Review of Effect of Chloride on Corrosion of Stainless Steels in Cementitious Environments
Report to NDA RWMD

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Review of Effect of Chloride on Corrosion of Stainless Steels in Cementitious Environments

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This report has been prepared by Serco under contract to Nirex and forms part of an ongoing programme of research commissioned by Nirex to underpin the long-term safety of a geological disposal facility for higher-active radioactive wastes. Before it was published Nirex was subsumed into the NDA.

The report has been reviewed by NDA. However, references to Nirex in the text have been retained as they are appropriate for the period when this research was being performed. The views expressed and conclusions drawn in this report are those of Serco and do not necessarily represent those of Nirex or the NDA.

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Executive Summary

A limited fraction of the ILW considered for disposal in a Geological Disposal Facility (GDF) may contain relatively high concentrations of chloride. There is a concern that the high concentrations of chloride in the porewater of any encapsulant grouts that may be used might promote localised corrosion of container materials. The objective of this report is to review the information available to evaluate the effect of high porewater chloride concentration on the corrosion of stainless steels.

The report reviews the relevant literature and summarises the experiments undertaken on 304L and 316L stainless steel in the Nirex Safety Assessment Programme. Most of the available information refers to the 300 series austenitic stainless steels, and to a lesser extent to duplex stainless steels. A small amount of information about low alloy ferritic stainless steels is given.

The data in the literature for long-term exposure tests indicate that stainless steel in cementitious environments has a high resistance to localised corrosion up to 5 wt% relative to cement. Electrochemical measurements indicate that the critical chloride concentration for pitting in alkaline porewater environments is >10% for 316SS at temperatures below 40 °C.

Evidence from the literature and from tests carried out for Nirex under the NSARP indicate that the critical chloride to hydroxide ratio for pitting corrosion of stainless steel 316L in a cementitious environment, CCl/OH, has a value of at least 14 at temperatures up to 70 °C.

There is no evidence for significant galvanic corrosion of stainless steel/carbon steel couples embedded in chloride-contaminated cement.

Only limited data are available on the corrosion performance of low alloy ferritic stainless steels but they appear to be more resistant to pitting than mild steels under similar conditions.

The presence of thiosulphate, which may be released from BFS grouts, is detrimental compared to chloride environments alone, resulting in severe pitting attack under neutral conditions. Increasing pH substantially reduces the effect but insufficient data are available to confirm resistance under the full range of possible conditions.

Slow strain rate testing has indicated that stress corrosion cracking may also occur in chloride/thiosulphate environments, even under alkaline conditions. This has not been confirmed under more realistic loading conditions.
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1 Introduction

In support of Government policy, the Nuclear Decommissioning Authority (NDA) is responsible for developing safe, sustainable and publicly acceptable solutions to the challenge of nuclear clean-up and waste management in the UK. As part of the NDA, the Radioactive Waste Management Directorate (RWMD) was established to develop and implement geological disposal as a long term solution for the management of the radioactive wastes generated by the country’s commercial, medical, research and defence activities. The wastes currently include high level waste (HLW), spent nuclear fuel (SF), intermediate level waste (ILW) and some low-level radioactive wastes (LLW) unsuitable for disposal in the Low Level Waste Repository.

In support of this remit, NDA RWMD has defined packaging standards and developed a methodology to give confidence that wastes that are conditioned and packaged will be suitable for safe storage, transport, handling and eventual disposal. Packaging proposals are assessed during the Letter of Compliance process, which includes an evaluation of the expected durability of waste packages on the basis of the corrosion resistance of container materials in contact with specific waste types.

A limited fraction of the ILW considered for disposal in a Geological Disposal Facility (GDF) may contain relatively high concentrations of chloride. There is a concern that the high concentrations of chloride in the porewater of any encapsulant grouts that may be used might promote localised corrosion of container materials. The subject of the concentration of chloride expected in porewater for a given concentration of chloride in the waste has been reviewed previously [1] and the objective of the current document is to review the information available about the effect of high porewater chloride concentration on the corrosion of stainless steels, which are the main encapsulation materials currently considered for ILW. In particular it presents the critical chloride concentrations and critical chloride/hydroxide ratios for the corrosion of stainless steel in cementitious environments.

In Section 2 of the report, relevant literature is reviewed. Most of the available information refers to the 300 series austenitic stainless steels and to a lesser extent to duplex stainless steels. In Section 3 the results of experiments undertaken on 304L and 316L stainless steel in the Nirex Safety Assessment Programme are summarised. Section 4 summarises the main conclusions arising from the review.

