Corrosion Resistance of Austenitic and Duplex Stainless Steels in Environments Related to UK Geological Disposal

A Report to NDA RWMD
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<th>Title: Corrosion Resistance of Austenitic and Duplex Stainless Steels in Environments Related to UK Geological Disposal</th>
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<td>Subtitle: A Report to NDA RWMD</td>
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<tr>
<td>Client: NDA RWMD</td>
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<tr>
<td>Document Number: QRS-1384C-R1</td>
</tr>
<tr>
<td>Version Number: Version 1.0 Date: November 2007</td>
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<td>Notes:</td>
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<td>Prepared by: Fraser King</td>
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<td>Reviewed by: Alan Paulley</td>
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<tr>
<td>Version Number: Version 1.1 Date: January 2009</td>
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<td>Notes: Incorporates changes based on review comments from NDA internal and external reviews.</td>
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<tr>
<td>Prepared by: Fraser King</td>
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<td>Reviewed by: Alan Paulley</td>
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<tr>
<td>Version Number: Version 1.2 Date: April 2009</td>
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<td>Notes: Incorporates changes based on review comments from additional NDA internal review prior to publication.</td>
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<td>Prepared by: Fraser King</td>
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Summary

A review has been carried out of the corrosion performance of austenitic and duplex stainless steels as container materials for the storage and disposal of ILW as part of the Phased Geological Repository Concept. Two grades have been selected as representative of each family, namely 304(L) and 316(L) austenitic stainless steels and 2304 and 2205 duplex alloys. Various forms of corrosion are considered, including: general corrosion, localised corrosion in the form of pitting and crevice corrosion, sensitisation-induced intergranular attack, stress corrosion cracking, microbiologically influenced corrosion, atmospheric corrosion, the effects of radiolysis and welding, and galvanic corrosion.

In general, the duplex alloys offer a number of advantages over the austenitic stainless steels, including:

▲ increased resistance of duplex alloys to localised corrosion due to the higher N content and, in some cases, higher Cr and Mo contents than “corresponding” austenitic stainless steels, although this benefit is reduced at temperatures >50°C;

▲ significantly improved resistance to chloride-induced stress corrosion cracking, with possible immunity of duplex grades at temperatures <100°C; and

▲ a higher threshold stress for stress corrosion cracking for duplex alloys which, combined with the significantly higher strength of duplex materials, results in a lower susceptibility to stress corrosion cracking as a result of mechanical damage during storage and handling.

Given these advantages of duplex alloys, the most significant difference between the behaviour of austenitic and duplex stainless steel waste containers would be expected (i) on external surfaces during storage and (ii) for internal surfaces in incompletely or non-grouted containers soon after backfilling and in the initial, aerobic, stages of repository saturation. In the latter case, however, duplex stainless steels appear to lose their enhanced resistance to localised corrosion at elevated temperatures (>50°C), so the advantage may be restricted to their lower susceptibility to stress corrosion cracking.

Although there are some advantages to the use of duplex alloys over austenitic grades, the expected environmental conditions are such that austenitic stainless steels should perform adequately during the various stages of the Phased Geological Repository Concept. Both families of material offer good corrosion resistance under atmospheric exposure conditions and the presence of cement grout backfill should ensure continued
excellent performance following repository closure. Duplex alloys provide an extra degree of corrosion resistance during those periods when the probability of localised corrosion and stress corrosion cracking is highest.
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1 Introduction

The Nuclear Decommissioning Authority (NDA) envisages the use of stainless steel containers for the encapsulation of intermediate level waste (ILW) as part of a Phased Geological Repository Concept. Within this concept, the containers are required to provide isolation of the waste during several different phases, including: a period of surface indoor storage, a period of underground atmospheric storage, and eventual disposal in a repository backfilled with cementitious material. The containers will be exposed to a wide range of environmental conditions during their service life and the corrosion behaviour of the stainless steel is, therefore, a key factor in selecting suitable materials for construction.

Stainless steels are iron-based alloys characterised by generally good corrosion resistance as a result of a minimum chromium content of 11-13 wt.% (Sedriks 1996). Different families of stainless steel are classified based on their crystallographic structure, e.g., austenitic, ferritic, martensitic, and duplex alloys, the latter containing approximately equal fractions of austenite and ferrite (ASM 1987, 2003, 2005). Whilst all of the stainless steels exhibit good resistance to general corrosion they can be susceptible, to different degrees, to various forms of localised corrosion and stress corrosion cracking. Within a given family of alloys, the resistance to localised corrosion, in particular, can vary depending upon the amount of alloying elements such as Cr, Mo, W, and N that are added.

In this report, the corrosion properties of common grades of austenitic and duplex stainless steels are compared and their suitability as container materials for ILW for the Phased Geological Repository Concept considered. The greatest body of available data is for the commonest grades from each family, namely Types 304 and 316 (and their low-carbon variants, 304L and 316L) for the austenitic alloys and alloys 2205, and to a lesser extent, 2304 for the duplex alloys. However, where useful, reference is made to other alloys within these two families of stainless steel.

It is not possible to compare the suitability of these various materials without some discussion of the expected environmental conditions and service requirements for the containers. Therefore, the environmental conditions at various stages in the service life of the containers are briefly reviewed, with particular emphasis on those stages during which conditions will be most aggressive and, hence, during which any difference in the corrosion properties of the two families of alloys might be most apparent. Next, the corrosion behaviour of the austenitic and duplex stainless steels are summarised for each form of corrosion that might be of concern for the Phased Geological Repository Concept. By necessity, this review is illustrative of the general properties of these two families of alloy, rather than being an exhaustive review of the respective corrosion properties. Finally, the inferences of the corrosion properties for the behaviour of these two families of alloy as
potential ILW container materials are considered, and the advantages and disadvantages of each material discussed.
2 Review of Environmental Conditions and Container Requirements

2.1 Environmental Conditions

The different types of environment to which ILW containers may be exposed during their service life have been summarised by Nirex (2003). Whilst there is still some uncertainty as to the exact nature of the environmental conditions (partly because no specific site has been identified) and the duration of each phase of the concept, the waste containers will be typically exposed to a period of surface storage under atmospheric conditions, a period of underground storage again exposed to ambient atmospheric conditions, and eventually disposal in a repository backfilled with cementitious material that will become saturated by incoming groundwater. In general, therefore, the outside of the containers will be exposed to atmospheric conditions of differing relative humidity and temperature, and a subsequent period of saturated conditions during which the near-field conditions, especially the pH, will be conditioned by the presence of cement-based grout. Corrosion may also occur on the inside of the grout-filled containers, which will also be subjected to first unsaturated and then saturated conditions.

From the perspective of the corrosion of stainless steels, the most important environmental parameters are the pH, redox conditions, chloride ion concentration, and temperature. Nirex (2003) describe a series of possible disposal environments, including:

- a period of relatively benign conditions during the surface storage phase of ambient temperature, aerobic, controlled humidity, and low Cl⁻ concentration;

- a operational period characterised by moderately elevated temperature (up to 50°C), control of Cl⁻ contamination in the form of aerosols, continued control of relative humidity (to <60% relative humidity), and aerobic; and

- following backfilling, an early stage of aerobic conditions with increasing temperature and Cl⁻ concentration (due to the curing of the cement and inflow of groundwater, respectively), but alkaline pH, followed by a long-term anaerobic phase of relatively high Cl⁻ concentration, alkaline pH, and a temperature falling to ambient.

Overall, the properties of the barriers that have been selected for the multi-barrier concept complement each other. Initially, the stainless steel containers provide good corrosion resistance to the relatively benign conditions in the early stages of the Phased Geological Repository Concept. Subsequently, the conditioning of the near-field pH by the cementitious backfill protects the stainless steel containers during the more aggressive
period immediately following backfilling, as the repository saturates with groundwater but conditions are still aerobic.

The most aggressive forms of corrosion of stainless steels occur in neutral or acidic aerobic chloride environments at elevated temperature. For the external and internal surfaces of the containers, the periods of most concern would appear to be:

- on the outside of the container, any period during which water and Cl\(^{-}\) are present in an aerobic atmosphere and an alkaline interfacial pH has not developed. These conditions could only occur during the operational phase if the proposed controls of the relative humidity and the level of Cl\(^{-}\) contamination fail. Alternatively, such conditions could develop immediately after backfilling if Cl\(^{-}\)-containing groundwater enters the vault prior to the development of the alkaline pore-water pH; and

- on the inside of the container, the period of most concern for non- or incompletely-backfilled containers will be the early post-backfilled period, when the system is still aerobic but the temperature is increasing due to the curing of the backfill. (Completely backfilled containers should be protected from aggressive forms of internal corrosion at all times because of the pH-conditioning by the cement grout).

