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**Chloride stress corrosion cracking in austenitic
stainless steel – recommendations for assessing
risk, structural integrity and NDE based on
practical cases and a review of literature**

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

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EXECUTIVE SUMMARY

Objectives

Chloride stress corrosion cracking (Cl-SCC) 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 practice in assessing the risk of Cl-SCC and in applying risk based inspection (RBI) to existing plant, in particular setting inspection intervals and carrying out non-destructive examinations (NDE).

To assess a case of extensive deterioration from Cl-SCC 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 Cl-SCC based on trials carried out by Mitsui-Babcock with samples from one of the reactors.

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

Recommendations for Risk Assessment of Cl-SCC

The risk of Cl-SCC is usually assessed on the basis of chloride content, pH and temperature. In our view there are additional factors that should be taken into account when assessing the risk with both new and existing pipework or vessels that have accumulated significant service. These include:

- Operation involves high temperature excursions. Risk should be determined by the highest temperature reached during any part of duty or maintenance operations, irrespective of the duration of the excursion.
- Liquid can dry out allowing chlorides to concentrate or form 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 the risk of CI-SCC 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 risk 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 NDE

Wrought austenitic stainless steels have high fracture toughness and for pipework and vessels Leak-Before-Break is the most likely consequence of CI-SCC. Leak detection is not a reliable indicator of CI-SCC 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 CI-SCC by NDE or by in-situ metallography.

CI-SCC 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 NDE, 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 CI-SCC 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 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 NDE technique for detecting CI-SCC. 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 CI-SCC in the reactor

It is likely that the following factors contributed to CI-SCC in the reactor:

- Residual stress from fabrication and welding
- A rough surface finish leading to a long period of slow localised corrosion.
- Initiation of CI-SCC on the process side when the depth of corrosion pitting was ~1mm.

- Short periods of rapid crack growth when the temperature $\geq 60^{\circ}\text{C}$ 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

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

The initiation of Cl-SCC 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 Cl-SCC. Furthermore, it also follows that more severe conditions will be required to initiate Cl-SCC than are needed to sustain crack growth. Recent work has clearly shown that Cl-SCC 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 Cl-SCC 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 Cl-SCC propagation can begin at low stress intensities in the range $2\text{MPa}\cdot\text{m}^{0.5}$ to $10\text{MPa}\cdot\text{m}^{0.5}$. For fabricated structures containing tensile residual stresses, the critical depth of localised corrosion to initiate Cl-SCC would be $<1\text{mm}$.

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

The majority of the reported practical instances of Cl-SCC have occurred where temperatures $\geq 60^{\circ}\text{C}$. 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 (Cl-SCC) is one of the most common reasons why austenitic stainless steel pipework and vessels deteriorate in the chemical processing and petrochemical industries. Deterioration by Cl-SCC 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 Cl-SCC, and by periodic inspection to monitor the extent of cracking. Although the deterioration of austenitic stainless steels by Cl-SCC is well known, recent incidents and inspection visits by HSE have found that risk 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 Cl-SCC 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 is an introduction to Cl-SCC in austenitic stainless steel.
- Section 2 gives the authors' conclusions and recommendations for assessing the risk of Cl-SCC. These include applying RBI, setting inspection intervals, structural integrity considerations and NDE.
- Section 3 summarises findings from a metallurgical investigation into extensive deterioration from (Cl-SCC) in austenitic stainless steel reactor vessels that had been 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 Cl-SCC in thin-walled austenitic stainless steel vessels with complex design and welded details. This includes the results of NDE trials carried out by Mitsui-Babcock on samples from two of the failed reactors.
- Section 5 is a literature review of published cases of Cl-SCC 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 Cl-SCC.

Austenitic stainless steel pipework and vessels are particularly vulnerable to Cl-SCC 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 Cl-SCC 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 with Cl-SCC 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 formation¹, 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.

| <i>AISI</i> | <i>Euronorm</i> | <i>DIN</i> | <i>British Standard</i> | <i>Description</i> |
|-------------|-----------------|-----------------|-------------------------|---|
| 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 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. Carbide 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.

1.3 CL-SCC MECHANISM

The mechanism of Cl-SCC is complex and the current understanding is discussed in Section 5 of this report. Essentially Cl-SCC 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 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.