2 Literature on Corrosion of Stainless Steels in Cement

The most common application of stainless steel in a concrete environment is as a substitute for carbon steel reinforcement bars. Stainless steel may be substituted where corrosion of carbon steel is likely in high chloride environments, for example where de-icing salts are present, or in marine environments [2,3]. Although the cost of stainless steel is higher, the increased durability of the stainless steel has long-term economic advantages when it is used selectively in the most susceptible regions of structures [2,4]. Bibliographies and reviews of the experience of stainless steel reinforcement in concrete structures and the results of relevant research programmes are available in references [5] and [6]. These references concluded that stainless steel is capable of maintaining excellent corrosion resistance in concrete in the severe chloride-containing environments. Stainless steels are resistant in carbonated concrete but may suffer pitting corrosion in chloride-containing concrete. The intensity of the pitting corrosion increases...
with chloride concentration. No cracking of concrete has been observed due to corrosion of stainless steel bars and no stress corrosion was observed in any of the research reviewed.

2.1 Corrosion of stainless steel rebar in concrete

In this section the results of a series of research programmes on the performance of stainless steel in concrete are summarised. The majority of these tests were long term exposure tests (~2-20 years), usually of concrete samples containing stainless steel reinforcing rods. Typical test environments were air, often in marine environments and sometimes with temperature cycling, aqueous chloride solutions or seawater. In several of the tests the concrete was mixed using chloride-containing water. Some electrochemical testing has also been carried out. The review is divided into long-term exposure tests and aqueous electrochemistry measurements.

2.1.1 Long-term exposure tests of stainless steel in concrete

1. Long-term tests on 302, 315 and 316 stainless steels embedded in chloride-contaminated concrete, with up to 3.2 wt% chloride present as calcium chloride in the cement and with the samples exposed at a marine coastal site, resulted in no visual evidence of corrosion after 22 years [7,8]. Two types of specimen were tested, namely concrete prisms and concrete bars. The weight loss for each test piece in the prisms was measured for each bar and found to be less than 0.05%. Based on the information given in the paper about the size of the test bars, this would correspond to a corrosion rate of <0.06 μm yr⁻¹. Electrochemical measurements showed that the potential of the steel was in the passive range (-27 to +124 mV SCE) and the passive current densities were 0.02 to 0.2 μA cm⁻², corresponding to a maximum corrosion rate of ~2 μm yr⁻¹.

2. Partly embedded 316L stainless steel in concrete exposed to seawater exhibited negligible corrosion after 12.5 years [9]. Two types of concrete were tested, namely an ordinary Portland cement (OPC) concrete and a Sulphate Resisting Portland Cement (SRPC). After 12 years, staining of the surface was observed in both types of cement. After removal of the staining it was apparent that the attack was superficial. After 12.5 years’ exposure one of the stainless steel bars had suffered crevice corrosion running from the surface of the SRPC concrete block along the interface between the specimen and the concrete block. The good corrosion resistance was attributed to the beneficial effects of the alkaline porewater.

3. Summers and Olsen [10] cast type 316 stainless steel rebars in poorly cured concrete made with 3.2% chloride. The rebars showed no significant weight loss after 12 years’ exposure in the Arabian Gulf, where high temperatures and extremes of humidity were experienced.

4. Gu and co-workers [2] carried out tests using U-bends of four stainless steel rebar materials: 316, 304, 2205 (duplex) and Nitronic 33. Experiments were carried out at chloride concentrations of 0, 0.5 and 2 wt% of the cement. The temperature was cycled over the temperature range 25°C to 65°C, with 80% relative humidity. No cracking of the concrete occurred after two years and electrochemical activity was negligible.

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1 It has not been possible to obtain a copy of the original reference and so it has not been possible to check the actual weight loss recorded.
5. Rosso [11] studied the performance of various grades of stainless steel reinforcement (304, 316 and two duplex grades) in concrete in the temperature range –27 to +60ºC. Temperature cycling was followed by immersion in chloride solution (20 wt% sodium chloride or 27 wt% calcium chloride), followed by drying. The cycle was repeated for 90 days. Slight corrosion was observed on the 304 stainless steel but no corrosion was observed on 316 or the two duplex grades.

6. Zoob [12] conducted tests using 304 stainless steel reinforcement mats in a concrete whose chloride concentration was 2.1 wt% relative to the weight of cement, at the level of the reinforcement bars. The slabs were placed in chloride solution for 3 days at 16-27ºC, followed by drying at 38ºC for 4 days. This cycle was repeated for 48 weeks, after which no signs of corrosion damage were detected.

7. Rasheeduzzafar [13] carried out tests on 304 stainless steel clad reinforcement bar in a seven year exposure site programme in concrete containing chloride at concentrations of 0.6, 1.2 and 4.8 wt%, relative to the mass of cement. The test blocks were exposed to the environment of Eastern Saudi Arabia. After seven years, no corrosion was detected on the 304 clad reinforcement bars.

8. Pastore [14] tested 304, 316 and duplex stainless steel in concrete at concentrations up to 3 wt% (referred to the weight of cement). Electrochemical measurements (open circuit potential, LPR and potentiostatic tests) showed that the stainless steels remained passive.

