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John Gauley
16 Hull St.
Hingham, MA 02043

March 7, 2019

May Ma
Office of Administration
Mail Stop: TWFN-7-A60M
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001

Dear Ms. Ma:

My Comments on the PSDAR License Transfer Application-Entergy to Holtec at Pilgrim Nuclear Power Plant

I write as a concerned citizen to thank you for your interest in the decommissioning of the Plymouth Nuclear Power Plant. As a resident of the "impacted area" around the plant, I am deeply concerned with all aspects of this process.

I would like to direct your attention to the safety concerns of those of us who live in the area and especially in regards to the type of steel being used for long term storage of the dangerous radioactive waste from the site. The type of steel used in Holtec's Dry Cask Storage has been proven to corrode and crack in salt air environments. This corrosion occurs in the welded areas and in the presence of high heat.

I believe the enclosed materials from the Health and Safety Executive in Great Britain and Coastal Salt Effects on the Stress Corrosion Cracking of Type 304 Stainless Steel convincingly demonstrate that this is an important safety issue to be considered in the licensing process. I respectfully request that you broaden the scope of your interest to include it.

Thank you for your kind attention to this matter.

Sincerely,

John Gauley

NACE Corrosion 2013
March 17-21, 2013
Orlando, FL

Coastal Salt Effects on the Stress Corrosion Cracking of Type 304 Stainless Steel

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ABSTRACT

Some U.S. nuclear power plants are storing spent nuclear fuel in dry cask storage systems (DCSS). In many cases, the DCSS consists of a metal storage canister inside a concrete vault or overpack for radiation shielding. Most canisters are made of austenitic stainless steel, including UNS S30400 (304 SS). The concrete vault or overpack is vented to the atmosphere for passive cooling, allowing interaction between the canister and the ambient environment. In coastal environments, airborne salts could deposit and accumulate on the surface of the canisters over time. Deliquescence of these salts in a humid environment could create a chloride-rich brine on the canister surface. This, in addition to the presence of residual tensile stresses, could make the canister susceptible to chloride-induced stress corrosion cracking.

The objective of this work is to evaluate how salt concentration, temperature, and relative humidity affect stress corrosion cracking initiation for austenitic SS used for dry storage canisters. To that end, simulated sea salt in quantities between 0.1 and 10 g/m^2 was deposited on the surface of type 304 SS U-bend specimens. Three material conditions were used in this evaluation: as-received, sensitized, and welded with type 308 SS filler metal. Once the salt was deposited, the specimens were exposed to a range of temperatures and both cyclic and static humidity conditions to examine crack initiation. The results indicate that both as-received and sensitized 304SS are susceptible to crack initiation at all salt concentrations from 0.1 to 10 g/m^2, and that cracks initiate attemperatures between 35 and 80 °c .

Keywords: Stress Corrosion Cracking, Atmospheric Corrosion, Stainless Steel, Dry Storage Containers, Dry Cask Storage, Spent Nuclear Fuel

INTRODUCTION

At a number of operating and decommissioned nuclear reactor sites in the U.S., the U.S. Nuclear Regulatory Commission[1] (NRC) has issued licenses for independent spent fuel storage installations (ISFSIs). At the ISFSIs, spent fuel removed from the reactor may be placed into dry cask storage systems (DCCS) after cooling for several years in the spent fuel pool. The spent fuel is typically confined in canisters fabricated from austenitic stainless steel (SS) of the types UNS S30400 (304 SS), UNS S30403 (304L SS), or UNS S31603 (316L SS).[1,2] The steel canister is in turn emplaced in a concrete or metal overpack or vault for radiation shielding and physical protection. The overpack or vault is vented to the ambient external environment to allow airflow for passive cooling. Inspections of DCCS have shown evidence of water intrusion and dust or particulate matter on the canister surfaces.[3]

Some ISFSI sites are located in areas where the atmosphere could contain a relatively high concentration of airborne chloride-rich salts, including coastal regions, near salted roads, or near cooling towers.[4] Salts could deposit on the spent fuel canister surface via the external vents. Further, it is expected that residual tensile stresses on the canister from welding or other fabrication activities could be relatively high. It is known that in certain conditions, austenitic SS materials under tensile stress are susceptible to chloride-induced stress corrosion cracking (SCC).[5,6,7] Such occurrences have been reported for external tanks and piping systems at a number of nuclear power plant sites near the ocean. SCC could affect the function of dry storage canisters by allowing leakage of radionuclides through a confinement barrier or by compromising structural integrity. Given this concern, NRC has undertaken research projects to better understand the conditions that could lead to SCC initiation.

In a previous scoping study, 304, 304L, and 316L SS U-bend specimens deposited with simulated sea salt were observed to undergo SCC at a temperature of roughly 45 °C while cracking was not observed at either 85 °C or 120 °c .[8,9] It was determined from these tests that the SCC susceptibility of the stainless steel samples was related to the deliquescence of the deposited simulated sea salt. The deliquescence of the deposited salt is dependent upon the relative humidity at the surface of the sample. The testing also showed that the relative humidity at the surface of the sample is not the same as the bulk environment relative humidity, but rather the absolute humidity (dependent upon both the relative humidity and temperature) at the surface of the sample was the same as the bulk absolute humidtiy. The bulk absolute humidity in these previous tests was measured to be roughly 65 g/m^3. At an absolute humidity of 65 g/m^3, the relative humidity at the surface of the 45, 85, and 120 °C samples is calculated to be roughly 99, 18, and 6 percent respectively. The main components of sea salt are

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[1] U.S. Nuclear Regulatory Commission , Washington, DC 20555-0001

sodium chloride and magnesium chloride which have deliquescence points at a relative humidity of roughly at 70 and 30 percent (dependent upon temperature), respectively. Due to the lower relative humidity at the surface of the 85 and 120 °c samples, no deliquescence could occur.

The applicability of scoping study test conditions to the actual condition of in-service canisters is uncertain. The tests used an absolute humidity of roughly 65 g/m^3, which is high compared to the natural environment humidity. A survey of absolute humidity measurements from coastal° regions around the United States indicated a maximum of about 26 g/m^3.[8] In addition to this data, one of the highest recorded absolute humidity occurred in Sharjah, United Arab Emirates located on the western shore of the Persian Gulf.[10] The dew point was recorded as 34 °C [93.2 °F]. Depending upon the temperature, the absolute humidity would be around 35 g/m^3. Moreover, Japanese data for austenitic stainless steel indicated that SCC could initiate at surface chloride concentration as low as 0.3 g/m^2.[11] The scoping study used a significantly higher chloride concentration, approximately 20 g/m^2. While the actual salt deposition on in-service canisters has not been well-studied, it would be useful to know whether there is a minimumchloride concentration needed for SCC initiation.

Given the conservatisms associated with the scoping study, NRC is sponsoring a follow-on study to more systematically evaluate the parameters that could affect crack initiation, including temperature, humidity, salt content, and material condition . This paper presents some of the preliminary results.

EXPERIMENTAL PROCEDURE

Tests were conducted using welded and unwelded alloy 304 SS. Single U-bend samples were cut out of a 0.125 in (0.318 cm) thick alloy sheet with the sample length perpendicular to the rolling direction. The U-bend samples had dimensions of 5 in (12.7 cm) length and 0.75 in (1.9 cm) width. After cutting, some unwelded samples were sensitized in air' at 650 °C for 2 hours to simulate the condition of the weld heat affected zone. The U-bend samples were bent around a 0.5 in (1.27 cm) diameter mandrlil, following the procedures of ASTM[2] G30, "Standard practice for Making and Using U-Bend Stress Corrosion Test Specimens." [12] The total train on the outside of the U-bend specimen can be closely approximated as 17 percent. After bending, all samples were inspected to ensure no cracks or fissures were present prior to testing.

An ASME[3] Code Section IX qualified welder and procedure were used to prepare the welded specimens.[13] Welding of specimens was performed using a gas tungsten arc welding process. The weld was roughly 0.64 cm [0.25 in] wide and the welded U-bends had the same dimensions as the other U-bend samples. All welds were examined using radiographic testing[14] in accordance with ASME Section III and the acceptance criteria in ASME Section III WB'-5000. Materials that passed the ASME criteria were then machined into U-bend specimens with the weld located at the apex of the specimen, following ASTM G58 procedure[15] Similar to the as-received specimens, each welded specimens was inspected after bending to ensure no cracks or fissures were present prior to testing.

Two different types of tests were conducted with the first being a cyclic humidity test. In the cyclic testing the specimens were mounted on cylindrical heaters and placed in the test chamber as has been described previously.[9] The full test matrix for the cyclic tests is shown in Table 1. The temperature set points for the specimens exposed to cyclic conditions included 35, 45, 52, and 60 °C. Specimens at 35 and 45 °C were examined after 1 and 4 month exposure periods. Some had only been examined after 1 month exposure The 60 °C specimens are yet to be examined in later stages of this project.

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[2] ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA

[3] ASME International, 3 Park Avenue, New York, NY 10016-5990

Different surface concentrations of simulated sea salt were deposited on the U-bend specimens. Past work by Shirai et al. indicated that the threshold for SCC to initiate is expected to be between 0.3 and 10 g/m^2.[11] As such, the tests described in this paper included specimens deposited with 0.1, 1, and 10 g/m^2 in an attempt to bound these conditions. The deposition was accomplished by placing the specimens in a chamber that was fogged using simulated sea water prepared per ASTM D1141-98.[16] During the deposition, all the specimens were maintained at 90 °C. The deposition procedure is shown in Table 2. The surface concentration was adjusted by increasing or decreasing the exposure time in the simulated sea salt fog. Once the salt was deposited, the specimens were heated to the appropriate temperature and the cyclic test was conducted. The cyclic test consisted of a high humidity cycle followed by a dry cycle. The high humidity was obtained by flooding the bottom of the environmental chamber and submerging heaters. Once the heaters were submerged, they were turned on to increase the humidity. The exposure condition maintained the absolute humidity below 30 g/m^3.

The second type of testing was performed under static environmental conditions. U-bend specimens were deposited with salt under the same procedure as previously described. Once deposited with salt, the U-bend specimens were placed in an environmental chamber with a constant temperature and relative humidity. In the static tests, only one surface salt concentration of 10 g/m^2 was used. The static test matrix is shown in Table 3. As can be seen from Table 3, specimens were exposed to 45, 60, and 80 °C. As will be explained later, some of the exposure conditions had an absolute humidity that exceeded 30 g/m^3.

After both the cyclic and static testing, the specimens were removed and examined with a stereomicroscope with at least 50 to 1000x magnifications. For some of the specimens, if cracks were observed, the samples were polished and etched to identify the type of cracking.

RESULTS

Cyclic Humidity Tests with Varying Surface Salt Concentrations

The preliminary results for the cyclic humidity testing at various surface salt concentrations are shown in Figures 1 through 3. As can be seen by Figure 1, the specimens deposited with 10 g/m^2 were extremely susceptible to SCC. Specimens held at 35, 45, and 52 °C were all observed to undergo SCC. The cracks observed in the welded specimens did not occur in the welded material but in the base material away from the weld. SCC susceptibility appears to be greater for sensitized specimens than as-received, with the welded specimens appearing to be the least susceptible. While cracks were observed to occur as early as 1-month after exposure, the cracking was much more severe at 4-months exposure as can be seen in Figure 1.

Figure 2 provides the results for the U-bend specimens deposited with 1 g/m^2 simulated sea salt. As can be seen from the figure, the specimens were susceptible to cracking at both 35 and 45 °C. In addition, the figure seems to show that the sensitized specimens are more susceptible than the as-received specimens; however both specimens showed cracking at the two temperatures when exposed for 4 months.

Figure 3 shows the results for the U-bend specimens deposited with 0.1 g/m^2 surface salt. As can be seen from this figure, the sensitized specimens were susceptible to cracking at both 35 and 45 °C. For the as-received samples, only the 45 °C samples were observed to undergo cracking and not the 35 °C samples. SCC initiated after 4 months of exposure suggesting that the amount of salt appears to affect the crack initiation time.

Figure 4 provides images of 4-month exposed U-bend specimens with different amounts of deposited salt. As can be seen in Figures 4a and 4b, the 10 and 1 g/m^2 specimens have a whitish color given the quantity of salt deposited on the surface. Further, pitting corrosion is clearly visible on those specimens, though cracks cannot be seen at this magnification. For the 0.1 g/m^2 specimens shown in Figure 4c, the surface appears to be nearly pristine as the quantity of salt is very low and there is little evidence of pitting. Photomicrographs of the specimen surfaces and cross-sections, howeve,r show SCC initiation at all of the surface salt concentrations, including 0.1 g/m^2 Figure 5 shows cracks on the surface at the apex of the U-bend specimens. It appears that cracks tend to grow between pits. In some cases, the pitting on the surface of the samples may mask visual observation of cracks so cross-sectional imaging is preferable for identifying cracking. Figure 6 shows the cross-section image of various U-bend specimens. Figures 6a, 6b, and 6c show cross-section imagesof U-bend specimens that were etched to reveal the grain boundaries. As can be seen in these three images, the cracks appear to have both transgranular and intergranular features.

Constant Humidity Tests

The results for the U-bend samples held at 45 °C and 45 percent relative humidity are not shown in a figure because only one test was conducted at this condition. The results indicate that the 304SS specimens exhibited SCC initiation in the static environmental conditions, which is consistent with the results of the cyclic test. At this temperature, both sensitized and as-received specimens cracked. The cross-sectional images of the U-bend specimens are shown in Figure 7. Similar to the cyclic testing the cracks appear to be of mixed mode with both intergranular and transgranular features.

Figure 8 provides the preliminary results for the U-bend specimens held at 60 °C. The results indicate that the sensitized and as-received 304 SS exhibited sec initiation at a relative humidity above 25 percent. After 1-month exposure to 60 °C and 22 percent relative humidity, not only were there no cracks, but there was no observable pitting either.

Figure 9 provides the preliminary results for the U-bend samples held at 80 °C. The results indicate that the sensitized and as-received 304SS samples are susceptible to SCC at a relative humidity at or above 35 percent.

The images of the sec for the U-bend specimens held at 60 and 80°C with different relative humidity are shown in Figures 10 and 11, respectively.

DISCUSSION

One of the main results observed in the testing was that the susceptibility for SCC tended to increase with increasing relative humidtiy. This can be rationalized by examining Figure 12, which is a plot of relative humidity versus temperature with constant absolute humidity lines plotted in black. In addition, the plot shows the calculated lines for the deliquescence relative humidity of the significant constituents of simulated sea salt, including calcium chloride, magnesium chloride, and sodium chloride. The red dots represent the constant environment tests where cracking has been observed. Although sodium chloride is the most abundant constituent of sea salt, SCC occurred at humidity levels below its deliquescence relative humidity. Rather, SCC was observed as long as the test relative humidity was above the deliquescence relative humidity of magnesium chloride or calcium chloride. In natural conditions where the absolute humidity is limited to about 30 g/m^3, such a relative humidity could only be reached at temperatures below approximately 60 °C. This suggests that colder canisters are likely to be more susceptible to sec.

In addition to evaluating how the constituents of sea salt affect the sec susceptibility of 304 SS, the effect of salt concentration on SCC initiation was assessed In certain temperature and relative humidity conditions , cracks initiated with a surface salt concentration as low as 0.1 g/m^2, where the unmagnified surface appeared pristine and no significant pitting was observed. This weight includes not only chloride but also other cations in the .total surface weight. This is a lower surface salt concentration than reported in previous work by Shirai et al., where the surface chloride concentration needed for sec to occur was 0.3 g/m^2.[11] Much more extensive cracking, however, was noted on the specimens with 10 or 1 g/m^2 surface salt concentration. It should be noted that no cracks were observed in the weld material or along the heat affected zone for the welded samples. Cracks that did initiate in the welded samples were located in the base material. These cracks took longer to initiate than observed in the as-received samples. However, the stress is less in the base material for the welded samples because it is along the side of the U-bend samples

CONCLUSION

The objective of this work was to evaluate the susceptibility of austenitic stainless steels typically used in nuclear waste dry storage containers for chloride SCC. Sea salt was deposited onto the surface of various U-bends held at 35, 45, 52, 60 and 80 °C. The samples were either exposed to cycling or constant relative humidity conditions. Samples were deposited with simulated sea salt at surface concentrations of 0.1, 1.0, or 10 g/m^2. The results showed that samples would undergo SCC between 35 and 80 °C as long as the relative humidity was maintained above the calcium chloride relative humidity deliquescence threshold. The results also indicated that SCC could initiate for surface salt concentration at or above 0.1 g/m^2.