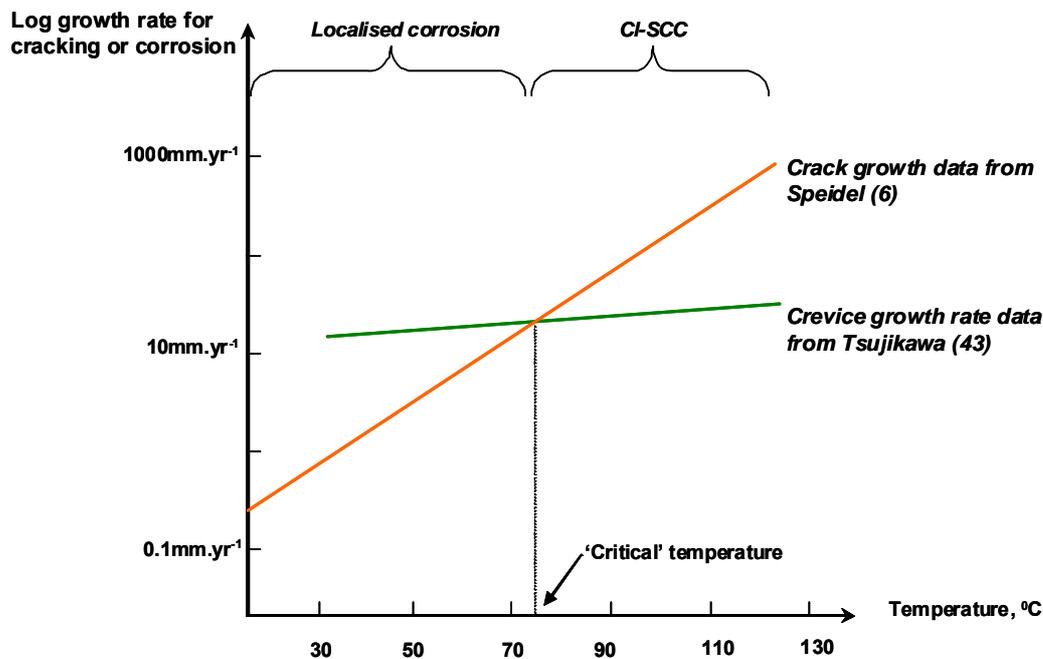
It is commonly accepted that Cl-SCC initiates from sites of active pitting or crevice corrosion [2] and therefore, cracks are considered to grow in the high chloride, strongly acidic, near-saturated solution that develops at sites of localised corrosion. One theory [43] proposes that Cl-SCC only occurs 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 Cl-SCC and the rate of localised corrosion. Crack growth is also restricted to a range of electrochemical potential which 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 Cl-SCC because crack growth increases more rapidly with temperature than the rate of localised corrosion. Figure 1 is a schematic description of Tsujikawa's theory. In our opinion, the competition theory reinforces the fact that localised corrosion is a prerequisite for Cl-SCC 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 Cl-SCC 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 Cl-SCC 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:

- (i) The initiation of Cl-SCC by localised corrosion.
- (ii) Crack propagation when the rate of Cl-SCC 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 Cl-SCC.



Note for Figure 1. Tsujikawa showed that the 'critical' temperature could range from 42°C to 130°C by varying the phosphorus and copper levels in the steel.

1.4 FACTORS AFFECTING CL-SCC

A range of environmental factors have been identified that can affect the development of Cl-SCC which include chloride content, temperature, pH and contact with dissimilar metals. Recent work [23] 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 Cl-SCC. A significant volume of literature has been published on how Cl-SCC is affected by environmental factors and by the factors affecting the resistance of specific grades. Part of the work described here 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 Cl-SCC

The main options for preventing or controlling Cl-SCC 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 Cl-SCC 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 Cl-SCC when the pipework or vessels are insulated [76]. Austenitic stainless steel heat exchanger tubes are also thought to be cathodically protected from pitting and Cl-SCC when used with carbon steel tube plates and shells [47].

When components are designed, the risk of Cl-SCC can be reduced by choosing more resistant alloys and by lowering the stress. Alloys with greater resistance to Cl-SCC include ferritic and duplex (austenitic-ferritic) stainless steels, and alloys containing >42% nickel. Resistance to Cl-SCC 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 Cl-SCC under severe conditions, e.g. where chloride solutions evaporate [37].

Stress in components can be lowered by down rating working pressures, but where pipework 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 RISK ASSESSMENT FOR CL-SCC

The risk of Cl-SCC 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 $\sim 50^{\circ}\text{C}$) and/or chloride concentrations to define conditions that lead to Cl-SCC and conditions that do not [81]. Tsujikawa [43] has successfully demonstrated a critical temperature for Cl-SCC 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 Cl-SCC and the literature shows that Cl-SCC can and does occur at near ambient temperatures. Compared with temperatures $>60^{\circ}\text{C}$, however, it would appear that near ambient temperature Cl-SCC is slower and that conditions needed to sustain cracking are more specific. At first sight, Cl-SCC 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 $\text{time}^{0.5}$ [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 Cl-SCC 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 Cl-SCC 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 risk indicator for Cl-SCC rather than as a precise threshold below which it can be safely assumed Cl-SCC will not occur. We recommend that additional factors should be taken into account when assessing the risk of Cl-SCC 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. Risk should be based on 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 the risk of CI-SCC is assessed by extending the API 581 '*Base resource document, Risk Based Inspection*' [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 API 581 method is shown in Figure 2. The 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 risk 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.