9. Sorensen [15] used electrochemical measurements to determine the critical chloride concentration ranges for corrosion of stainless steel in mortar containing sodium chloride and sulphate resistant Portland cement (SRPC) at ambient temperature. The corrosion currents were measured for 304 and 316 stainless steel, with and without welds, at potentials fixed near the free corrosion potential. For 304 steel the critical concentrations were 2-5% and 4-8% for welded and parent material respectively, expressed as a percentage of the weight of cement [15], whereas for 316 the corresponding ranges were 2-5% and 4 to >8 %. These results show that (a) 316 stainless steel is more resistant to corrosion in cement than 304, and (b) the presence of welds, and in particular the different surface condition in the weld area (e.g. oxide thickness, porosity) effect the corrosion resistance of the weld. The values reported by Sorensen [15] are somewhat lower than those obtained in the NSARP using Nirex Reference Vault Backfill (NRVB) (see Section 3.1), where no corrosion of unwelded 316 was observed with over 23 wt% chloride present. This may reflect the fact that SRPC binds less chloride than other forms of cement, including NRVB. Iron deposits or swarf on the surface of stainless steel embedded in mortar were found to be provide good initiation sites for crevice corrosion [15].

2.1.2 Electrochemical measurements

1. Nurnberger [16] measured the pitting potential for welded reinforcement bars made from a number of different stainless steels, including 320 (1.4571), which is similar in composition to 316 with an addition of up to 0.7 wt% titanium, as well as duplex and ferritic stainless steels. The pitting potential became more negative with increasing chloride concentration and carbonation, indicating a greater risk of pitting corrosion. Deformed, ribbed bar was found to give more negative pitting potentials than plain bar. On the basis of the pitting potential measurements and the expected corrosion potential, no pitting would be expected for 320 grade stainless steel in concrete with a chloride content of less than ~5% (relative to the cement content), even for deformed material, or if the concrete were carbonated. This was confirmed by field tests over 2.5 years in carbonated concrete with a chloride content of
up to 2.5% (relative to the cement content), in which no corrosion occurred on ribbed and welded reinforcement bars made from 320 stainless steel or duplex stainless steel (1.4462).

2. In simulated concrete porewater (saturated calcium hydroxide solution, pH 12.5) Bertolini found that the pitting potential of 304(L) and 316(L) stainless steel was greater than 300 mV vs SCE at 20 °C, at chloride concentrations, in the form of sodium chloride, up to 10% [17]. The pitting potentials became more negative at 40 °C, and were most negative at the highest chloride concentrations tested (10% Cl). The critical chloride concentrations for pitting, for 304(L) and 316(L) at a controlled potential of +200 mV (vs SCE), which is a conservative upper bound for the rest potential, are shown in Figure 1 for 20 °C and 40 °C.

All these investigations have shown that stainless steels are highly resistant to localised corrosion in a cementitious environment. Experiments have been reported at concentrations up to 5 wt% (relative to cement) at ambient temperature without any indications of corrosion. Electrochemical measurements (Figure 1) suggest that at room temperature the critical porewater chloride concentration for pitting corrosion of 316 is above 10% in fresh, high alkalinity porewater, at 20 °C and 40 °C. As expected, 304 has a lower critical porewater chloride concentration than 316. The critical porewater chloride concentration decreases with lower pH and increasing temperature.

There are no accurate methods of predicting the concentrations of chloride in the porewater of the concretes used in the literature reports summarised above. The papers reviewed did not report the actual porewater concentration or pH. However, on the basis of the review of porewater concentrations of chloride and hydroxide carried out by Simmons [1] it is possible to estimate an approximate porewater concentration. For NRVB the plot of porewater chloride concentration, as a function of the proportion of chloride as a fraction of the weight of solids in NRVB is shown in Figure 2 [1]. The weight of OPC in NRVB is approximately 40%, so the scale on the abscissa should be multiplied by 2.5 to obtain the dose of chloride as a function of the OPC content. On this basis 2.5 wt% chloride in relation to the weight OPC would give a porewater concentration of 14,000 ppm chloride (i.e. 1.4 wt% chloride). If it is assumed that the equivalent porewater chloride concentration in concrete is similar to that in NRVB it can be estimated that for 5 wt% OPC the porewater chloride concentration in the concrete would be of the order of 50,000 ppm or 5 wt%. The literature evidence therefore suggests that no corrosion of stainless steel occurs with a porewater chloride concentration up to at least 50,000 ppm in cementitious material at ambient temperatures.

In the electrochemical measurements made by Bertolini (Figure 1), a value of 100,000 ppm chloride at temperatures up to 40 °C was acceptable (i.e. no corrosion occurred) in highly alkaline porewater (i.e. pH 13.9). The critical chloride concentration would have been higher than this. For a porewater pH value of 13.9, 100,000 ppm chloride corresponds to a $C_{\text{ClOH}}$ value of 3.6, meaning that the critical $C_{\text{ClOH}}$ value would have been higher than 3.6. At pH 12.6 and a temperature of 40 °C, when corrosion of 316L stainless steel occurred at a critical chloride concentration of ~4.5 wt% chloride (Figure 1), the $C_{\text{ClOH}}$ value would have been ~32. On the basis of these results the threshold $C_{\text{ClOH}}$ value for corrosion of 316L stainless steel at 40 °C was greater than 3.6 in the first measurement and about 32 in the second measurement.