### 2.2 Container Requirements

The Generic Waste Package Specification report (Nirex 2005) defines a detailed series of requirements for the waste container and the waste form contents (together referred to as the waste package). From a structural integrity point of view, the most important requirements are that the waste package must be capable of being moved and handled safely during all phases of the storage and repository operations leading to backfilling and sealing of the repository, a period that could be extended for as long as 500 years. The waste packages should also “not exhibit any permanent deformation” when stacked either six (for shielded packages) or seven (unshielded packages) high.\(^1\)

There is also a requirement that the total gas generation from a waste package should not exceed several tens of litres per day (Nirex 2005), but this requirement refers more to the stability of the waste form than the generation of H\(_2\) by anaerobic corrosion of the waste container material.

\(^1\) It is unclear whether the term “permanent deformation” implies plastic deformation, i.e., a load exceeding the yield strength of the material, or simply any degree of elastic deformation whilst still under load, i.e., loads less than the yield strength.
It is important to note that, unlike high-level waste containers, there is no requirement for absolute containment of the waste form. Indeed, the waste container will be vented for waste forms that can potentially generate gas (Nirex 2005).

It is important to bear these waste package specifications in mind when deciding whether austenitic and/or duplex stainless steels are suitable container materials. Because absolute containment is not a requirement, a limited degree of localised corrosion prior to final backfilling of the repository would not necessarily violate the waste package specifications. On the other hand, extensive localised corrosion or a stress corrosion crack along a welded seam might well compromise the structural integrity of a waste package sufficiently that it could not be safely moved or handled.
3 Corrosion of Austenitic and Duplex Stainless Steels

3.1 Introduction to Austenitic and Duplex Stainless Steels

Tables 1 and 2 give the chemical composition and mechanical properties of a number of common austenitic and duplex stainless steels.

Austenitic stainless steels are among the most widely used types of stainless steel. The most commonly used grades are the American Iron and Steel Institute (AISI) 300 series of alloys (Sedriks 1996). Starting from the basic 304 alloy (Fe-19Cr-10Ni), Mo is added to improve resistance to pitting (2-3 wt.% in the case of type 316 and 3-4 wt.% in type 317). Sensitisation due to Cr depletion during welding and other heat treatments, and the possible resultant intergranular corrosion, can be avoided through the use of low-carbon grades (304L, 316L, 317L, in which C is limited to 0.03 wt.% max.) or by adding Ti (type 321) or Nb and Ta (type 347) to precipitate C at higher temperatures. The addition of Cr also imparts greater oxidation resistance, whilst Ni improves the ductility and workability of the material at room temperature.

The 200-series stainless steels also exhibit an austenitic microstructure, but with lower Ni content than the 300-series. There are also higher austenitic alloys containing increased levels of Cr, Ni, Mo, and/or N for enhanced corrosion resistance, including the so-called super-austenitic alloys. However, neither the 200-series nor the higher austenitic alloys will be discussed further here.

Duplex stainless steels are alloys containing approximately equal proportions of austenite and ferrite (Sedriks 1996). Compared with the austenitic alloys, they are characterised by their higher strength, significantly greater resistance to chloride stress corrosion cracking. They also have good toughness (resistance to crack growth) and resistance to sensitisation-induced intergranular corrosion. The proportion of ferrite to austenite is achieved during production by controlling the cooling rate or by adding austenite stabilisers, such as Ni or N.

Modern duplex stainless steels contain N to stabilise the austenite phase and to create suitable austenite-ferrite balance. The presence of ferrite prevents sensitisation through Cr carbide (Cr$_2$C$_6$) formation because of the high diffusivity of Cr in the ferrite phase (which prevents concentration differences). Carbide precipitation can still occur at austenite-austenite grain boundaries. The ferrite phase has a lower solubility for carbon than the austenite phase. The 2205 grade has a specified lower limit for C.
Super-duplex stainless steels contain higher concentrations of Cr, Mo, and N for improved resistance to localised corrosion, and have Pitting Resistance Equivalent (PREN) values of greater than 40 (see below).

### 3.2 General Corrosion

The containers will be subject to general corrosion at all stages during the service life of the waste package. Thus, general corrosion will occur under humid atmospheric conditions during surface and below-ground storage, and under saturated conditions following backfilling and sealing of the repository. These conditions represent a broad range of environments, ranging from thin well-aerated moisture films with low Cl\textsuperscript{-} content, to fully immersed systems with high Cl\textsuperscript{-} content that will evolve from aerobic to eventually anaerobic.

For the environments of interest here, the general corrosion behaviour of stainless steels is primarily determined by the following parameters: temperature, pH, Cl\textsuperscript{-} concentration, and redox potential (or O\textsubscript{2} content). In general, the corrosion rate increases with increasing temperature, Cl\textsuperscript{-} concentration, and degree of aeration and with decreasing pH.

There are relatively few measurements of the general corrosion rate of austenitic and duplex stainless steels under the environmental conditions of interest. Although of interest for the long-term performance of nuclear waste containers, the rate of general corrosion of stainless steels in atmospheric and cementitious environments is so low that few researchers have attempted the difficult task of measuring rates that are typically of the order of 0.01-0.1 µm/y.

Table 3 provides a summary of reported corrosion rates of 304(L) and 316(L) stainless steels in alkaline and near-neutral pH solution and under atmospheric conditions. For a given set of conditions, the reported rates vary significantly, presumably as a consequence of differences in surface preparation technique, duration of the experiment, and the inherent inaccuracy of weight-loss measurements for determining such low corrosion rates. Reliable studies, i.e., those based on long-term measurements based on H\textsubscript{2} evolution, or using direct surface analytical measurements of the growth of the oxide film, suggest corrosion rates of the order of 0.01 µm/y under alkaline conditions (Table 3(a)), 0.1-1 µm/y in saturated environments at near-neutral pH (Table 3(b)), and 0.01-0.1 µm/y under atmospheric conditions (Table 3(c)). Blackwood et al. (2002b) have demonstrated the important effect of pH on the passive current density (expressed as a corrosion rate) of 316L stainless steel (Figure 1). These measurements were made under non-steady-state conditions and the long-term corrosion rate is likely to be lower.
Although there are few reports in the literature of the corrosion rate of duplex stainless steels under the conditions of interest, the rates are likely to be of the same order of magnitude as for austenitic alloys. The corrosion resistance of these alloys is provided by the Cr(III)-rich passive film (Clayton and Olefjord 1995) and, since the Cr content of the duplex alloys is typically higher than that for the austenitic materials (Table 1), there is no reason that duplex stainless steels should not also exhibit the excellent general corrosion resistance of the austenitic alloys. Souto et al. (2001) have studied the nature of the passive film on a duplex alloy similar in composition to Uranus 50 (Table 1) and found it to comprise Cr(III), Fe(II)/Fe(III), and Ni(II). Under active conditions, Fe is present as Fe(II), possibly in the form of Fe(OH)$_2$, with Fe(III) (as FeOOH) formed at more-positive potentials.

Where direct measurements of the corrosion rates of austenitic and duplex alloys have been made, the duplex alloys are found to have a similar corrosion rate to austenitic alloys. Blanco et al. (2006) compared the behaviour of 304, 316L, and 2205 in saturated Ca(OH)$_2$ solution to simulate cement grout pore water. Figure 2 shows a series of voltammograms for the different alloys (along with a Type 204 austenitic alloy) in the presence of 0.5% NaCl. The duplex alloy clearly has the lowest passive current density, implying that this alloy has the most protective passive film. Evidence from electrochemical impedance spectroscopy (EIS) measurements supports this conclusion (Figure 3), although the difference in the value of the charge-transfer resistance (inversely proportional to the corrosion rate) for the duplex 2205 alloy and that for one of the 316L samples is not significant. Corrosion current densities from short-term tests were of the order of $10^{-8}$-$10^{-7}$ A/cm$^2$, equivalent to corrosion rates of 0.1-1 µm/y. The corrosion rate decreases with time as the passive film thickens (Table 3), and these short-term rates would be expected to continue to decrease with increasing exposure time.