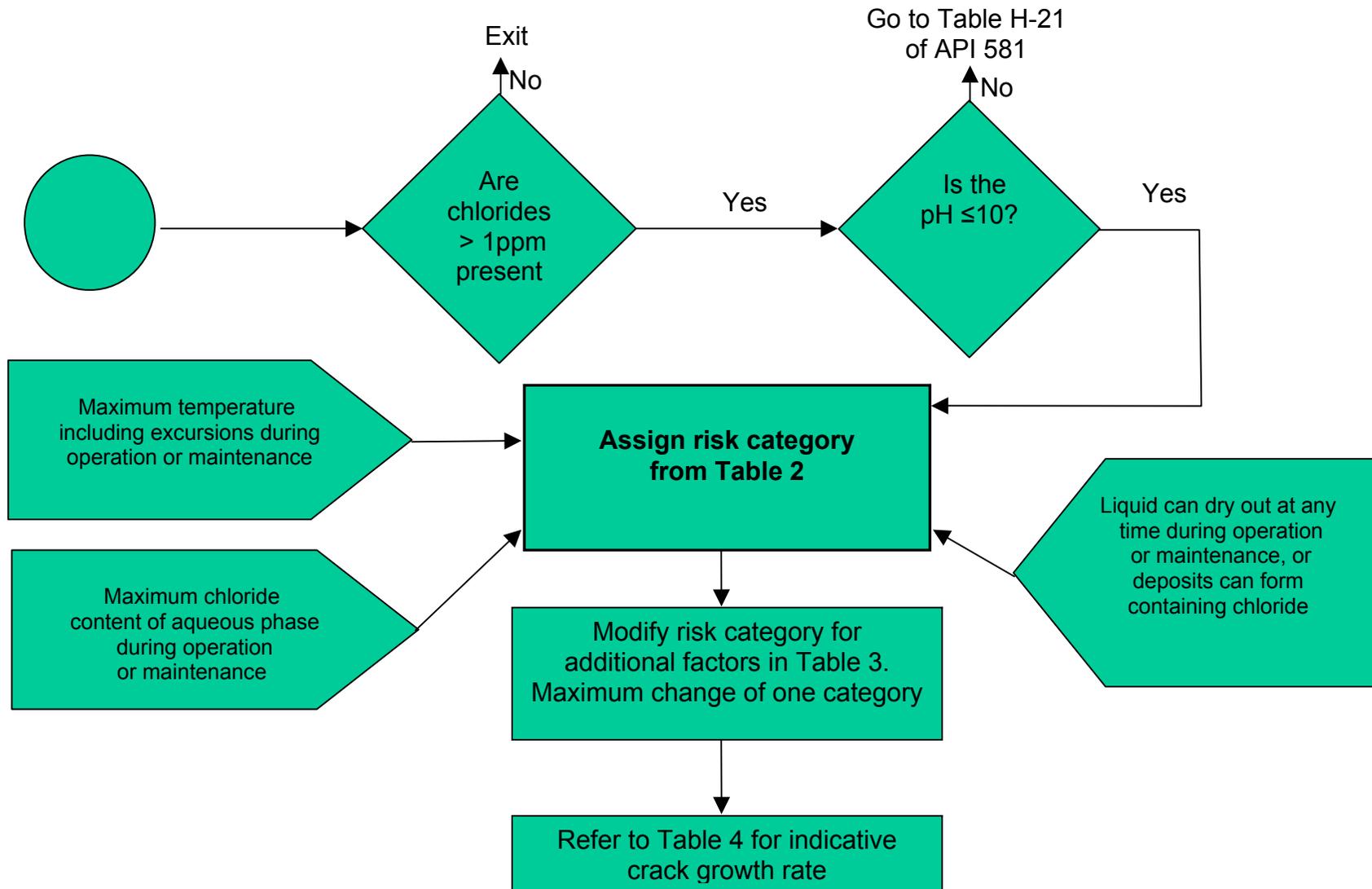


Figure 2 Proposed modification to risk assessment for CI-SCC given in API 581, section H

Table 2. Proposed scheme for CI-SCC risk categories in aqueous media where $\text{pH} \leq 10$, and in conditions where chloride rich deposits may form by drying out or by deposition.

| <i>Temperature, °C</i> | <i>Chloride concentration, ppm</i> | | | | Drying out / deposition |
|------------------------|------------------------------------|-----------|-------------|--------|-------------------------|
| | 1 to 10 | 11 to 100 | 101 to 1000 | >1000 | |
| 10 to 35 | Low | Low | Low | Medium | High |
| 36 to 65 | Low | Medium | Medium | High | High |
| 66 to 95 | Medium | Medium | High | High | High |
| 96 to 150 | Medium | High | High | High | High |

Notes for Table 2: 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 risk category for additional factors.

| <i>Increase risk category</i> | <i>Decrease risk category</i> |
|---|--|
| Sensitisation is likely | Coating or wrapping with aluminium foil |
| History of progressive cracking where mode has not been established | Continuous control of chloride level, pH, or temperature during all operational and non-operational periods. |
| Surface contamination with iron or poor surface finish | Continuous dosing with appropriate corrosion inhibitor during all operational and non-operational periods. |
| 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 for Table 3: The risk category should be changed by a maximum of one category.

Table 4. Suggested CI-SCC growth rates for determining inspection intervals

| <i>Risk category</i> | <i>Crack growth rate,</i> | |
|----------------------|---------------------------|-------------------------------------|
| | <i>mm.yr⁻¹</i> | <i>m.s⁻¹</i> |
| Low | 0.6 | 2×10^{-11} |
| Medium | >0.6 and <30 | $>2 \times 10^{-11}$ and $<10^{-9}$ |
| 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 risk, it is possible for cracks to grow slowly to a structurally damaging size over long periods of service under conditions classified as low risk.
- (ii) With present knowledge of CI-SCC, it is not possible to predict the time required for crack initiation from a smooth surface. In fact the time to initiate CI-SCC probably depends on factors similar to those that affect crack growth rate. For low risk conditions, a crack growth rate of 0.6mm.yr^{-1} is likely to underestimate crack initiation time and give conservative inspection intervals. There is some evidence to suggest that initiation times can be relatively short with high chloride concentrations and temperatures $>80^{\circ}\text{C}$.