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Table 1
Environmental Cycling Test Matrix

Temperature, (°C)	Salt Concentration, (Q/m^2)	Fabrication
35	0.1, 10	As-Received, Sensitized, Welded
	1.0	As-Received , Sensitized
45	0.1, 10	As-Received, Sensitized, Welded
	1.0	As-Received, Sensitized
52	1, 10	As-Received, Sensitized

Table 2
Atmospheric Test Chamber Protocol During Salt Deposition Phase

Cycle#	Chamber Cycle	Time, minutes	Chamber Temp, °C	Comments
	Salt fog	5	27	Deposit Salt on specimens
2	Hold	15	27	Dry specimens after fog cycle

Table 3
Static Environmental Test Matrix

Temperature	Relative Humidity	Fabrication
45	44	As-Received, Sensitized
60	22, 25, 30, 35, 40	As-Received, Sensitized
80	35,40	As-Received, Sensitized

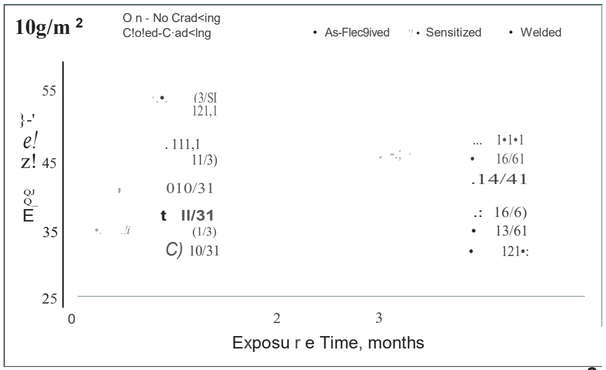

Figure 1: Cycling environment SCC susceptibility map for 10 g/m^2 simulated sea salt U-bend samples (number in brackets indicates number of specimens observed to have cracked versus the number that were inspected).

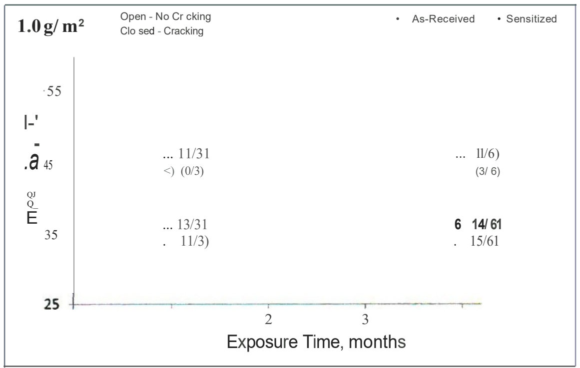

Figure 2: Cycling environment SCC susceptibility map for 1 g/m^2 simulated sea salt U-

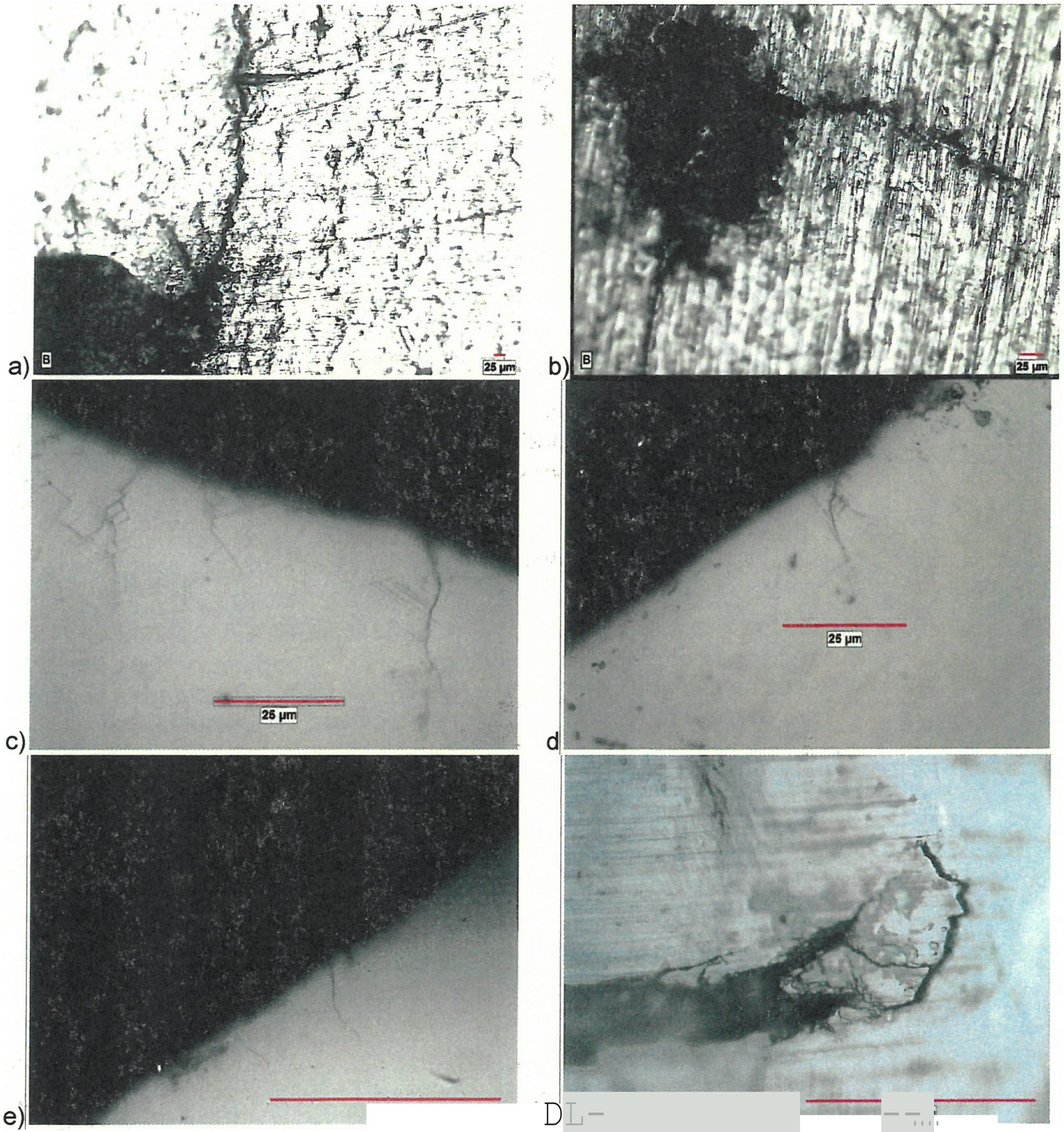

Figure 10: Images of cracked U-bends held at 60 °C and deposited with 10 g/m ^{2} of simulated sea salt. 40 percent relative humidity a) as-received and b) sensitized; 35 percent relative humidity c) as-received and d) sensitized; 25 percent relative humidity e) as-received and f) sensitized

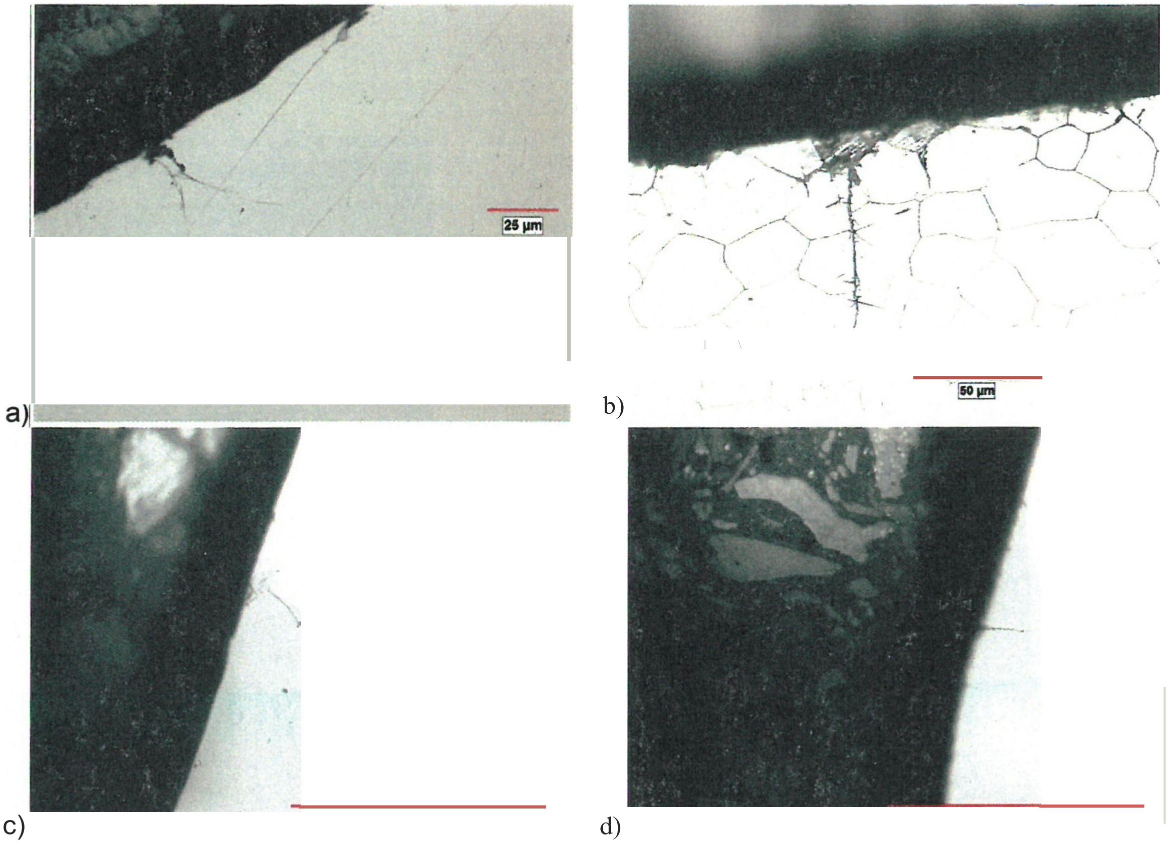

Figure 11: Images of cracked U-bends held at 80 °C and deposited with 10 g/m^2 of simulated sea salt. 40 percent relative humidity a) as-received and b) sensitized; 35 percent relative humidity c) as-received and d) sensitized

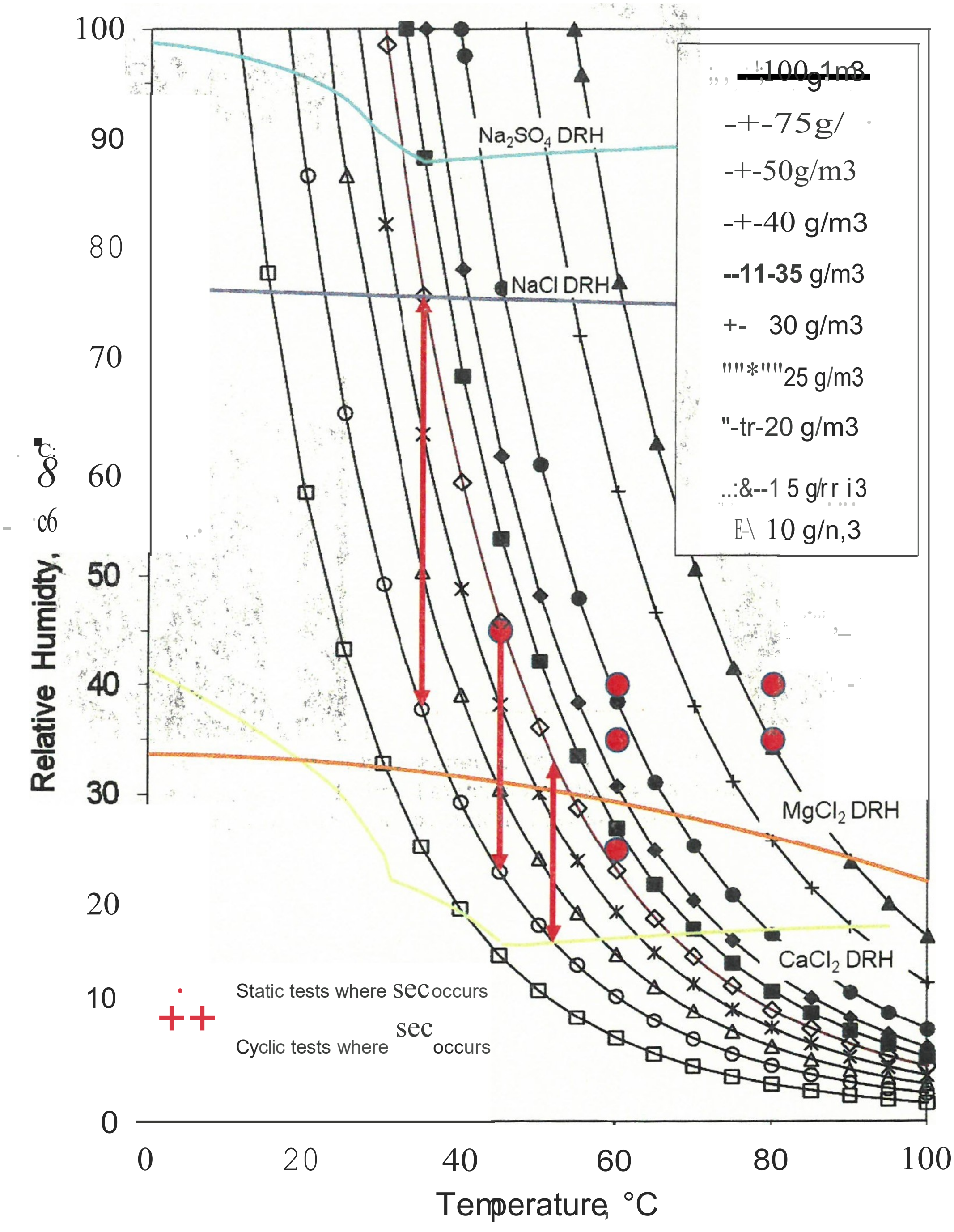

Figure 12: Test conditions relative to the salt deliquescent conditions necessary to form salt brine

HSE

Health and Safety
Executive

Chloride stress corrosion cracking in austenitic stainless steel

Assessing susceptibility and structural integrity

Prepared by the **Health and Safety Laboratory**
for the Health and Safety Executive 2011

RR902
Research Report

HSE

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Executive

Chloride stress corrosion cracking in austenitic stainless steel

Assessing susceptibility and structural integrity

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Chloride stress corrosion cracking (CLSCC) is one the most common reasons why austenitic stainless steel pipework and vessels deteriorate in the chemical processing and petrochemical industries. Deterioration by CLSCC can lead to failures that have the potential to release stored energy and/or hazardous substances. Failures of plant can be prevented by an awareness of the onset and evolution of CLSCC, and by periodic inspection to monitor the extent of cracking. Although the deterioration of austenitic stainless steels by CLSCC is well known, recent incidents and inspection visits by HSE have found that susceptibility assessments were inconsistent and did not always take account of current knowledge. Discussions between HSE, dutyholders and competent bodies identified that the technical justification for setting inspection intervals and the effectiveness of periodic non-destructive examination (NOE) for monitoring CLSCC were additional areas of concern.

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(i) The chemical manufacturing company for providing detailed background information on the operation of two stainless steel reactors that developed chloride stress corrosion cracking.

(ii) The company's insurer for supplying details of a metallurgical investigation carried out on the reactors.

(iii) Mitsui-Babcock who carried out an assessment of NOE techniques on samples from the reactors.

CONTENTS

EXECUTIVE SUMMARY

Objectives

Chloride stress corrosion cracking (CLSCC) is one of the most common reasons why austenitic stainless steel pipework and vessels deteriorate 'in the chemical processing and petrochemical industries. The objectives of this work-were:

To draw conclusions and give recommendations for best practic;e in assessing susceptibility to CLSCC and in applying risk based inspection (RBI) to existing plant, in particular setting inspection intervals and carrying out non-destructive examinations (NOE).

To assess a case of extensive deterioration from CLSCC in austenitic stainless steel reactor vessels that operated at ambient temperature. This part of the work included metallurgical testing and an engineering critical assessment of the reactors' structural integrity.

To review NDE techniques for detecting and sizing CLSCC based on trials carried out by Mitsui-Babcock with samples from one of the reactors.

To review literature on published cases of CLSCC at near ambient temperatures and of factors affecting the mechanism of CLSCC. The purpose of the review was to assess published data as a basis for control measures and for RBI decisions in the management of CLSCC.

Recommendations for assessing,,susceptibiltiy to CL CC

The susceptibility to CL CC ls. ustfa yll ssessed on the basis of chloride content, pH and temperature. In our view there ¥e additional factors that should be taken into account when assessing the susceptibility with both new and existing pipework or vessels that have accumulated significant service. These include:

- Operation involves high temperature excursions. Susceptibility should be determined by the highest temperature reiiched during any part of duty or maintenance operations, irrespective of the duration of the excursion .
- Liquid can dry out allowing chlorides to concentrate orform chloride -rich solid films.
- Pitting and/or crevice corrosion already exist.
- The steel was manufactured before 1970 with possible higher levels of impurities.
- Possibility of sensitisation.
- Free machining grades.
- Surface finish has deteriorated since manufacture.
- Iron contamination of surfaces.
- Welding during manufacture, modification and repair.

- Design or manufacturing details where chlorides can accumulate, e.g. roots of partial penetration welds.

