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Stress Corrosion Cracking of Duplex Stainless Steels in Concentrated Brines – A Critique of Testing

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ABSTRACT

A critical evaluation has been made of methods for testing susceptibility of duplex stainless steels to stress corrosion cracking in concentrated salt solutions relevant to oil and gas production. Testing in submerged conditions in concentrated salts and also under evaporation conditions is discussed. Recommendations for future work are proposed.

CONTENTS

1   INTRODUCTION

Stress corrosion cracking (SCC) in concentrated salt solutions has resulted in a number of failure incidents in offshore oil and gas production[1-3]. 'Leak before break' occurred and safety was not compromised. The high temperatures associated with topside, about 130 °C, and downhole conditions, up to 200 °C, suggest chloride stress corrosion cracking as the likely mechanism. Failure associated with completion brines would seem readily avoidable by control of oxygen level and use of inhibitors. However, where the concentrated solution derives from evaporation of seawater or of formation water (unforeseen in the latter case) the uncontrolled nature of this and uncertainty in the relevance of laboratory testing has proved more of a concern.

1.1   STRESS CORROSION CRACKING ASSOCIATED WITH COMPLETION FLUIDS

The completion fluids in the annulus are most often based on chlorides or bromides of Ca, Na, K and Zn with an inhibitor/oxygen scavenger commonly used but "eco-friendly" caesium, potassium and sodium formates have also been adopted. A typical annulus completion fluid might contain 0.12 kg/l (11.9 M) of $CaCl_2$. Problems are perceived to be experienced in these conditions only where there is significant oxygen ingress or possibly decomposition of inhibitor/scavenger to provide an additional reactant[3].

1.2   CHLORIDES - INTERNALLY INITIATED CRACKING

In view of the significance of the HSE safety report[1], the comments in that report are reproduced verbatim, where appropriate.

'Some observations suggest that cracks initiated beneath deposited chlorides left by evaporated formation waters. Reduction of pressure on passing level control valves (LCVs) resulted in water evaporation, creating a chloride supersaturated liquor in the downstream flow. This led to localised deposition of chlorides. This could be exacerbated by the physical layout of the local pipework (close coupled orthogonal bends, hard Tees). Failures were highly localised. Each occurred where a pressure drop, which caused water flash with chloride concentration and salt deposition, coincided with a weld.'

The composition of formation water will vary according to the particular field. Examples of the chemistry of fields in varied locations are given in Appendix 1. Notably, Ca and Mg levels are often quite different and this will significantly influence the chemistry under evaporative conditions. The relevant partial pressure of gases can be defined in relation to the well but by implication of the pressure drop resulting in vaporisation of the water, the actual partial pressures will be lower. Problems have been experienced in conditions where oxygen is believed to be absent or at least very low in concentration[1,2].

1.3   CHLORIDES - EXTERNALLY INITIATED CRACKING

'External cracks of pipework initiated within pipe support trunnions where seawater (e.g. from deluge testing) entered the support tubulars through small vent holes provided for fabrication. These holes were not sealed after installation. The internal surfaces of the supports, particularly attachment weld areas, were not protected by paint or other coating. Evaporation of the seawater gradually concentrated the chloride solutions if the seawater was unable to drain away.

Cracks developed where these highly concentrated chloride solutions were in direct contact with the welds of support plates (i.e. high stress areas) and where temperatures were elevated. The cracks propagated through the process pipework until containment was lost.'

1.4   GENERAL

Depending on the field chemistry and partial pressures of gaseous species, duplex stainless steel (22 Cr and 25 Cr) or super martensitic stainless steel (13 Cr steel) may be used for the tubulars and topside pipework. Stress corrosion cracking of 22 Cr steel has been reported in all of the conditions above under specific conditions and for 25 Cr duplex stainless steel downhole in the annulus and under wet insulation[2]. The SMSS would be anticipated to be less resistant than these materials though there is no published report of service cracking as yet.

In a number of the cases of failures under evaporative conditions reported by the HSE, the point of failure was at, or adjacent to, welds with no apparent detrimental metallurgical structures. There were no clearly defined 'metal' initiation sites (e.g. pits, crevices) other than proximity of welding. Stress corrosion cracking has also occurred in 22 Cr re-heater tubes with no welds, associated with scratches on the tube surface. Cold-work has also been implicated in failure of a 25 Cr tubing.

Externally initiated cracking occurred in locations open to atmospheric oxygen. Internally initiated cracking, however, occurred in extremely low oxygen environments. The levels are estimated to be a few parts per billion or less. Subsequent laboratory tests (reference not reported by HSE) have not identified a threshold for oxygen levels below which cracking does not occur. However, the time taken to initiate cracking is extended at lower oxygen levels.

An underpinning issue is the relevance of laboratory testing. The purpose of this overview is to critically evaluate the different approaches to testing for these varied service conditions.

2   OVERVIEW OF THE LITERATURE ON TESTING

2.1   COMPLETION BRINES

For completion brines, this is comparatively straightforward insofar as the environment is essentially well-defined. There is evidence that with certain scavenger/inhibitor

combinations (NaSCN/NH$_4$HSO$_3$) decomposition at temperature can lead to generation of H$_2$S. The temperature will determine whether autoclave or conventional glassware facilities are required. Examples of boiling points for various fluids are shown[4,5] in Figure 1.
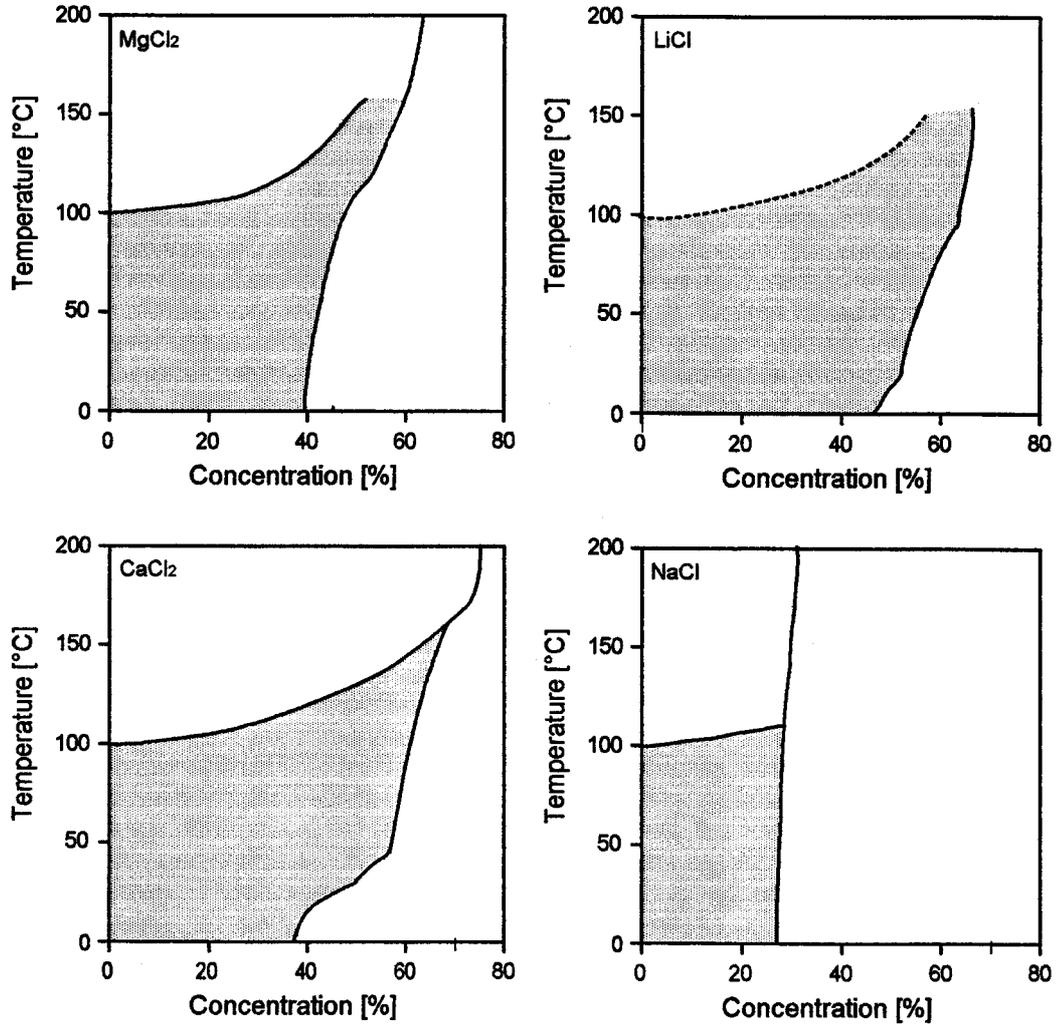