2.2 STRUCTURAL INTEGRITY ASSESSMENT

In general, wrought austenitic stainless steels have high fracture toughness with a very low risk 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 1 of this report. Austenitic components and structures can therefore remain stable when they contain large through-wall defects generated by CI-SCC ($>100\text{mm}$ in the case of the reactor). Clearly, for pipework and vessels Leak-Before-Break (LBB) is the most likely consequence of CI-SCC. 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 CI-SCC by NDE 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 CI-SCC 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 CI-SCC 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 CI-SCC. Its structural integrity had been seriously compromised to the extent that some 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 CI-SCC 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 modes 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 CI-SCC in austenitic stainless steel is dye penetrant testing (PT). This method requires that a surface under inspection is clean, accessible and visible to the inspector [82]. Disadvantages of PT in detecting CI-SCC are:

- (i) A high standard of surface cleanliness is required and it is relatively slow.
- (ii) Cracks must break the surface 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 CI-SCC can be increased by applying dye penetrant to one surface and developer to the opposite surface [80]. PT can be effective in locating CI-SCC but sizing through thickness cracks will 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 CI-SCC. 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 example as covered by BS EN 1714:1998 "*Non-destructive testing of welds —Ultrasonic testing 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 CI-SCC. 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 and CI-SCC 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:

- 1 ECT using standard and purpose designed probes had limited penetration and significant sensitivity to surface imperfections 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 REACTOR VESSELS

3.1 HISTORY

Recent interest in the degradation of austenitic stainless steels by CI-SCC was raised by the condition of reactor vessels at a chemical manufacturing facility. The vessel of most interest was had been manufactured from grade 321S12 austenitic stainless steel. A hydraulic test at 40 psig was carried out in 2002 when the vessel had been in service for approximately 24 years. The hydraulic test revealed that the vessel was 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 CI-SCC [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 fusion 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 11⁰C and 21⁰C. 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 70⁰C to 75⁰C. The vessel was also cleaned once or twice a year with sodium hydroxide, at a maximum of 12% concentration, and at a temperature of 85⁰C to 90⁰C. 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 11⁰C to 21⁰C. In terms of total service therefore, the vessel operated at a temperature between 70⁰C and 90⁰C 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 CI-SCC, and localised corrosion. Metallographic examination revealed no evidence of sensitisation.

3.2 DISCUSSION OF CL-SCC IN THE REACTORS

The traditional engineering view is that transgranular Cl-SCC 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 Cl-SCC propagation $\geq 60^\circ\text{C}$. One of the constituents in the reaction was described as containing 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 Cl-SCC occurred during the reactor operation between 11°C and 21°C, during the cleaning cycles $\geq 60^\circ\text{C}$, 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 Cl-SCC. 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 rapid at the start but they tend to decrease as the site of corrosion enlarges and the distance for outward diffusion of metal ions lengthens. According to the competition theory, the transition between localised corrosion and crack propagation occurs at a growth rate of $\sim 10\text{mm.yr}^{-1}$. In fracture mechanics terms, an area of localised corrosion would have to become large enough such that the stress intensity exceeded the critical threshold, K_{ISCC} , for Cl-SCC. Crack growth thresholds for Cl-SCC in austenitic stainless steels are quoted [6, 23, 29] as ranging from $1\text{MPa.m}^{0.5}$ to $30\text{MPa.m}^{0.5}$. If localised 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 3mm for $K > K_{\text{ISCC}}$, assuming that there was $\sim 290\text{MPa}$ residual tensile stress from welding and/or fabrication. On this basis, therefore, it is possible that sufficient depth of localised corrosion could have existed in the reactor after the first year of service. This analysis is probably a considerable oversimplification because 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 Cl-SCC propagation could have developed relatively early in the service life of the reactor.

The rate at which cracks propagate by Cl-SCC has been found to vary by a factor of approximately 500. For example, laboratory tests with pre-cracked specimens have obtained Cl-SCC growth rates ranging from $\sim 300\text{mm.yr}^{-1}$ to $\sim 0.6\text{mm.yr}^{-1}$. The highest growth 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 Cl-SCC could have grown through the vessel wall thickness ($\sim 6\text{mm}$) in that time. An alternative scenario is for a higher rate of Cl-SCC propagation to have caused crack extension through the full wall thickness during the high temperature cleaning cycles. For example the accumulative time of the cleaning cycles is approximately 6 months out of the 24 years reactor service. Crack growth at $\sim 12\text{mm.yr}^{-1}$ 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 $>90^\circ\text{C}$. It is also possible that fatigue cracking, due to the $\sim 150,000$ 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 CI-SCC 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 CI-SCC 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 $\frac{2}{3}$ 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 CL-SCC

4.1 BACKGROUND

The assessment of NDE techniques was carried out on two CSG reactors by Mitsui-Babcock. The aim of the work was to identify techniques for detecting CI-SCC in austenitic stainless steel vessels with the fabrication details and wall thickness found in the CSG 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 NDE 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 NDE ISSUES FOR CL-SCC

The assessment by Mitsui-Babcock showed that the sizing and detection of cracks from CI-SCC 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 CI-SCC 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 CI-SCC 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 CI-SCC 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 CI-SCC in fabrications with complex design details.

5 LITERATURE REVIEW

5.1 CURRENT UNDERSTANDING OF THE CL-SCC MECHANISM

Cl-SCC 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”. Cl-SCC 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 Cl-SCC as well as microvoid coalescence.

The initiation of Cl-SCC 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 Cl-SCC include:

Metal removal by:

- (a) Strain or slip-step accelerated dissolution
- (b) Brittle film rupture
- (c) A combination of (a) and (b)

Metal separation by:

- (a) Hydrogen embrittlement
- (b) Adsorption

Reviews of candidate mechanisms for Cl-SCC propagation have been published [29, 37] but a detailed evaluation is outside the scope of this report. Newman and 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 description of the mechanism of Cl-SCC 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 cell with:

- A higher chloride level than the bulk solution.
- A very low pH (~0).
- Nearly saturated with complex metal ions containing chloride 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, Cl-SCC 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_{ISCC} , at a low crack propagation rate, for example Speidel [6] adopted a minimum crack growth rate of 1mm.yr^{-1} ($3 \times 10^{-11}\text{m.s}^{-1}$). The lowest sustained rate of crack propagation was 0.6mm.yr^{-1} ($1.8 \times 10^{-11}\text{m.s}^{-1}$) as reported by Turnbull [23].