Although corrosion rates are observed to decrease with exposure time over laboratory timescales (a maximum of 3-5 years), the question remains as to whether long-term aging of the passive film will result in time-dependent changes in the corrosion behaviour. Corrosion potentials typically ennoble with time, a possible result of film thickening, defect annealing, or other structural or chemical changes to the passive film. Some passive films are known to crystallise after long exposure periods (e.g., passive films on Ti alloys, Mattsson and Olefjord 1990, Mattsson et al. 1990), resulting in a less-protective film and possible increase in corrosion rate. The composition and protectiveness of passive films is also generally a strong function of temperature, with the degree of hydration in particular affected by temperature. The question of the long-term stability of passive films remains an area of some uncertainty.

Overall, however, the evidence from the literature is that the general corrosion rate of duplex stainless steels is similar to, and possibly slightly lower than, that of the common
300-series austenitic alloys 304L and 316L. On this basis, there is no apparent advantage to choosing duplex alloys over austenitic stainless steels for the waste container material.

3.3 Localised Corrosion

Localised corrosion, in the form of pitting or crevice corrosion, is an important degradation mechanism for stainless steels. Although the mechanisms of pitting and crevice corrosion differ to some degree, they are generally treated in a similar manner and are discussed here together.

Various factors lead to the initiation of localised corrosion, including (Sedriks 1996, Szklarska-Smialowska 2005):

- the presence of MnS inclusions;
- Cr-depleted zones around grain boundaries;
- the presence of $\sigma$ and chi phases, small amounts of $\delta$-ferrite, and other metallurgically distinct phases; and
- defects and other types of damage to the passive film.

Pits initiate on the bold exposed surface of the alloy. The initiation of crevice corrosion is also thought to occur at inclusions, distinct phases, or defects in the film, with the occluded geometry and distinct chemical environment inside the crevice helping to sustain initiation and propagation of the localised sites of attack. Consequently, the critical temperature and chloride concentration for pitting are higher than those for crevice corrosion.

Manganese sulphide inclusions, in particular, are common locations for the initiation of localised attack. In duplex alloys, MnS inclusions tend to form at the ferrite/austenite grain boundaries. Pits may propagate preferentially into either the ferrite or austenite phase. Figure 4 shows preferential crevice corrosion of the austenite phase, which tends to occur in low N-containing alloys because a higher proportion of the Cr and Mo remains in the ferrite phase. With increasing N content, a greater fraction of these elements remain in the austenite phase making it more resistant and promoting attack of the ferrite. In austenitic alloys, this preferential distribution of MnS inclusions at grain boundaries does not occur. One remedy for duplex alloys is to lower the Mn content below 0.5 wt.% (Sedriks 1996).

A number of methods have been developed for ranking the susceptibility of different alloys to localised corrosion (Szklarska-Smialowska 2005). The most common methods are:
the pitting resistance equivalent number (PRE or PREN) that accounts for the effect of alloy composition on localised corrosion susceptibility;

the critical pitting (CPT) or crevice (CCT) temperature, an experimentally determined threshold temperature dependent on the composition of the test solution; and

comparison of the breakdown or repassivation potential for pitting or crevice corrosion and the corrosion potential $E_{\text{CORR}}$.

The PREN method is useful for comparing the effect of composition, particularly the beneficial effects of increasing Cr, Mo, and N content of the alloy. The general form of the expression is

$$\text{PREN} = \%\text{Cr} + a \cdot \%\text{Mo} + b \cdot \%\text{N} \quad (1)$$

The values of $a$ and, in particular, $b$ tend to vary depending on whether corrosion takes the form of pitting or crevice corrosion, on the nature of the environment, and to some degree of the alloy family (Pettersson and Flyg 2004). The value of $a$ tends to be the same for austenitic and duplex alloys and commonly falls in a narrow range between 3 and 3.33, but with extreme values reported of 2.4 to 5.0. There is much greater variability in the $b$ parameter, which depends strongly on the nature of the corrosion and of the environment. The value is typically higher for duplex alloys (having a value of ~30), with a value of between ~10 and 30 for austenitic alloys (generally 16, Szklarska-Smialowska 2005), although some authors have reported the reverse (i.e., 30 for austenitic and 16 for duplex alloys, Oberndorfer et al. 2004).

Examination of the nominal alloy compositions in Table 1 indicates that the duplex stainless steels will generally be more resistant to localised corrosion based on the PREN than the equivalent austenitic alloy. For alloys with similar Mo contents (e.g., type 304L and 2304 or type 316L and 2205), the duplex steel will exhibit a higher PREN because of the higher Cr content and, particularly, the presence of N. The common type 304L and 316L austenitic alloys have PREN values in the range 18-25, whereas the duplex alloys have PREN values of 30-35. Super-duplex stainless steels are alloys with PREN values >40.

The predicted superior resistance of the duplex alloys is also evident from the critical pitting and crevice temperatures. Figure 5 shows CCT and CPT values (measured in 10% ferric chloride solution according to the ASTM G48 test method) for various austenitic, super-austenitic, duplex, and super-duplex alloys (IMOA 2001). The CCT and CPT values are consistently lower for austenitic stainless steels of a given Mo content, reflecting the beneficial effect of both the higher Cr content and the addition of N to the duplex alloys.

Mechanistically, pitting or crevice corrosion should only occur if the $E_{\text{CORR}}$ exceeds the critical potential for localised attack. Although the breakdown potential ($E_{\text{p}}$ or $E_{\text{crev}}$ for...
pitting and crevice corrosion, respectively) is strictly speaking the potential at which localised corrosion initiates, the corresponding re-passivation potentials (E_{RP} and E_{RCREV} for pitting and crevice corrosion, respectively) are often used as conservative measures of initiation. (The re-passivation potential is the potential below which a propagating pit or crevice will cease to grow). The criterion for localised corrosion is then

\[
E_{\text{CORR}} > E_{\text{P}}, E_{\text{CREV}} \quad (2a)
\]

based on a film breakdown criterion, or

\[
E_{\text{CORR}} > E_{\text{RP}}, E_{\text{RCREV}} \quad (2b)
\]

based on re-passivation. Figure 6 illustrates the concept for the pitting of 316L stainless steel in Cl\textsuperscript{-} solutions at 95\textdegree C (Dunn et al. 1996). Pitting is possible (based on a comparison of \(E_{\text{CORR}}\) and \(E_{\text{RP}}\)) in aerated solution, but not in deaerated solutions.

Film breakdown potentials \((E_b)\) have been reported for type 316L and 2205 duplex stainless steels in static seawater (Neville and Hodgkiess 1996). Although the duplex alloy is clearly superior at ambient temperature, the greater temperature sensitivity of alloy 2205 results in a similar susceptibility for the two alloys at temperatures >40\textdegree C (Figure 7). The difference between \(E_b\) and \(E_{\text{CORR}}\) is a measure of the susceptibility to localised corrosion. Both \(E_b\) and \((E_b - E_{\text{CORR}})\) decrease rapidly with temperature for alloy 2205 below 20\textdegree C, whereas the 316L alloy exhibits relatively little temperature dependence. These data suggest that the superiority of duplex over austenitic alloys may be lost at elevated temperatures.

It is found that the PREN, CCT and CPT, and critical potentials for pitting and crevice corrosion are related. Figure 8 shows the correlation between PREN and critical pitting temperature (Oberndorfer et al. 2004) and Figure 9 shows a similar dependence between PREN and \(E_p\). Note in the latter figure that the duplex (2205) and super-austenitic (20Cb3, 254, 3127) alloys exhibit pitting potentials that are 300-400 mV more positive than those for the 300-series austenitic alloys, again illustrating the beneficial effects of elevated Cr and added N.

The threshold conditions for localised corrosion can also be expressed in terms of “corrosion maps” that define environments in which pitting or crevice corrosion can and cannot be expected. Figure 10 shows one such map for 316L, duplex alloy 2205, and super-austenitic alloys 904L and 254 SMO, defining the threshold temperature for pitting or crevice corrosion as a function of Cl\textsuperscript{-} concentration. The duplex stainless is clearly superior to the austenitic 316L alloy in respect to both pitting and crevice corrosion. It is interesting to note that the Cl\textsuperscript{-} concentration dependence for pitting is greater than that for crevice corrosion for all alloys. This figure refers specifically to O\textsubscript{2}-saturated systems and would show greater corrosion resistance for lower O\textsubscript{2} concentrations, although the relative ranking of the alloys
would be expected to be the same. Figure 11 shows a similar corrosion map for pitting and SCC as a function of Cl⁻ concentration and temperature (Oberndorfer et al. 2004).