- Operation causes stress cycles.

It is recommended that susceptibility to CLSCC is assessed by extending the API 581 approach to take account of these factors. A flow diagram for the proposed extension of the API 581 method, and crack growth rates are suggested for susceptibility categories. These proposals are outlined in Section 2 of this report; in particular Figure 2, Table 2, Table 3 and Table 4.

Recommendations for Structural Integrity and NOE

Wrought austenitic stainless steels have high fracture toughness and for pipework and vessels Leak-Before-Break is the most likely consequence of CLSCC. Leak detection is not a reliable indicator of CLSCC because cracks are highly branched and may be filled with corrosion products. Nevertheless, it is recommended that where pipework or vessels develop leaks in service, they should always be investigated for possible CLSCC by NOE or by in-situ metallography.

CLSCC can generate very large cracks in structures where, as in the case of reactors, the residual stress from welding dominates and operational stresses are low by comparison. If undetected by NOE, the large cracks might introduce failure modes with consequences that were not anticipated by the original design, e.g. complete separation of attachments, toppling of tall columns under wind loading or collapse of long pipe runs due to self-weight.

The simplest and most effective NDE technique for detecting CLSCC is dye penetrant testing. Eddy Current Testing (ECT) is effective with purpose-designed probes that have been calibrated on known defects. ECT was found to be ineffective on the samples from the reactor due to limited penetration of the current and sensitivity to surface imperfections that could not be distinguished from cracking

Crack sizing by eddy current testing may be limited and is not possible by penetrant testing.

Ultrasonic flaw detection can be applied as a manual or an automated NOE technique for detecting CLSCC. For structures with complex design features and Welds as on the reactors, the trials indicated that ultrasonic testing would require a range of probes, several complimentary scans and be very time consuming. Ultrasonic flaw detection did not cover all design details and possible crack position orientations found on the reactor, and crack sizing was difficult.

Main findings on CLSCC in the reactors

It is likely that the following factors contributed to CLSCC in the reactors:

- Residual stress from fabrication and welding

- A rough surface finish leading to a long period of slow localised corrosion.

- Initiation of CLSCC on the process side when the depth of corrosion pitting was - 1mm.

- Short periods of rapid crack growth when the temperature 60°C during the cleaning cycles.

- Long periods of very slow crack growth at the normal reactor operating temperature.

- Periodic reactivation of cracking due to low frequency load cycles and the temperature excursions during cleaning.

From the Literature Review

CLSCC initiates from sites of localised pitting or crevice corrosion. CLSCC propagation occurs when cracks grow more quickly from the pit or crevice than the rate of corrosion.

The initiation of CLSCC has been shown to involve a competition between localised corrosion, which is strongly dependent on chloride concentration but has a weak dependence on temperature, and crack growth which has a strong dependence on temperature but is relatively unaffected by chloride concentration and pH.

It follows from the competition approach that environmental factors, which affect localised corrosion, are also likely to affect the initiation of CLSCC. Furthermore, it also follows that more severe conditions will be required to initiate CLSCC than are needed to sustain crack growth. Recent work has clearly shown that CLSCC crack growth can be sustained at a chloride concentration and temperature significantly below those required to initiate cracking.

There is a large amount of published work on various aspects of CLSCC in austenitic stainless steels. However, no data were found that could be used to predict the time required for crack initiation by localised corrosion in real structures.

Fracture mechanics tests have shown that CLSCC propagation can begin at low stress intensities in the range 2MPa.m ^{05} to 10MPa.m$^{0\ 5}$. For fabricated structures containing tensile residual stresses, the critical depth oflocalised corrosion to initiate CLSCC would be <Imm.

The rate of crack propagation is strongly dependent on temperature but is relatively unaffected by stress intensity. Rates of CLSCC propagation can vary from 0.6mm.yr"^{1} at near ambient temperatures to >30mm.yr-^{1} at temperatures -100°c. In laboratory tests CLSCC has been observed in samples at temperatures between 25°C and 40°C.

The majority of the reported practical instances of CLSCC have occurred where temperatures 60°C. However, a significant number of failures below 60°C have also been reported although in these instances there appear to have been other contributory factors which include:

- The use of highly cold worked and/or free-machining grades.

- Iron contamination of the surface.

- The presence of a highly corrosive film containing chloride compounds.

1 INTRODUCTION

1.1 BACKGROUND

Chloride stress corrosion cracking (CLSCC) is one the most common reasons why austenitic stainless steel pipework and vessels deteriorate in the chemical processing and petrochemical industries. Deterioration by CLSCC can lead to failures that have the potential to release stored energy and/or hazardous substaqces. Failures of plant can be prevented by an awareness of the onset and evolution of CLSCC, and by periodic inspection to monitor the extent of cracking. Although the deterior tion of austenitic stainless steels by CLSCC is well known, recent incidents and inspection visits by HSE have found that susceptibility assessments were inconsistent and did not always take account of current knowledge. Discussions between HSE, dutyholders and competent bodies identified that the technical justification for setting inspection intervals and the effectiveness of periodic non-destructive examination (NDE) for monitoring CLSCC were additional areas of concern.

This report describes work carried out for Mr R Breen, Principal Inspector for Mechanical Engineering in the Hazardous Industries Directorate of the Health and Safety Inspectorate. The report is in five parts:

- Section 1 gives the background for this work and an overview of the mechanism of CLSCC
- Section 2 gives the authors' conclusions and recommendations for assessing susceptibility to CLSCC. These include applying RBI, setting inspection intervals, structural integrity corrsiderationsand NDE.
- Section 3 summarises findings *ftoin* a metallurgical investigation into extensive deterioration from (CLSCC) in austenitic stainless steel reactor vessels that operated at ambient temperature. This includes an engineering assessment of the reactor structural integrity. The results from the laboratory examination are in Appendix 1 and the engineering assessment is in Appendix 2.
- Section 4 is a short review of non-destructive testing techniques for detecting CLSCC in thin-walled austenitic stainless steel vessels with complex design and welded details. This includes the results ofNDE trials carried out by Mitsui-Babcock on samples from two of the failed reactors.
- Section 5 is a literature review of published cases of CLSCC at near ambient temperatures and of factors that affect the mechanism. the purpose of the review was to assess published data as a basis for control measures and risk based inspection (RBI) decisions in the management of CLSCC.

Austenitic stainless steel pipework and vessels are particularly vulnerable to CLSCC if they are covered with an insulation material that contains moisture, i.e. conditions that normally cause corrosion under insulation (CUI) of carbon and low alloy steels. This report is primarily concerned with CLSCC from the process environment and from the outside due to the external environment where no insulation material is involved. Nevertheless, some comparisons will be made between CLSCC of insulated and un-insulated austenitic stainless steel.

1.2 AUSTENITIC STAINLESS STEEL

Austenitic stainless steels are iron-based alloys that contain nominally 19% chromium and 9% nickel. As implied by the name, austenite is the predominant microstructural phase in austenitic stainless steels at room temperature. The chemical composition can be varied, for example by lowering the carbon content, and by adding titanium, niobium or tantalum to prevent carbide formation[1], or by adding molybdenum to increase resistance to localised corrosion. Table 1 lists the grades of austenitic stainless steels that are most widely used in chemical processing. Table 1 is not an exhaustive list and the grade designations are closest matches based on chemical composition rather than exact equivalents. For the purposes of this report, the American Iron and Steel Institute numbering system has been used when referring generally to a grade.

AISI	*Euronorm*	*DIN*	*British Standard*	*Description*
304	1.4301	X5CrNi18-10	304S31	The general-purpose grade, widely used where good formability and corrosion resistance are required.
304L	1.4306	X2CrNi19-11	304S11	As 304 but with lower carbon content to minimise carbide precipitation during welding.
301 & 302	1.4310	X12CrNi18 10	301S21	Higher strength versions of 304 that are often cold worked to give higher strength.
303 & 303Se	1.4305	X10CrNiS18-9	303S31	General purpose grades with sulphur or selenium added to improve machinability
321	1.4541	X6CrNiTi18-10	321S12 321S31	As 304 with an addition of titanium to prevent carbide precipitation during welding.
347	1.4450	X6CrNiNb18-10	347S31	As 304 with addition of niobium and or tantalum to prevent carbide precipitation during welding.
316	1.4401	X5CrNiMo17-12-2	316S31	As 304 but with molybdenum added to increase resistance to localised corrosion in marine and chemical environments.
316L	1.4404	X2CrNiMo17-13-2	316S11	As 316 but with lower carbon content to minimise carbide precipitation during welding.

Table 1 Grades of austenitic stainless steel most widely used in chemical plant.

1.3 CLSCC MECHANISM

The mechanism of CLSCC is complex and the current understanding is discussed in Section 5 of this report. Essentially CLSCC involves a combination of the electrochemistry of metal dissolving over a highly localised area, i.e. at the base of a pit or crevice, and microstructural

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[1] *The formation of chromium carbide or other complex carbides at grain boundaries in austenitic stainless steels causes a loss of corrosion resistance and increased susceptibility to intergranular corrosion. Carbides are formed when austenitic stainless is exposed to temperatures between 450°C and 800°C. This phenomenon is known as* ***'sensitisation'.*** *Further information on sensitisation is in Section 5.6.3.*

processes that separate the metal structure "in a region of highly localised plastic strain, i.e. at the crack tip. A detailed review of candidate mechanisms is set out.in the literature survey. For the purposes of this report, the mechanism will be described simply in terms of an *initiation stage,* dominated by electrochemical mechanisms, and a *crack propagation* stage in which both electrochemistry and metal separation are involved.

The high corrosion resistance of austenitic stainless steels in most atmospheric and aqueous environments is due to passivation by a thin (-2nm)° layer of chromium oxide [2]. Wet and humid environments containing chloride ions can cause pitting corrosion and crevice corrosion of austenitic stainless steel components. Components under an applied or residual stress can deteriorate further by stress corrosion cracking in these conditions. Pitting is simply a breakdown of the chromium oxide layer followed by localised corrosion that produces pits, which may cause perforation of a vessel or pipework. Pitting is mainly associated with microscopic heterogeneities in a surface rather than macroscopic physical features of a component. Crevice corrosion is also a breakdown of the chromium oxide layer followed by localised corrosion but in contrast to pitting, it occurs at specific physical features where a surface is partly shielded and stagnant solution exists at an interface with the shielded area.

Where pitting or crevice corrosion causes localised metal loss, the geometry and the local environment are critical in ensuring that metal loss becomes self-sustaining. Localised corrosion: in an active pit or inside a crevice produces a solution with the following characteristics.

(i) Higher chloride level than the bulk solution because negatively charged chloride ions migrate into the pit to balance the positively charged metal ions.

(ii) Strongly acidic with a very low pH (-0).

(iii) Nearly saturated with complex ions produced from dissolved metal, chloride and water.

This demonstrates an essential feature of localised corrosion on stainless steels, i.e. the region inside a pit, a crevice or a crack is an isolated electrochemical cell that contains a much more aggressive environment than the bulk solution.

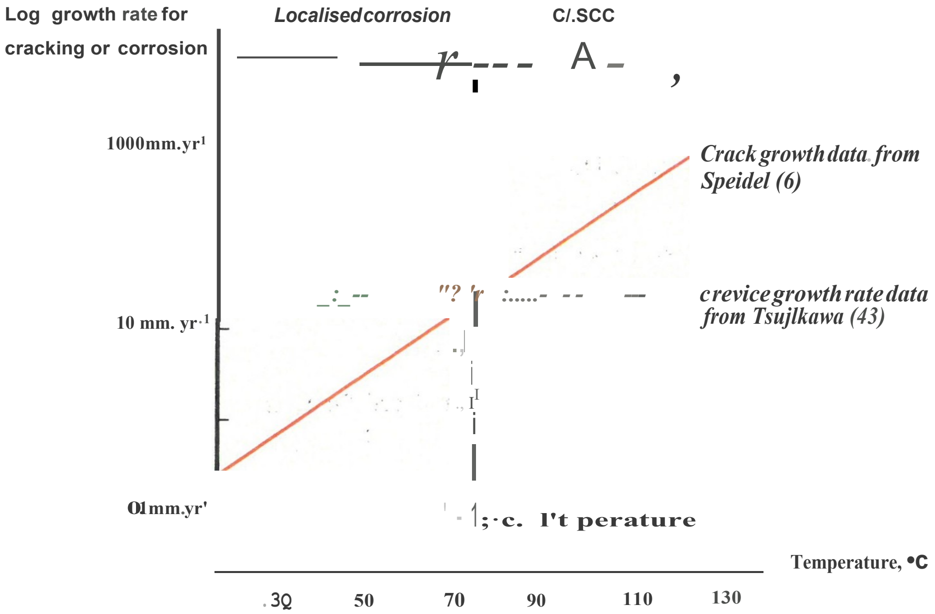
It is commonly accepted that CLSCC initiates from sites of active pitting or crevice corrosion [2] and therefore, cracks are considered to grow in the high chloride, strongly acidic, near-saturated solution that develops at sites of localised corrosion. One theory [43] proposes that CLSCC only occurs when a crack grows more quickly than the rate of metal removal by localised corrosion from the base of a crevice or pit; in other words there is a competition between the rate of CLSCC and the rate of localised corrosion. Crack growth is also restricted to a range of electrochemical potential that is defined by an upper limit where dissolution exceeds crack growth and a lower limit set by re-passivation. This approach has been used by Tsujikawa to demonstrate a temperature dependency of CLSCC because crack growth increases more rapidly with temperature than the rate of localised corrosion. Figure I is a schematic description of Tsujkawa's theory. In our opinion, the competition theory reinforces the fact that localised corrosion is a prerequisite for CLSCC propagation in austenitic stainless steels. Stress corrosion tests carried out by Tsujikawa and recent tests carried at HSL [77] have confirmed that it is very difficult to initiate CLSCC on bare, smooth specimens under laboratory conditions when there is no localised corrosion of the surface under stress.

The susceptibility of austenitic stainless steels to CLSCC depends on a range of environmental vai:iables that include chloride concentration; temperature and pH. Other variables include, for example, stress level, surface finish and the metallurgicalco11ditior1 of the steel. The approach in this report is therefore based on assessing how variables are likely to affect:

(i) The initiation of CLSCC by localised corrosion.

(ii) Crack propagation when the rate of CLSCC exceeds the rate of localised corrosion.

Figure 1. Schematic graph to demonstrate the competition concept proposed by Tsujikawa [43]. Note how changes in crack growth rate or corrosion rate can alter the 'critical' temperature for CLSCC.



Note that Tsujikawa foun<;l that the 'critical' temperature could range from 42°C to 130°C by varying the phosphorus anq coppe.r levels in the steel.

1.4 FACTORS AFFECTING CLSCC

A range of environmental factors have been identified that can affect the development of CLSCC which include chloride content, temperature, pH and contact with dissimilar metals. Recent work has also identified the importance of transient conditions such as high temperature excursions. Alloying element content, impurity levels and the degree of cold working are factors that affect the intrinsic resistance of a particular austenitic stainless steel to CLSCC. A significant volume of literature has been published on how CLSCC is affected by environmental factors and by the factors affecting the resistance of specific grades. Part of this work has been to review published literature to assess the range of factors involved including:

Temperature, pH, chloride content, oxygen level humidity

Electrode potential effects, e.g. galvanic coupling and cathodic protection.

Applied and residual stress

Alloying and impurities in the steel

Sensitisation

Cyclic conditions

1.5 CONTROLLING CLSCC

The main options for preventing or controlling CLSCC are management of chloride levels, temperature, and pH. Inhibitors can also be effective where the process allows it. As noted above, electrode potential has a major effect on CLSCC susceptibility and while positive potentials increase cracking, lowering the potential can prevent cracking by cathodic protection [29]. Wrapping with aluminium foil or coating with thermally sprayed aluminium are established techniques for preventing external CLSCC when the pipework or vessels are insulated [76]. Austenitic stainless steel heat exchanger tubes are also thought to be cathodically protected from pitting and CLSCC when used with carbon steel tube plates and shells [51].

When components are designed, the susceptibility ofCLSCC can be reduced by choosing more resistant alloys and by lowering the stress. Alloys with greater resistance to CLSCC include ferritic and duplex (austenitic-ferritic) stainless steels, and alloys containing >42% nickel. Resistance to CLSCC is usually assessed by ranking alloys on their performance in accelerated tests using conditions that promote cracking. The three most common tests, in order of increasing severity, are boiling acidified sodium chloride, evaporation of sodium chloride using droplets or a wick on a heated surface, and boiling magnesium chloride. Even high alloy grades of austenitic and duplex stainless steel containing >22% chromium and >5% molybdenum can crack in less than 24 hours when tested in boiling magnesium chloride [74]. It should be recognised, however, that while duplex grades and highly alloyed grades are more resistant than the common austenitic types, they might not be immune to CLSCC under severe conditions, e.g. where chloride solutions evaporate[37].