Tsujikawa [43] has demonstrated that Cl-SCC 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 Cl-SCC and the rate of localised corrosion. This approach has been used by Tsujikawa to demonstrate a temperature dependency of Cl-SCC 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 Cl-SCC 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 Cl-SCC by localised corrosion.
- Crack propagation when the rate of Cl-SCC 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_{ISCC} , for sustained crack propagation by Cl-SCC. However, according to the competition theory of Tsujikawa, even if $K > K_{ISCC}$, 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, Cl-SCC propagation will be assumed to be possible when $K > K_{ISCC}$ and localised corrosion is slower than crack growth. The initiation phase of Cl-SCC will be assumed to be defined by $K < K_{ISCC}$ 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 Cl-SCC 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 Cl-SCC 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 Cl-SCC growth rates have a strong dependency on temperature. The highest growth rate [6] was $\sim 300\text{mm.yr}^{-1}$ measured in saturated magnesium chloride concentrations at 130°C , but the lowest crack growth rate was $\sim 0.3\text{mm.yr}^{-1}$ near K_{ISCC} for a low chloride concentration and a temperature of 40°C [23]. Published crack growth thresholds range from $1\text{MPa.m}^{0.5}$ to $30\text{MPa.m}^{0.5}$. Based on the work of Speidel and Turnbull, it should be reasonably conservative to expect typical crack growth rates to lie within the range 0.3mm.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 Cl-SCC 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 not reported but it is clear that the temperature is likely to have been between 80°C and 100°C. 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 Cl-SCC.

Recent work by Turnbull [23] has added to the current understanding of the respective contributions of the initiation and propagation stages of Cl-SCC. 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 the Turnbull cautions against drawing broad conclusions, the work suggests that high temperature excursions can accelerate structural deterioration of type 321 by allowing Cl-SCC to continue at lower temperatures.

The identification of Cl-SCC is normally based on the path of the cracks when viewed microscopically on a prepared section. Cracks formed by Cl-SCC 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 Cl-SCC 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 CL-SCC BELOW 60°C

It is commonly asserted that Cl-SCC of austenitic stainless steel 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 Cl-SCC 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 Cl-SCC 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 Cl-SCC 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 Cl-SCC 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 Cl-SCC 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 Cl-SCC 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 Cl-SCC of stainless steel from Kure Beach, North Carolina. Two type 303 stainless steel nuts had cracked following 14 years service and contained numerous transgranular, 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 301 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 Cl-SCC 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 ¼ 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 Cl-SCC in the marine atmosphere.

Kain stated that the overwhelming body of data demonstrated Cl-SCC resistance of annealed and ¼ hard austenitic stainless steels exposed to a coastal marine atmosphere. However, there were exceptions with crevices being implicated in initiating Cl-SCC 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 [65]. Following tests in the Mont Blanc Road Tunnel, he issued a warning to avoid the use of type 303 where chlorides are present due to Cl-SCC at room temperature.

In 1987 the Hilti Corporation initiated a test programme with five types of stainless steel to study resistance to Cl-SCC. 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 Cl-SCC 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 α' -martensite by cold working. The corrosion rate of α' -martensite was reported to be much higher than that of austenite in the active state. It concluded that selective corrosion of the α' -martensite resulted in lowered pH and increased chloride concentration within local pits, and this could lead to crack formation.

A further conclusion was that up to 10 years could pass before Cl-SCC 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 wire in 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, ¼ inch diameter. An investigation revealed that once a sufficient number of rods had failed by Cl-SCC, 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 Cl-SCC 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 indoor pools and leisure centres.

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

On 9 June 2001 in Steenwijk, The Netherlands, [63] the whole ceiling and air channels collapsed into the pool overnight. The author noted that in the interim period, many incidents had occurred, most of them unreported. Replacement fasteners were manufactured from type 304 or 316. The author reported that 30 swimming pools were inspected in the Netherlands after the incident and six were found to be at immediate risk due to Cl-SCC below rust spots.

In September 2003, the ceiling above the main pool in a spa-resort hotel in Finland entirely collapsed due to the fracture of stainless steel suspension wires as a result of Cl-SCC [45]. Type 304 was originally selected for the wire but the 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 Cl-SCC 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 an 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 [0]. 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 Cl-SCC.

Baddoo and Cutler [35, 59] 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 Cl-SCC, 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 Cl-SCC 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 Cl-SCC at temperatures below 50°C to determine the key factors in the swimming pool environment. Arlt showed that Cl-SCC 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 Cl-SCC 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 CI-SCC

CI-SCC 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 CI-SCC 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 MTI-5 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 have a significant influence on CI-SCC behaviour under test conditions and this has been recognised by numerous workers [6, 7, 8, 14, 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 Cl-SCC. With constant axial load specimens and slow strain rate testing, the effect of parameters with time on Cl-SCC 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 Cl-SCC 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, K_{ISCC} , 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 Cl-SCC 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 Cl-SCC 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 ($>1.5 \times$ 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 Cl-SCC 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 Cl-SCC 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 Cl-SCC 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 Cl-SCC in ceiling support rods made from type 304, type 316 and a German titanium stabilised type 316 (DIN1.4571). 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 is clear, therefore, that while temperature is a critical factor in the development of Cl-SCC, other factors such as chloride concentration are also involved.