Corrosion maps and measurements of the CCT and CPT can be used to assess whether the alloys are immune to localised corrosion at a given service temperature, regardless of the Cl⁻ concentration. This type of assessment is useful because it is generally difficult to predict the maximum Cl⁻ concentration that could be generated as a result of evaporation processes, for example during the long-term atmospheric storage period.

The data in Figures 5, 8, 10, and 11 clearly show that the duplex alloys 2304 and 2205 exhibit greater resistance to localised corrosion than the corresponding austenitic alloys 304L and 316L. However, based on the CCT and CPT data, it is not possible to claim that these duplex alloys would be immune to crevice or pitting attack during the atmospheric storage phase (maximum temperature 50°C). For example, based on the data in Figure 5, the CPT in 10 wt.% ferric chloride solution (ASTM G48 standard test solution) is 20°C and 33°C for the 2304 and 2205 duplex alloys, respectively, and 3°C and 10°C for the 304L and 316L austenitic alloys, respectively. The critical crevice temperature values are 20-25°C lower. Although the conditions of the ASTM G48 procedure are very aggressive, the data in Figure 10 support the conclusion that even the more-resistant 316L and 2205 alloys would be susceptible to localised corrosion at 50°C at Cl⁻ concentrations of a few thousand ppm, which could conceivably be formed on the surface of a container by repeated dripping/evaporation cycles during the long-term atmospheric storage period. In order to claim immunity to localised corrosion during long-term storage, it would be necessary to consider the use of a super-austenitic or super-duplex alloy containing 4-6 wt.% Mo (e.g., 904L or 254 SMO austenitic grades or 2507 duplex).

Although the PREN and critical pitting and crevice corrosion temperatures are useful measures of relative susceptibility, they do not indicate the important role of redox conditions in localised corrosion. The concentration of dissolved O₂ (or that of other oxidants present in the system, e.g., Fe(III), radiolytic oxidants, H⁺, etc.) determines the value of $E_{\text{CORR}}$, the more positive the value the more likely localised corrosion is to occur. In this sense, the most useful indicator of localised corrosion is that based on a comparison of $E_{\text{CORR}}$ and $E_{\text{P}}/E_{\text{CREV}}$ or $E_{\text{RP}}/E_{\text{RCREV}}$ (Equation (2)). As clearly shown in Figure 6, pitting of 316L stainless steel in O₂-containing Cl⁻ solutions is possible in aerated solution, but not under anaerobic conditions. Measurement of $E_{\text{CORR}}$ as a function of O₂ concentration (or the concentration of other oxidants) would then allow a critical redox potential to be defined below which localised corrosion would not be expected at a given Cl⁻ concentration. In general, however, neither the austenitic nor duplex alloys would be expected to be susceptible to localised corrosion under anaerobic conditions.

Bertolini et al. (1996) studied the localised corrosion of austenitic, martensitic, and duplex stainless steels in simulated cement grout porewater solution containing Cl⁻ ions. Based on a
conservative estimate of the $E_{\text{CORR}}$ value for stainless steel in concrete structures of +200 mV$_{SCE}$, the authors concluded that 304, 304L, 316, 316L, and 2304 alloys would not be susceptible to localised attack in cement environments at 20°C. However, results at 40°C suggested possible localised attack for the austenitic alloys at Cl$^-$ concentrations between 4 and 6 wt.%, with attack of the duplex 2304 alloy in 6 wt.% Cl$^-$. It is interesting to note that the higher Cr and N content of the 2304 alloy provides greater resistance to localised corrosion than the Mo added to 316/316L stainless steel.

The susceptibility of stainless steels to localised corrosion decreases with increasing pH primarily because of the increase in the threshold potential for pitting (Figure 12). The pitting potential is found to increase significantly at pH >10 for 316 stainless steel and pH 11.5 for the 304 alloy. The resistance of stainless steels to localised corrosion in alkaline solutions typical of the pore water in cement grout is confirmed by tests performed in the Nirex/NDA program. Smart (2002) reports no pitting of 304, 304L, 316, or 316L austenitic stainless steels in cements containing up to 10 wt.% Cl$^-$. The stifling of localised corrosion is currently an area of active research in the corrosion community. The term stifling is used here to describe the observation that the rate of localised penetration decreases with time. Various factors may account for the observation that the rate of propagation of pits and crevices slows with time, including:

- the ohmic drop in deep pits which shifts the potential at the bottom of the pit or crevice below the repassivation potential;
- decreasing cathode:anode surface area ratio;
- mass-transport limitation of aggressive species to the bottom of actively growing pits and crevices;
- loss of critical pit or crevice chemistry;
- preferential migration of inhibitive anions into the pit or crevice; or
- passivation of actively growing pits or crevices due to enrichment of the alloying elements stable at low pH.

Of these various factors, two are worthy of more discussion. First, the issue of the necessary cathode:anode surface area ratio is of interest for localised corrosion under atmospheric conditions. In unsaturated systems, the extent of crevice or pit propagation can become cathodically limited since the aerial extent of the cathode is limited because of the limited water availability in unsaturated atmospheres. Mathematical models can be developed to estimate under what conditions a pit or crevice might be anodically or cathodically limited (Cui et al. 2005, Kelly et al. 2006). Factors such as the high resistivity of thin liquid layers
and suppression of the rate of $O_2$ reduction due to the increase in pH in the cathodic electrolyte can serve to inhibit localised corrosion under atmospheric conditions.

The second area of interest here is the role of different alloying elements in promoting passivation within the acidic pit or crevice environment. Typically, alloying elements that are soluble in the acidic chloride environment within the pit or crevice will sustain localised corrosion, whereas those that are less soluble will promote stifling through the formation of either a salt film or protective oxide. The solubility of chromium is affected less by the presence of $Cl^-$ than for other metal ions (Strehlow 1995). Molybdenum is relatively insoluble in acidic solutions (Pourbaix 1974) and there is an apparent synergistic effect of $N$ and Mo in promoting passivity of stainless steels (Clayton and Olefjord 1995). These combined effects might result in enrichment of Cr and Mo inside the crevice or pit, which could then promote passivation. These apparently beneficial properties of Cr, Mo, and $N$ in suppressing pit and crevice propagation suggest that duplex alloys might be more prone to the stifling of localised corrosion than the corresponding austenitic alloys.

Overall, there is substantial evidence and sufficient mechanistic understanding to support the position that duplex stainless steels, such as 2304 and 2205, are more resistant to localised corrosion than the corresponding austenitic alloys, such as 304(L) and 316(L).

### 3.4 Intergranular Attack

The basic type 304 stainless steel is susceptibility to sensitisation-induced intergranular attack (IGA) (Sedriks 1996). Precipitation of $M_23C_6$ carbides during welding and other thermal treatments depletes the Cr concentration near grain boundaries, and increases the susceptibility to local dissolution. Corrosion is evident as etching of the grain boundaries leading to the release of entire grains or, in the presence of a tensile stress, as intergranular SCC.

Various strategies have been developed for minimising the effect of chromium carbide precipitation. Low-carbon grades (e.g., 304L, 316L, 317L, etc.) are available that contain <0.03 wt.% carbon. Carbide stabilising elements, such as Ti (type 321) or Nb+Ta (type 347), can also be used to preferentially precipitate C and prevent depletion of the Cr.

One of the main advantages of duplex alloys is that they exhibit a high resistance to sensitisation and IGA (Sedriks 1996). The major reason for this resistance involves the relative diffusivities of Cr in the ferrite and austenite phases. Chromium diffuses ~100 times faster in ferrite than in austenite. Therefore, Cr-depleted regions do not develop at the edges of ferrite grains and are limited to a narrow range at austenite grain boundaries. This narrow region of Cr depletion at austenite grain boundaries is readily reversed by diffusion
of Cr in the austenite grain. More significant Cr depletion can occur at austenite-austenite grain boundaries in duplex alloys and elongated austenite grains should be avoided if possible.

Femenia et al. (2003, 2004) have reported small galvanic differences between the austenite and ferrite particles in duplex stainless steels. A difference in the Volta potential (the potential of the surface measured in air related to the surface work function, and thought to be linearly related to the corrosion potential measured in solution) of 20-70 mV was reported, with the ferrite grains being more active and the austenite grains more noble. This potential difference was interpreted as indicating possible micro-scale galvanic coupling between the different crystallographic phases which, presumably, could lead to some degree of non-uniform corrosion. The magnitude of this possible micro-scale galvanic coupling and the consequences for the corrosion behaviour of duplex alloys is uncertain. Austenitic alloys, being single phase, would not exhibit this behaviour.