Stress in components can be lowered by down rating working pressures, but where pipe work and vessels are fabricated by welding, there is likely to be residual stress (with a magnitude approximately equal to the parent metal proof stress) from welding. Residual stresses may also arise from cold working during manufacture. A stress relief heat-treatment can lower residual stress but its application is often limited by concerns over distortion, surface finish and sensitisation

2 RECOMMENDATIONS

2.1 ASSESSING SUSCEPTIBILITY TO CLSCC

Susceptibility to CLSCC is usually assessed from knowledge of environmental variables, i.e. temperature, chloride content, temperature, pH and oxygen level (60). Some sources give a maximum temperature (typically -50°C) and/or chloride concentrations to define conditions that lead to CLSCC and conditions that do not (81). Tsujikawa (43] has successfully demonstrated a critical temperature for CLSCC in laboratory tests and described a competition theory to explain it, Figure 1. The competition theory states simply that crack propagation does not occur below the critical temperature because crack growth is outpaced by crevice corrosion or pitting. Another way of viewing the competition is that crevice corrosion blunts a crack tip more rapidly than it can be kept sharp with sufficient strain concentration to maintain crack growth.

Tsujikawa also showed how the critical temperature can be raised and lowered by factors that affect crack propagation and/or crevice corrosion. Our review of the practical cases of CLSCC and the literature shows that CLSCC can and does occur at near ambient temperatures. Compared with temperatures >60°C, however, it would appear that near ambient temperature CLSCC is slower and that conditions needed to sustain cracking are more specific. At first sight, CLSCC at near ambient temperatures would appear to contradict the competition principle. Tsujikawa used a crevice geometry that remained sharp and produced a rate of localised corrosion that was constant with time. However, real structures and components are unlikely to have the same severe crevice geometry and it is reasonable to expect that localised corrosion will slow down with time as a practical crevice deepens and the diffusion distance lengthens. In fact numerical models of pits in austenitic stainless steel, supported by measurements with miniature electrodes, have shown that the depth of a hemispherical corrosion pit increases as time^{05} [76). Furthermore, as an area of local corroded area deepens, the stress intensity factor will also rise and increase the crack growth rate. Applying Tsujikawa's competition principle, therefore, the likelihood of CLSCC propagation from an area of localised corrosion should increase with time as the depth of metal loss increases. More importantly, however, this reasoning suggests that when CLSCC propagation is underway, i.e. metal separation is faster than localised corrosion; it will become increasingly difficult to arrest a crack by blunting the crack tip. Turnbull's recent study of temperature excursions (23) gives some support to this reasoning and to the corollary that crack growth can continue under less severe conditions (i.e. lower temperatures and lower chloride contents) than were required to initiate cracking.

In our opinion, therefore, temperature should be seen as a key indicator for susceptibility to CLSCC rather than as a precise threshold below which it can be safely assumed CLSCC will not occur. We recommend that additional factors should be taken into account when assessing the susceptibility of CLSCC based on service temperature, chloride content, pH and oxygen level. The recommendations apply to new plant and particularly to existing pipework and plant that have accumulated significant service. These factors include:

(i) Temperature excursions. Susceptibility should be assessed from the highest temperature reached during any part of duty or maintenance operations, irrespective of the duration of the high temperature excursion.

(ii) Formation of chloride-rich layers by evaporation or deposition.

(iii) Evidence that pitting and/or crevice corrosion already exists.

(iv) Steel manufactured before 1970 with possible higher levels of impurities.

(v) Possibility of sensitisation

(vi) Heavily cold worked and/or free machining grades of steel

(vii) Mechanical deterioration of surface finish

(viii) Iron contamination of surfaces

(ix) Welding during manufacture, modification and repair.

(x) Design features that trap water and may allow chloride concentration when plant is nominally dry, e.g. roots of partial penetration welds.

We recommend that CLSCC susceptibility is assessed by extending the API RP 581 *'Risk-Based Inspection Technology'* [60] approach to take account of these factors and in particular the cases of cracking that have been reported at ambient temperatures. A flow diagram for the proposed extension of the approach in API RP 581 Part 2 is shown in Figure 2. Key features of this proposal are:

(i) Initial assessment based on the highest temperature experienced during any stage in the vessel/pipework history, including short-term excursions rather than the nominal operating temperature, see Table 2.

(ii) Introduction of additional categories for ambient temperature and for conditions where a deposit may form or liquid may evaporate.

(iii) Increasing the initial susceptibility category from low to medium or medium to high where other factors are taken into account as proposed in Table 3.

(iv) Using typical crack growth rates from the literature as a basis for setting inspection intervals, Table 4.

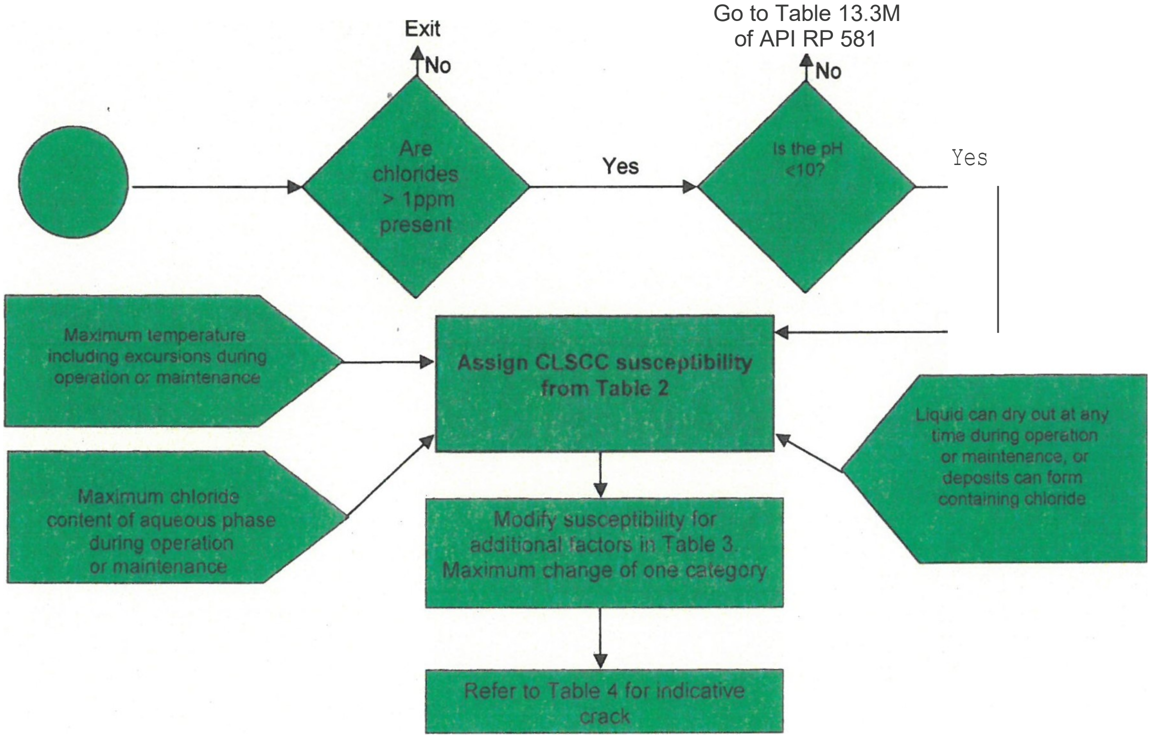


Figure 2. Proposed extension of susceptibility assessment for CLSCC in API RP 581(2008), Part 2, section 13.

Table 2. Proposed scheme for CLSCC susceptibility categories in aqueous media where pH :S 10, and in conditions where chloride deposits may form by drying out or by deposition. (The scheme is derived from Table 13.3M in API RP 581.(2008)., with the API v;:ilues shown in blue.)

1'e,nJJerature, °c;	*C:hloride concentration,JJJJm*				
	I to 10	iit ioo	IOI to 1000	>1000	Drying out / deposition
					High
					High
					High
					High

Note: The pH, temperature, chloride concentration and drying out/deposition rankings should be based on the worst-case scenario including up-set conditions and short-term excursions during operation, shut down, or: maintenance.

Table 3. Change in susceptibility category for additional factors.

Increase susceJJtibility category	*Decreas susceJJtibility category*
Sensitisation is likely	Coating or wrapping with aluminium foil
History of progressive cracking Wher mode has not been established	Contirnim.i co trol ofchloride level, pH, or temperature during all operational and non-operational periods.
Poor surface finish	tontinuo s dosing with appropriate corrosion inhibitor during all operational and non-operational periods.
Surface contamination with iron	
Steel manufactured before 1970	
Highly cold worked and/or free-machining steel	
Pits and/or crevice corrosion already exist	
Crevice-like design features, e.g. roots of partial penetration welds	
Galvanic coupling to a more noble metal	
Cyclic conditions - temperature or stress	

Note: The susceptibility category should be changed by a maximum of one category.

Table 4. Suggested CLSCC propagation rates for determining inspection intervals

Susceptibility *category*	***Crack growth rate,*** *mm.yr1*	***m.s·I***
Low	0.6	1.8x 10-11
Medium	>0.6 and <30	>1.8 :x $10^{\cdot 11}$ and <$10^{\cdot 9}$
High	>30	>10^{9}

Notes for Table 4:

(i) Crack growth rates can vary by more than the factor of 50 given here. It is also important to recognise that while cracks can propagate rapidly under conditions classified as high susceptibility, it is possible for cracks to grow slowly to a structurally damaging size over long periods of service under conditions classified as low susceptibility.

With present knowledge of CLSCC, it is npt possible to predict the time required for crack initiation from a smooth surface. In fact the time to initiate CLSCC probably depends on factors similar to those that affect crack growth rat!:). For low susceptibility conditions, a crack growth rate of 0.6mm.yr$^{\cdot 1}$ is likely to underestimate crack initiation time and give conservative inspection intervals. There is *some* evidence to suggestthat initiation times can be relatively short with high chloride concentrations and temperatures > 80° .

2.2 STRUCTURAL INTEGRITY ASSESSMENT

In general, wrought austenitic stainless steels have high fracture toughness with a very low susceptibility of brittle fracture down to cryogenic temperatures. Fracture toughness is also usually high in austenitic weld metal and weld heat affected zones, as was found in the laboratory examination of the reactor described in Appendix I of this report. Austenitic components and structures can therefore remain stable when they contain large through-wall defects generated by CLSCC (>100mm in the case of the reactor). Clearly, for pipework and vessels Leak-Before-Break (LBB) is the most likely consequence of CLSCC. Note that a plausible but less likely failure mode would arise if pressures/stresses were high and cracks reached a critical size for rapid ductile failure before LBB. It is recommended, therefore, that through-wall leaks developing in service with austenitic stainless pipework or vessels should always be investigated for possible CLSCC by NOE or by in-situ metallography. It is also important to recognise that leakage is not a reliable indicator of either the presence or the size of through-wall cracks because cracks formed by CLSCC tend to be narrow and highly branched. The quantity of the fluid that escapes from a crack will also depend on its viscosity and the pressure difference. Furthermore, leakage into the process stream (e.g. coolant leaking into reactants) could be more difficult to detect than a visible escape of liquid or audible escape of gas.

When CLSCC is a recognised mode of deterioration for a vessel or pipework, the absence of leakage does not guarantee that cracks are not present; and in particular, it does not obviate a requirement for periodic NDE. The reactor investigated in this work contained numerous very long, through thickness cracks as a result of CLSCC. Its structural integrity had been seriously compromised to the extent that soine nozzles and attachments appeared to be close to full separation under static loading from the reactor. body. This demonstrates that very large cracks can form by CLSCC in structures whereas in the case of the reactors, the dominant stress was residual stress from welding and operational stresses would have been low by comparison. If undetected by NDE, the large cracks can introduce failure tnodes which were not anticipated by the original design, for example complete separation of attachments, toppling of tall columns under wind loading and collapse of long pipe runs due to self-weight.

2.3 NON-DESTRUCTIVE EXAMINATION

The simplest and most common manual NDE technique for detecting CLSCC in austenitc stainless steel is dye penetrant testing (PT). This' method requires that a surface under inspection is clean, accessible and visible to the inspector [82]. Disadvantagesof PT in detecting CLSCC are:

(i) A high standard of surface cleanliness is required and it is relatively slow.

(ii) Cracks must break thesurface being inspected.

(iii) It can be difficult to differentiate cracks from volumetric defects such as corrosion pits or welding pores.

Where both surfaces can be inspected , the effectiveness of PT in finding through-wall CLSCC can be increased by applying dye penetrant to one surface and developer to the opposite surface [80]. PT can be effective in locating CLSCC but sizing through thickness cracks will not be possible unless both surfaces can be inspected.

Eddy current testing (ECT) is also a common NDE technique which can be applied manually and automatically for detecting CLSCC. It can be particularly effective when automated with purpose-designed probes that have been calibrated on test samples containing known defects. ECT is used for heat exchanger tubing and pipework where the surface condition and geometry are fairly consistent over long distances [83). The disadvantage of ECT is that it will only find surface breaking cracks and cracks just below the surface. In other words the penetration is limited in steels [25) and it is most effective when testing surfaces from which cracks have initiated rather than the opposing surface. Crack sizing by ECT will be limited in the through thickness direction.

Ultrasonic flaw detection (UT) of fabricated and welded austenitic stainless steel requires a specialised technique because weld metals are coarse grained and this causes high sound attenuation and false signals. Normal methods of UT, for !;lXample as covered by BS EN 1714:1998 *"Non-destructive testing of welds - Ultrasonictesting of welded joints" ,* are normally based on ferritic materials. An appropriate UT procedure for austenitic stainless steel can be applied as a manual or an automated NDE technique for detecting CLSCC. Providing access is available, UT can be applied to a surface from which cracks have initiated and/or from the opposing surface. If accurate drawings are available and an appropriate technique is used, UT may be capable of obtaining information on the crack size and orientation.

The reactor that was studied as part of this work was fabricated from 5mm to 7mm thick material d CLSCC was found in a range of welded details, As described in Section 4 of this report, Mitsui-Babcock compared the effectiveness of PT, ECT and UT on samples cut from the reactor [25). The conclusions of the report were:

ECT using standard and purpose designed probes had limited penetration and significant sensitivity to surface imperfection that could not be distinguished from cracking.

2 Manual UT was more promising but the procedure required qualified personnel, a range of probes, and several complimentary scans. The procedure was considered to be very time consuming and would not cover all design details and possible crack position orientations found on the reactor. Sizing of defects was found to be difficult due to access limitations.

3 PT was the recommended method of NDE.

3 CRACKING Of THE REACTORS

3.1 HISTORY

Interest in the degradation of austenitic stainless steels by CLSCC was raised by the condition of reactor vessels at a chemical manufacturing facility. The vessel of most interest had been manufactured from grade 321S12 austenitic stainless steel. A hydraulic test at 40 psig was carried out in 002 when the vessel had been in service for approximately 24 years. The hydraulic test revealed that the vessel was found to be leaking. NDE revealed extensive cracking, with many instances of through-wall cracking around a significant proportion of the circumference of welded nozzles. A laboratory examination of the failed vessel confirmed that the cracks were branched and transgranular, characteristic of CLSCC [28].

It was reported that the vessel had been manufactured to BS 1515:1968 *"Fusion welded pressure vessels for use in the chemical, petroleum and allied industries"*. Note BS 5500:1976 *"Unfired fasion welded pressure vessels"* superseded BS 1515:1968.

3.1.1 Reactor duty cycle and environment

The reactor vessel had been used for an ambient temperature, batch process chemical reaction. The reactants contained chloride and the vessel operating temperature during the reaction was given as between 11°C and 21°C. According to the operator, the variation in vessel temperature was caused by ambient temperature changes in the works building and not from any exothermic/endothermic aspects of the reaction.

Approximately once a week the vessel was cleaned for between 2 hours and 3 hours, using either cooling water heated with steam or more usually CHP condensate. The temperature during cleaning was given as approximately 70°C to 7 °C. The vessel was also cleaned once or twice a year with sodium hydroxide, at a maximum of 12% concentration, and at a temperature of 85°c to 99°c. Again, a cleaning time of between 2 hours and 3 hours was used.

When in normal operation, the vessel pressure cycled from 10 psig to vacuum and there could be up to 25 pressure/vacuum cycles per day. It was estimated that the vessel had been in service for approximately 24 years and would have experienced approximately 150,000 pressure/vacuum cycles and approximately 1,300 higher temperature cleaning cycles.

From the information supplied, the majority (98.2%) of the vessel life was under vacuum at an operating temperature of 11°C to 21°C. In terms of total service therefore, the vessel operated at a temperature between 70°C and 90°C and atmospheric pressure for only **1.8%** of its life.

3.1.2 Metallurgical assessment

The results of the metallurgical assessment are in Appendix 1. The investigation revealed that the microstructure, chemical analysis and tensile strength of the reactor material were all consistent with the specified 321S12 grade material. There was extensive transgranular cracking, characteristic of CLSCC, and localised corrosion. Metallographic examination revealed no evidence of sensitisation.