The relationship between pH, chloride concentration, in ppm, and the resulting molar chloride : hydroxide ratio, $C_{\text{ClOH}}$, is shown schematically in Figure 3.
2.2 Galvanic coupling of stainless steel in cement

Within the civil engineering community there is an interest in replacing some regions of corroded carbon steel reinforcement with stainless steel reinforcement, and so the possible effects of galvanic interactions between carbon steel and stainless steel in chloride-contaminated concrete have been investigated [4,18]. Experimental work has shown that although carbon steel and stainless steel are separated in the galvanic series, galvanic coupling does not cause a significant increase in the corrosion rate of carbon steel, compared to coupling with areas of passive carbon steel. Stainless steel may even be beneficial when connected to carbon steel that is actively corroding in the presence of chloride, because it is a poorer cathode for the reduction of oxygen than passive carbon steel [15,19].

2.3 Corrosion of low alloy ferritic stainless steels

It has been found that the critical chloride concentration for corrosion in cement is at least 10 times higher for 304 and 316 than it is for carbon steel [15] and so it is expected that 3CR12 (1.4003) would also be more resistant to localised corrosion than carbon steel in cement. The form of attack is likely to be different; for example, the pits formed on 3CR12 are likely to be narrower and deeper than on carbon steel. In one study, 3CR12 reinforcement bars mounted in concrete blocks and subjected to a weekly cycle of salt spray exposure and drying in the atmosphere for 4.5 years did not show any significant signs of corrosion or cracking [20], whereas mild steel bars subjected to the same testing suffered significant corrosion leading to cracking of the concrete.

Nurnberger [16] included 3CR12 in his study of pitting potential and long-term exposure in concrete. The performance of 3CR12 was superior to mild steel but electrochemical tests suggested that 1% chloride (relative to cement content) would be sufficient to cause corrosion in concrete. This was confirmed by field tests. The welded material was more susceptible than the unwelded.

3 Experimental Results from the NSARP

3.1 Pitting of stainless steel in cement

The aim of the work carried out under the Nirex Safety Assessment Research Programme (NSARP) was to determine the critical chloride concentrations and critical temperatures required for the initiation of pitting corrosion of stainless steel in Nirex Reference Vault Backfill (NRVB). This was addressed by carrying out long-term tests on metal samples embedded in NRVB over a range of temperatures and chloride concentrations.

Two types of specimens were used for the tests, namely 304L and 316L bullet specimens and plate specimens. The bullet specimens were used for most of the tests and sheet specimens were only used in the last year of the programme for tests on stainless steel. Prior to testing, the specimens were abraded with 280 grit abrasive paper, then degreased in acetone. The rods were then sheathed in heat shrink tubing and a thin layer of a proprietary masking agent (‘Turco-lacquer’) was applied to seal the insulation-specimen interface and reduce the risk of crevice corrosion.
The plate specimens were designed to maximise the surface area available for pitting. The samples were either 304L or 316L stainless steel. They consisted of 50 × 40 mm pieces of 1.5 mm thick stainless steel plate, connected to 1 mm diameter 316L stainless steel wire by spot welding. The spot welded region was coated with epoxy resin and the connection wire was encased in heat shrink insulation. The sheet was used in the 'as received' condition, corresponding to a grade 2B finish. Full details of the experimental arrangements for these tests are given in [21].

The results from the pitting tests on stainless steel in a range of test environments are presented in Table 1. The results are shown graphically, as a function of temperature and the concentration of chloride as a percentage of the weight of Ordinary Portland Cement (OPC), in Figure 4. Table 1 includes estimates of $C_{Cl}/OH$, the ratio of chloride ion and hydroxide ion concentrations in the porewater, based on measured values and values predicted from calibration experiments [21]. Values of $C_{Cl}/OH$ based on a pH value of 13 are also given; this pH is typical of a fresh NRVB porewater. There were some experimental difficulties in accurately determining the true pH of porewater samples extracted from cement, due to reaction with carbon dioxide in the air. A porewater chloride concentration of 50,000 ppm corresponds to a molar $C_{Cl}/OH$ value of 14.1, based on an assumed porewater pH of 13. The actual porewater chloride concentration in the tests at 80°C was probably considerably higher than this value, due to the effect of temperature on the dissociation of Friedel’s salt.

The only experiments in which pitting of stainless steel was observed were at approximately 60°C, with a high concentration of chloride present. Sample SS9, composed of 304L, suffered severe corrosion when $C_{Cl}/OH$, based on the room temperature prediction of chloride concentration and assuming a porewater pH of 13, was over 29. One 304L sample (SS11) showed mild corrosion at a calculated $C_{Cl}/OH$ value of over 13. The actual ratios would probably have been considerably higher, in view of the increase in porewater chloride concentration with increasing temperature as a result of decomposition of Friedel’s salt [21].