Figure 1.   Solubilities (lower line) and boiling points (upper line) of chloride solutions with shaded area representing ambient pressure conditions[4,5]

Clearly, in laboratory testing, any system should be fully deaerated prior to connecting the test gas. The primary issue is often to define and maintain levels of oxygen when examining its impact on SCC. In both autoclave and atmospheric pressure testing this is best achieved by continuous passage of a relevant gas mixture through the solution with the water content maintained by a condenser system. For autoclave conditions, the gas output is via the condenser with a pressure relief valve just down stream and set so that the relief pressure is just below that for the sealed system. This will allow a continuous passage of gas, thus compensating for any loss of oxygen due to reaction.

Measurement of oxygen in this system with concentrated solutions is difficult though feasible. However, in a well-controlled system with gas flow-through, it is reasonable to assume equilibrium conditions. The challenge is to define the time to achieve such conditions. For stress corrosion studies over 30 days this may not be so critical but for electrochemical measurements of short duration it is more important. The time to achieve subsequent uniform equilibrium conditions will depend on the solution volume, the interfacial area between gas and liquid, and the rate of solution mixing. A large diameter vessel with the same volume will charge up quicker than a smaller diameter vessel. Solution stirring also helps and is advisable also for autoclave testing in avoiding temperature gradients. The use of fritted discs to generate lots of small bubbles and enhance the interfacial area is not recommended because of salt plugs so standard tubing such as 6.35 mm tubing would often be adopted. In the absence of direct measurement of oxygen concentration an estimate of the time to steady state for the system could be made with a platinum electrode. Here the platinum electrode would be polarised into the diffusion limiting regime for oxygen reduction. This would be obscured by hydrogen ion reduction in the concentrated brine so it is necessary to undertake a reference test in neutral pH, relatively dilute, solution. The time to attain the steady state current under diffusion limiting conditions would be determined.

It should be noted that the oxygen concentration in solution will decrease with temperature due to decreasing solubility but there is no effect of the salt concentration on the solubility. Confusion often arises because the *concentration* of oxygen decreases with salt concentration. However, the *activity* of oxygen does not change. It is the activity that is relevant in defining solubility and reaction kinetics.

2.2   EVAPORATIVE CONDITIONS

Evaporative conditions present a bigger challenge in laboratory representation because of the varied origin of the process in service. This could involve washing of the topside decks with seawater, testing of seawater fire protection systems, dripping of seawater, vaporisation of internal formation fluids.

2.2.1   Internal

In the case of internal environment fluctuations, the temperature may not vary significantly in the sense of a cooling effect as with seawater spray since it is usually a pressure drop, or run-down, that induces the vaporisation. However, in the former the associated partial pressure of the gases may not be known. The pressure drop may occur at a level control valve. From the viewpoint of boiling of the aqueous phase, it is the vapour pressure that is important. That will drop along with the total pressure and induce a net transfer of water molecules from the aqueous phase to the gas phase until such time as the concentration of the solution attains a value such that the boiling point of the concentrated solution is greater than the internal temperature. For formation waters relatively low in Ca and Mg, it may lead to complete drying out. It is important to establish the relative boiling point temperature for the field chemistry and identify the frequency with which pressure drops occur. Any information on the drop in total pressure during such an excursion would help to define the test conditions for laboratory simulation. It is also not clear what happens in a flowing system; is there a region of stagnation that sustains the salt concentration for a period? The indication from the HSE report[1] is that salt crusts were observed.

Laboratory simulation may involve simply testing in an autoclave at the test temperature[6]. The basic field chemistry would simply be concentrated up to a manageable amount, sufficient to cause dissolution of all salts at the test temperature. To be conservative, the partial pressure of gases associated with normal operation conditions would represent a worst case. However, in the case of CO_2 it may well be the case that this has modest impact because the pH in the solution may become dominated by ionic strength effects, particularly if the Ca and/or Mg concentration in the base solution are significant, as salts of these cations are known to cause a significant lowering of pH when concentrated. This may outweigh any effect of dissolved CO_2 in such cases. The role of H_2S in the overall process is less clear, the assumption has often been made that it is not a dominant factor for field failures under these conditions. This needs to be verified.

The challenge in this set-up may be associated with the type of specimen used and problems of crevice corrosion. This may occur at roller points in 4-point bend testing or at the restraining fixtures if using C-rings for example. The effect of such crevice corrosion may be to lower the potential of the specimen and indirectly sacrificially protect the highly strained region. Overcoming this is a challenge as it can be difficult to protect in the crevice regions. An artificial crevice can be created around the strained region by tape or other means. The issue will be repeatability and the arbitrariness of it. Nevertheless, in the absence of any artificial crevice, reasonable results were reported by Huizinga et al[6], using both 4-point bend and C-ring tests in concentrated formation water with a pH of about 3.4. It was shown that failure of UNS S31803 could occur in the absence of oxygen at the test temperature of 140 °C with 2 bar CO_2. A salt concentration greater than 6 M was considered necessary for cracking, corresponding to about 50% evaporation. In the oxygen-free case, very little corrosion attack was found associated with the cracks.

An important question is the extent to which actual salt deposits form in service or whether the solution simply concentrates. The former could lead to restricted mass transfer, similar to under-deposit attack and a crevice arrangement might seem pertinent. It would be preferable to try to simulate service conditions more effectively. However, any evaporation test usually involves a change of temperature rather than pressure and some innovative thinking is required if the pressure is to be cycled in a controlled manner. A simpler approach may be to undertake alternate immersion at constant temperature of both metal and solution.

2.2.2 External

In the case of external exposure to seawater, the wetting and drying "cycle" is wholly irregular and the associated fluctuation in temperature in service unknown. The latter will be completely different for a washing/spraying situation compared with a dripping source. It may be of interest to set up a test with a pipe with a controlled internal temperature at 130 °C and assess the impact on the external surface temperature of varying wetting procedures.

The highly variable nature of the overall process means that a laboratory test has to have a degree of arbitrariness about it but should be designed to discriminate materials and to be just conservative for fitness for service purposes. A single laboratory test may

fulfil the former but not the latter requirement. There is also the issue of encrusted salts hygroscopically absorbing water vapour from the atmosphere.

From the viewpoint of stress corrosion cracking the factors of relevance would be:

wetting and drying cycle;
salt concentration/composition attained, including calcareous scales;
extent of washing off deposits (under-deposit corrosion issue);
oxygen reduction especially in latter stages of drying;
temperature fluctuation.

These are all interrelated.

The generic approaches to laboratory simulation have involved mainly testing in a simulated concentrated solution or intermittent wetting of the surface with seawater (dripping or spraying).

2.2.1.1 *Concentrated solution*

Here, a solution deemed to represent the concentrated solution at the metal surface is prepared and tests under fully submerged conditions undertaken. Crevice corrosion issues as discussed in Section 3.2.1 are relevant here also. Clearly, salt deposition is not reproduced with the associated scaling effects nor is the possible role of oxygen in the drying out stage. The latter may be less relevant in simulated concentrated seawater because of the acidity generated by the Mg^{2+} cation at high concentrations. Reduction of hydrogen ions would then be the dominant cathodic reaction (but see 3.2). It is important to recognise that the hydrolysis constant for Mg^{2+}, and for Ca^{2+}, is small. It is not the hydrolysis of these cations that leads to acidification. The lowering of the pH is related to the increased activity coefficient of the hydrogen ion in concentrated salts due to the increased ionic strength of the solution.