3.2 DISCUSSION OF.CLSCC IN,THI; ,REACTORS

The traditional engineering view is that transgranular CLSCC does not normally occur in solutions of near-neutral pH below a temperature of 60°C (29] unless the steel is in a sensitised condition, in which case, intergranular cracking can occur at temperatures approaching ambient. According to the metallurgical report from the company's insurer (28], cracks were found to be branched and transgranular, which is consistent with CLSCC propagation 60°C. One of the constituents in the reaction was described ,as cbntaining chloride but the concentration of chloride ions was not stated. The cleaning cycles used steam and/or condensate with low levels of chloride. Cracking of the reactor poses the question of whether CLSCC occurred during the reactor operation between 11°c and 21°c , during the cleaning cycles 60°C, or during both stages?

3.2.1 Rate of degradation

As discussed in Section 1.3, sites of crevice corrosion or pitting are necessary to initiate CLSCC. It seems reasonable to suppose, therefore, that cracking of the reactors involved an initial period of localised corrosion followed by a period of crack growth. Rates of crevice corrosion and pitting can be rapiq at the start but they ten d t o decrease as the site of corrosion enlarges and the distance for outward diffusion of metal ions lengthens. According to the Co mpetition theory; the transition between localised COtrosion and crack propagation OCClirS at a growth rate of - 10mm.yr^{1}. In fracture mechanics tehns, an area of localised corrosion would - have to become large enough such that the stress intensity exceeded the critical threshold, K1scc, for CLSCC. Crack growth thresholds for CLSCC in austenitic stainless steels are quoted (6, 23, 29] as ranging from 1 MPa.m^{05} to 30MPa.m^{05} • If iocalised corrosion is considered as a surface breaking crack to estimate its stress intensity, the depth of corrosion would have to lie between 0.8mm to 3rhm for K> K_{1}scc; assuming thatthere was :...290 MPa residual tensile stress from welding and/or fabrication. *bn* this basis, therefore; it is possible that sufficient depth of localised corrosion could have existe din the reactor after the first year of service. This analysis is probably a considerable oversimplification becallse pitting and crevice corrosion are stochastic, and as -discussed above, the rate at which pits or crevices deepen is likely to become slower with time. Nevertheless, it demonstrates that localised corrosion and the conditions required for CLSCC propagation could have developed relatively early iri the service life of the reactor.

The rate at which cracks propagate by CLSCC has been found to vary by a factor of approximately 500. For example, laboratory tests with pre-cracked specimens have obtained CLSCC growth rates ranging from - 300mm'.yr^{1} to - 0.6 inm.yr"^{1}. The highest gro rate was measured by Speidel (6] in high chloride concentrations and at high temperatures (90°C to 110°C), whereas the lowest rate was found for a low chloride concentration and a temperature of 40°C by Turnbull [23]. However even if cracks propagated at the slowest rate of 0.6mm.yr"^{1} over the full 24 years service, it is quite feasible that CLSCC could have grown through the vessel wall thickness (- 6mm) in that time. An alternative scenario is for a higher rate of CLSCC propagation to have caused crack extension through the full wall thickness during the high temperatur cleaning cycles. For example the accumulative time of the cleaning cycles is approximate,ly 6 months out of the 24 years reactor service. Crack growth at - 12mm.yr^{1} would therefore have been required if propagation only occurred during the cleaning cycles. This rate is towards the upper end of the crack growth rate range found in laboratory tests for high chloride concentrations and temperatures >90°C. It is also possible that fatigue cracking, due to the - 150,000 pressure/vacuum cycles that the reactor would have experienced, could have contributed to the failure.

3.2.2 Non-Destructive Examination

It is our understanding that the reactor vessels had been examined periodically by NDE using dye penetrant testing. The effectiveness of this technique, of ultrasonic flaw detection and of eddy current testing in the detection of CLSCC were investigated by Mitsui-Babcock using samples cut from the reactor vessels, Section 4. The Mitsui-Babcock report (25] gives an assessment of the effectiveness and limitations of the three inspection techniques. The report also gives recommended procedures for detecting CLSCC in welded thin wall, austenitic stainless steel vessels like the reactors.

3.2.3 Structural integrity

Cracking in the reactor vessel was found to be extensive. Through-wall cracks were found around three nozzles in the vessel base; in two cases the cracks extended around $^{2}/_{3}$rds of the circumference. There were also four positions of through-wall cracking on the top main circumferential seam. It was considered that the structural integrity of the vessel was severely compromised.

4 AN ASSESSMENT OF NDE TECHNIQUES FOR CLSCC

4.1 BACKGROUND

The assessment of NDE techniques was carried out on two reactors by Mitsui-Babcock. The aim of the work was to identify techniques for detecting CLSCC in austenitic stainless steel vessels with the fabrication details and wall thickness found in the reactors. Given the location of the cracking, NDE techniques were required that could be used for cracks lying in the surface being inspected and also for cracks in the opposite face.

4.2 CONCLUSIONS FROM THE NOE ASSESSMENT

The Mitsui-Babcock conclusions as given in Section 2.3 were:

- Eddy current testing was not recommended due to the lack of penetration and significant sensitivity to surface imperfections.
- Manual ultrasonic testing was more promising but the procedure required qualified personnel, a range of probe types and several complimentary scans. The procedure was likely to be very time consuming and would not cover all the vessel and nozzle details. Sizing of defects would be difficult due to the access limitations.
- Dye penetrant testing was recommended.

4.3 OVERVIEW OF NOE ISSUES FOR CLSCC

The assessment by Mitsui-Babcock showed that the sizing and detection of cracks from CLSCC can be difficult using eddy current testing where a structure has complicated design features and a rough surface. The manufacture of test pieces and special probes may need to be considered in similar circumstances. Eddy current testing is routinely applied to detect CLSCC in components that are of relatively simple shape and regular geometry, for example long runs of pipework and large diameter vessels where welds have been dressed flush.

The procedure developed for detecting CLSCC in the reactors was complicated and had some limitations due to the geometry of the design features and access. However, the general principles of using qualified technicians, multiple probes, complimentary scans and test pieces that accurately represent the design under inspection are likely to be needed in similar circumstances.

Cracks produced by CLSCC are often tight and filled with corrosion products so that dye penetrant may not be effective in all circumstances. It has been reported [80) that when through-thickness cracking is suspected in thin wall thicknesses, the effectiveness of dye penetrant testing can be improved by applying dye to the internal surface and the developer on the external surface.

The findings from the work carried out by Mitsui-Babcock, Section 4.2, indicate the range of issues that must be considered in selecting and applying different NDE techniques to detect CLSCC in fabrications with complex design details.

5 LITERATURE REVIEW

5.1 CURRENT UNDERSTANDING OF THE CLSCC MECHANISM

CLSCC requires the presence of a residual or applied tensile stress and the presence of chloride ions under specific environmental conditions. Cracks form and propagate with time at approximately right angles to the direction of the tensile stress. Cracks propagate at stress levels much lower than those required to cause normal tensile failure. Cracks that run across the grain boundaries are called "transgranular" and those that follow the grain boundary and are termed " intergranular". CLSCC normally progresses until the remaining ligament of material separates by ductile overload fracture. Hence the fracture surface will contain both areas of brittle fracture that are characteristic of CLSCC as well as microvoid coalescence .

The initiation of CLSCC by localised .corrosion is widely accepted [2, 37, 43] but the mechanism of crack propagation is complicated and not yet fully understood. Most authors accept that crack propagation involves a combination of electrochemistry, whereby metal dissolves over a highly localised area, and atomistic processes that fracture the metal structure. Possible mechanisms for CLSCC include:

Metal removal by:
  (a) Strain 'Or slip-ste p accelerated dissolution
  (b) Brittle film rupture
  (c) A combination of(a) and (b)

Metal separation by:
  (a) Hydrogen embrittlemeni
  (b) Adsorption

Reviews of candidate mechanisms for CLSCC propagation have bee n published[29, 37] but a detailed evaluation is outside the scope of this rep'oit. Newman {lnd Cottis [37] have given a critical review of current models and provided arguments in favour of a discontinuous model of metal separation, which involves periodic film-induced cleavage. This model involves the formation of a thin de-alloyed layer which is rich in nickel, and which periodically nucleates fracture.

As might be expected,therefore, any descriptionof the mecbanism of CLSCC propagation stage should be based on electrochemical and fracture mechanics considerations. It is generally accepted that the region inside a pit; a crevice or a crack is an isolated electrochemical ceUwith:

- A higher chloride level tllan the bulksolution.
- A very low pH (---0).
- N e arly saturated with complex metal ions containing chlotide and water.

Crack growth is also restricted to a narrow range of electrochemical potential. The upper limiting potential is set by the condition where localised corrosion in the crevice or pit is stimulated and metal dissolves faster than the crack growth rate. The lower limiting potential is thought to correspond to re-passivation of the internal surface of the pit or crevice where corrosion is occurring.

Clearly, CLSCC must initiate and propagate in this aggressive environment. Fracture mechanics testing has demonstrated that crack initiation can be described in terms of a critical stress intensity- factor, K_{1scc}, at a low crack propagation rate, for example Speidel [6] adopted a minimum crack growth rate of 1mm.yr^{-1} (3 x 10^{-11}m.s^{-1}). The lowest sustained rate of crack propagation was 0.6mm.yr^{-1} (1.8 x 10^{-11}m.s^{-1}) as reported by Turnbull [23].

Tsujikawa [43] has demonstrated that CLSCC only occurs when a crack grows more quickly than the rate of metal removal by localised corrosion from the base of a crevice or pit; in other words there is a competition between the rate of CLSCC and the rate of localised corrosion. This approach has been used by Tsujikawa to demonstrate a temperature dependency of CLSCC because crack growth increases more rapidly with temperature than the rate of localised corrosion. Figure 1 (Section 1) is a schematic description of Tsujikawa's theory.

The susceptibility of austenitic stainless steels to CLSCC depends on a range of environmental variables that include chloride concentration, temperature and pH. Other variables include, for example, stress level, surface finish and the metallurgical condition of the steel: The approach in this report is therefore based on assessing how variables are likely to affect:

- The initiation of CLSCC by localised corrosion.
- Crack propagation when the rate of CLSCC exceeds the rate of localised corrosion.

It is reasonable to assume that crack propagation will be possible when the pit depth attains a critical size such that the stress intensity factor, K, exceeds the critical value, K_{1scc}, for sustained crack propagation by CLSCC. However, according to the competition theory of Tsujikawa, even if $K > K_{1scc}$, a crack will only extend if the environment is such that crack growth is more rapid than the rate of localised corrosion. For the purposes of this report therefore, CLSCC propagation will be assumed to be possible when $K > K_{1scc}$ and localised corrosion is slower than crack growth. The initiation phase of CLSCC will be assumed to be defined by $K < K_{1scc}$ and/or localised corrosion is faster than crack growth. This is similar to the approach adopted by Cottis and Newman [37].

It is reasonable to expect that localised corrosion will slow down with time as a corroded area deepens and the diffusion distance lengthens. For example, numerical models of diffusion in pits in austenitic stainless steel, supported by measurements with miniature electrodes, have shown that the depth of a hemispherical pit increases as $t^{0.5}$ [78]. Furthermore, as a locally corroded area becomes deeper, the stress intensity factor will also increase and increase the crack growth rate. Applying the Tsujikawa reasoning, therefore, the likelihood of CLSCC propagation from an area of localised corrosion should increase with time as the depth of metal loss increases. More importantly, however, this reasoning suggests that once CLSCC propagation is underway, i.e. metal separation is faster than electrochemical dissolution; it will become increasingly difficult to arrest a crack by re-passivating the crack tip.

Laboratory tests with pre-cracked specimens have shown that CLSCC growth rates have a strong dependency on temperature. The highest growth rate [6] was - 300mm.yr^{-1} measured in saturated magnesium chloride concentrations at 130°C; but the lowest crack growth rate was - 0.6mm.yr^{-1} near K_{1scc} for a low chloride concentration and a temperature of 40°C [23]. Published crack growth thresholds range from 1MPa.m$^{0.5}$ to 30MPa.m$^{0.5}$. Based on the work of Spiedel and Turnbull, it should be reasonably conservative to expect typical crack growth rates to lie within the range 0.6mm.yr^{-1} to 30mm.yr^{-1} for most practical applications. The lower end of the range would represent small cracks and/or mild environments whereas the high end of the range would apply to longer cracks and more severe conditions.

Unlike the results from pre-cracked specimens, there is little quantitative data to describe the initiation phase of CLSCC by localised corrosion. Time to failure data can be produced by testing samples under constant deflection (i.e. U bend samples), constant load, or slow strain rate testing (SSRT). However all of these test use samples with smooth; bare surfaces and the time to failure results will include a period of localised corrosion to initiate cracking followed by crack growth. Platts and Adams [1] have related T_i, time to crack initiation for a sensitised 316 steel to chloride concentration with the equation:

$$T_i = 1.15\ [\text{Cl concentration}]^{-0.69}$$

The temperature and pH used in measuring crack initiation times were are not reported but it is clear that the temperature is likely to have been between 80°C and 100C. The authors used the equation to estimate that crack initiation could occur in approximately 200 hours in oxygenated water containing 12ppm chloride. It is interesting to note that if the chloride concentration was increased to 120ppm, the initiation period would reduce to 50 hours. While this equation could have wider application, no other author has attempted to predict crack initiation times for real structures in this way. In our opinion, the value of the equation is in showing that crack initiation periods at high temperatures can be very short compared with the time required for cracks to reach a significant size during the propagation stage of CLSCC.

Recent work by Turnbull [2] has added to the current understanding of the respective contributions of the initiation and propagation stages of CLSCC. Working with pre-cracked samples of grade 321 steel, it was found that once crack propagation had been initiated at 130°C, the growth rate increased when the temperature was reduced first to 60°C, and then crack growth continued after further cooling to 40°C despite reducing the chloride level to 35ppm. In the case of 316 steel, the 130°C to 60°C temperature change reduced the crack growth rate to a level that was not likely to affect structural integrity, and propagation did not continue at 40°C. While Turnbull cautions against drawing broad conclusions, the work suggests that high temperature excursions can accelerate structural deterioration of type 321 by allowing CLSCC to continue at lower temperatures.

The identification of CLSCC is normally based on the path of the cracks when viewed microscopically on a prepared section. Cracks formed by CLSCC are usually very narrow and have two characteristics, i.e. they follow a transgranular path that is relatively unaffected by grain boundaries, and there is extensive crack branching. It is possible for CLSCC to be intergranular where cracks propagate mainly along grain boundaries. Intergranular fracture usually indicates that an austenitic stainless steel is in a 'sensitised' condition. An austenitic stainless steel is described as being sensitised if a heat-treatment or welding procedure allows holding or slow cooling between 900°C and 480°C. Holding or slow cooling through this temperature range leads to chromium depletion at grain boundaries because chromium carbides are formed. Sensitisation impairs resistance to localised corrosion significantly and leads to intergranular attack in a wide variety of environments that would otherwise cause little or no metal loss.

5.2 PRACTICAL CASES OF CLSCC BELOW 60°C

It is commonly asserted that SCC does not occur in chloride environments below 60°C. One justification, based on Tujikawa's competition theory, is that below this temperature localised corrosion occurs more rapidly than crack propagation. However, exceptions do occur and there are many published instances of CLSCC at near ambient temperatures.

5.2.1 Vessels, pipes, connector and associated equipment

Jha et al [51] have reported that a number of bellows made from grade 304 were found to be leaking during pressure testing following 6 years storage at ambient temperature. The temperature and humidity were not stated. The bellows had been made from 1.3mm thick cold rolled plies that had been TIG welded to forged and machined rings. Small pinholes were found along the circumference of the weld fusion line and transgranular cracking had initiated from these pits.

Kain [66] reported ambient CLSCC of high pressure hose connectors following 18 months intermittent operation in air with an ambient temperature from 32°C to 36°C. The hoses with the cracked connectors did not carry particularly aggressive water, but from time to time were sprayed inadvertently with the supplied seawater and/or concentrated brine. The hose connectors were found to be a free machining grade such as type 302 or 303 with high sulphur contents.

Three cases of failure by CLSCC of stainless steel components exposed to ambient coastal atmospheres were reported by Gnanamoorthy [70]. The components were found to be cracked before they were put into service; The components included a sheathed heater coil, where approximately 20% out of a batch of 552 heaters were cracked. Cracking also occurred in a 10" diameter type 304 pipe and in several type 304L dished ends for vessels.

In all three cases the common causative factors were believed to be

(a) Rusting of the surface due to iron contamination
(b) Presence of chloride in coastal environment
(c) Stresses arising from fabrication or fit-up

The coastal area in which the failures occurred had a monthly temperature from 25 C to 32°C with relative humidity between 70% and 80%.