Extensive testing on 316L (see Table 1) showed that no corrosion was observed on any of the specimens up to a temperature of 70 °C for a $C_{Cl}/OH$ value up to a measured value of about 14, which was the maximum value of the $C_{Cl}/OH$ tested. The actual ratios would probably have been considerably higher, in view of the increase in porewater chloride concentration with increasing temperature as a result of decomposition of Friedel’s salt [21]. It is possible that actual threshold values would be significantly higher than 14. The temperature value of 70 °C is likely to be significantly higher than the temperature that may be experienced by ILW packages during their lifetime (recent modelling shows that peak temperatures of about 39 °C are likely to be experienced after closure, if a cement-based backfill is used [22]). This suggests that a threshold value of 14 for the $C_{Cl}/OH$ for 316L is likely to be conservative. At room temperature, for example, corrosion was not observed at values of the $C_{Cl}/OH$ up to about 29. These data broadly agree with the estimated values of $C_{Cl}/OH$ where corrosion did not occur, based on literature information (see Section 2.1). In particular, from data reported by Bertolini [17], a value of the critical $C_{Cl}/OH$ of about 32 for 316L for 40 °C can be inferred (see Section 2.1.2),

2 Note: the nominal external temperature during this experiment was 80 °C but the internal temperature in the cement block was approximately 60 °C [21].

3 Note: the nominal external temperature during this experiment was 80 °C but the internal temperature in the cement block was approximately 70 °C [21].
which is considerably higher than the conservative value of 14 estimated based on the NSARP data.

Based on this information, it is suggested that a value of the chloride to hydroxide concentration \((C_{\text{ClOH}})\) of 14 can be adopted as a conservative value below which pitting corrosion of stainless steel grade 316L in cement is unlikely to occur. This grade has been considered so far for the manufacture of most container parts.

For 304L, corrosion was observed in the NSARP at a nominal temperature of 80 °C at an estimated \(C_{\text{ClOH}}\) value of 13.90, but no data were obtained for 304L in this programme for lower chloride concentrations. Data from Bertolini [17] showed that at 40 °C the critical \(C_{\text{ClOH}}\) value for 304L was similar to that of 316L (4.5 wt%, equivalent to a \(C_{\text{ClOH}}\) value of about 32 – see section 2.1.2). Further data, however, are needed to confirm appropriate threshold values for this grade.

3.2 Pitting in thiosulphate – chloride solutions

In neutral and alkaline environments, it has been demonstrated that the addition of thiosulphate to chloride-containing causes severe pitting of 304L and 316L stainless steels, provided the ratio of the sum of the sulphate and chloride concentrations to the thiosulphate concentration falls within a critical range [23 -27]. 316 stainless steel is more resistant to thiosulphate pitting than 304 stainless steel. At higher pH, the pitting of austenitic stainless steels is significantly reduced by the high concentration of \(OH^-\) ions but not entirely eliminated up to a pH of about 12.

At pH greater than 12.5 (relevant to typical BFS/OPC grouts, which may contain thiosulphate), the pitting behaviour of stainless steel has not been fully examined at the temperatures and concentrations of thiosulphate and chloride relevant to grout encapsulation. The only data available suggests that thiosulphate corrosion is significantly inhibited if the pH is raised above 12.5 [23].

3.3 Stress corrosion cracking of stainless steels in BFS cements

BFS-based grouts can release thiosulphate into porewater. Work within the NSARP has been investigating the effect of mixed alkaline solutions of chloride and thiosulphate ions on the susceptibility of 304L and 316L stainless steels to SCC at 80 °C [28,29]. Slow strain rate test and U-bend specimens fitted with crevice formers were used to induce crevice corrosion. For the slow strain rate specimens, a galvanostatically controlled current was passed to ensure that crevice corrosion persisted. Summaries of the test results obtained for non-welded 304L and 316L stainless steels (i.e. stainless steel which had not been subjected to a simulated weld heat treatment) are presented in Table 2 and Table 3 respectively. The main conclusions from the work on the slow strain rate specimens are as follows:

- SCC was not observed in 316L or 304L stainless steel in 0.5M NaCl at 80 °C at pH 7 or 11 (measured at 25°C).
- the addition of 0.03M Na\(_2\)S\(_2\)O\(_3\) (sodium thiosulphate, 3360 ppm S\(_2\)O\(_3\)) to 0.5M NaCl (17,750 ppm Cl) led to SCC in 316L and 304L stainless steel at 80 °C for both neutral and pH 12 solutions.
• the severity of SCC in 0.03M Na₂S₂O₃ + 0.5M NaCl (as shown by the parameters measured during slow strain rate tests, i.e. time to failure, maximum load, reduction in area, etc.) was found to increase with decreasing pH.