The use of a concentrated seawater has been explored by Sintef[7] using the apparatus of Figure 2 with the stress just above yield for the material. The authors used a solution (Table 1) that corresponded to reduction of the liquid phase of about 60:1 by evaporation of seawater. By inference of their testing temperatures in an ambient pressure system, it can be assumed that the boiling point was about 140 °C. The pH was about 4.0 at 20 °C, which is to be expected at this concentration (typically 4 M $MgCl_2$ gives a pH of 4) but decreased to between 1.6-2.5 at 100 °C. It is not indicated how the pH was measured at 100 °C. A modest lowering of the solution pH is expected with increase in temperature because the ionisation constant for water decreases with temperature, so that neutral pH would be lower than 7 in pure water. However, the decrease at 100 °C would be modest and could not explain the unusually large decrease measured for the salt solution. The specimen was loaded to yield.

Table 1

Composition of seawater concentrated by evaporation[7]

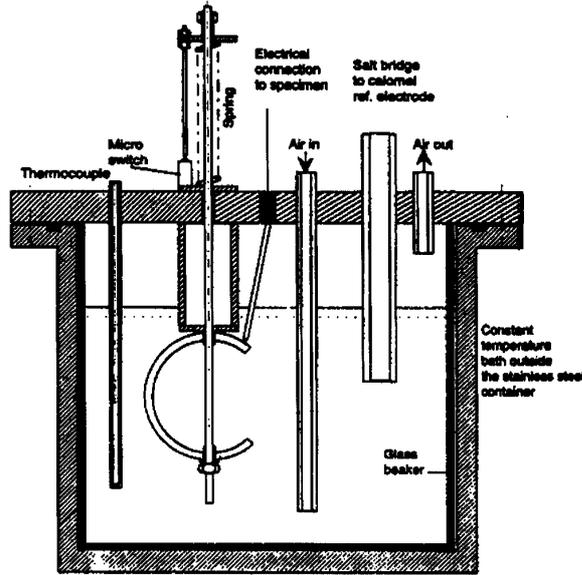| Units	NaCl	MgCl$_2$	Na$_2$SO$_4$	KCl	CaCl$_2$	Cl$^-$	SO$_4^{2-}$	Mg^{2+}	Na$^+$	K$^+$	Ca^{2+}
M/l	0	4.52	0.23	0.49	0.003	9.52	0.22	4.77	0.44	0.49	0.005
g/L	0	4.3	31.1	36.2	0.36	355	21.1	115.9	10.1	19.2	0.2

Figure 2.   Arrangement for C-ring testing in concentrated seawater solution[7]

The test is essentially a ranking test in a concentrated solution and gives comparable ranking to the drop evaporation test. It might be expected to generate quite repeatable and reproducible results, provided the crevice problem is satisfactorily resolved, as indicated in Figure 3. All tests here were conducted with unwelded material.
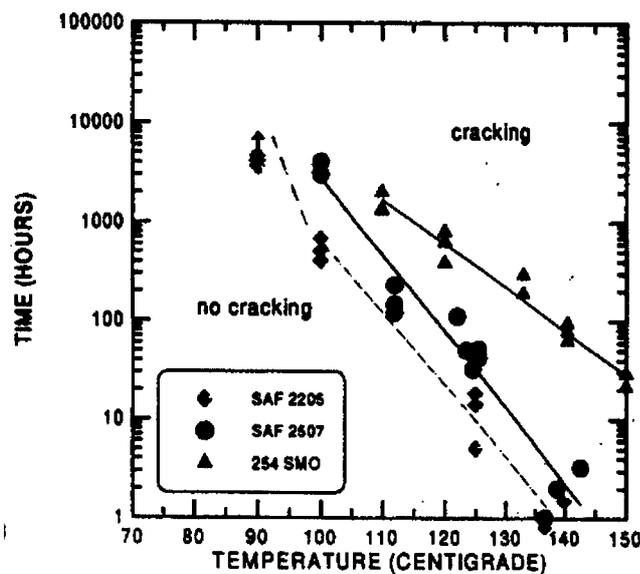
Figure 3. Time to failure as function of temperature in concentrated seawater solution[7]

The authors claim the scatter in the time to failure was small compared with the drop evaporation test and other methods reported in the literature. However, the authors' results clearly demonstrated that this is a much more severe test than the drop evaporation test, with much shorter time to failure. Hence, a reduced scatter is not unexpected. It is not clear why the conditions should actually be more severe than the drop evaporation test as the temperature in the latter is apparently quite high unless it is a transient dilution effect in the latter case. As described below, the temperature was quite high but measurements were not made directly on the wetted surface.

Jergelius-Pettersson et al[5] also explored the use of concentrated seawater, in this case by evaporating to 1/25 of the original volume of ASTM D1141 seawater. Their analysis yielded 66.7 g/l Na^+, 15.6 g/l K^+, 17.0 g/l Mg^{2+}, 0.2 g/l Ca^{2+} and 209 g/l Cl^-. No values for sulphate were reported nor was the pH of the final solution. The majority of the calcium was considered to have precipitated. The results should be compared with Table 1 with the Mg^{2+} notably lower and the Na^+ higher. On the basis of their analysis, the authors then made up a solution for SCC testing by dissolving 168 g/l NaCl, 30 g/l KCl, 66 g/l $MgCl_2$ and 0.4 g/l $CaCl_2$ and then adjusting the pH to 2. The SCC tests were performed at the boiling point of 107 °C. It is not clear why the adjustments to the concentration were made or why the pH was set to a value of 2. The SCC tests gave the expected ranking of the three alloys tested (UNS S32304, S31803 and S32750).

However, the authors noted that testing in chlorides of Ca, Li and of Mg on their own did not always give consistent behaviour depending on the concentration and temperature and emphasised the need to test in more relevant environments.

2.2.1.2 *Drop evaporation*

Avesta developed a method for studying the SCC of steel under evaporation conditions which was referred to as the drop evaporation test[8,9]. A sodium chloride solution is dripped onto and evaporated on a horizontally mounted specimen under constant tensile load. In general, the solution is dripped through a vertical glass capillary (typically, ID 0.4 mm, OD 4.0 mm) terminating 10 to 15 mm above the specimen. This is exemplified by Figure 4.
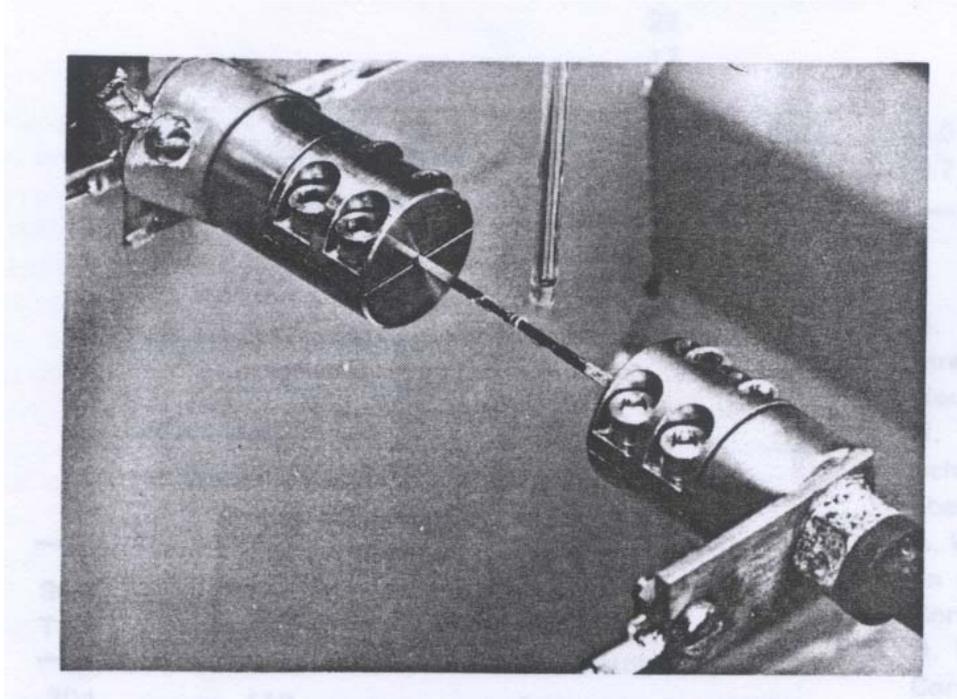
Figure 4.   Illustration of drop evaporation test[9]

The current to the specimen is adjusted to ensure that each drop evaporates completely before the next drop. Typical temperature variation is shown in Figure 5.