Smart [52] has reviewed two reports from Japan that gave numerous instances of CLSCC in plant and pipework that were insulated and un-insulated. Cracking was reported for cases without insulation at temperatures below 50°C and down to room temperature. Cracking was predominantly found in the heat-affected zones of welds and cold worked areas. The reports of CLSCC applied mainly to type 304 stainless and to a lesser extent to type 316, but this could have been a reflection of its less common use. It would appear, therefore, that the cracking found in these instances was mainly due to sensitisation.

The lowest reported temperature for CLSCC is -20°C in methylene chloride, although the aggressive species was considered to be almost certainly hydrochloric acid formed by hydrolysis [24].

5.2.2 Fasteners (general)

Kain [69} described several examples of CLSCC of stainless steel from Kure Beach, North Carolina. Two type 03 stainless steel nuts had cracked following 14 years service and contained numerous trans ular, branching cracks. The material had a high inclusion content suggesting that it was a high sulphur, free machining grade. Cracking was attributed to air-borne and spray-borne chlorides with cracks initiated in the threads, possibly involving crevice corrosion in the initiation stage.

Kain also described cracking of cold worked grade 30l stainless steel band clamps. He also provided information on grade 303 and 316 stainless steel studs which also suffered delayed fractures. The author conjectured that CLSCC and crevice corrosion had contributed to the failure of the studs but no further details were given.

Kain also reported on U-bend testing over a 5 year period of exposure at Kure Beach. They considered alloy composition, metallurgical processing and atmospheric sheltering. A total of 306 annealed and welded, cold worked 1/.i hard specimens and as-welded specimens were all found to resist cracking. However, exposure of furnace-sensitised material produced a high incidence of cracking in the stainless steels, but not in four higher nickel alloys. The author stated that, of the sensitised austenitic stainless steels tested, types 210, 301, 302, and 309 were most prone to intergranular CLSCC in the marine atmosphere.

Kain stated that the overwhelming body of data demonstrated CLSCC resistance of annealed and *Y4* hard austenitic stainless steels exposed to a coastal marine atmosphere. However, there were exceptions with crevices being implicated in initiating CLSCC in some stainless grades. Furnace sensitised austenitic steels as opposed to as-welded were found to be susceptible to chloride-assisted cracking even without crevice corrosion.

Sedriks [29] comments that common factors in the marine atmosphere failures included a hot, humid atmosphere, contamination by iron that had rusted and residual stresses from fabrication and fit-up. Whilst the UK climate is not hot and humid, it is plausible that such an environment could exist for example in the roof space of a factory and this group of factors cannot therefore be ignored. Clearly this type of environment can occur in the roof space of UK swimming pools.

A completely different set of conditions is discussed by Haselmair [651. Following tests in the Mont Blanc Road Tunnel, he issued a warning to avoid the use of type 3Q where chlorides are present due to CLSCC at room temperature.

In 1987 the Hilti Corporation initiated a test programme with five types of stainless steel to study resistance to CLSCC. A series of samples were stressed to 90% yield strength by springs and a second series were unloaded. The test location was 1 km inside a tunnel entrance in France. The test location and an annual mean temperature of 18.5°C, mean humidity of 72% and enormous amounts of dust, causing large deposits of soot, rubber, minerals and up to 3.5% water soluble chloride. A suspension of water including the dust had a pH value 3.8 to 5.3.

After 11 months all exposed materials showed extensive pitting and crevice corrosion; cracks were found in unstressed type 303 specimens. Following 19 months further exposure, unstressed 303 specimens had cracked and after 38 months one 303 sample had fractured. The cracking was typical of transcrystalline propagation due to CLSCC with the crack orientation reflecting the main direction of stressing. Cracks originated predominantly from local pits.

The study found that type 316 had a higher resistance than type 304 and the higher number of sulphide inclusions in the surface of type 303 acted as nuclei for localised corrosion. Attention was also drawn to the formation of a' -martensite by cold working. The corrosion rate of a' -martensite was reported to be much higher than that of austenite in the active state. It concluded that selective corrosion of the o.'-martensite resulted in lowered pH ahd increased chloride concentration within local pits, and this could lead to crack formation.

A further conclusion was that up to 10 years coul-d pass before CLSCC causes austenitic steels to fail in environments containing chlorides. The time to failure was considered to be very dependent on the pH value and chloride content of the surroundings.

5.2.3 Fasteners and suspension wirein swimming pools

On the 9th May 1985 in Uster Switzerland, the suspended roof above a swimming pool collapsed, resulting in 12 fatalities. It had been constructed from a concrete slab that was supported by a large number of 1.4301 (304) stainless steel rods, inch diameter. An investigation revealed that once a sufficient number of rods had failed by CLSCC, the remaining rods were unable to support the roof and it collapsed. The British Stainless Steel Association website [58) states that subsequent research has shown that CLSCC could occur at 25°C in conditions of high chloride content plus acidity, or very high chloride near-neutral conditions. There have subsequently been similar incidents associated with the use of stainless steel in safety critical load bearing applications in ind◇or pools and leisure centres.

In 1987 an acoustic ceiling collapsed adjacent-to a swimming pool in South Wales. This was attributed to CLSCC of 2mm diameter supporting wires manufactured from type 304 stainless steel [35).

On 9 J e 2001 in Steenwijk, The Netherlan s, [6,] tp.e whole ceiling and air channels collapsed into the pool oyemight. The auth,or noted tliat in the interim period, many incidents had occurred, most of thefm unreported. Replacement fasteners were manufactured from type 304 or 316. The author :repqrted t4at30 wipiming p ols were inspected in the Netherlands after the incident and six were fotll}d to be at immediate susceptibility due to CLSCC below rust spots.

In September 2003, t4e ce,iling above the main pool in a spa-resort hotel in Finland entirely collapsed due to the fra tuie of stainless steel suspension wires as c:1 result of CLSCC [45). Type 304 was originally selected for the wire but (he authors considered that grade 316 would not have been a significantly better solution.

Failures of 304 wire and strip, and 316 wire have also been reported in swimming pools in Germany, Denmark, Sweden [68) and the USA [61).

5.2.3.1 The swimming pool environment

Oldfield and Todd [68) commented that whilst stainless steels had been used for swimming pool components for many years, the problem of room temperature CLSCC appeared to be relatively recent and could suggest a change in the corrosive environment. A survey of pools in the UK was carried out to investigate such a possibility and this revealed a lack of reliable information on pool atmospheres. The disinfectant used in most UK pools was chlorine, which until 1987 was usually supplied using gas cylinders. Following government recommendations a change to the use of compounds took place and the most commonly used were sodium and calcium hypochlorites. The main effect has been an increase in the total dissolved solids in the pool water.

In the 1970s the introduction of leisure pools led to an increase in water temperature and this changed the operating conditions [62, 68]. Leisure pools had higher air temperatures with larger water surfaces. There was also extended splash zone, more moisture evaporating and higher usage of disinfectants. It was concluded that the resulting environment has become more physically aggressive and should be classified as corrosivity class C4 [79]. This environment class is comparable to severe industrial environments, for example in pulp and paper manufacturing plants.

Organic chemicals called chloramines are formed by the interaction of chlorine-based pool disinfection chemicals and organic compounds from bathers [58]. It is thought that chloramines evaporate and condense on surfaces and can be highly concentrated depending on the combination of temperature and humidity in the pool area. Areas in the roof space are particularly vulnerable as there is no opportunity for natural washing or easy maintenance of such components. The article states that immersed, components are not susceptible to CLSCC.

Baddoo and Cutler [35, 9] have stated that 304 and 316L are not suitable for safety critical, load bearing components that are not constantly wetted and in a highly corrosive environment. Some grades of stainless steel have long been recognised as susceptible to CLSCC, but only above about 55°C. The unusual feature of these failures has been that they have occurred at around 30°C. The components were highly stressed and had not been frequently cleaned. The authors conclude that three factors lead to CLSCC in the swimming pool environment:

- The use of susceptible grades 304 and 316.
- A relatively high tensile stress relative to the yield strength (0.2% proof strength), either from structural loading or present as residual stresses from forming or welding operations during manufacture and installation.
- The presence of a specific highly corrosive film containing chloride compounds from by-products of disinfection.

Arlt et al [32) and Fielder et al [67) have studied CLSCC at temperatures below 50°C to determine the key factors in the swimming pool environment. Arlt showed that CLSCC could occur in 304 and 316 under chloride rich deposits on U-bend samples and in highly concentrated chloride (>20%) solutions with constant axial load samples even though the surface remained passive. pH and cation type appeared less important than the total chloride activity. A critical level of humidity was required with chloride rich deposits; enough moisture being needed to form a thin film of saturated solution underneath the deposit, but not so much as to dilute the solution. Fielder showed that CLSCC could initiate in 304 and 316 steels at temperatures below 50°C under conditions of partial passivity in an environment of very low pH (<2) and high chloride ion concentration. He considered that initiation would also be possible in less severe environments where passivity was stronger if the conditions inside the pit or crevice were more severe than the bulk conditions at the metal surface.

5.3 EFFECT OF TESTING TECHNIQUE

5;3.1 Accelerated testing for ranking resistance to CLSCC

CLSCC in austenitic stainless steels is a well known phenomenon and consequently has been studied extensively [29]. Early studies, starting in 1945, used a boiling solution of magnesium chloride and this has become a standardised environment, e.g. ASTM G36 - 94(2006) *'Standard Practice for Evaluating Stress-Corrosion-Cracking Resistance of Metals and Alloys in a Boiling Magnesium Chloride'* . It is usually considered that a stainless steel that survives a long period of exposure in this test is not likely to exhibit CLSCC in service. Although this is a simple and rapid test which enables comparisons between results from different laboratories, it has some limitations. The main limitations are that slight changes in temperature or chloride concentration affect the relative rankings of types 304 and 316, and it is a severe environment that is unlikely to replicate service conditions. Even high alloy grades of austenitic and duplex stainless steel containing >22% chromium and >5% molybdenum can crack in less than 24 hours when tested in boiling magnesium chloride[74].

Although any type of stress corrosion test specimen can be used in the magnesium chloride test, the U-bend to ASTM G30::97(2009) *"Standard Practice for Making and Using U-Bend Stress-Corrosion Test Specimens"* has been popular because it provides a severe configuration but is also simple and relatively inexpensive to make and use. ASTM G123 describes a standardised corrosion test employing a solution of boiling acidified sodium chloride. The test is considered to be less severe than the magnesium chloride tests and is believed to correlate better with service experience in sodium chloride environments.

Tests based on the evaporation of sodium chloride solution, using either droplets or a wick on a heated surface, are considered to give rankings that reflect service behaviour in many environments. The two main techniques are method MTia5 in Materials Technology Institute *"Corrosion testing of iron and nickel-based alloys - Part 1: Test Methods"*, and ASTM C692-08 *"Standard Test Method for Evaluating the Influence of Thermal Insulations on External Stress Corrosion Cracking Tendency of Austenitic Stainless"*.

5.3.2 Test specimen type

Specimen design and the loading regime hav ll significant influence on CLSCC behaviour under test conditions and this has been recognised by numerous workers [6, 7, 8,)4, 53]. The main combinations of test specimen and loading condition are:

- U bend or other constant deflection design
- Constant axial load
- Slow strain rate
- Pre-cracked specimens

It is generally recognised that U bend or constant deflection specimens are best for comparing materials and screening environments. However, these specimens normally use smooth surfaces so they do not differentiate between the initiation phase (i.e. localised corrosion) and propagation phases of CLSCC. With constant axial load specimens and slow strain rate testing, the effect of parameters with time on CLSCC can be determined. Results from these tests have been used to study the role of environmental variables (e.g. chloride concentration, pH or temperature) on CLSCC and on the time to failure [7, 8, 53]. It is important to recognise, that the results from constant axial load specimens and slow strain rate testing cannot generally be used to predict crack initiation times or rates of crack propagation in practical applications. The results from pre cracked specimens can be used to determine "the critical stress intensity for crack initiation, K1scc, and the crack growth rate in the propagation stage; both of which can be used in structural integrity calculations [6, 23]. The limitation of data from tests with pre-cracked specimens is that it does not include the time taken for a crack to initiate by pitting or crevice corrosion from a smooth surface:

Bruemmer [53]' compared the CLSCC resistance of sensitised 304 using constant axial load, slow strain rate tests, U-bend samples and crevice corrosion tests. The purpose of the work was to simulate a service failure by intergranular CLSCC at low temperatures in very dilute chloride solutions. Constant axial load tests were found to give a better simulation of the service failure and produced intergranular cracking under a wider range of conditions than the other samples. However, all test methods produced some intergranular cracking in the low temperature dilute chloride environments. The authors used high stress levels (>1.5 X proof stress) but considered that the cracking would have also occurred at lower stresses if the test duration had been longer.

The authors stated that the test results depended on surface condition because crack initiation was the critical step particularly at lower temperature. They also considered that the strain rate in slow strain rate testing must be slow enough for the necessary corrosion reactions to occur, thus promoting crack initiation and propagation. Results from slow strain rate tests and crevice corrosion tests indicate that surface defects could reduce the incubation time for localised corrosion and crack initiation. A similar effect has been observed when testing duplex stainless steels. The critical temperature for CLSCC is reported to be significantly lower at a strain rate of 10^{-8} compared with 10^{-6} that is commonly adopted in laboratory tests [84].

5.4 ENVIRONMENTAL FACTORS

In 1969 Truman (22) stated that the combination of variables, which could affect behaviour, include - chloride content, temperature, cation species, oxygen content and pH of solution, applied stress and composition and metallurgical condition of steel. Several other authors have studied the importance of these and additional environmental factors.

5.4.1 Temperature, chloride concentration and oxygen

The conventional view was that CLSCC did not occur in non-sensitised austenitic stainless steels at temperatures below about 60°C in near-neutral chloride solutions (29). However, as described in Section 5.2, instances of transgranular CLSCC in service have been reported to occur in atmospheres above indoor swimming pools, in the marine atmosphere and in a heavily polluted road tunnel atmosphere and in low temperature process applications. Swimming pool atmospheres have caused CLSCC in ceiling support rods made from type 304, type 316 and a German titanium stabilised type 316 (DINI.4571). Common factors in the marine atmosphere failures included a hot, humid atmosphere, contamination by iron that rusted and residual stresses from fabrication and fit-up. It i dear, therefore, that while temperature is a critical factor in the development of CLSCC, other factors such as chloride concentration are also involved.

Truman's work identified temperature as the most important factor in any occurrence of CLSGC; in fact the times to failure that Qe obtained with consti\llt axial load specimens appeared to show that chloride concentration was of less importance. While the role of chloride concentration has become clearer, recent work confirms the significant increase in CLSCC susceptibility of austenitic stainless steel with temperature. Temperature susceptibility is displayed by increases in crack growth rate measured with pre-cracked Samples [6] and by decreases in time to failure of smooth specimens under constant axial load (10). Crack growth rates range from - 300mm.yr^{-1} at n0^{0}c (6) to - 0.6mm.yr^{1} at 40°C [23]. Recent work also shows a general inverse trend between chloride concentration and temperature, such that at temperatures >100°C, the chloride concentration required to initiate CLSCC falls to a few ppm [34]. Immersion tests suggested that a concentration of approximately 400ppm chloride is required for CLSCC ilt 20°c decreasing to IOOppm at I00°C [24]. It is interesting to note that an area of $CC research in the nuclear industry is the behaviour of sensitised 304 or 316 grades for n;actor pipework in high purity oxygenated water at temperatures up 288°C (5, 70, 72]. These studies have shown that intergranular SCC can occur in the absence of chloride. Conversely, very high chloride concentrations are required for cracking to develop at <50°C [11, 66). From the work carried out by Alrt (32] and Fielder (67) it is clear that these high chloride concentrations can be produced either in thin films of moisture beneath chloride rich deposits, or inside pits and crevices by concentration from the bulk solution.

Sedriks (29) notes that CLSCC susceptibility under immersion conditions is increased by raised chloride concentrations but that the relationship is not simple. The maintenance of low chloride levels cannot ensure freedom from CLSCC under conditions in which chloride can concentrate in crevices or shielded areas. Platts also (1) considers that CLSCC initiation is more likely and crack propagation rates are generally faster with increasing temperature, stress and chloride concentration. The possibility that chlorides could concentrate in crevices or vapour spaces where water is evaporated or consumed should also be taken into account. Surface films can also absorb or occlude chlorides and increase their concentration by several orders of magnitude compared with the bulk solution. For example, a bulk chloride concentration of 0.02ppm was found to have been concentrated to 10,000ppm by aluminium oxide films (24).

Temperature and chloride concentration are factors that also influence localised corrosion behaviour [29] and accelerated tests can be used to define Critical Pitting Temperatures (CPT) and Critical Crevice Corrosion Temperatures (CCT) (74]. It is important to recognise that these tests are used either as acceptance standards or for comparing different grades of stainless steel. Critical temperatures obtained from accelerated testing are not equivalent to safe operating temperatures that will ensure that pitting or crevice corrosion does not occur in practical applications. Some authors infer that a critical temperature exists for CLSCC and that this can be demonstrated experimentally based on a competition between the rate of localised corrosion and the rate of crack growth [2, 43]. However, it is clear that practical situations and laboratory tests can produce conditions where CLSCC is possible over a wide range of temperatures. The existence of a critical temperature threshold that could be applied to CLSCC over a wide range of practical conditions is therefore an over-simplification [1].