• in 0.0625M thiosulphate solutions (7,000 ppm) at pH 12, SCC was observed for 304L with only $2.82 \times 10^{-5}$ M chloride (1 ppm) present. For 316L, cracking was observed at 0.0028M chloride (100 ppm) present, but not at $2.82 \times 10^{-5}$ M chloride (1 ppm).

• in 0.5634M chloride solutions (20,000 ppm) the minimum concentrations of thiosulphate required for cracking of 304L and 316L stainless steels were $>8.93 \times 10^{-5}$ M (10 ppm) and $>8.93 \times 10^{-4}$ M (100 ppm) respectively.

• failure occurred by both transgranular SCC (TGSCC) and intergranular SCC (IGSCC).

Tests performed in the same chemical conditions on U-bend specimens, however, did not show signs of SCC. It is important to recognise that slow strain rate testing in the presence of crevice formers and impressed currents is a severe test in which corrosion is deliberately induced. The results on U-bend specimens indicate that the susceptibility observed in the slow strain rate tests may not be observed in practice.

Tests on U-bend samples were carried out in the NSARP, in which highly deformed, statically loaded smooth specimens of 304L and 316L were exposed to a range of alkaline solutions containing thiosulphate and chloride ions at 80°C, under freely corroding conditions. Crevice corrosion was induced on the specimens using a PTFE tape crevice former. In this case, no stress corrosion cracking was observed after a period of approximately three months’ exposure, even though in some experiments the test environments were the same as those used for the slow strain rate tests. Slow strain rate tests are recognised as producing non-conservative results (i.e. they are a very severe test which may not reflect the susceptibility to SCC in practical statically loaded applications, for which a U-bend test is more applicable).

Other workers have shown that SCC of austenitic stainless steels occurs in chloride-thiosulphate mixtures at pH 12.5, but not at pH 13, because of a lack of crevice corrosion to act as an initiation site [30]. The test solutions for this work were 0.5M NaCl, with and without 0.03M Na₂S₂O₃, at pH values of 7, 12, 12.5 and 13. The test temperatures were 25, 55 and 80 °C.

Overall, the results indicate that there is a risk of SCC of austenitic stainless steels in alkaline solutions containing thiosulphate and chloride at elevated temperatures, but the susceptibility is reduced at higher pH and when the stress intensity is low.
4 Conclusions

1. Data reported in the literature from testing of stainless steel embedded in concrete indicate a high resistance to localised corrosion for chloride levels up to 5 wt% relative to the cement content (i.e. wt% OPC).

2. Electrochemical measurements by Bertolini et al indicate that the critical chloride concentration for pitting in alkaline porewater environments is >10% for 316 grade stainless steel at temperatures below 40 °C, at a porewater pH value of 13.9. The critical chloride concentration decreases with increasing temperature and decreasing pH. Corrosion of 316L and 304L was observed at 40 °C at about 4.5 wt% chloride, which is equivalent to a $C_{\text{Cl/OH}}$ value of 32.

3. Tests in cementitious backfill carried out within the NSARP indicate that pitting corrosion of stainless steel in a Nirex Reference Vault Backfill environment is insignificant for 316L below a critical chloride : hydroxide ratio, $C_{\text{Cl/OH}}$ value of 14, at temperatures up to 70 °C. These results are consistent with the results reported in the literature and it is suggested that this figure is used for NDA guidance on acceptable levels of chloride for 316L stainless steel in encapsulant porewater.

4. There is no evidence for significant galvanic corrosion of stainless steel/carbon steel couples embedded in chloride-contaminated cement.

5. Only limited data are available on the corrosion performance of low alloy ferritic stainless steels but they appear to be more resistant to pitting than mild steels under similar conditions.

6. The presence of thiosulphate, which may be released from BFS grouts, is detrimental compared to chloride environments alone, resulting in severe pitting attack under neutral conditions in certain ranges of concentrations. Increasing pH substantially reduces the effect but insufficient data are available to confirm resistance under the full range of possible conditions.

7. Slow strain rate testing has indicated that stress corrosion cracking may also occur in chloride/thiosulphate environments, even under alkaline conditions. This has not been confirmed under realistic loading conditions.
5 References


Table 1  Results of 304L and 316L stainless steel pitting tests in NRVB [21]