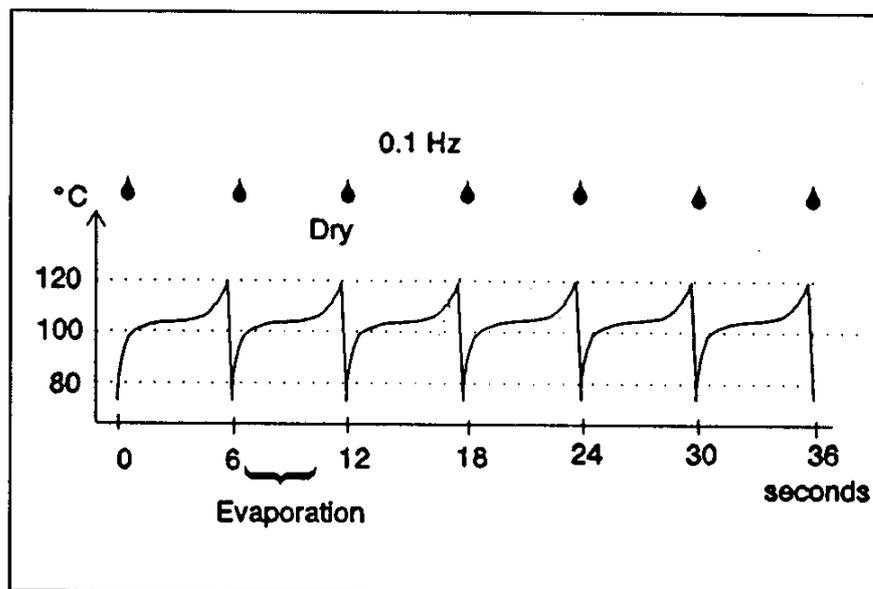Figure 5.   Typical time variation of temperature in response to dripping of 0.1 M NaCl onto heated specimen in drop evaporation test[9].

The waisted region of the specimen acts not only to increase the stress but also the resistance so that the temperature will be proportionally higher relative to the adjacent region of the specimen. The material is heated by passing an electrical current through the

specimen. Time to fracture at a certain stress level is used as a measure of the susceptibility to SCC of the specimen material. The Avesta technique has since been adopted with some modification as a MTI test method[10]. Cihal[11] has also conducted tests similar to that of Avesta. Subsequent work at NPL[12] led to an improvement of the basic method, leading to an ISO standard[13].

The primary distinction between the different approaches relates to the surface temperature measurement before the onset of dripping and the time of application of load. The distinction is summarised in Table 2. The use of 40 drops/min in the MTI test results in significantly lower mean temperature unless adjustment is made to the applied current. This is not indicated in the MTI method and tests at NPL on a 2304 DSS did not show any susceptibility to cracking with this drop rate in contrast to that observed for 6 drops/min.

Table 2

Comparison of key features in drop-evaporation testing

Avesta   Set-up T=300°C (contact therm.); 10 drops/min (peristaltic pump)   Load defined in relation to 0.2% σ_y at 200°C   Load *before* wetting   0.1 M NaCl   Electropolished samples
MTI-5 Test   As Avesta but 40 drops/min.
Ostrava (Cihal)   Set-up T - unspecified; 10 drops per minute (gravity fed)   Procedure not specified in detail.
NPL(ISO 15324)   Set-up T=300°C (wax/paint "calibrated" contact thermometer); 10 drops/min (gravity fed)   Load defined in relation to 0.2% σ_y at 100°C   Load *after* wetting;   Current increased by 25% after dripping started to ensure drying out but to avoid too high a temperature initially.   0.1 M NaCl (seawater optional)   Finish optional; ground finish acceptable

Contact thermometers are inappropriate for reliable measurement at high temperature because they draw heat away from the specimen in the measurement process. Using temperature sensitive waxes and paints it is possible to compare the measurement using contact thermometer with more accurate measures. In measurements at NPL, at 300 °C as measured by a contact thermometer, the actual temperature was 500 °C. With load before wetting adopted also for the Avesta and MTI methods, this could lead to quite erroneous results due to preliminary yielding of the specimen. Once wetting is obtained, the temperature range is usually quite modest (typically 90 °C to about 120 °C) and errors in

temperature measurement less significant. Most of these tests are based on 0.1 M NaCl and are designed as a sorting test but the ISO standard does allow for testing in seawater.

There is no ideal method of measuring the temperature during dripping of the solution. Optical methods can be used but are uncertain due to the changing emissivity and small size of the sample in its gauge length. The use of a contact thermometer at these lower temperatures is satisfactory for giving an indication when applied for short intervals but can still produce errors, the extent of which will depend on the location of the probe. In testing cylindrical specimens each drop of solution normally flows along the specimen onto one of the shoulders of the specimen. The presence of a probe can retain the drop in the centre of the gauge length and thus greatly reduce the temperature whilst the probe is in position. If measurements are made in the wet zone, the presence of the probe, even for a short period, can cause the behaviour of the solution drops to change and markedly alter the surface temperature. Nevertheless, the temperature of the specimen at the dry edge of the specimen can be monitored occasionally with a calibrated probe.

Provided the test conditions are well controlled, materials can be discriminated with respect to their resistance to SCC. An example of results for a 22Cr DSS steel from Cihal[11] is shown in Figure 6.
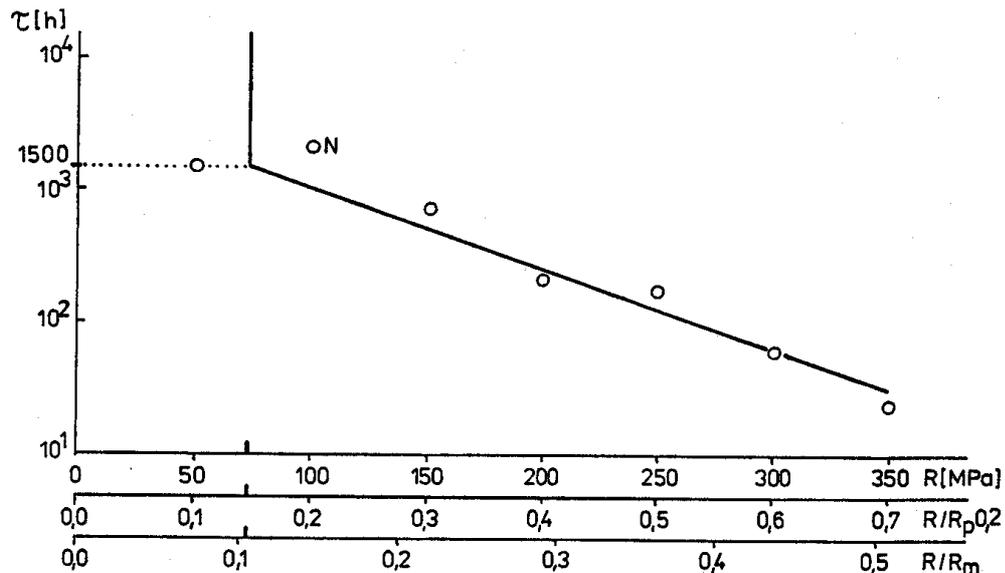

Figure 6   Example of test results for a DSS in drop evaporation testing using 0.1 M NaCl[11].