Truman's work identified temperature as the most important factor in any occurrence of Cl-SCC; in fact the times to failure that he obtained with constant 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 Cl-SCC 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 $\sim 300\text{mm.yr}^{-1}$ at 130°C [6] to $\sim 0.6\text{mm.yr}^{-1}$ at 40°C [23]. Recent work also shows a general inverse trend between chloride concentration and temperature such that at temperatures $>100^{\circ}\text{C}$, the chloride concentration required to initiate Cl-SCC falls to a few ppm [34]. Immersion tests suggested that a concentration of approximately 400ppm chloride is required for Cl-SCC at 20°C decreasing to 100ppm at 100°C [24]. It is interesting to note that an area of SCC research in the nuclear industry is the behaviour of sensitised 304 or 316 grades for reactor pipework in high purity oxygenated water at temperatures up to 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 $<50^{\circ}\text{C}$ [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 Cl-SCC 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 Cl-SCC under conditions in which chloride can concentrate in crevices or shielded areas. Platts also [1] considers that Cl-SCC 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 Cl-SCC 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 Cl-SCC is possible over a wide range of temperatures. The existence of a critical temperature threshold that could be applied to Cl-SCC 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 Cl-SCC in type 321 and 316 stainless steels. When crack propagation had been initiated at 130⁰C in type 321 steel, the authors found that the growth rate increased when the temperature was reduced to 60⁰C, and then crack growth continued after further cooling to 40⁰C. Type 316 steel had a higher crack growth rate at 130⁰C than type 321. However, decreasing the temperature to 60⁰C reduced the crack growth rate to a level that was not likely to affect structural integrity, and propagation did not continue at 40⁰C. While the authors caution against drawing broad conclusions, the work suggests that high temperature excursions can accelerate structural deterioration of type 321 by allowing Cl-SCC 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 be 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 risk of Cl-SCC. Arlt [32] considered chloride rich deposits and reported that a deposit of zinc chloride was the most effective promoter of Cl-SCC because the pH of its solution is acidic. In drop evaporation tests, sodium chloride on its own did not initiate Cl-SCC 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 MgCl₂, even if it was present in minor amounts.

Oldfield and Todd [68] discussed the likely mechanism of Cl-SCC 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 Cl-SCC.

The relationship between chloride rich deposits and the humidity required to cause Cl-SCC 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 particles 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 Cl-SCC can occur under atmospheric exposure below 50⁰C 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

Cl-SCC 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 electrode potential. Hersleb [16] demonstrated the synergistic relationship between oxygen concentration, electrode potential and chloride concentration in tests with solutions at 100⁰C. 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 Cl-SCC in natural waters at very high temperatures, i.e. 250⁰ to 300⁰C. If free from oxygen, solutions will not cause Cl-SCC 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 Cl-SCC.

5.4.2 Cathodic protection and contact with other metals

Electrode potential has a very significant influence on the susceptibility to Cl-SCC of austenitic stainless steel [29]. The use of impressed current systems, sacrificial anodes and sacrificial coatings has been used to provide cathodic protection against Cl-SCC [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 Cl-SCC 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 Cl-SCC 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 Cl-SCC [24].

One very effective form of cathodic protection is wrapping of pipework and vessels with aluminium foil to prevent external Cl-SCC under insulation [76].

It is also the case that inadvertent contact with more noble metals can increase susceptibility to Cl-SCC. A recent case [75] of Cl-SCC occurred in cold forged 304 fasteners which were coupled to a larger area of a nickel-chromium-molybdenum alloy (Hastelloy).

5.4.3 pH

Various researchers have demonstrated in the laboratory that with very low pH and high chloride solutions, Cl-SCC can occur below 50⁰C [67, 68]. In general, therefore a low pH increases the risk of cracking. However, as discussed by Arlt [32] and demonstrated by Fielder[67], at very low pH values, passivity is lost and general corrosion occurs. At pH >0, it could be the case that the rate of general corrosion prevents the localised pitting or crevice attack necessary to initiate Cl-SCC. The range from pH 2 to pH 0 in the bulk solutions was regarded as being the most harmful. However, both authors note that in bulk solutions with pH<2, the pH will fall significantly inside pits and crevices when localised corrosion is active.

The susceptibility of austenitic stainless steels to Cl-SCC in high temperature water is highly dependent on pH. Nishimura showed that the time to failure for constant load samples was reduced when the pH was increased from 0 to 2 at 80⁰C. Elevated pH (>7) especially in buffered solutions can significantly inhibit both pit initiation and growth and hence prevent Cl-SCC [1]. In Turner's work [22], a near neutral pH appeared to be best for resisting cracking.

The upper pH limit for Cl-SCC in austenitic stainless steels is ~pH 10. At higher pH levels, there is an increased risk of stress corrosion by the caustic cracking mechanism [24, 26, 29, 59].

5.4.4 Sulphides

Hydrogen sulphide appears to have a synergistic effect on Cl-SCC in grades 304 and 316 such that transgranular cracking may be observed at ambient temperatures with relatively low (<500ppm) chloride concentrations [24]. In the absence of hydrogen sulphide, these chloride concentrations would not cause cracking at ambient temperature.

5.4.5 Inhibitors

Chemical inhibitors have been extensively studied [29] and in practice it has been found that silicates, nitrates, phosphates, carbonates, iodides [55] and sulphites can all be effective in preventing Cl-SCC if present in certain concentrations [24]. Complex organic molecules can also prevent Cl-SCC. It seems likely that most inhibitors will prevent the initiation stage by preventing the acidification at sites of local corrosion, by stimulating passivation, or by moving the electrochemical potential outside the restricted range for Cl-SCC.