5.4.1.1 Temperature excursions

The recent work by Turnbull and Zhou (23] revealed that a short-term temperature excursion can affect the propagation of CLSCC in type 321 and 316 stainless steels. When crack propagation had been initiated at 130°C in type 321 steel, the authors found that the growth rate increased when the temperature was reduced to 60°C, and then crack growth continued after further cooling to 40°C. Type 316 steel Had a higher crack growth rate at 130°C than type 321. However, decreasing the temperature to 60°C reduced the crack growth rate to a level that was not likely to affect structural integrity; and propagation did not continue at 40°C. While the Turnbull and Zhou caution against drawing broad conclusions, the work suggests that high temperature excursions can accelerate structural deterioration of type 321 by allowing CLSCC to continue at lower temperatures.

5.4.1.2 Humidity and cation type

Truman [22] gave time to failure results for samples immersed in 1% solutions of magnesium, calcium and sodium chlorides. Although the testing conditions were not clear, magnesium chloride gave the shortest time to failure; a slightly longer time was obtained with calcium chloride; and the longest time was obtained with sodium chloride. This effect is observed with accelerated testing and is thought to lie due to differences in solubility and chloride activity between the different salts. Magnesium and calcium chlorides are more soluble than sodium chloride.

Truman and Pirt [11] reported on the difference between using a test solution and cracking under deposits and found that a deposit of zinc chloride produced the greatest susceptibility of CLSCC. Arlt [32] considered chloride rich deposits and reported that a deposit of zinc chloride was the most effective promoter of CLSCC because the pH of its solution is acidic. In drop evaporation tests, sodium chloride on its own did not initiate CLSCC whereas drops of artificial marine salt containing magnesium chloride did. The authors concluded that the effect of a salt mixture was determined by the most aggressive salt, usually $MgCl_2$, even if it was present in minor amounts.

Oldfield and Todd (68] discussed the likely mechanism of CLSCC under chloride rich deposits and regarded the most likely transfer mechanism to be hydrolysis of the salts. Of the salts considered they suggest calcium as the most likely cause of room temperature CLSCC.

The relationship between chloride rich deposits and the humidity required to cause CLSCC under atmospheric exposure at ambient temperatures was reviewed by Smart [52]. Cracking was most prevalent at the equilibrium humidity for a saturated solution of the salt concerned but could occur over a specific narrow humidity range. For cracking at ambient temperature, chloride containing particles were a prerequisite; the potency of particle being critically related to the relative humidity and the composition of the chloride (which was cation dependent), but not highly sensitive to the concentration of the chloride above a certain critical level. There was a strong dependence on humidity; at high humidity a surface solution was considered to be too dilute to breakdown the passive film whereas at low humidity there would be insufficient water to form continuous film. The range of critical humidity was wider at higher temperatures. Smart concluded that CLSCC can occur under atmospheric exposure below 50°C but over a narrow and low range of humidity that is outside normal operating conditions for most practical applications.

5.4.1.3 Dissolved oxygen and electrode potential

CLSCC occurs within a restricted range of electrochemical potential; the range being defined by increased localised corrosion at the anodic end and at the cathodic end by re-passivation of the internal surface of the pit or crevice. The main effect of dissolved oxygen is on electode potential. Hersleb [16] demonstrated the synergistic relationship between oxygen concentration, electrode potential and chloride concentration in tests with solutions at 100°C. The tests measured the time to failure of smooth, constant axial load samples produced from sensitised 304 type steel. The results showed that the time to failure was reduced by increasing chloride concentration and by increasing the applied stress. The shortest times to failure were obtained over a narrow range of electrode potential (-0.3V). Cathodic potentials (or a reduced oxygen concentration) caused a marked increase in the time to failure with many specimens remaining intact at the end of the 1000 hour tests.

The role of oxygen appears to be of fundamental importance to CLSCC in natural waters at very high temperatures, i.e. 250° to 300°C. If free from oxygen, solutions will not cause CLSCC even at high chloride concentrations [24]. At lower temperatures and with chloride solutions containing other oxidising ions, the presence of dissolved oxygen does not appear to be necessary for CLSCC.

5.4.2 Cathodic protection and contact with other metals

Electrode potential has a very significant influence on the susceptibility to CLSCC of austentic stainless steel [29]. The use of impressed current systems, sacrificial anodes and sacrificial coatings has been used to provide cathodic protection against CLSCC [24, 73]. Impressed current systems are more difficult to apply because they need close control via a reference electrode and this is only possible with some applications where surfaces are continually immersed. In heat exchangers, it has been found that CLSCC of austenitic stainless steel tubes is rarely experienced with carbon steel tube plates and shells. This is because the carbon steel adopts a relatively low electrode potential that is well below that required to cause SCC or pitting of austenitic stainless steel, and which is thereby cathodically protected. When the all-stainless tube, tube sheet and shell construction is adopted, this unintentional electrochemical protection is lost and CLSCC failures occur in the tubes [73]. The use of carbon steel as a sacrificial anode is not always effective because corrosion products accumulate over time reducing current density. Consequently the potential shift is not sufficient to protect the austenitic steel surfaces against CLSCC [24].

One very effective form of cathodic protection is wrapping of pipework and vessels with aluminium foil to prevent external CLSCC under insulation [76]. It is also the case that inadvertent contact with more noble metals can increase susceptibility to CLSCC. A recent case

5.5 OTHER FACTORS

5.5.1 Stress and stress intensity

Clearly the magnitude of tensile stress level is a principal factor that will affect the initiation and propagation of CLSCC. Several authors have measured a threshold stress for CLSCC with smooth specimens (1, 10, 19, 22, 27]. Threshold stresses ranged from 80MPa to 100MPa [27], with Platts and Adams [1] reporting values from some authors as low as 10% of the 0.2% proof stress. Platts and Adams also recognised that non-stress relieved structures that have been fabricated by welding are likely to contain residual tensile stress with a magnitude up to or just above the yield strength. They state that initiation rates are highly dependent on stress level although threshold stress levels, where determined by either authors, tended to be much lower than yield.

Fielder [67] reported a threshold stress of -100MPa but recognised that results obtained from smooth specimens under constant axial load depend on the duration of the test. Thus with longer exposure times, the threshold stress could be below 100MPa. Leinonen (19] reported threshold stress values of between 100MPa and 130MPa.

Truman (22] recognised that the threshold for CLSCC could be defined for some conditions but that its magnitude would differ with every change of corrosive condition. The lowest values of threshold stress reported by Truman were - 15MPa in boiling magnesium chloride and in boiling sodium chloride but he questioned whether or not it was realistic to define a threshold for such CLSCC under such severe conditions.

A number of workers have studied CLSCC using a fracture mechanics approach and pre-cracked samples to observe how crack growth rate varied as function of stress intensity and to determine the threshold stress intensity factor, $K_{1}scc$ [5, 6, 23, 41, 42]. The lowest values reported ranged from 1MPa.$m^{0.5}$ to 5MPa.$m^{0.5}$ for sensitised grade 304 material at high temperatures. The highest values ranged from 10MPa.$m^{0.5}$ to 30MPa.$m^{0.5}$. The most extensive assessment of crack growth rate as a function of stress intensity was carried out by Speidel [6]. He found that crack growth rates were - 1mm.yr^{-1} near $K_{1}scc$, but the rate increased steeply to >100mm.yr^{-1} for a relatively small increase in K.

This approach would suggest that, in less aggressive conditions where pit growth rates are expected to be slower, initiation could be an extended process. If local stresses were around the 0.2% proof stress in the vicinity of welds (e.g. between 250MPa and 300MPa) a pit of only 0.3mm deep could be sufficient to provide an initiation site with $K_{1}scc$ in region of 10MPa.$m^{0.5}$. Conversely, with $K_{1}scc$ of approximately 30MPa.$m^{0.5}$ a pit - 3mm deep would be needed to initiate crack propagation.

Stress cycles are rarely considered in the context of CLSCC but it is known that stress cycles at a low frequency can significantly lower the threshold for stress corrosion cracking in other metal environment systems, e.g. carbon manganese structural steel in seawater [24]. Shoji et al [72] have shown that low frequency load cycles reactivated stress corrosion cracking of sensitised 304 even in a relatively mild environment, i.e. pure water at 85°C.

It is worth mentioning that the effect of tensile stress on CLSCC can be offset by introducing compressive residual stress into the surface of austenitic stainless steel components. Compressive residual stress is usually produced by shot peening, but there are other processes that also produce permanent deformation of the surface layer [24].

5.5.2 Surface finish

Surface finish can be just as critical in determining the corrosion resistance of austenitic stainless steel as the grade [58]. Poor quality finishes can lead to disappointing performance of stainless steel and a bright polished surface will usually give the best performance in any specified environment.

Coarse polished finishes with surface roughness values greater than I micron have been shown to contain deep grooves where chloride ions can accumulate and destroy the passive film, thereby initiating corrosion attack. In contrast, fine polished finishes with surface toughness values less than 0.5 micron will generally have fewer sites where chloride ions can accumulate.

The standard of surface finish is an important consideration with fabrications like the reactor vessels. The inner surface of the reactors had been ground in the areas around openings and welds but the surface finish was poor with coarse grinding marks still visible.

Austenitic stainless components that are fabricated by welding are likely to have heat tint colouration. The colouration is due to a thickening of the normal chromium oxide surface layer at the welding temperature. The increased thickness of the oxide leaves the metal just below the surface with a reduced chromium level, which can adversely affect corrosion resistance of the steel in aqueous environments [58].

Surface contamination with iron [70, 71] leads to localised corrosion and this has been cited as an explanation for the initiation and propagation of CLSCC at ambient temperature.

5.6 METALLURGICAL FACTORS

5.6.1 Alloy content

Stainless steels are iron alloys containing a minimum of approximately 11% chromium, which prevents the formation of rust in unpolluted atmospheres. Austenitic stainless steels are iron-based alloys that contain nominally 19% chromium and 9% nickel. As implied by the name, the predominant microstructure of austenitic stainless steels at room temperature is the phase known as austenite. The high corrosion resistance of austenitic. stainless steels in most atmospheric and aqueous environments is due to passivation by a thin (- 2nm) self-healing layer of chromium oxide [2]. Almost 200 different alloys are now recognised with modifications appearing all the time. In addition to chromium and nickel, many other elements are added to provide specific properties.

The role of nickel is to stabilise a fully austenitic microstructure by countering the effect of chromium, a ferrite stabiliser. The effects on the microstructure of changing the relative proportions of nickel and chromium are normally described by the Schaeffler diagram [29]:

Compositional modifications that improve corrosion resistance are:

(a) Additions of molybdenum and/or nitrogen, to improve pitting and crevice corrosion resistance.
(b) Lowering the carbon content or stabilising with either an addition of titanium, or niobium and tantalum to reduce sensitisation in welded components.
(c) Further increases of nickel and chromium to improve high temperature oxidation resistance and strength

(d) Additions of nickel to improve stress corrosion resistance.
(e) Small additions of copper, which can improve corrosion resistance in sulphuric acid.

The compositions of the 300 series are balanced according to the Schaeffler diagram in order to minimise formation of 8-ferrite phase. Whilst 8-ferrite causes difficulty in hot working and is known to decrease pitting resistance, a proportion is retained in weld filler metals because it reduces hot tearing when the weld pool solidifies. Other deliberate alloying additions to austenitic stainless steel include sulphur, selenium and calcium to improve machinability.

There has been an extensive research effort to investigate the effects of major and minor alloying additions on the CLSCC resistance of austenitic stainless steels and each element can be classified as detrimental, beneficial or variable [29].

5.6.1.1 Major alloying additions

Nickel additions have a strong but variable effect on resistance to CLSCC [6, 29] as measured by the time to failure of smooth specimens under constant axial load, or by K1scc and crack growth rate obtained with pre-cracked samples. The lowest resistance is found with alloys having from 10% to 25% nickel; but increasing the nickel content to 32% appears to make alloys fully resistant [6].

Chromium additions are beneficial up to about 15 (in a 10% nickel matrix) but there is a minimum in CLSCC resistance of alloys containing around 18%Cr [30]. Raising the chromium content from 18% to 25% does not make stainless steel resistant to CLSCC [6].

Molybdenum additions are strongly beneficial to CLSCC resistance and an addition of approximately 5% can increase K_1scc to the point that austenitic stainless steel can be considered fully resistant for many purposes [6]. There is some evidence that molybdenum additions in the lower composition range, i.e. up to 2% Mo, can be deleterious in boiling MgClz solutions.

5.6.1.2 Minor alloying additions and impurities [29, 30}

Manganese is present in most stainles steels in the 1% to 2% range. It is variable in its effect on CLSCC, but in the range of 2% to 4% Mn a clear deleterious effect has been found. Silicon appears to improve the resistance to cracking in boiling MgClz solutions, partly via the formation of a protective compound, thought to be magnesium silicate, on the surface of the specimen. Some authors have stated that silicon does not sustain the resistance to CLSCC unless it coexists with 0.045% or more solute carbon. Thus silicon may lose its positive effect resulting from sensitisation when carbon precipitates as a carbide e.g. during welding. Excessive silicon, e.g. from 3.5% to 5.5% in **18-8** steels causes the formation of significant amounts of 8-ferrite.

Nitrogen is unusual in having a strongly beneficial effect on resistance to localised corrosion but being detrimental to CLSCC. Phosphorus has a detrimental effect similar to nitrogen [43] and it has been suggested that stainless steels containing less than 0.003%P could be immune to SCC in boiling MgC'2 solutions.

Carbon at up to 0.1% appears to improve SCC resistance of 18-10' steels in boiling MgClz solutions with a minimum resistance at approximately 0.06%.

Sulphur is detrimental to CLSCC but its effect is not as pronounced as nitrogen, phosphorus and carbon. Sulphides are generally detrimental to pitting resistance and crevice corrosion resistance -in all grades of stainless steel. Furthennore, manganese sulphide inclusions are preferred sites for pitting and crevice corrosion so sulphur would be expected to enhance the initiation of CLSCC. The susceptibility of c LSCC increases with a high sulphur content, as there is a higher density of sulphide inclusions, which act as initiation sites for pitting and/or stress corrosion cracks [52]. It is for this reason that type 303 stainless steel, the high sulphur free-machining grade, has a lower resistanc-e t o pitting, crevice corrosion and CLSCC than 304 or 316.

Laycock et al [17) have discussed the role of manganese sulphide inclusions as sites for the initiation of pitting and crevice corrosion. The authors considered the possibility that oxidation of the inclusion in the crevice could generate thiosulphate ions or reduced sulphur compounds that could contribute to the localised corrosion mechanism.

The carbide formers niobium and titanium are added to obtain resistance to sensitisation, but ey have been found to decrease the resistance to CLSCC [29).

Austenitic stainless steels are currently manufactured by melting scrap or primary alloys in an electric arc furnace and refining by argon oxygen decarburisation (AOD). AOD refining, which was introduced in the early 1970's, produce's significantly lower levels of carbon and impurity elements' such as sulphur and phosphorus. It is reasonable to expect, therefore, that stainless steels manufactured by the AOD process wiil be more' resistant to localised corrosion and CLSCC than those made by earlier steel making woce ses.

5.6.2 Microstructure

Many microstructural features such as second phases, inclusions and grain boundaries can all affect CLSCC in austenitic stainless steels [29). The most likely second phases are o-ferrite and a '-martensite. Resistance to CLSCC is generally improved by o-ferrite but a considerable amount, e.g. -50% as in duplex grades, must be present in the microstructure before there is any beneficial effect. The improvement in CLSCC resistance of duplex stainless steels is due to a combination of electrochemical and mechanical differences between the austenite and ferrite phases. Martensite can be'producedwhen austenitic stainless steels are col<l'worked at ambient tempera ture. It is reported that a' -martensite has a lower corrosion resistance than austenite and that this can lower the resistance to pitting. Haselmair [65) concluded that selective corrosion of a' -martensite in cold forged fasteners resulted in lowered pH and increased chloride concentration Within local pits, and this could lead to CLSCC.

5.6.3 Sensitisation [29)

It is possible for CLSCC to be intergranular where cracks propagate mainly along grain boundaries. Intergranular fracture usually indicates that an austenitic stainless steel is in a 'sensitised' condition. An austenitic stainless steel is described as being sensitised if a heat-treatment or welding procedure allows holding or slow cooling between 900°C and 480°C. Holding or slow cooling through this temperature range leads to chromium depletion at grain boundaries because chromium carbides are formed. Sensitisation impairs corrosion resistance significantly and leads to intergranular attack in a wide variety of environments that would otherwise cause little deterioration. The intergranular attack is caused by the chemical and physical differences between the grain boundaries and the bulk material. These differences are the result of precipitation of carbides, depletion of alloying elements, and segregation of impurities at the grain boundaries. Sensitisation is therefore very detrimental to CLSCC susceptibility.