Further examples from NPL, including unpublished work, are shown in Figure 7.
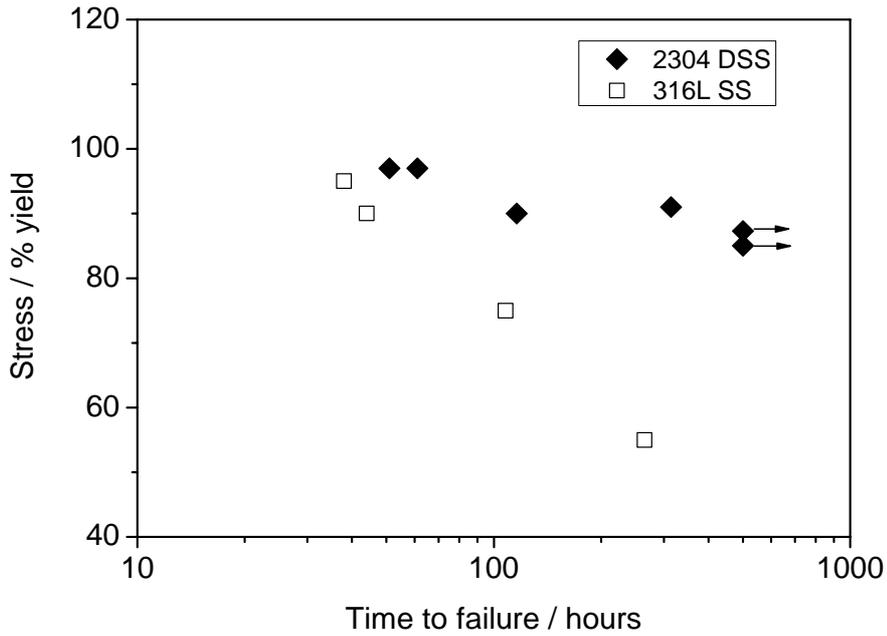
Figure 7. Results from drop evaporation testing at NPL on a 2304 DSS and a 316 L SS[12]

There can be a significant spread in the time-to-failure near the threshold stress. Such scatter is to be expected in the approach to threshold and is apparent also in corrosion fatigue studies. Also, as localised corrosion is a likely precursor of SCC under these conditions the statistical nature of this can be significant. Nevertheless, definition of the minimum stress at a specific failure time and discrimination between materials was readily possible as was distinction of different alloys as exemplified[8] also by Figure 8.

Figure 8. Ranking of materials by the drop evaporation test[9]

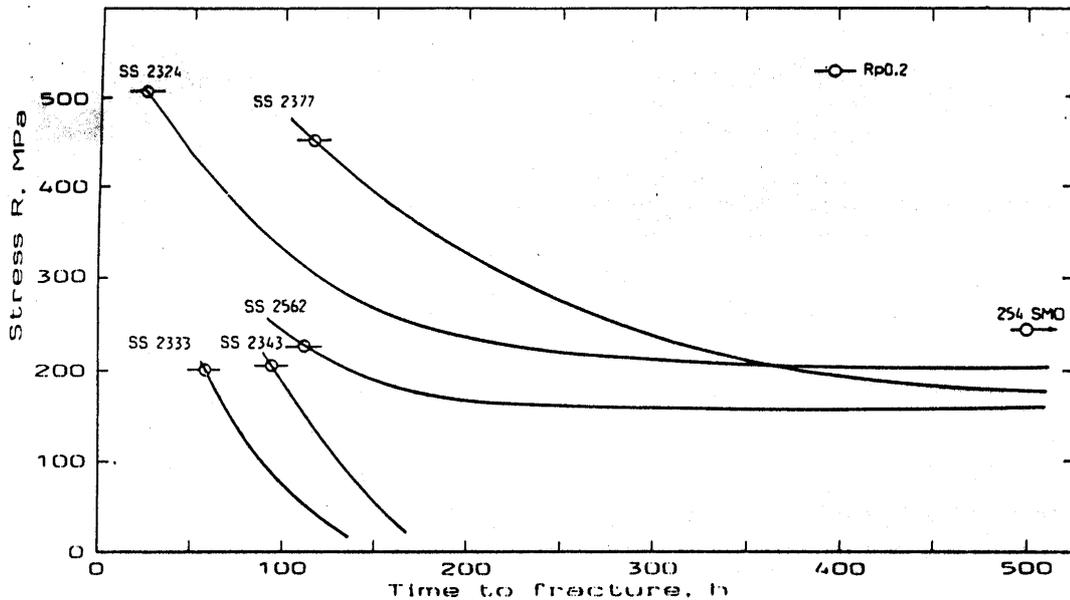These results indicate that the drop evaporation test when conducted with care can give internally consistent results. However, whilst repeatability in an individual laboratory should be achievable, reproducibility from one laboratory to another will depend critically on the specimen dimensions and will be quite different for cylindrical specimens compared with flat specimens and for specimens of different thickness, as this will affect the thermal mass.

The maximum exposure time in the Avesta work and in the ISO standard is set at 500 h. Of course this is arbitrary but since this is an accelerated test, there is need for a balance. The issue is whether no failure would occur at longer time at a lower stress level. If no pitting occurs then this is not likely. If pitting does occur, it is possible that with longer exposure time the conditions for the pit-to-crack transition may be met and a lower threshold obtained. Stress corrosion cracking does not occur in the immediate region of impact of the drop, which is continuously washed but close to the edge of the salt zone as the liquid spreads and dries out forming a significant crust.

Clearly for any fitness for purpose evaluation for topside application, it is essential to use seawater (albeit artificial seawater) and to restrain the maximum temperature to 130 °C. In addition to the possible difference in pH associated with concentration of seawater compared with 0.1 M NaCl, the nature of the salt layer will be different with more hydgroscopic salts and carbonates. This will lead to a different wetting and drying cycle from that of the NaCl solution under equivalent test conditions.

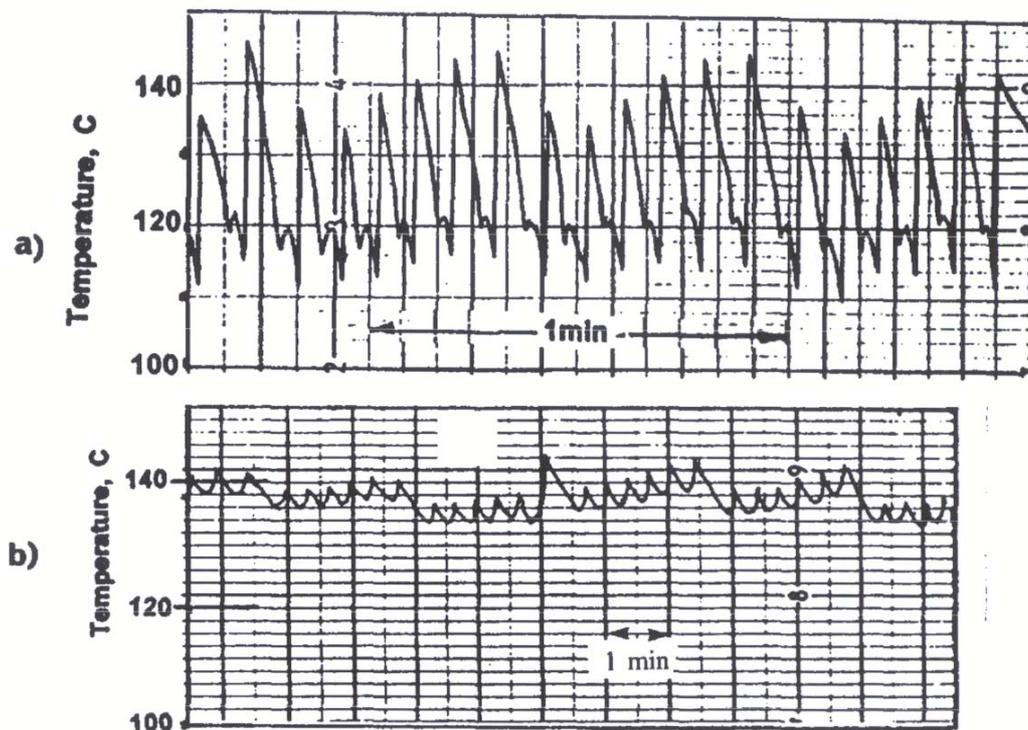This is exemplified by the data[14] of Figure 9.