Failing to maintain the correct concentration of an inhibitor may actually reduce the time to failure [24] particularly with inhibitors that shift the potential. Batch or slug treatments may not be sufficient to maintain protection under all conditions. Continuous injection of the inhibitor with continuous monitoring of its concentration is essential to ensure that protection is provided at all times.

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 Cl-SCC. Several authors have measured a threshold stress for Cl-SCC 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 other 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 Cl-SCC 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 Cl-SCC under such severe conditions.

A number of workers have studied Cl-SCC 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_{ISCC} [5, 6, 23, 41, 42]. The lowest values reported ranged from $1\text{MPa}\cdot\text{m}^{0.5}$ to $5\text{MPa}\cdot\text{m}^{0.5}$ for sensitised grade 304 material at high temperatures. The highest values ranged from $10\text{MPa}\cdot\text{m}^{0.5}$ to $30\text{MPa}\cdot\text{m}^{0.5}$. 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 $\sim 1\text{mm}\cdot\text{yr}^{-1}$ near K_{ISCC} , but the rate increased steeply to $>100\text{mm}\cdot\text{yr}^{-1}$ 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_{ISCC} in region of $10\text{MPa}\cdot\text{m}^{0.5}$. Conversely, with K_{ISCC} of approximately $30\text{MPa}\cdot\text{m}^{0.5}$ a pit ~3mm deep would be needed to initiate crack propagation.

Stress cycles are rarely considered in the context of Cl-SCC 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 Cl-SCC 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 1 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 roughness 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 Cl-SCC 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 δ -ferrite phase. Whilst δ -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 CI-SCC 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 CI-SCC [6, 29] as measured by the time to failure of smooth specimens under constant axial load, or by K_{ISCC} 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 CI-SCC resistance of alloys containing around 18%Cr [30]. Raising the chromium content from 18% to 25% does not make stainless steel resistant to CI-SCC [6].

Molybdenum additions are strongly beneficial to CI-SCC resistance and an addition of approximately 5% can increase K_{ISCC} 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 $MgCl_2$ solutions.

5.6.1.2 Minor alloying additions and impurities [29, 30]

Manganese is present in most stainless steels in the 1% to 2% range. It is variable in its effect on CI-SCC, 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 $MgCl_2$ 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 CI-SCC 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 δ -ferrite.

Nitrogen is unusual in having a strongly beneficial effect on resistance to localised corrosion but being detrimental to CI-SCC. 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 MgCl_2 solutions.

Carbon at up to 0.1% appears to improve SCC resistance of 18-10 steels in boiling MgCl_2 solutions with a minimum resistance at approximately 0.06%.

Sulphur is detrimental to Cl-SCC 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. Furthermore, manganese sulphide inclusions are preferred sites for pitting and crevice corrosion so sulphur would be expected to enhance the initiation of Cl-SCC. The risk of Cl-SCC 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 resistance to pitting, crevice corrosion and Cl-SCC 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 they have been found to decrease the resistance to Cl-SCC [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, produces 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 will be more resistant to localised corrosion and Cl-SCC than those made by earlier steel making processes.

5.6.2 Microstructure

Many microstructural features such as second phases, inclusions and grain boundaries can all affect Cl-SCC in austenitic stainless steels [29]. The most likely second phases are δ -ferrite and α' -martensite. Resistance to Cl-SCC is generally improved by δ -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 Cl-SCC resistance of duplex stainless steels is due to a combination of electrochemical and mechanical differences between the austenite and ferrite phases. Martensite can be produced when austenitic stainless steels are cold worked at ambient temperature. It is reported that α' -martensite has a lower corrosion resistance than austenite and that this can lower the resistance to pitting. Haselmair [65] concluded that selective corrosion of α' -martensite in cold forged fasteners resulted in lowered pH and increased chloride concentration within local pits, and this could lead to Cl-SCC.

5.6.3 Sensitisation [29]

It is possible for Cl-SCC 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 Cl-SCC 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 Cl-SCC 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 Cl-SCC [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.

6 CONCLUSIONS

6.1 CL-SCC IN THE REACTORS

- 1 It is likely that a number of factors contributed to the deterioration of the austenitic stainless steel reactors by Cl-SCC. These include:
 - Residual stress from fabrication and welding.
 - A rough surface finish leading to a long period of slow localised corrosion.
 - Initiation of Cl-SCC on the process side when the depth of corrosion pitting was ~1mm.
 - Short periods of rapid crack growth when the temperature $\geq 60^{\circ}\text{C}$ 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 Cl-SCC 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 CSC 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.
- 3 The most effective NDE technique for detecting Cl-SCC 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 Cl-SCC in the reactors because it was sensitive to other surface imperfections and did not have sufficient penetration.

6.2 FROM THE LITERATURE REVIEW

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

The initiation of Cl-SCC 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 Cl-SCC. Furthermore, it also follows that more severe conditions are required to initiate Cl-SCC than are needed to sustain crack growth. Recent work has clearly shown that Cl-SCC crack growth can be sustained at a chloride concentration significantly below that required to initiate cracking.

There is a large amount of published work on various aspects of Cl-SCC in austenitic stainless steels. However, no data was 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 Cl-SCC propagation can begin at low stress intensities in the range $2\text{MPa}\cdot\text{m}^{0.5}$ to $10\text{MPa}\cdot\text{m}^{0.5}$. For fabricated structures containing tensile residual stresses, the critical depth of localised corrosion to initiate Cl-SCC could be $<1\text{mm}$.