<table>
<thead>
<tr>
<th>Duration of test (days)</th>
<th>Sample†</th>
<th>Nominal Temp</th>
<th>CaCl₂·2H₂O (g/l in make-up water)</th>
<th>Predicted [Cl]₁₀₀ (mg/l)</th>
<th>Measured [Cl]₁₀₀ (mg/l)</th>
<th>Measured alkalinity (N)</th>
<th>C⁺ClOH M for pH 13</th>
<th>C⁺ClOH M for pH 13 &amp; predicted [Cl]₁₀₀</th>
<th>Potential results - failure rate</th>
<th>Visual inspection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bullet specimens</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>707 SS1 RT</td>
<td>10.96</td>
<td>447</td>
<td>950</td>
<td>0.189</td>
<td>0.14</td>
<td>0.27</td>
<td>0.13</td>
<td>0/6</td>
<td>no corrosion</td>
<td></td>
</tr>
<tr>
<td>1046 SS3 RT</td>
<td>19.30</td>
<td>2874</td>
<td>4100</td>
<td>0.142</td>
<td>0.81</td>
<td>1.15</td>
<td>0.81</td>
<td>0/6</td>
<td>no corrosion</td>
<td></td>
</tr>
<tr>
<td>1076 SS2 RT</td>
<td>29.60</td>
<td>5873</td>
<td>5400</td>
<td>0.37</td>
<td>0.41</td>
<td>1.52</td>
<td>1.65</td>
<td>0/6</td>
<td>no corrosion</td>
<td></td>
</tr>
<tr>
<td>1036 SS4 RT</td>
<td>70.97</td>
<td>17923</td>
<td>14000</td>
<td>0.033</td>
<td>11.95</td>
<td>3.94</td>
<td>5.05</td>
<td>0/6</td>
<td>no corrosion</td>
<td></td>
</tr>
<tr>
<td>983 SS5 RT</td>
<td>178.80</td>
<td>49328</td>
<td>52000</td>
<td>0.03</td>
<td>48.83</td>
<td>14.65</td>
<td>13.90</td>
<td>0/6</td>
<td>no corrosion, tarnish near masking</td>
<td></td>
</tr>
<tr>
<td>964 SS6 RT</td>
<td>363.55</td>
<td>103138</td>
<td>nm</td>
<td>nm</td>
<td></td>
<td></td>
<td>29.05</td>
<td>0/6</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>1663 SS7 50</td>
<td>178.80</td>
<td>49328</td>
<td>50000</td>
<td>0.038</td>
<td>37.06</td>
<td>14.08</td>
<td>13.90</td>
<td>0/6</td>
<td>no corrosion</td>
<td></td>
</tr>
<tr>
<td>752 SS10* 50</td>
<td>178.80</td>
<td>49328</td>
<td>nm</td>
<td>nm</td>
<td></td>
<td></td>
<td>13.90</td>
<td>0/6</td>
<td>no corrosion</td>
<td></td>
</tr>
<tr>
<td>872 SS8 80</td>
<td>178.71</td>
<td>49303</td>
<td>48000</td>
<td>0.038</td>
<td>35.58</td>
<td>13.52</td>
<td>13.89</td>
<td>0/6</td>
<td>no corrosion, tarnish near masking</td>
<td></td>
</tr>
</tbody>
</table>

* In these tests distilled water was added to the top surface of the NRVB blocks at regular intervals during the tests, to prevent dry-out.
† Tests shown in italics (SS9 and SS11) used 304L specimens. All other specimens were 316L.
Table 1 (contd). Results of 316L stainless steel pitting tests in NRVB [21]

<table>
<thead>
<tr>
<th>Duration of test (days)</th>
<th>Sample</th>
<th>Nom. Temp</th>
<th>CaCl₂.2H₂O (g/l in make-up water)</th>
<th>Predicted [Cl]pw (mg/l)</th>
<th>Measured [Cl]pw (mg/l)</th>
<th>Measured alkalinity (N)</th>
<th>C_{ClOH} M analysed</th>
<th>C_{ClOH} M for pH 13 &amp; predicted [Cl]pw</th>
<th>Potential results - failure rate</th>
<th>Visual inspection</th>
</tr>
</thead>
<tbody>
<tr>
<td>751</td>
<td>SS11*</td>
<td>80</td>
<td>178.71</td>
<td>49303</td>
<td>nm</td>
<td>nm</td>
<td>13.89</td>
<td>6/6</td>
<td>some corrosion at tip</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>SS12*</td>
<td>80</td>
<td>178.71</td>
<td>49303</td>
<td>nm</td>
<td>nm</td>
<td>13.89</td>
<td>0/6</td>
<td>no corrosion</td>
<td></td>
</tr>
<tr>
<td>709</td>
<td>SS9</td>
<td>80</td>
<td>363.55</td>
<td>103138</td>
<td>105000</td>
<td>0.052</td>
<td>56.88</td>
<td>29.58</td>
<td>29.05</td>
<td>6/6</td>
</tr>
</tbody>
</table>