Figure 9   Temperature trace at 40 mins (a) and 5 hours (b) after start of the test with seawater dripped onto a C-ring[14].

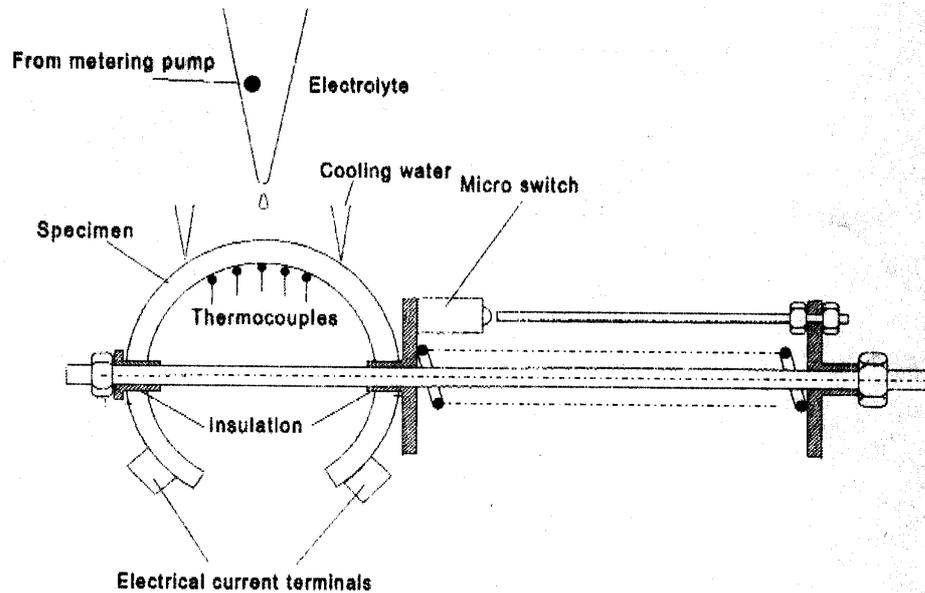The measurements were made using a C-ring test as shown by Figure 10.

Figure 10. Drop evaporation test on C-ring with cooling water used to control the temperature gradient[14].

Measurement of temperature beneath the specimens is not ideal, though the authors are commended for trying to determine the distribution. It would have been useful to have attached one thermocouple on the wetted surface at least transiently.

Here, as the salt layer builds up, the system did not appear to dry out between each drop as the concentrated solution formed now begins to stabilise at the test temperature. The mean temperature correspondingly rises. It would have been informative to establish the time to dry out by allowing a longer interval between drops.

The authors had tested in both welded and unwelded conditions. In the former case, failure occurred about 2 mm from the fusion line. It was suggested that the increased thickness of the weld itself led to a lower stress at the weld itself. Thus, the test would give no insight as to the role of weld microstructure with respect to SCC susceptibility. The lower corrosion resistance of the welded UNS S31803 and UNS S32760 was assumed to be related to oxidation of the surface during welding, favouring initiation of localised corrosion.

2.2.1.3 *Continuous feed evaporation*

The distinction between this approach and that of drop evaporation is the continuous supply of seawater to the hot tensile specimen. This can be achieved by the wicking method[15] or by directly pumping solution on to the specimen at a controlled slow rate. In both cases the effective supply rate of solution is controlled to ensure evaporation, with salt deposits forming a short distance form the source.

Directly pumping the solution onto the specimen using a peristaltic pump with very low flow rate of 2.6 ml/hour was explored briefly at NPL. The glass tube or PTFE tube was mounted above a horizontally loaded tensile specimen and in constant contact at the mid-point of the gauge length. This method was observed to give more consistent behaviour in terms of temperature fluctuation than the drop method (unpublished work).

The wicking method forms a part of ASTM C692-00. The method consists of using a wick of glass wool to draw a chloride ion solution containing 1500 ppm chloride up to the surface of a heated U-bend specimen of the alloy being evaluated. The latter specimen form is not the key issue here, just the wetting method. The standard states that the level of the solution should be approximately 1/2" (12.7 mm) below the bottom of the stressed specimen. The wicking solution (1500 ppm chloride ion) is replenished daily to maintain a relatively constant liquid level. In the particular standard, it is specified that the specimen temperature is controlled to the local boiling point ±6 °C but with no indication as to where the temperature sensor is located.

The disadvantage of the wicking method is the lack of control of the flow rate of the solution on a continuous basis so that overnight the temperature can rise significantly because of the fall in water level. Direct slow pumping would seem preferable if a continuous feed were considered preferable to the dripping method.

2.2.1.4 *Other methods*

Jargelius-Pettersson et al[5] used an atomising spray nozzle that was directed at a slow strain rate specimen heated to 150 °C (Figure 11). With intermittent spraying (1 s spray followed by 20 s recovery period) with 1% NaCl, the temperature cycled from about 90 °C to 150 °C with a period of 21 s. A stress fluctuation of about 20 MPa induced by thermal cycling was noted. No such measurements were reported for the drop evaporation test but since the temperature range is less for the latter with 6 drops per minute, it would be less significant.
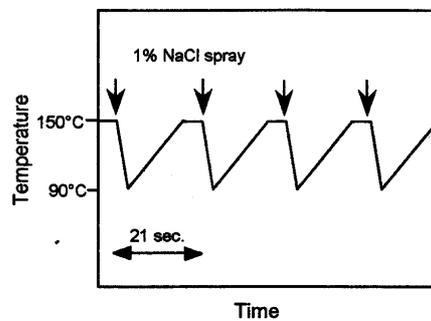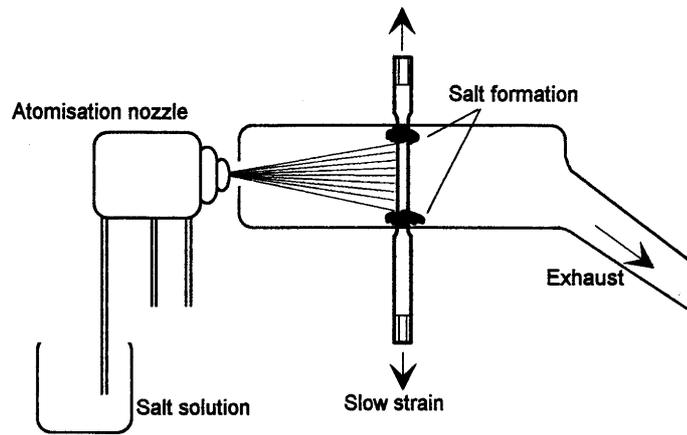
Figure 11. Slow strain rate testing of heated specimen subjected to intermittent spraying[5].

3   DISCUSSION

3.1   GENERAL

In relation to completion brines, testing is comparatively straightforward with the only issue being that of defining and controlling the concentration of oxygen. As indicated above, for autoclave testing, the maintenance of a controlled oxygen level is best achieved by using a mixed gas, with the appropriate level of oxygen, and a pressure release valve on the outlet side of a condenser set so that there is always a regular throughput of gas. Testing at ambient pressure conditions is straightforward but with care to avoid unintentional uptake of oxygen.

The more significant challenge is assessing how best to test under evaporative conditions. Here, the major differences in approach arise in the context of submerging the test specimen in simulated concentrated solution deemed to form at the metal-solution interface versus some means of directly inducing evaporation by dropping or spraying a salt solution onto a heated specimen. Most studies have focused on seawater or NaCl, rather than formation waters and mainly using NaCl.

