

Stress Corrosion Cracking of Carbon Steel Used Fuel Containers in a Canadian Deep Geological Repository in Sedimentary Rock

NWMO TR-2010-21

November 2010

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Integrity Corrosion Consulting Ltd.

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ABSTRACT

Title: Stress Corrosion Cracking of Carbon Steel Used Fuel Containers in a Canadian Deep Geological Repository in Sedimentary Rock
Report No.: NWMO TR-2010-21
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Date: November 2010

Abstract

Carbon steel has been proposed as a used fuel container material for a deep geological repository in sedimentary rock. The container will be subject to a number of corrosion mechanisms including stress corrosion cracking (SCC). An assessment is presented of the probability that SCC will lead to through-wall penetration of the container in the repository.

Stress corrosion cracking of carbon steel has been reported in a number of environments. The environmental conditions associated with cracking are reviewed and the controlling factors and threshold environmental and stress-related conditions identified. Cracking of pipeline steels due to the presence of either dilute or concentrated carbonate/bicarbonate solutions appear to be the most relevant for the SCC of containers in the repository.

Various mechanisms have been proposed to account for the SCC of carbon steel and , more generally, for various metal/environment systems. These mechanisms are reviewed, both in relation to the SCC of carbon steel and in terms of whether they will operate in the repository environment.

Based on the environmental and mechanistic evidence, the implications for SCC of carbon steel containers in the repository are considered. The evidence is reviewed in the context of the inherent susceptibility of the material, the corrosiveness of the environment, and the aggressiveness of the mechanical loading conditions. Possible mitigation strategies are also reviewed.

Overall, it is concluded that the probability of through-wall penetration of the container due to stress corrosion cracking is low.

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1. INTRODUCTION

The Nuclear Waste Management Organization (NWMO) is responsible for the long-term management of Canada's used nuclear fuel. The selected approach for the long-term management of used fuel is Adaptive Phased Management (APM). One of the options being considered is the use of carbon steel (C-steel) as a container material for a possible deep geological repository (DGR) in sedimentary rock (King 2005a, Mazurek 2004).

A requirement for the development of the used fuel container (UFC) is that an assessment be carried out of any corrosion process that could potentially limit the service life of the container. A conceptual model for the corrosion behaviour of a C-steel UFC in a DGR in sedimentary rock has been developed (King 2007). Various corrosion processes were considered, including: uniform and localized corrosion, hydrogen effects, stress corrosion cracking (SCC), microbiologically influenced corrosion, the corrosion behaviour of welds, and low-temperature oxidation. It was concluded that through-wall penetration by SCC is unlikely because of the absence in the DGR of both an appropriate cracking environment and the cyclic loading found to be necessary to support crack propagation.

Stress corrosion cracking is the result of the conjoint action of a tensile stress on a susceptible material in a specific aggressive environment. Each of these three factors must be present for cracking to occur. The cracking process is often divided into separate crack initiation and propagation phases, which typically involve different mechanisms.

Different approaches are taken to the management and prediction of SCC in different industries and applications. For example, in the pipeline industry it is typical to manage the growth of cracks rather than their initiation. This approach is possible because, compared with the service life of a pipeline, cracks grow relatively slowly and because periodic inspection to assess the extent of crack growth is possible. However, where the rate of crack growth is fast relative to the service life or where periodic inspection is not possible, it is necessary to manage SCC at the initiation stage. This is the case for the SCC of used fuel containers in a DGR. The most appropriate approach to manage SCC of UFC, therefore, is to demonstrate that the containers will not be susceptible to cracking in the repository environment.

This report builds on the preliminary analysis of the susceptibility of C-steel containers to SCC in a DGR in sedimentary rock presented by King (2007). Two approaches are taken to address the question of whether SCC is a threat to the integrity of the containers (Section 2). First, as briefly summarized by King (2007), the environmental, metallurgical, and stress conditions under which the SCC of C-steel has been observed are discussed in Section 2.1, including cracking in carbonate/bicarbonate, nitrate, phosphate, and caustic, as well as miscellaneous other environments. Second, the prerequisite conditions for different cracking mechanisms, some of which have been proposed to account for the SCC of C-steel, are discussed in Section 2.2, including slip dissolution (film rupture), stress-assisted intergranular corrosion, film-induced cleavage, surface mobility, and corrosion fatigue.

