ISO 15156 and NACE MR0175, MR0176 do provide bibliographies that are better, to varying degrees, in explicitly referencing their source data.

6. The evidence indicates that current advances in corrosion theory are being considered by some operators and some of the guidelines do now refer specifically to recent work where concentrated chlorides might lead to SCC at temperatures lower than those currently set in Standards such as Norsok. Another example, where current advances are being included, are the recommendations that ageing processes are carried out on components to develop a robust passive film prior to immersion in chlorinated seawaters.

7. In certain operator guidelines and International Standards, the bottom line for the specification of stainless alloys is always that, where doubt exists, technical expertise must be consulted, and or specific testing carried out on the alloy in question under the proposed service conditions.

8. There are many fewer data in the operator guidelines regarding localised corrosion (pitting and crevice corrosion) temperature limits, but where stated, the data are in slightly better agreement than is the case for CSCC.

4 APPENDICES

4.1 APPENDIX 1 - FIELD TERMS USED IN THE SPREADSHEET

Each record is comprised of a series of fields which has allowed the entry of sufficient environmental, and materials detail to allow the user to make useful judgements. Table 4.1 below lists the field terms:

Table 4.1 Field terms used in the Spreadsheet Database

	Field Name	Description
Administrative information	Database Number	
	Date	Date of the source reference
	Endnote reference number	From the literature reference database set up for this project.
	Source	Publisher or author
Environmental information	Environment – Laboratory	Data derived in a laboratory environment – mainly standard tests
	Environment – Laboratory - detail	Detail regarding the testing and environment.
	Environment – Service - external	Data derived from external corrosion under service conditions
	Environment – Service – external – detail	Detail regarding the external service conditions
	Environment – Service – internal	Data derived from internal corrosion under service conditions
	Environment – Service – internal – detail	Detail regarding the internal service conditions
Materials information	Product	From which either laboratory samples were manufactured or from which service generated data were derived
	Application	Under which the product was used
	UNS Grade Name	
	Common name	
	Steel type	
	Steel condition	Heat treatment and processed condition for the steel
Temperature limits	Non-specific temperature threshold, experimental temperature range or service condition	Catch-all for service and laboratory data that have not derived the specific ‘critical’ temperature limits
	Critical Pitting Temperature	
	Critical Crevice Temperature	
	Critical Stress Corrosion Cracking Temperature	
	Notes	More information regarding the data – this field is significant and provides more background and explanation than the other fields can do. This field would not be used as a search field.
	Further	Reference type – review etc….

4.2 APPENDIX 2 - SOURCES OF DATA

a) National/International Corrosion and Technical Organisations (including Governmental):

National Physics Laboratory (NPL)
British Standards and ISO (BS EN ISO)
Institute of Corrosion
Corrosion Source.com
NACE International)
American Petroleum Institute (API)
ASTM International
ASM International
Institute of Metals (now IOM3)
European Commission (EC)
Health and Safety Executive (HSE)
European Federation of Corrosion (EFC)
SERCO
NIREX

b) Industry Associations and Operator Guidelines

British Stainless Steel Institute (BSSI)
NORSOK
Energy Institute (EI)
Society of Petroleum Engineers (SPE international)

8 offshore operators

c) Text Books and Technical Monographs

Corrosion of Stainless Steels, A J Sedriks, Corrosion Monograph Series, 1996
Oilfield Metallurgy and Corrosion, Bruce D Craig, MetCorr, 1992
ASM Metals Handbook 9 – Volumes 13b, Corrosion: Materials. 2005ASM Speciality Handbook – Stainless Steels. 1999
Shrier's Corrosion, Volume 3. Corrosion and degradation of engineering materials. 2010

Technical Publications (books) by Organisations:

Stress Corrosion Cracking. Ed. Russell Jones, ASM International, 1992
Survey of Literature on Crevice Corrosion (1979–1998), F P Ijsseling, EFC, 30, 2000
Intergranular Corrosion of Steels and Alloys, V Cihal, Materials Science Monograph, 18, 1984
Corrosion Resistant Alloys for Oil and Gas Production: Guidance on General Requirements and Test Methods for H_2S service. EFC, 17, 2002
Seawater Corrosion of Stainless Steels – Mechanisms and experiences. EFC - IOM, 1996
Marine Corrosion of Stainless Steels, D Feron, EFC, 33, 2001

d) Journals and Conference Proceedings that have been consulted

Advanced Materials and Processes
ASTM STP 518 Stress Corrosion Cracking of Metals
ASTM STP 821 Environmental Sensitive Fracture: evaluation and comparison of test methods
Advanced Materials and Processes
ASM Metals Handbook 9th Edition [update]
BSSA
Corrosion
Corrosion 93, 95 - 2001 – 2003, 2005, 2008 [what of 2009 and 2010 to be current?]
Corrosion of Austenitic Stainless Steels – Mechanism, Mitigation and Monitoring
Corrosion Engineering
Corrosion Engineering Science and Technology
Corrosion Management
Corrosion Monograph series
Corrosion Review
Corrosion Science
Corrosion Science and Technology
Desalination 2005, 2007
Engineering Solutions to Industrial Corrosion Problems
Eurocorr 97
Eurocorr 2006
European Corrosion Congress
European Federation of Corrosion Publications
International Congress on Surface Modifications
International Joint Power Generation Conference
ISIJ International
Journal of Materials Engineering and Performance
Marine Corrosion of Stainless Steels
Materials and Corrosion
Materials Performance
Materials Protection and Performance
Materials Science and Engineering A
Materials Selection and Design
Metal Transactions A
Metallic Materials for sucker rod pumps
The 2nd NACE Asian Conference
Nuclear Regulatory Commission Report
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