Duplex alloys are clearly superior to austenitic stainless steels in terms of resistance to grain boundary sensitisation and IGA. However, the use of low-carbon or carbide-stabilised austenitic grades can sufficiently reduce the susceptibility of austenitic alloys to this form of corrosion.

### 3.5 Stress Corrosion Cracking

The other major reason for the use of duplex alloys is their enhanced resistance to Cl-induced SCC (Sedriks 1996). The principal reason behind this resistance is the difference in the electrochemical potential at which the two phases are susceptible to cracking (Newman 1995). Ferrite cracks at lower potentials than the austenite phase. Because the potential in a crack has a single value, it cannot be at the optimum potential for cracking of both phases, so cracking in one phase is arrested as soon as the crack encounters a grain of the other phase. This resistance is apparent as a much higher stress intensity factor for SCC ($K_{SCC}$) for duplex alloys than for austenitic stainless steels.

Figure 13 shows a corrosion map for the susceptibility of different austenitic and duplex alloys to SCC in aerated chloride solutions as a function of temperature. Based on practical experience, a threshold temperature of 40-60°C has been established below which the Cl-induced SCC of austenitic stainless steels is not observed regardless of the Cl-concentration (McIntyre 1987). This threshold temperature exceeds 100°C for 2305 and 2205 duplex stainless steels.

From a practical viewpoint, the threshold stress for cracking of duplex alloys is higher than for austenitic alloys. For example, under aggressive evaporative concentration conditions at
120°C, the threshold stress for types 316, 2205, and 2507 stainless steels are approximately 4%, 35%, and 75% of the yield strength, respectively. Combined with the higher strength of duplex alloys, the absolute threshold stress value for the duplex stainless steels is significantly higher than for the lower-strength austenitic alloys.

Various mechanisms have been proposed for the SCC of duplex stainless steels under the aggressive conditions where cracking is observed (Kangas and Nicholls 1995). Tsai and Chou (2000) report both SCC and hydrogen-assisted cracking of 2205 duplex stainless steel in an aggressive 26 wt.% Cl solution at pH 2 (Figure 14). The ferrite phase was found to be more susceptible to crack initiation and growth than the austenite grains.

Both austenitic and duplex stainless steels are susceptible to SCC in sulphide- and thiosulphate-containing environments. The susceptibility of 304L and 316L austenitic stainless steels has been determined in simulated cementitious environments containing chloride and/or thiosulphate ions for the Nirex/NDA program (Smart 2002). Thiosulphate could be produced in the repository by the microbial reduction of sulphate or be released from cement containing blast-furnace slag. The severity of cracking increased with decreasing pH and with increasing thiosulphate and/or chloride concentrations. Thiosulphate enhances the effect of Cl. The susceptibility of duplex alloys has not tested over the same range of conditions, but less-severe cracking might be expected given the enhanced resistance of duplex alloys to chloride-induced SCC and their greater pitting resistance, pits often acting as initiation sites for stress corrosion cracks.

Overall, there appears to be an advantage to the selection of duplex stainless over the austenitic alloys because of their greater resistance to Cl–SCC. This increased resistance is characterised by higher threshold temperatures for SCC at a given chloride concentration and a higher threshold stress for crack initiation and stress intensity factor for crack growth.

### 3.6 Microbiologically Influenced Corrosion

The key to microbiologically influenced corrosion (MIC) is microbial activity. If microbes are not active then they cannot produce aggressive metabolic by-products (such as sulphide ions or organic acids) or the extracellular polymeric substance (i.e., slime) that creates localised environments.

A number of environmental factors can limit microbial activity. In the present context, the elevated pH in the cement pore water and the limited availability of water under atmospheric conditions will limit the extent of microbial activity (Brown 1990). All microbes have a threshold relative humidity or water activity ($a_w$) below which they are not active, with a threshold of 90-95% RH for many bacteria and an absolute threshold of 60% RH (or
aw = 0.60) for all microorganisms. Even if the relative humidity is above the absolute threshold, the diversity of the microbial population decreases with decreasing %RH. In many microbially active systems, it is the diversity of the microbial population that is important, as this diversity allows the consortium to survive adverse external stressors and to act symbiotically. The diversity of the microbial population will be further diminished in cementitious environments as most microbes are not active in alkaline environments at pH >10.

Stainless steels are susceptible to MIC in active microbial environments (Little et al. 1991). Although stable Cr-rich passive films minimise the impact of microbial activity (Lloyd et al. 2005), the slight difference in Cr content of the austenitic and duplex stainless steels is insufficient to markedly differentiate their resistance to MIC. The greater overall resistance of the duplex alloys to localised corrosion should translate into a corresponding improved resistance to corrosion under biofilms.

However, a deeper understanding of the effect of the expected disposal environments on microbial activity (and, if there is any, on MIC) is warranted.

### 3.7 Atmospheric Corrosion

The waste containers will be exposed for the early part of their service life to atmospheric conditions, either in surface or below-ground storage. During these periods, the containers will be subject to possible atmospheric corrosion because of the deliquescence of moisture on salt particles and other contaminants on the container surface. During below-ground storage, there is also the possibility of contact by, and evaporation of, groundwater species.

Much is known about the deliquescence behaviour of different salts, and the critical temperature and %RH at which these salts will first absorb moisture and possibly cause corrosion can be predicted with some degree of certainty (BSC 2004b, King 2006, Rard et al. 2005). Furthermore, the atmospheric behaviour of stainless steels waste containers has been reviewed (Smart 2000), measurements made (Smart 2005), and a workshop on the subject was held in 2004 (Smart 2004).

More recently, Tani and Mayuzumi (2007) have compared the behaviour of austenitic and duplex stainless steels exposed to humid atmospheres following contamination by salts contained in seawater. Surface corrosion took the form of pitting at isolated salt crystals formed by the evaporation of seawater and which subsequently deliquesced when exposed to a humid atmosphere. Figure 15 shows that the duplex alloys S31254 and S31260 suffer less localised corrosion that the 316L (S31603) material because of their greater Cr, Mo, and N contents (S31260: 25.7Cr, 6.9Ni, 0.01C, 0.41Si, 0.45Mn, 0.024P, 0.001S, 0.49Cu, 3.33Mo,
The corrosion observed by Tani and Mayuzumi (2007) is the result of the deliquescence of MgCl$_2$ and possibly CaCl$_2$, because the major component of evaporated seawater (NaCl) does not deliquesce under these test conditions. Figure 16 shows the deliquescence behaviour of a number of chloride salts. Magnesium chloride deliquesces at a relative humidity of ~20-35% at temperatures between 0 and 100°C. Sodium chloride deliquesces at much higher %RH and would not have formed an aqueous phase for the test conditions in Figure 15 (35% RH). It is also interesting to note that although the fractional corroded area increased with temperature for the S31254 and S31260 alloys, this is despite the fact that the adsorbed water film would have been more dilute (as indicated by the decrease in deliquescence %RH with increasing temperature for MgCl$_2$).

The architectural applications of austenitic stainless steels have been summarised by Smart and Wood (2004). The use of duplex stainless steels for architectural applications is relatively new and there are few reports in the literature of the extent of atmospheric corrosion following extended periods in service. However, these alloys are being used for architectural purposes, especially in bridge construction (Figure 17). Type 2205 duplex stainless steel was also selected for the upper 120 metres of the towers of the Stonecutters Bridge in Hong Kong harbour (Figure 18). This alloy was selected because of its superior strength compared with austenitic alloys combined with its excellent corrosion resistance.

### 3.8 Effects of Radiolysis

Radiation and radiolysis can affect the corrosion behaviour of materials in a number of ways. Because of the nature of the waste forms under consideration here, radiation damage by neutrons and high-energy sources can be ignored. Alpha-, beta-, and gamma-radiation can produce oxidants and reductants through the radiolysis of aqueous solutions. The yield of radiolysis products is typically estimated using homogeneous radiolysis models (Smart et al. 2006), but this is erroneous as the presence of a reactive (corroding) interface invalidates the assumptions underlying these models.