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The distinction with seawater, relative to NaCl is the lower pH that can be obtained if the Mg^{2+} concentration increases significantly, calcareous deposits, the hygroscopic nature of the precipitated salts of the cations, and the higher boiling point of the concentrated fluid formed on the metal surface. Thus, in assessing the performance of materials for service, it would be deemed a more relevant environment, although the indications from testing are that ranking of materials is similar. The key issue is whether to test in submerged conditions vs an evaporation system.

Drop evaporation with seawater led to a build up of product, with uncertainty as to whether the solution dried out between drops. The mean temperature also rose. Presumably in the latter case this reflects retention of hot liquid and a consequent damping of the effect on the metal temperature of further drops. The issue for the concentrated solution is the pH to be expected. It may seem apparent that it will be low because of the high concentration of Mg^{2+} ions but this ignores the dynamic effect of the corrosion reaction, which would tend to raise the pH due to cathodic consumption of hydrogen ions and reduction of oxygen, and the solution chemistry cycling induced by the drop process. In the latter case, the oxygen concentration on addition will be that of the ambient temperature drop and far greater than the equilibrium value at temperature. Hence, the chemistry will be more "dynamic" than that of the fully immersed situation. In the latter case there is a large reservoir of solution of low pH. Indeed it may be retention of the liquid salt phase for longer at a high temperature is the key factor in the drop evaporation case rather than the lower pH and the bulk solution approach may not reflect this.

Nevertheless, the advantage of submerged testing is that the conditions are readily definable. However, what concentration to test at seems a little arbitrary. It is also a concern whether simply evaporating off water in a beaker type test is equivalent to the process on a heated surface because of the possible role of reactions, as discussed above, in affecting the pH and precipitation processes including the higher than equilibrium oxygen concentration. There is a concern about activating crevice attack at the loading points in the fully immersed case but that does not seem to have been significant.

The net conclusion for the seawater studies would seem to be that the fully immersed conditions gives less scatter than the drop evaporation test (based on one study!) but with the same ranking of materials. There was an indication that the submerged specimen test was more severe. The effect of oxygen level was not assessed, the focus being on replicating external SCC rather than internal SCC.

Of the evaporation tests, there is the issue of dropping the solution onto the specimen, feeding it directly at a slow rate to the surface, spraying it on, or using the wick test. The wick test is the least satisfactory as the supply rate is not well controlled but can fluctuate as the level fluctuates. In principle this could be balanced by automatic maintenance of water level but it has no clear advantage over the drop test or the continuous feed test. The drop test can give satisfactory results provided the drop rate is maintained constant and the procedure adopted to avoid overheating of the specimen. Anecdotal reference to scatter is sometimes quoted. However, the evidence of the studies reported above is that it can be controlled but recognising that on the approach to threshold stress, large variations in time to failure are inevitable and are apparent in other studies.

The spray method would need to be tested over a long period to ensure no salting out in the nozzle and subsequent blockages. Our own experience at NPL suggested problems of this kind in longer term testing but we did not explore this fully and it is feasible this could have been resolved. If working correctly it should result in a more uniform distribution of fluid to the surface and of temperature. Measuring the surface temperature presents more problems in this case.

Testing in evaporative conditions internal to the topside piping or downhole tubing presents the same issue of whether to test in a submerged simulate concentrated environment or under evaporative conditions. The challenge with the latter is that the vaporisation may be due to a pressure drop so there is not the same temperature cycling effect associated with a cold fluid on a hot surface. Controlled cyclic variation of such a pressure fluctuation would present a challenge and it may seem preferable to test under submerged conditions in this case with the appropriate partial pressure of gases. The degree to which the solution should be concentrated then needs to be resolved. In this case, the effect of oxygen concentration needs to be evaluated as has been reported previously by Huizinga et al[6]. An alternative approach is to devise an alternate immersion test with the metal temperature and solution temperature fairly similar. The partial pressure of gas has to be well maintained.

The reported observation in the HSE report[1] of a significant effect of oxygen even at low concentrations is interesting because it might be anticipated that if the solution were acidic, the role of oxygen would become marginal. It may be the case that the role of oxygen as a cathodic reactant is less significant than its influence on the nature of the oxidation states of the corrosion product and the characteristics of the oxide film (see below). Electrochemical studies combined with SCC measurements would be pertinent.

It is evident from the above that on the whole ranking of the materials is in general terms consistent for the different testing approaches. All of the tests are accelerated with respect to exposure conditions and the materials can be made to fail depending on the approach to testing. For example, at 130 °C in a simulated concentrated seawater, failure of the 22 Cr and 25 Cr DSS occurred in about 10 hours or so. The issue then is which test could be considered to most effective for qualification purposes and what the qualification criterion should be. Also, to what extent can intermittent damage be tolerated.

To resolve both aspects we need to understand more about the actual water chemistry and the cumulative damage process under conditions that reflect more realistically the transient nature of the exposure process. However, in parallel with this there is a need to look more carefully at the test specimens and in particular evaluation of welded specimens for topside application.

3.2   ROLE OF OXYGEN

The solubility of oxygen decreases with temperature, but is not affected by salt concentration at a specific temperature. The solubility must be considered in assessing the effect of temperature and in comparing boiling solutions of different salts, which will be at somewhat different temperatures.

The role of oxygen in stress corrosion cracking in concentrated salts is often confusing because of lack of measurement of actual values of oxygen in solution and of the corrosion potential. Oxygen can influence the potential directly as a cathodic reactant or indirectly by oxidising ferrous ions to ferric ions. In the latter case, there are two consequences: the ferric ions can be reduced to ferrous ions, thereby providing a cathodic reaction that does not involve the oxygen directly (though there is no net gain in cathodic reactivity); the ferric ions can hydrolyse to generate a lower pH. The hydrolysis constant for ferric ions is very much greater than ferrous ions and at low concentrations can significantly lower the pH. For example, a very carefully prepared solution of saturated $FeCl_2$ in extremely low oxygen conditions will give a pH of about 4. Moderately low levels of oxygen (values uncertain), which can easily develop in conventional deaeration, where additional precautions are not taken, can result in a pH of about 1. Of course this will be supported further by hydrolysis of Cr^{3+} ions from dissolution of the DSS. This lowering of the pH can enhance initiation and stabilise local attack and possibly more general active corrosion. Local acidity in salt layers may explain the behaviour at low concentrations of oxygen[1], associated with internal formation waters, though this needs verifying. However, if the concentrated chloride solution is sufficiently acidic oxygen may not be a necessary factor.

In terms of cathodic reactions, we may have reduction of oxygen, reduction of ferric ions and reduction of hydrogen ions all deriving from the supply of oxygen. The significance will depend on the nature of the chloride. Cottis and Newman[16] suggest that with boiling $MgCl_2$ the role of ferric ions may be assumed to have less significance because of the dominant effect of hydrogen on reduction associated with the lower pH – assuming that indeed the pH is sustained constant in the test.

As indicated previously, the pH of $MgCl_2$ at 4 M concentration is about 4 at ambient temperatures. The quoted values[7] of 1.6-2.5 for a similar solution at 100 °C are unlikely to be meaningful and may be an experimental artefact. It is still feasible that oxygen could have an effect.

Now consider the distinction between a fully immersed condition and a drop evaporation condition.

Under evaporation conditions, a salt film will form. The consequence of this is that we have then an underdeposit situation. The restricted mass transport for metal ions in the thin liquid layer will encourage concentration of the dissolving metal solution that will act as a precursor to local attack and cracking. Furthermore, consider the situation just before dry out. The liquid layer will be thin, perhaps enhancing oxygen replenishment from the air because there is a reduced thickness of liquid and hence a smaller diffusion layer thickness. In addition to any effect on the cathodic reduction of oxygen, any ferrous ions will be oxidised because the oxygen is passing through a solution layer with dissolved metal cations en-route to the surface. The solution pH may then be reduced quite considerably in locations where the ferrous ion concentration is high. There may be regions of acidity and alkalinity depending on the balance of reaction processes. In the drop evaporation test, the addition of fresh aerated solution in the sequential drop will dilute the solution on the metal surface somewhat but of course will maintain the surface wet, thereby sustaining reaction, and introduce higher levels of oxygen associated with the lower temperature of the feed solution.