5.6.4 Cold working

Heavily cold worked components made from austenitic stainless steel, for example wire products and cold forged fasteners, can be particularly vulnerable to CLSCC in swimming pool environments [59,74]. It is difficult to separate deformation (slip), martensite formation and increased yield strength due to work hardening, in understanding how cold working might increase susceptibility to CLSCC [29]. The current understanding is that up to 10% prestrain can decrease the time to failure. However high levels of deformation (- 35%) can increase the time to failure in accelerated tests at high temperature and high chloride concentrations such as boiling solutions of calcium or magnesium chloride. The failure of cold forged fasteners would therefore appear to contradict the beneficial effect of high levels of deformation that has been observed in accelerated tests.

� CONCLUSIONS

6.1 CLSCC IN THE REACTORS

1 It is likely that a number of factors contributed to the deterioration of the austenitic stainless steel reactors by CLSCC. These include:

- Residual stress from fabrication and welding,
- A rough surface finish leading to a long period of slow localised corrosion.
- Initiation of CLSCC on the process side when the depth of corrosion pitting was-Imm.
- Short periods of rapid crack growth when the temperature �60°C during the cleaning cycles.
- Long periods of very slow crack growth at the normal reactor operating temperature.
- Periodic reactivation of cracking due to low frequency load cycles and the temperature excursions during cleaning.

2 Given the published crack growth rates for CLSCC and the effect of temperature, it seems likely that cracks of significant size would have been present for a considerable time prior to their discovery during the hydrotest.

3 The fracture mechanics tests carried out on the parent metal and weld metal from the reactor revealed very high fracture toughness values, as would be expected for austenitic stainless steel at room temperature. Structural integrity assessments to API 579 and BS 7910 for typical defects indicated that the reactors could withstand very long, through-thickness defects without experiencing rapid fracture and Leak Before Break was the most likely mode of failure.

4 The most effective NDE technique for detecting CLSCC in the reactors was the dye penetrant method. A promising ultrasonic flaw detection procedure was developed but it was very time consuming because complimentary scans with several different probe types were required. The procedure could not be applied to every position and all crack orientations. Eddy current testing was found to be an ineffective means of detecting CLSCC in the reactors because it was sensitive to other surface imperfections and did not have sufficient penetration.

6.2 FROM THE LITERATURE REVIEW

CLSCC initiates from sites of localised pitting or crevice corrosion. CLSCC propagation occurs when cracks grow more quickly from the pit or crevice than the rate of corrosion.

The initiation of CLSCC has been shown to involve a competition between localised corrosion, which is strongly dependent on chloride concentration but has a weak dependence on temperature, and crack growth which has a strong dependence on temperature but is relatively unaffected by chloride concentration and pH.

It follows from the competition approach that environmental factors, which affect localised corrosion, are also likely to affect the initiation of CLSCC. Furthermore, it also follows that more severe conditions will be required to initiate CLSCC than are needed to sustain crack growth. Recent work has clearly shown that CLSCC crack growth can be sustained at a chloride concentration and temperature significantly below those required to initiate cracking.

There is a large amount of published work on various aspects of CLSCC in austenitic stainless steels. However, no data were found that could be used to predict the time required for crack initiation by localised corrosion in real structures.

Fracture mechanics tests have shown that CLSCC propagation can begin at low stress intensities in the range 2MPa.m^{05} to fOMPa.rrt^{5}. For fabricated structures containing tensile residual stresses, the critical depth of localised corrosion to initiate CLSCC would be <Imm.

The rate of crack propagation is strongly dependent on temperature but is relatively unaffected by stress intensity. Rates of CLSCC propagation can vary from 0.6mm.yr^{-1} at near ambient temperatures to >30mm.yr^{-1} at temperatures ......,! Q0°C. In laboratory tests CLSCC has been observed in samples at temperatures between 25°C and 40°C.

The majority of the reported practical instances of CLSCC have occurred where temperatures 60°C. However, a significant number of failures below 60 °C have also been reported although in these instances there appear to have been other contributory factors, which include:

- The use of highly cold worked and/or free-machining grades.
- Iron contamination of the surface.
- The presence of a highly corrosive film containing chloride compounds.

7 APPENDICES

7.1 APPENDIX 1- METALLURGICAL EXAMINATION

7.1.1 Visual examination

Dimensions are for indication only unless accompanied by a statement of accuracy.

Two pieces cut from the reactor vessel were received at HSL and for the purposes of this report the two pieces were identified as 1 and 2 respectively

It was noted that the internal and external surfaces of the vessel had a poor surface finish with coarse grinding marks evident particularly in the welded regions. It was clear that the samples had been subjected to dye penetrant flaw testing and remains of crack like indications were visible. Residues of an adhesive substance were present inside some cracks. Areas of scattered corrosion pitting were present on the inside surface of the two samples.

The welds were a combination of fillet and butt joints: The wall thickness of the main part of the vessel was approximately 4.5mm to 5mm while the heads and set on flanges were 6.5mm to 7.0mm thick. The internal welds appeared to have been ground smooth and flush with the surface but the external welds were as-welded: The appearance of the external welds was variable with an uneven weave pattern, prominent stop/start imperfections; and areas of slight undercutting.

7.1.2 Dye penetrant flaw detection

The two samples were cleaned and inspected by applying a red visible dye penetrant fluid, Ely Chemicals Checkmor 222. The surplus fluid was removed with a solvent and a dry powder developer, Ely Chemicals LD3, was applied. Numerous indications were revealed on the internal and external surfaces of the two samples. The indications were mainly associated with the welds but more scattered indications were visible on the inside surface which appeared to be due to corrosion pitting.

The penetrant indications indicated that there were through-wall cracks around three nozzles in the vessel base; in two cases the cracks extended around $^{2}/_{3}$rds of the circumference. There were also four positions of through-wall cracking on the top main circumferential seam. Many other penetrant indications had corresponding indications on the both surfaces, which indicated that smaller areas of through-wall cracking were present around other welds.

7.1.3 Microscopic examination

Sections were cut for microscopic examination from the sites where dye penetrant flaw detection had revealed imperfections. The samples were prepared metallographically for microscopic examination before and after electrolytic etching in 10% oxalic acid solution.

Microscopic examination revealed that the parent materials for the vessel, flanges and nozzles had a single phase grain structure characteristic of austenitic stainless steel. The weld filler metals had a columnar appearance and mixed austenite-ferrite microstructures. The heat affected zones showed evidence of recrystallisation. There was no evidence of carbide formation at grain boundaries due to sensitisation in the heat-affected zones. Some welding imperfections were visible which included gas pores and irregular cavities in the root regions where there was incomplete penetration. Some joints had significant voids in the spaces between set-on plates and the vessel wall.

This examination confirmed that indications revealed by dye penetrant testing were due to branched transgranular cracking as observed in the insurer's laboratory examination [28] and e Mitsui-Babcock NDE assessment [25]. The cracks appeared to have initiated in areas close to welds but were not associated with specific microstructural features. In many instances, cracks had propagated through the full wall thickness. Most of the cracks appeared to have initiated at a site of localised -corrosion, and in some cases, this occurred within the weld metal. The cracks had multiple macroscopic and microscopic branches, characteristic of CLSCC.

7.1.4 Reactor material properties

Samples from the vessel shell were cut for chemical analysis and tensile testing by Sheffield Testing Laboratories Ltd. The results of the tests are summarised in Table *5* and Table 6 below.

Table 5. Results from tensile testing on samples from the reactor

Test number	***Proof stress Nmm^{-2}***	***Maximum stress Nmm^{-2}***	***Elongation*** %
E280	293	5 5	49
E280A	294	584	52
E2808	293	585	52
Average	**293**	**585**	**51**
Typical values for ASTM 321	*205*	*515*	*40*

Table 6. Results from chemical analysis of the reactor

Element	***Mass %***	***Tolerance***	***ASTM321***
Carbon	0.066	±0.005	*0.08 max*
Silicon	0.60	±0.0 3	*0.75 max*
Manganese	1.58	±0.05	*2.0 max*
Phosphorus	0.027	±0.004	*0.045 max*
Sulphur	0.008	±0.002	*0.030max*
Chromium	17.23	±0.40	*17.00to 19.00*
Molybdenum	0.36	±0.01	*n!s*
Nickel	10.31	±0.20	*7.00 to 12.00*
Titanium	0.62	±0.01	*5x* %C *min*

The results in Table *5* and Table 6 show that the mechanical properties and chemical composition of the vessel material were typical of those for ASTM grade 321 stainless steel. There were no indications of any material or manufacturing deficiencies in the vessel material, therefore, that might have contributed to the development of CLSCC.

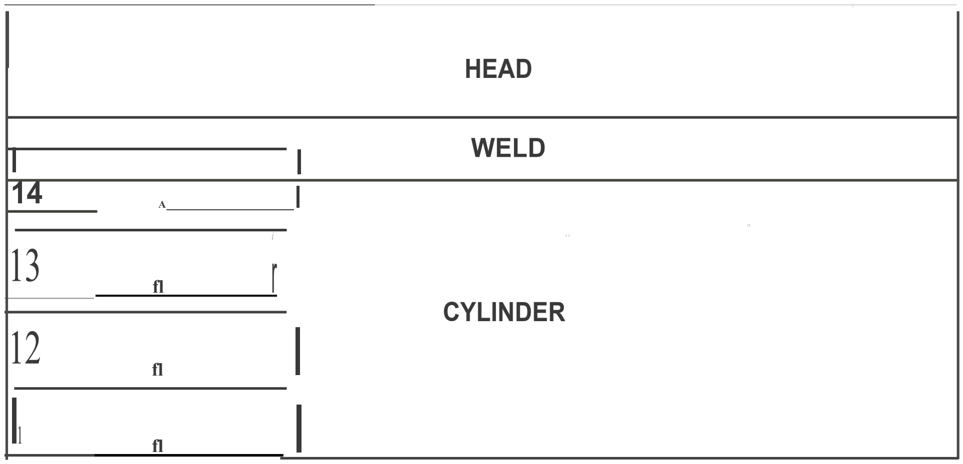
7.2 APPENDIX 2 - ENGINEERING ASSESSMENT

7.2.1 Fracture toughness testing

four specimens were removed from the vessel material for fracture toughness testing. The orientation and positions of the four specimens are shown in Figure 3. As can be seen, the fourth specimen was orientated so that the remaining ligament (the section not pre-cracked) was taken from a weld. All the specimens were approximately 6 mm thick (the thickness of the vessel), 12 mm in height and 55 mm long.

Assessments were performed on the vessels to determine the maximum crack sizes tolerable in the vessel under different conditions. Two locations were analysed; in the region of one of the nozzles in the cylinder head and along the longitudinal weld. The testing methodology was based on BS 7448: Part 1:1991 *"Fracture mechanics toughness tests"*. The tests did not conform to the standard for a number of reasons; (i) the specimens geometry did not meet the standard due to the thin curved material available from the vessel, (ii) the clip gauge used to measure the displacement was not calibrated for use at 0 °C and did not meet the 1% accuracy requirement for the room temperature tests. However, the tests still provide a useful estimate of the fracture toughness. The results from the tests are shown in Table 7.

Figure 3. The positions of the fracture toughness specimens



-Table7. Results from the fracture toughness tests.

Specimen.	*Test Temp ("C)*	*Critical* *CTOD,o(mm)*	*Equivalent Kma1 from AP/ 579 (MPa-»n)*	*Equivalent K,,,,,Jrom BS7910 (MPa-»n)*
I	0	0.231	181	110
2	0	0.212	173	105
3	Room Temp	0.658	305	196
4	Room Temp	0 .744	325	208

7.2.2 Structural integrity assessments

Assessments, based on the fracture toughness results, were performed using the American Petroleum Institute (API) document .579:" *Fitness-for,-service"* . This document provides more comprehensive procedure than BS 7910 *"Guide to methods for assessing the acceptability of flaws in met //ic structures'.'* . For example, BS7910 gives no guidance on the analysis of cracking around nozzles or on the residual stresses in welds.

7.2:2.1 Nozzle Crack

The case of the crack!i around a nozzle was represented by a crack located at ¢.e toe of pie fillet weld connecting the reinforcing pad to the vessel. The crack was t4fough thickness and followed the arc of the weld around the reinforcing pad.

API 579 recommended using the solution for a cracked flat plate for the case of.a crack growing from the toe ofa weld around a nozzle or reinforcing pad. The main difference bet.ween the flat plate solution and the case of the crack growing around. the nozzle was the shape of the crack. In the case of the nozzle, the crack was curved, growing around an arc that would eventually grow to form a complete circle. Once this happened for a through thickness crack, the nozzle would then be completely detached from the main part of the vessel.

7.2.2.2 Boundary element analysis

As this case is significantly different to the flat plate solution used in the API 579 assessment, the boundary element method (BEM) was used to check that the flat plate solution was conservative. Models were created representing a nozzle reinforcement pad welded to a flat plate with through thickness cracks extending for various lengths around the pad. The results for the three different crack lengths are listed in Table 8. For short cracks, the boundary element results were marginally higher then the flat plate solution. This may be due to the effect of the reinforcing pad or the hole acting as a stress concentrator. For longer crack lengths, the flat plate solution becomes increasingly conservative. The API solution assumes that the crack is growing straight across a finite width plate, so as the crack grows, the remaining ligament carrying the load decreases. With the case of the crack growing in an arc around a nozzle, as the crack increases in length, the load will flow around the crack and the remaining ligament, rather than across the ligament. Therefore, at longer crack lengths, the API solution is likely to be more conservative, yielding shorter critical defect sizes.

Table 8. Results from the boundary element analysis compared to the flat plate solution contained in API 579.

Crack Length (mm)	***Flat Plate SIF Soludon*** *(N.mm·312)*	***Boundary Element SIF Solution*** *(N.mm-3^{12})*
52	12.9	13.9
104	18.5	15.6
156	24.3	9.4

From the API analysis, it was estimated that a crack could grow to over 600 mm in length before the vessel would fail. The residual' stress distribution for this analysis was taken from Appendix E of API 579, for a fillet weld. The plate width used in the assessment was assumed to be the circumference of the reinforcing pad, i.e. 835 mm. Therefore, the critical crack length would have extended around approximately :Y. of the pad circumference. As discussed in the previous section, this analysis is conservative due to the difference in geometry between the API solution and the actual case. This means that an even longer crack would be tolerable before any sudden failure of the vessel. It is likely that the vessel would leak from a crack this large.

This critical crack length figure was obtained assuming the pressure in the vessel was the hydrotest pressure of 40 psi. Longer crack lengths could be tolerated under the operating pressure, although the effect of the pressure change is slight due to the residual stress in the weld being the most significant factor.

7.2.2.3 Longitudinal weld

For the longitudinal weld, API 579 contains a solution for the exact case, therefore there was no need to verify the solution with boundary element models. The residual stresses used for the analysis were based oil the residual stress distribution for a single v:groove longitudinal weld and a double V-groove weld found in Appendix E.

The critical flaw size, based on a single V-groove weld was approximately 160 mm, although for a double V-groove weld this would reduce to 80 mm. Again, these figures were obtained assuming the pressure in the vessel was the hydrotest pressure of 40 psi. A slight increase in lengths would be achieved under operating pressure.

7.2.2.4 Comparison with BS7910

The main difference between the assessments performed using API 579 and an assessment using BS7910 would be in the conversion of critical crack *tip* opening distance (CTOD) to a Kma1 value. Due to the conversion used by BS7910, the equivalent K mat value would be approximately 30% lower, as shown in Table I, resulting in smaller critical crack lengths. For the longitudinal crack cases, this would reduce the critical crack length to approximately 50 mm. As BS79 IO does not contain specific residual stress distributions for different weld types, this assumes the worst case of the residual stress equalling yield, as in the double V-groove weld example.

For the crack around the stiffening plate of the nozzle, the critical crack length would not be significantly affected as in this case, the vessel would fail in a ductile manner and the critical fracture toughness is not so important. In this case, the critical crack length would reduce to approximately 540 mm.

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Chloride stress corrosion cracking in austenitic stainless steel

Assessing susceptibility and structural integrity

Chloride stress corrosion cracking (CLSCC) is one the most common reasons why austenitic stainless steel pipework and vessels deteriorate in the chemical processing and petrochemical industries. Deterioration by CLSCC can lead to failures that have the potential to release stored energy and/or hazardous substances. Failures of plant can be prevented by an awareness of the onset and evolution of CLSCC, and by periodic inspection to monitor the extent of cracking. Although the deterioration of austenitic stainless steels by CLSCC is well known, recent incidents and inspection visits by HSE have found that susceptibility assessments were inconsistent and did not always take account of current knowledge. Discussions between HSE, dutyholders and competent bodies identified that the technical justification for setting inspection intervals and the effectiveness of periodic non-destructive examination (NDE) for monitoring CLSCC were additional areas of concern.

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