Shoesmith and King (1999) reviewed the available information on the effects of radiolysis on the corrosion of nuclear waste container materials. The minimum absorbed dose rate at which any effect of radiolysis has been observed on any material, including 304L stainless steel, is ~1 Gy/h (equivalent to a gamma-radiation dose rate of 1 Sv/h). The Generic Waste Package Specification (Nirex 2005) specifies a maximum surface dose rate of 2 mSv/h for shielded containers. Furthermore, the surface dose rate for unshielded containers is likely to
be greater than 1 Gy/h for only a limited period of time. Therefore, since the maximum external surface dose rate is ~3 orders of magnitude lower than the threshold above which any effect has been observed, it is concluded that the effects of radiolysis on waste container corrosion can be neglected. (It is assumed that the dose rate for internal surfaces of the waste container are also below the observed threshold for radiolysis effects.)

3.9 Effects of Welding

Poorly designed or performed welding procedures can lead to enhanced susceptibility to corrosion of stainless steels. In austenitic materials, a common corrosion problem is the sensitisation resulting from the precipitation of chromium carbides. As discussed above, this problem can be largely overcome through the use of low-carbon grades or the use of grades containing alternative carbide stabilisers (types 331 and 347).

In duplex grades, most welding-related corrosion problems are associated with the heat-affected zone (IMOA 2001). For example, chromium depletion in the ferrite grains in 2304 duplex stainless steel resulted in a decrease in the resistance to localised corrosion compared with the parent material (Garzón et al. 2007). Not only was the mean Cr content of ferrite grains in the HAZ lower than in similar grains in the parent material, but there was also local Cr depletion due to nitride precipitation. Corrosion resistance can be restored, at least partially, through post-weld heat treatment. Enhanced susceptibility to SCC has also been reported for the HAZ in 2205 stainless steel (Liou et al. 2002). This is, in part, due to the enhanced susceptibility to pitting (with pits acting as crack initiation sites) and is related to the N content of the alloy. This susceptibility can be minimised by using a N₂-containing atmosphere during welding (Sedriks 1996).

The susceptibility of both austenitic and duplex stainless steels to localised corrosion and SCC can be affected by welding. However, for both types of material, the proper selection of welding procedures and materials and post-weld heat treatment can result in restoration of the corrosion resistance of the alloy.

3.10 Galvanic Corrosion

Galvanic corrosion may result from contact between metallic waste forms and the internal surface of the waste container. Passive stainless steels are noble relative to most of the potential metallic waste forms, such as aluminium, and carbon- and low-alloy steels. In a galvanic couple, therefore, the stainless steel will be the cathode and the waste form will be
the anode, the dissolution of which will effectively cathodically protect the stainless alloy. There is little difference between the relative positions of austenitic and duplex stainless steels in the galvanic series.

There are two possible mechanisms by which galvanic coupling could impact the service life of the waste package. First, under aerobic conditions, the oxidation and hydrolysis of dissolved corrosion products can lead to locally acidic and oxidising conditions resulting in an increased probability of localised corrosion of the stainless steel. In the case of the coupling of carbon and stainless steels, the reactions of interest are:

\[
\begin{align*}
    \text{Fe} & \rightarrow \text{Fe}(\text{II}) + 2e^- \quad (3a) \\
    4\text{Fe}(\text{II}) + \text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{Fe}(\text{III}) + 4\text{OH}^- \quad (3b) \\
    \text{Fe}(\text{III}) + 3\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ \quad (3c)
\end{align*}
\]

with the cathodic reduction of \( \text{O}_2 \) occurring remotely on the stainless steel surface. Thus, locally aggressive acidic ferric environments can be produced at the point of contact between the carbon and stainless steels. Apart from carbon steel waste forms, this issue can also be caused by the use of carbon or low alloy steel tools for fabrication and handling of the stainless steel containers (so-called “smeared-” or “embedded-iron” corrosion), the use of which should be controlled during repository operations.

The second mechanism of concern is the hydrogen embrittlement of stainless steel coupled to a more active metal. Because the stainless steel is cathodically polarised by the galvanic couple, the reduction of \( \text{H}_2\text{O} \) and the possible absorption of atomic hydrogen can occur under anaerobic conditions. If sufficient hydrogen is absorbed then the material can become embrittled. This problem would tend to be of more concern for the higher-strength duplex alloys, since the potentially higher stress levels would tend to concentrate hydrogen at defects in the material. On the basis of the data in Figure 14, hydrogen-assisted cracking of alloy 2205 occurs at potentials more negative than \(-800 \text{ mV}_{\text{SCE}}\), although a more-negative limit of \(-900 \text{ mV}_{\text{SCE}}\) has been proposed by Zucchi et al. (2006) in acidified seawater (pH 6.5). Regardless of the precise potential threshold, such a limit is unlikely to be exceeded by galvanic coupling with carbon steel since the \( E_{\text{CORR}} \) for the latter material in anaerobic natural waters is approximately \(-750 \text{ mV}_{\text{SCE}}\). Hydrogen embrittlement of the stainless steel container is only possible, therefore, if it becomes galvanically coupled to Al, Mg, or galvanised alloys or, possibly, carbon steel in the presence of sulphide ions.

The potential for galvanic corrosion of the stainless steel waste containers is considered to minimal. Even if a galvanic couple was established, it is unlikely to be sufficiently long-lived that extensive damage would result. However, it is good design practice to avoid such a possibility in the first place, through appropriate waste form loading and care with the use of carbon steels tools during manufacture and handling.
4  Behaviour of Austenitic and Duplex Stainless Steels under Phased Geological Repository Conditions

Based on the above discussion, the expected behaviour of austenitic and duplex stainless steels during various stages of the Phased Geological Repository Concept is summarised in Table 4 (based on the various disposal phases identified by Nirex 2003). The expected rates of general corrosion have not been specifically defined in Table 4, but are expected to be approximately the same for both families of alloys and to be of the order of magnitude defined by Smart et al. (2006).

Table 4 does not distinguish between the different grades of austenitic or duplex stainless steels. In general, type 304(L) stainless steel will be more susceptible to localised corrosion and SCC than the 316(L) alloy. The use of the low-carbon grade of each alloy will minimise any differences between the two in terms of sensitisation-induced IGA. For the duplex alloys, the higher Mo content of the 2205 alloy provides greater resistance to localised corrosion and SCC compared with the 2304 stainless steel, despite the higher Cr content of the latter.

As discussed in more detail in the previous section, the advantages of the duplex alloys over the austenitic alloys from a corrosion viewpoint are:

- lower susceptibility of duplex alloys to sensitisation-induced intergranular attack;
- increased resistance of duplex alloys to localised corrosion due to the higher N content and, in some cases, higher Cr and Mo contents than “corresponding” austenitic stainless steels, although this benefit is reduced at temperatures >50°C;
- significantly improved resistance to chloride-induced SCC, with possible immunity of duplex grades at temperatures <100°C; and
- higher threshold stress for SCC for duplex alloys which, combined with the significantly higher strength of duplex materials, results in a lower susceptibility to SCC caused by mechanical damage during storage and handling.

Given these advantages of duplex alloys, the most significant difference between the behaviour of austenitic and duplex stainless steel waste containers would be expected (i) on external surfaces during storage and (ii) for internal surfaces in incompletely or non-grouted containers soon after backfilling and in the initial, aerobic, stages of repository saturation. In the latter case, however, duplex stainless steels appear to lose their enhanced resistance to localised corrosion at elevated temperatures (>50°C), so their advantage may be restricted to their lower susceptibility to SCC.
Although there are some advantages to the use of duplex alloys over austenitic grades, the expected environmental conditions are such that austenitic stainless steels should perform adequately during the various stages of the Phased Geological Repository Concept. Both families of material offer good corrosion resistance under atmospheric exposure conditions and the presence of cement grout backfill should ensure continued excellent performance following repository closure. Duplex alloys provide an extra degree of corrosion resistance during those periods when the probability of localised corrosion and SCC is highest.
5 Summary and Conclusions

A review has been carried out of the corrosion performance of austenitic and duplex stainless steels as container materials for the storage and disposal of ILW as part of the Phased Geological Repository Concept. Two grades have been selected as representative of each family, namely 304(L) and 316(L) austenitic stainless steels and 2304 and 2205 duplex alloys. Various forms of corrosion have been considered, including: general corrosion, localised corrosion in the form of pitting and crevice corrosion, sensitisation-induced intergranular attack, stress corrosion cracking, microbiologically influenced corrosion, atmospheric corrosion, the effects of radiolysis and welding, and galvanic corrosion.