The contrast with testing in immersed solutions is that there is no representation of the heat transfer and of the build up of corrosion products. Fluid flow induced by thermal convection, boiling or forced flow will mix the solution at the surface more effectively so that metal ion build up may be less significant. The diffusion layer thickness for oxygen will be different and the possibility of generating low pH due to oxidation of ferrous ions less likely.

In the above discussion, the implicit assumption in relation to formation waters is that H_2S has no influence That has to be validated and the possible role of oxygen reacting with H_2S considered.

3.3   PRECURSOR OF SCC

In order to initiate a stress corrosion crack, film breakdown is essential. This can occur by localised attack in the form of corrosion pits or crevice attack or if the environment/temperature combination is very aggressive a form of active corrosion may ensue. At high enough stress levels in a sufficiently aggressive environment, strain induced film rupture may be the crack precursor. In all cases, the solution pH is a critical factor in addition to the chloride content and temperature. The observation of the failure in the HSE report[1] suggests that initiation occurred without much localised attack. It may indeed be the case that the change in film characteristics in the thin liquid layer, allied with dynamic strain associated with the high stress state or small thermal fluctuations, were sufficient to induced cracking.

4   CONCLUSIONS

- Testing of the performance of materials in completion brines at elevated temperature is comparatively straightforward provided that there is control of the partial pressure of gases and no unwarranted ingress.

- For internal production fluids concentrated by pressure drops and vaporisation of the water phase, there is a need to consider the relevant partial pressures for testing purposes but there is also insufficient information to define the concentrated solution chemistry for a specific field chemistry. Unlike a seawater spray or dripping situation, temperature fluctuations would not be expected to be so important. However, the role of oxygen is less clear.

- In relation to external stress corrosion cracking of hot piping exposed to seawater, the adoption of concentrated seawater formed by evaporation of water makes laboratory testing of hot piping simpler. However, its relevance to service is unclear as it does not account for the dynamic processes associated with reaction kinetics and the role of deposits. The degree of concentration of the solution is also a little arbitrary. Nevertheless, it does rank materials effectively. The test is very aggressive with respect to the exposure conditions and failure occurs in a very short timescale at 130 °C.

- The drop evaporation method can give repeatable measurements when used with proper control of the variables and gives consistent materials ranking. It has more of the characteristics of service conditions provided that seawater is used. The

acceleration factor is the sustained regular supply to the specimen. However, most studies have used 0.1 M NaCl (which also gives good ranking) and there is insufficient range of studies in seawater to comment on repeatability. Nevertheless, the higher concentration of cations such as Mg^{2+} formed under evaporation conditions with seawater will lead to a higher boiling point of the liquid layer. This could mean slower drying out and higher mean temperatures in a drop test.

- There is no specific advantage of using a wick test. The current standard would result in a variable wetting rate because the reservoir level is allowed to decrease overnight. This could be modified. However, with modern pumps capable of delivering slow flow rates it would be better simply to have a continuous pump-driven feed to the specimen with the end of the tube in contact with the surface but allowing the liquid to spread.

- The role of oxygen in thin liquid layers can be variable leading to enhanced reduction kinetics as the layer dries out because of a small diffusion layer thickness (important if in diffusion limited regime) or oxidation of ferrous ions with then increased acidity. The local acidity associated with hydrolysis of ferric ions could be an explanation for the impact of oxygen at low concentration at which its role as a cathodic reactant itself would seem insignificant.

- None of the tests simulating seawater exposure give a satisfactory basis for material qualification for service. There are no agreed qualification criteria and it is a matter of judgement for the user.

- The optimum way of testing of welds needs to be addressed.

5 ACKNOWLEDGEMENTS

6 REFERENCES

1. HSE Offshore Division Safety Notice 3/3003, Issue data: Dec. 2003.

2. A Leonard, 'Review of external stress corrosion cracking of 22%Cr duplex stainless steel, HSE Research Report 129 - ISBN 0-7176-2718-7

3. R. Mack, C. Williams, S. Lester and J Cassava, 'Stress corrosion cracking of a cold worked 22 Cr duplex stainless steel production tubing in a high density clear brine $CaCl_2$ packer fluid', Paper No. 02067, Corrosion 2002, Denver, NACE Int., Houston, TX., 2002.

4.	Gemelin, Handbuch der Anorganischen Chemie, 1972, Max Planck Institute fur Anorganische Chimie

5.	R.F. A. Jargelius-Pettersson, J. Linder and S. Hertzman, Ranking the resistance of duplex stainless steels to chloride-induced stress corrosion cracking, Paper no 025, Duplex Stainless steels '97, Stainless Steel World, KCL Publishing, 1998.

6.	S Huizinga, B. McLoughlin, W.E. Like and J.G. de Jong, Corrosion 2003, Paper No. 03129, NACE Int., Houston, Tx, 2003.

7.	J.M. Drugli and U. Steinsmo, 'Assessment of susceptibility to chloride stress corrosion cracking of highly alloyed stainless steel. Part II: A new immersion test method', Paper no. 194, Corrosion 97, New Orleans, NACE Int., Houston, Tx., 1997.

8.	S. Henrikson and M. Asberg, Corrosion, 35 (1979) 429.

9.	B.M. Svensson and T. Andersson, 'The drop evaporation test – An accelerated test method for stress corrosion cracking of stainless steel in chloride media', Proc. 10th Scandinavian Corrosion Congress, Stockholm, 297, 1986.

10.	'Laboratory testing of iron- and nickel-based alloys for relative resistance to stress corrosion cracking in a sodium chloride drop evaporation system', MTI-5 Test method (Revised 1995).

11.	V. Cihal, Werkstoffe und Korrosion, 43 (1992) 532.

12.	P.E. Francis, A.J. Griffiths and A. Turnbull, "Development of an improved test method to measure stress corrosion cracking under evaporation conditions", Eurocorr '97, Trondheim, 1997.

13.	ISO-15324:2000, Evaluation of stress corrosion cracking by the drop evaporation test.

14.	U. Steinsmo and J. M. Drugli, 'Assessment of susceptibility to chloride stress corrosion cracking of highly alloyed stainless steel – Part I: Drop evaporation test method', Paper no. 193, Corrosion 97, New Orleans, NACE Int., Houston, Tx., 1997.

15.	ASTM C692-00, 'Standard test method for evaluating the influence of thermal insulations on external stress corrosion cracking tendency of austenitic stainless steel', ASTM Int., West Conshoshocken, PA.

16.	R.A. Cottis and R.C. Newman, Stress corrosion cracking resistance of duplex stainless steels, HSE Report, OHT 94 440, 1995.

Appendix 1.

Representative field chemistries in different locations and typical make-up chemistries.

Field 1.

Water Analysis Data			Test Solution Compositon	
Chemical Species	(mg/l)		Reagent	(g/l)
Sodium	45908		$CaCl_2.6H_2O$	194.6
Potassium	3339		$MgCl_2.6H_2O$	56.79
Calcium	35602		KCl	6.37
Magnesium	6791		$SrCl_2.6H_2O$	2.68
Barium	34		$BaCl_2.2H_2O$	0.0605
Strontium	880		NaCl	114.7
Iron	-		Na_2SO_4	0.1065
Chloride	156123		$NaHCO_3$	4.662
Sulphate	72			
Bicarbonate	3386			
Barium	34			

Field 2

Water Analysis Data			Test Solution Compositon	
Chemical Species	(mg/l)		Reagent	(g/l)
Sodium	10,296		$CaCl_2.6H_2O$	0.13
Potassium	139		$MgCl_2.6H_2O$	0.109
Calcium	24		KCl	0.27
Magnesium	13		$SrCl_2.6H_2O$	0.014
Barium	1		$BaCl_2.2H_2O$	0.0018
Strontium	4.5		NaCl	19.185
Iron	-		Na_2SO_4	0.50
Chloride	11,848		$NaHCO_3$	7.14
Sulphate	337.5		Acetate	2759µl/l
Bicarbonate	5183			
Barium	1			
Organic Acid	2758			