Based on these two approaches, the implications for SCC of C-steel containers in the DGR are then considered (Section 3). In Section 3.1, the evidence for and against the cracking of containers is presented in terms of the susceptibility of the material, the nature of the environment (both during the initial thermal and moisture transients and following saturation of the repository), and the mechanical loading requirements for crack initiation and growth. Mitigation strategies for SCC are briefly discussed in Section 3.2, followed by a summary of the

overall likelihood of cracking in Section 3.3, including an assessment of when, if at all, cracking is most likely to occur.

2. STRESS CORROSION CRACKING OF CARBON STEEL

2.1 SCC OF CARBON STEEL IN VARIOUS ENVIRONMENTS

Stress corrosion cracking of C-steel has been reported in a number of different environments. Table 1 summarizes the environmental and mechanical loading conditions associated with each form of cracking.

2.1.1 Carbonate/bicarbonate

The SCC of C-steel in carbonate/bicarbonate ($\text{CO}_3^{2-}/\text{HCO}_3^-$) environments is a major issue for underground pipelines (Parkins 2000) and is relevant here both because of the presence of $\text{CO}_3^{2-}/\text{HCO}_3^-$ in bentonite pore waters (McMurray et al. 2003) and because of the similarity between pipeline steels and the grade of C-steel likely to be used for manufacture of a UFC.

Two apparently distinct forms of SCC are observed in pipeline steels, which are generally distinguished by the pH range associated with the electrolytes in which cracking is observed. Figure 1 illustrates the ranges of pH and potential (E) in which the so-called near-neutral pH and high-pH forms of cracking have been observed. The general characteristics of these forms of cracking are summarized in Table 2.

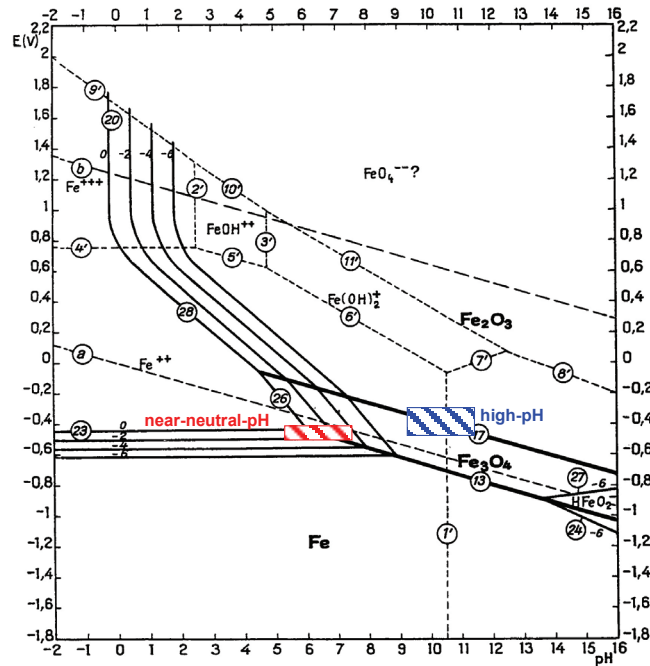


Figure 1: Potential-pH Diagram for Iron Showing the Regions of Susceptibility for the Two Forms of Stress Corrosion Cracking of Pipeline Steels (King 2005a).

Table 1: Summary of Stress Corrosion Cracking Systems Reported for Carbon Steels.