Compared with austenitic stainless steels, the duplex alloys provide significantly higher strength, greater resistance to chloride-induced SCC, and at temperatures up to ~50°C, improved resistance to localised corrosion. These advantages should provide additional assurance of acceptable waste package performance during various stages of the Phased Geological Repository Concept, most notably during the period of surface and below-ground storage and during the transient aerobic phase immediately following backfilling and closure of the repository.

However, the design of the repository concept and the selection of engineered barriers should ensure acceptable waste package performance for either austenitic or duplex grades of stainless steel. In particular, the presence of cement grout should protect both the internal and, eventually, the external surfaces of the containers from localised corrosion and SCC.
References


model environments simulating the manufacturing conditions of the synthetic resin KFE. Mat. Primen. No. 3, p. 59.


Table 1: Compositions of Common Austenitic and Duplex Stainless Steels

<table>
<thead>
<tr>
<th>UNS Number</th>
<th>Common name</th>
<th>Composition (wt.%)&lt;sup&gt;2&lt;/sup&gt;</th>
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<td></td>
<td></td>
<td>Cr</td>
<td>Ni</td>
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<td>18-20</td>
<td>8-10</td>
</tr>
<tr>
<td>S30403</td>
<td>304L</td>
<td>18-20</td>
<td>8-12</td>
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<td>SAF 2304</td>
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<td>Uranus 50</td>
<td>20.5-22.5</td>
<td>5.5-8.5</td>
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<sup>1</sup> After Sedriks (1996)

<sup>2</sup> Maximum unless otherwise indicated, balance Fe.

<sup>3</sup> Minimum
### Table 2: Mechanical Properties of Common Austenitic and Duplex Stainless Steels

<table>
<thead>
<tr>
<th>UNS Number</th>
<th>Common name</th>
<th>Yield Strength (0.2% Offset) (MPa)</th>
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<th>Elongation (%)</th>
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1 Minimum  
2 Maximum  
3 Rockwell C
Table 3: Literature General Corrosion Rates for Austenitic Stainless Steels.

(a) Highly Alkaline Solutions.

<table>
<thead>
<tr>
<th>Grade</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>[Cl⁻] (µg·g⁻¹)</th>
<th>Redox conditions</th>
<th>Other</th>
<th>Rate (µm·yr⁻¹)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>304</td>
<td>12.8</td>
<td>10.5</td>
<td>30, 45</td>
<td></td>
<td>200 days 60 days</td>
<td>0.0003 0.01</td>
<td>Fujisawa et al. 1999</td>
</tr>
<tr>
<td>304</td>
<td>13</td>
<td>Ambient</td>
<td>18,400</td>
<td>Aerated</td>
<td>28 days</td>
<td>0.3</td>
<td>Mcdonald et al. 1995</td>
</tr>
<tr>
<td>304</td>
<td>13</td>
<td>30</td>
<td>50, 80</td>
<td>Deaerated</td>
<td></td>
<td>0.06 0.18 0.82</td>
<td>Blackwood et al. 2002a</td>
</tr>
<tr>
<td>304</td>
<td>10</td>
<td>12.5 13.5</td>
<td>50</td>
<td>Deaerated</td>
<td>230 days</td>
<td>0.009 0.0055 0.0063</td>
<td>Wada and Nishimura 1999</td>
</tr>
<tr>
<td>304</td>
<td>12.8</td>
<td>30</td>
<td></td>
<td>Deaerated</td>
<td>Calculated 1 yr 10 yrs 1000 yrs 10⁴ yrs</td>
<td>0.055 0.010 0.002 0.0003 0.00006</td>
<td>Fukaya and Akashi 2003</td>
</tr>
<tr>
<td>316</td>
<td>13</td>
<td>Ambient</td>
<td>18,400</td>
<td>Aerated</td>
<td>28 days</td>
<td>0.6</td>
<td>Mcdonald et al. 1995</td>
</tr>
<tr>
<td>316L</td>
<td>&gt;13</td>
<td>Ambient</td>
<td>10,000</td>
<td>Deaerated</td>
<td>0.1 MPa H₂</td>
<td>0.03</td>
<td>Smart et al. 2004</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>13</td>
<td>Ambient</td>
<td>Deaerated</td>
<td>0.1 mol·dm⁻³ KOH agar gel, 50 days</td>
<td>0.4-1.6</td>
<td>Sharland 1991</td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td>13.4</td>
<td>Ambient</td>
<td>Aerated</td>
<td></td>
<td></td>
<td>1-6</td>
<td>Rubinshtejn et al. 1977</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>12.9</td>
<td>25-80</td>
<td>10,000</td>
<td>Deaerated</td>
<td></td>
<td>&lt;0.1</td>
<td>Naish et al. 1995</td>
</tr>
</tbody>
</table>
(b) Neutral to Slightly Alkaline Solution.

<table>
<thead>
<tr>
<th>Grade</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>[Cl⁻] (µg·g⁻¹)</th>
<th>Redox conditions</th>
<th>Other</th>
<th>Rate (µm·yr⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>Ambient</td>
<td>90</td>
<td>7,000-43,000</td>
<td>Aerated</td>
<td>10 hrs</td>
<td>10-130</td>
<td>Morsy et al. 1979</td>
</tr>
<tr>
<td>304L</td>
<td>Ambient</td>
<td>25-100</td>
<td>“Freshwater”</td>
<td>Aerated</td>
<td></td>
<td>0.21</td>
<td>BSC 2004a</td>
</tr>
<tr>
<td>304L</td>
<td>Ambient</td>
<td>27 90</td>
<td>“Saltwater”</td>
<td>Aerated</td>
<td></td>
<td>11.4 5.82</td>
<td>BSC 2004a</td>
</tr>
<tr>
<td>304</td>
<td>Ambient</td>
<td>25 50 75</td>
<td>Interstitial clay water</td>
<td>Aerated</td>
<td></td>
<td>0.2-0.96</td>
<td>Casteels et al. 1986</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.22-0.23</td>
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<td></td>
<td></td>
<td>0.3-0.35</td>
<td></td>
</tr>
<tr>
<td>316</td>
<td>Ambient</td>
<td>Ambient 19,000</td>
<td>Aerated</td>
<td>8 yrs, Pacific Ocean seawater</td>
<td>4</td>
<td></td>
<td>Alexander et al. 1961</td>
</tr>
<tr>
<td>316L</td>
<td>Ambient</td>
<td>30 50-100</td>
<td>“Freshwater”</td>
<td>Aerated</td>
<td></td>
<td>0.01 0.25</td>
<td>BSC 2004a</td>
</tr>
<tr>
<td>316L</td>
<td>Ambient</td>
<td>27 “Saltwater”</td>
<td>Aerated</td>
<td></td>
<td></td>
<td>1.94</td>
<td>BSC 2004a</td>
</tr>
<tr>
<td>316</td>
<td>Ambient</td>
<td>25 50 75</td>
<td>Interstitial clay water</td>
<td>Aerated</td>
<td></td>
<td>0.1-0.24</td>
<td>Casteels et al. 1986</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1-0.34</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1-0.17</td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td>Ambient</td>
<td>25-40 Seawater 19,000</td>
<td>Deaerated</td>
<td>120 days</td>
<td>0.8</td>
<td>White et al. 1966</td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td>Ambient</td>
<td>25-40</td>
<td>7.7 µg·g⁻¹ O₂ 2.17 µg·g⁻¹ O₂</td>
<td>Deaerated</td>
<td></td>
<td>0.55 4.8</td>
<td>White et al. 1966</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>9.8 9.4</td>
<td>25 80</td>
<td>2,000</td>
<td>Deaerated</td>
<td></td>
<td>0.025-0.23</td>
<td>Hoch et al. 1992</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.01-0.034</td>
<td></td>
</tr>
</tbody>
</table>
(c) Under Atmosphere Conditions.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Temperature (°C)</th>
<th>Redox conditions</th>
<th>Other</th>
<th>Rate (µm·yr⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>Ambient</td>
<td>Aerated</td>
<td>Urban, 5-15 yrs</td>
<td>&lt;0.03</td>
<td>Johnson and Pavlik 1982</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Urban, 5-15 yrs</td>
<td>0.022</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Marine, 5-15 yrs</td>
<td>0.05-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Industrial/urban, 5-15 yrs</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>304</td>
<td>Ambient</td>
<td></td>
<td>Industrial/urban</td>
<td>0.03-3</td>
<td>Kearns et al. 1984</td>
</tr>
<tr>
<td>316</td>
<td>Ambient</td>
<td>Aerated</td>
<td>Urban, 5-15 yrs</td>
<td>&lt;0.03</td>
<td>Johnson and Pavlik 1982</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>Ambient</td>
<td>Aerated</td>
<td>Various atmospheres</td>
<td>0.05</td>
<td>Dechema 1990</td>
</tr>
</tbody>
</table>
Table 4: Expected Corrosion Behaviour of Austenitic and Duplex Stainless Steels During Various Stages of the Phased Geological Repository Concept.