**Plate specimens**

<table>
<thead>
<tr>
<th></th>
<th>Sample</th>
<th>Nom. Temp</th>
<th>CaCl₂.2H₂O (g/l in make-up water)</th>
<th>Predicted [Cl]pw (mg/l)</th>
<th>Measured [Cl]pw (mg/l)</th>
<th>Measured alkalinity (N)</th>
<th>C_{ClOH} M analysed</th>
<th>C_{ClOH} M for pH 13 &amp; predicted [Cl]pw</th>
<th>Potential results - failure rate</th>
<th>Visual inspection</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>SS16</td>
<td>25</td>
<td>80.01</td>
<td>20555</td>
<td>nm</td>
<td>nm</td>
<td>5.79</td>
<td>0/6</td>
<td>no corrosion</td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>SS13</td>
<td>50</td>
<td>36.93</td>
<td>8008</td>
<td>nm</td>
<td>nm</td>
<td>2.26</td>
<td>0/6</td>
<td>no corrosion</td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>SS17</td>
<td>50</td>
<td>80.01</td>
<td>20555</td>
<td>nm</td>
<td>nm</td>
<td>5.79</td>
<td>0/6</td>
<td>no corrosion</td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>SS14</td>
<td>65</td>
<td>36.93</td>
<td>8008</td>
<td>nm</td>
<td>nm</td>
<td>2.26</td>
<td>0/6</td>
<td>no corrosion</td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>SS18</td>
<td>65</td>
<td>80.01</td>
<td>20555</td>
<td>nm</td>
<td>nm</td>
<td>5.79</td>
<td>0/6</td>
<td>no corrosion</td>
<td></td>
</tr>
<tr>
<td>102</td>
<td>SS15</td>
<td>80</td>
<td>36.93</td>
<td>8008</td>
<td>nm</td>
<td>nm</td>
<td>2.26</td>
<td>0/6</td>
<td>minor corrosion observed</td>
<td></td>
</tr>
</tbody>
</table>

* In these tests distilled water was added to the top surface of the NRVB blocks at regular intervals during the tests, to prevent dry-out.

nm = not measured  
RT = room temperature (15-25ºC)

Concerning the sheet specimens - six 304L and 316L specimens were embedded in each NRVB block, which was saturated with calcium hydroxide. The chloride concentrations for the specimens were chosen to be representative of typical Sellafield groundwater compositions.
Table 2. Summary of results from slow strain rate stress corrosion tests on 304L in chloride / thiosulphate solutions at 80 °C. The specimens were fitted with PTFE crevice formers and a galvanostatically controlled anodic polarisation at a current of 12.5 µA/cm² was applied [29]

<table>
<thead>
<tr>
<th>pH</th>
<th>Chloride (M)</th>
<th>Thiosulphate (M)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.5</td>
<td>0</td>
<td>no SCC</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>0.03</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.5</td>
<td>0.03</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.5</td>
<td>0.03</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>0.03</td>
<td>no SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.5634</td>
<td>0.004464</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.5634</td>
<td>0.000446</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.5634</td>
<td>8.93 × 10⁻⁵</td>
<td>no SCC</td>
</tr>
<tr>
<td>12</td>
<td>2.82 × 10⁻⁵</td>
<td>0.0625</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>2.82 × 10⁻⁴</td>
<td>0.0625</td>
<td>no SCC</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>0.03</td>
<td>no SCC</td>
</tr>
<tr>
<td>13</td>
<td>0.5</td>
<td>0.03</td>
<td>SCC</td>
</tr>
</tbody>
</table>
Table 3. Summary of results from slow strain rate stress corrosion tests on 316L in chloride / thiosulphate solutions at 80 °C. The specimens were fitted with PTFE crevice formers and a galvanostatically controlled anodic polarisation at a current of 12.5 µA/cm² was applied [29]

<table>
<thead>
<tr>
<th>pH</th>
<th>Chloride (M)</th>
<th>Thiosulphate (M)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.5</td>
<td>0</td>
<td>no SCC</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>0.03</td>
<td>SCC</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
<td>0.03</td>
<td>SCC</td>
</tr>
<tr>
<td>11</td>
<td>0.5</td>
<td>0</td>
<td>no SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.5</td>
<td>0.03</td>
<td>no SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.5</td>
<td>0.03</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.5</td>
<td>0.03</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.4225</td>
<td>0.0625</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.0282</td>
<td>0.0625</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.0028</td>
<td>0.0625</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>$2.82 \times 10^{-5}$</td>
<td>0.0625</td>
<td>no SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.5634</td>
<td>0.008929</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.5634</td>
<td>0.004464</td>
<td>SCC</td>
</tr>
<tr>
<td>12</td>
<td>0.5634</td>
<td>0.000893</td>
<td>no SCC</td>
</tr>
</tbody>
</table>
Figure 1. Critical chloride content for 304(L) and 316(L) stainless steels based on potentiostatic tests in aqueous solutions at +200 mV (vs SCE) at various pHs, at 20 °C and 40 °C [17]. The ↑ symbol indicates that no pitting was observed at 10 wt% chloride, and that the critical chloride concentration must be higher than this value.
Figure 2. Chloride and hydroxide composition of NRVB pore water at 28 days as a function of chloride dose [1].
Figure 3. Relationship between pH, chloride concentration and molar chloride : hydroxide ratio
Figure 4. Pitting corrosion of stainless steel in NRVB as a function of temperature, and chloride concentration as a proportion of the weight of OPC [21].