The rate of crack propagation is strongly dependent on temperature but is relatively unaffected by stress intensity. Rates of Cl-SCC propagation can vary from $0.6\text{mm}\cdot\text{yr}^{-1}$ at near ambient temperatures to $>30\text{mm}\cdot\text{yr}^{-1}$ at temperatures $\sim 100^\circ\text{C}$

The majority of the reported practical instances of Cl-SCC have occurred where temperatures $\geq 60^\circ\text{C}$. 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 type 303 free-machining grades.

- Iron contamination of the surface.

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

A range of environmental and metallurgical factors can affect the initiation and propagation stages of Cl-SCC and these should be taken into account when assessing the risk of failure.

7 APPENDICES

7.1 APPENDIX 1 – METALLURGICAL EXAMINATION OF THE REACTOR

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 showed that there were through-wall cracks around three nozzles in the vessel base; in two cases the cracks extended around $\frac{2}{3}$ 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 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 the 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 with little or no visible region of final overload failure. 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 CI-SCC.

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

| <i>Test number</i> | <i>Proof stress Nmm⁻²</i> | <i>Maximum stress Nmm⁻²</i> | <i>Elongation %</i> |
|--|--|--|-------------------------|
| E280 | 293 | 585 | 49 |
| E280A | 294 | 584 | 52 |
| E280B | 293 | 585 | 52 |
| Average | 293 | 585 | 51 |
| <i>Typical values for ASTM 321</i> | 205 | 515 | 40 |

Table 6. Results from chemical analysis of the reactor

| <i>Element</i> | <i>Mass %</i> | <i>Tolerance</i> | <i>ASTM 321</i> |
|----------------|---------------|------------------|-----------------|
| Carbon | 0.066 | ±0.005 | 0.08 max |
| Silicon | 0.60 | ±0.03 | 0.75 max |
| Manganese | 1.58 | ±0.05 | 2.0 max |
| Phosphorus | 0.027 | ±0.004 | 0.045 max |
| Sulphur | 0.008 | ±0.002 | 0.030 max |
| Chromium | 17.23 | ±0.40 | 17.00 to 19.00 |
| Molybdenum | 0.36 | ±0.01 | n/s |
| Nickel | 10.31 | ±0.20 | 7.00 to 12.00 |
| Titanium | 0.62 | ±0.01 | 5 x %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 CI-SCC.

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 of the four specimens is shown in Figure 3. The positions of the fracture toughness specimens. 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 vessel 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

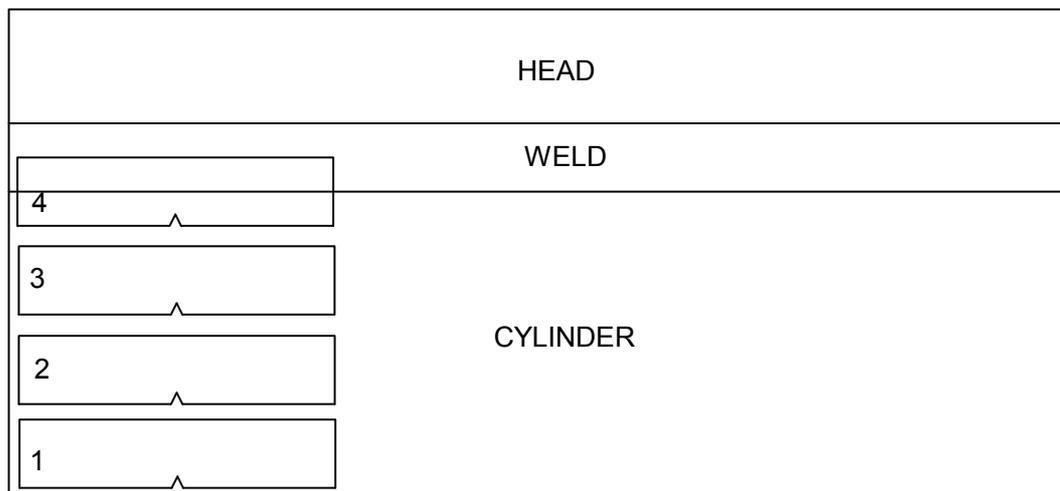


Table 7. Results from the fracture toughness tests.

| <i>Specimen</i> | <i>Test Temp (°C)</i> | <i>Critical CTOD, δ (mm)</i> | <i>Equivalent K_{mat} from API 579 (MPa \sqrt{m})</i> | <i>Equivalent K_{mat} from BS7910 (MPa \sqrt{m})</i> |
|-----------------|------------------------|--|---|--|
| 1 | 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 metallic 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 cracks around a nozzle was represented by a crack located at the toe of the fillet weld connecting the reinforcing pad to the vessel. The crack was through-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 of a weld around a nozzle or reinforcing pad. The main difference between 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 whether 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. Results for the three different crack lengths are listed in Table 8. For short cracks, the boundary element results were marginally higher than 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.

| <i>Crack Length (mm)</i> | <i>Flat Plate SIF Solution (N.mm^{-3/2})</i> | <i>Boundary Element SIF Solution (N.mm^{-3/2})</i> |
|--------------------------|--|--|
| 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 $\frac{3}{4}$ 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 on 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 BS 7910

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 K_{mat} value. Due to the conversion used by BS7910, the equivalent K_{mat} value would be approximately 30% lower, as shown in Table 1, resulting in smaller critical crack lengths. For the longitudinal crack cases, this would reduce the critical crack length to approximately 50 mm. As BS7910 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 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 be approximately 540mm.

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