<table>
<thead>
<tr>
<th>Disposal phase</th>
<th>Internal or external surface</th>
<th>Austenitic stainless steels</th>
<th>Duplex stainless steels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage (surface and below-ground)</td>
<td>External</td>
<td>Low rate of general corrosion under atmospheric conditions. Possibility of localised corrosion and SCC if humidity is high enough to permit deliquescence of surface contaminants.</td>
<td>Low rate of general corrosion under atmospheric conditions. Greater resistance to localised corrosion and SCC than austenitic alloys if humidity is high enough to permit deliquescence of surface contaminants.</td>
</tr>
<tr>
<td></td>
<td>Internal</td>
<td>Very low rate of general corrosion and absence of localised corrosion and SCC for grouted waste packages. Possibility of localised corrosion and SCC for incompletely or non-grouted packages at high relative humidity.</td>
<td>Very low rate of general corrosion and absence of localised corrosion and SCC for grouted waste packages. For incompletely or non-grouted packages, lower probability of localised corrosion than for austenitic alloys. Immune to SCC at expected storage temperatures.</td>
</tr>
<tr>
<td>Repository operation after backfilling</td>
<td>External (aerated)</td>
<td>Protected from localised corrosion and SCC by alkaline grout pH. Low rate of general corrosion.</td>
<td>As for austenitic alloys.</td>
</tr>
<tr>
<td></td>
<td>Internal (aerated)</td>
<td>Protected from localised corrosion and SCC by alkaline grout pH. Low rate of general corrosion.</td>
<td>As for austenitic alloys. For incompletely or non-grouted packages, increased temperature renders duplex alloys as susceptible to localised corrosion as austenitic alloys.</td>
</tr>
<tr>
<td>Post-closure after resaturation</td>
<td>Internal and external (aerated)</td>
<td>Period of susceptibility to localised corrosion and SCC due to elevated temperature (up to 80°C) and ingress of Cl⁻ from groundwater, although surfaces in contact with cement grout should be immune.</td>
<td>Similar susceptibility to localised corrosion as austenitic alloys if temperature exceeds critical pitting or crevice corrosion temperature for the particular alloy. Immune to SCC at temperatures &lt;100°C.</td>
</tr>
<tr>
<td></td>
<td>Internal and external (anaerobic)</td>
<td>Very low rate of general corrosion and absence of localised corrosion or SCC.</td>
<td>As for austenitic alloys.</td>
</tr>
</tbody>
</table>
Figure 1: Effect of pH and temperature on the passive current density (expressed in terms of a corrosion rate) of 316L stainless steel (Blackwood et al. 2002b).
Figure 2: Comparison of the voltammetric behaviour of various austenitic and a duplex stainless steel in saturated Ca(OH)$_2$ solution with the addition of 0.5\% NaCl at room temperature (Blanco et al. 2006).
Figure 3: Time dependence of the charge-transfer resistance for various austenitic and a duplex stainless steel in saturated Ca(OH)$_2$ solution containing 1% NaCl (Blanco et al. 2006).

![Graph showing charge-transfer resistance for different steels over time](image)

Figure 4: Crevice corrosion test on duplex alloy 2205 stainless steel in 1 mol·dm$^{-3}$ NaCl illustrating preferential attack on austenite phase (Pettersson and Flyg 2004).

![Image showing crevice corrosion test results](image)
Figure 5: Comparison of the critical crevice and pitting temperatures for a range of austenitic and duplex stainless steels in 10 wt.% ferric chloride solution (after IMOA 2001).
Figure 6: Comparison of the pitting and pit repassivation potentials for type 316L stainless steel to the corrosion potential $E_{\text{CORR}}$ in aerated and deaerated chloride solutions at 95°C (Dunn et al. 1996).
Figure 7: The temperature dependence of the film breakdown potential and the susceptibility to localised corrosion for types 316L and 2205 stainless steels in static seawater (after Neville and Hoghkiess 1996).
Figure 8: Correlation between the PREN and critical pitting temperature (Oberndorfer et al. 2004).

Figure 9: Correlation between the pitting resistance equivalent number and pitting potential for various austenitic, duplex, and super-austenitic stainless steels (Malik et al. 1996).
Figure 10: Corrosion map illustrating critical pitting and crevice corrosion temperatures as a function of chloride concentration for various austenitic, duplex, and super-austenitic stainless steels (ASM 2005). Critical conditions for pitting and crevice corrosion indicated by solid and dashed lines, respectively.

Figure 11: Domains of immunity and susceptibility to pitting and stress corrosion cracking as a function of chloride concentration and temperature for austenitic, duplex, and super-austenitic alloys (Oberndorfer et al. 2004).
Figure 12: Dependence of the pitting potential on pH for types 304 and 316 stainless steel in 3% NaCl solution (from Sedriks 1996).
Figure 13: Corrosion map for the susceptibility of various austenitic and duplex stainless steels to stress corrosion cracking in aerated chloride environments as a function of temperature (Sedriks 1996).
Figure 14: Potential dependence of SCC and hydrogen-assisted cracking of 2205 duplex stainless steel in 26 wt.% NaCl solution at pH 2 (Tsai and Chou 2000).
Figure 15: Dependence of the fractional surface area of different austenitic and duplex stainless steels corroded in a humid atmosphere as a function of exposure temperature (Tani and Mayuzumi 2007).
Figure 16: Deliquescence behaviour of various single chloride salts.
Oregon Bridge Uses Stainless

A highway bridge in Oregon that uses duplex stainless steel is designed to last 120 years.

The state of Oregon in the northwestern United States is using S32205 stainless steel as an anode to the corrosion problems that plague some of its older bridges along the Pacific coastline.

A $581.2-million bridge now under construction over an estuary near Coos Bay will contain 360 tonnes of stainless steel rebar, believed to be the largest quantity of stainless steel used for any bridge in North America.

The Oregon marine environment is hard on bridges reinforced by carbon steel rebar. Wind blows salty, moist air under the deck and 7-bears, where it condenses and causes corrosion. The resulting cracking along the contact between the rebar and the concrete is exacerbated by tensile cracking caused by heavy traffic loads. Eventually, rust forms and the concrete begins to crumble, weakening further the bond between the metal and the concrete. Structural failure has been known to occur in as little as 17 years.

Usually, designers recommend S31653 or S34400 stainless steel to prevent these problems. But Oregon has gone a step further. By choosing the S32205 alloy, which has much greater corrosion resistance, the state hopes to extend the maintenance-free life of the bridge to 120 years while providing the structure with enough strength to withstand potentially damaging seismic activity in the earthquake-prone area.

The S32205 was supplied by Carpenter Technology Corp. of Reading, Pa., U.S.A. It contains 25% chromium, 55% nickel and 3% molybdenum. The alloy has superior fatigue resistance because it exceeds the elongation requirement that allows bridges to withstand movement and stress under heavy traffic loads. Its yield strength is also considerably higher than the 410 megapascals typical of S31653 and S34400 stainless.

Even though the state stands to save a considerable amount on maintenance costs by using S32205, the choice of material did not add significantly to the capital cost of the project. The rebar represents only about 13% of the US$12 million budget.

The designer, James Ballinas, decided to use a stronger reinforcing bar than usual, to reduce the total weight and cost of the stainless steel,” says Frank Nelson in the bridge engineering section of Oregon’s Department of Transportation. “At the 520 megapascals yield strength, the steel mill and the contractor agreed on using this specific alloy.

Another, much larger (664-tonne) tonnage of uncoated carbon steel rebar will support areas of the substructure where corrosion is less of a concern. The 235-meter-long bridge, a series of three spans of concrete dock anchorage, will carry an estimated 14,000 vehicles per day. The five-lane structure replaces a two-lane timbered bridge that has reached the end of its life and is being removed.

Figure 17: Use of duplex stainless steels for bridge applications (Anonymous 2003).
Figure 18: The Stonecutters Bridge in Hong Kong harbour.