Environment	Crack path*	Mechanism**	Environmental Conditions	Stress/strain Conditions	Typical References
Near-neutral pH SCC	TGSCC	CF	Dilute HCO_3^- solution (of the order of a $0.001\text{-}0.01 \text{ mol}\cdot\text{dm}^{-3}$), with a pH in the range 5.5 to 7.5; potentials corresponding to E_{CORR} in anaerobic environments (-0.685 to $-0.715 V_{\text{SCE}}$); no effect of temperature	$\Delta K_{\text{th}} \cong 10\text{-}15 \text{ MPa}\cdot\text{m}^{1/2}$, threshold corrosion fatigue limit $(\Delta K)^2 \Delta K_{\text{max}} f^{0.1} \cong 10^4 \text{ MPa}^3\cdot\text{m}^{3/2}\cdot\text{s}^{0.1}$	Been et al. (2008); Chen et al. (2008, 2009b); King (2010); NEB (1996); Parkins (2000)
High-pH SCC	IGSCC	SD	Concentrated $\text{CO}_3^{2-}/\text{HCO}_3^-$ solution (0.1 to $>1.0 \text{ mol}\cdot\text{dm}^{-3}$) with a pH > 9.3 ; occurs in a specific range of potentials which is temperature dependent (-0.525 to $-0.675 V_{\text{SCE}}$ at room temperature); crack growth rate increases exponentially with temperature with an activation energy of $\sim 40 \text{ kJ/mol}$	$\sigma_{\text{th}} = \sigma_{\text{YS}} - 750(1 - R) \text{ MPa}$, $K_{\text{ISCC}} \cong 21 \text{ MPa}\cdot\text{m}^{1/2}$, threshold strain rate $\cong 10^{-8} \text{ s}^{-1}$, threshold crack-tip displacement rate $\cong 10^{-10} \text{ mm}\cdot\text{s}^{-1}$	King (2010), King et al. (2003), Leis and Parkins (1998), Parkins (2000)
Nitrate	IGSCC	SD	Concentrated NO_3^- solutions ($0.01\text{-}10 \text{ mol}\cdot\text{dm}^{-3}$) of various cations, Cl^- inhibits effect of NO_3^- ; cracking occurs in a wide potential range with values typically more positive than $-0.4 V_{\text{SCE}}$; crack growth rate increases with temperature with many studies performed in boiling solutions	$\sigma_{\text{th}} = 45 + 1800(\%C) \text{ MPa}$ for annealed C-steel $\sigma_{\text{th}} = 16\text{-}200 \text{ MPa}$ for $0.05\%C$ steel in boiling $(\text{NH}_4)\text{NO}_3$, $\text{Ca}(\text{NO}_3)_2$, LiNO_3 , NaNO_3 , KNO_3 at concentrations of $0.5\text{-}8 \text{ mol}\cdot\text{dm}^{-3}$	Parkins (1977)

... continued

Table 1: Summary of Stress Corrosion Cracking Systems Reported for Carbon Steels (concluded).

Environment	Crack path*	Mechanism**	Environmental Conditions	Stress/strain Conditions	Typical References
Caustic	IGSCC	SD	Concentrated hydroxide solutions with threshold concentration of ~4 wt.% NaOH; cracking occurs over a range of potentials (typically $-0.95 \pm 0.3 V_{SCE}$), width of potential window increases with increasing T and hydroxide concentration; severity increases with increasing T		Ciaraldi (1992), Parkins (1977), Uhlig (1977)
High-temperature water	TGSCC	SD	Cracking in low-conductivity water; trace levels of O ₂ control potential in cracking range; temperatures from 200-320°C	Requires dynamic strain	Ciaraldi (1992)
CO-CO ₂	TGSCC	SD, decohesion	Occurs in dilute solutions containing CO and CO ₂ , low levels of salts and CH ₄ can also be present; cracking occurs at E _{CORR} over a relatively narrow range of potentials (-0.475 to $-0.575 V_{SCE}$); severity decreases with increasing temperature	$\sigma_{th} = 270$ MPa with 0.076 MPa CO $\sigma_{th} = 180$ MPa with 0.15 MPa CO	Brown et al (1977) Kowaka and Nagata (1977)
Ferric chloride	TGSCC	SD	Presence of Fe(III) species, such as FeCl ₃ or FeOOH in a high-temperature aqueous phase; temperature range similar to that for SCC in high-temperature water	$\sigma_{th} \geq \sigma_{YS}$	Strauss and Bloom (1960)
Phosphate	IGSCC	SD	Cracking in Na and ammonium phosphate solutions, pH 3-7; cracking in a range of potentials, -0.6 to $0 V_{SCE}$; crack velocity decreases with increasing temperature		Beavers et al. (1985), Parkins et al. (1978)

* TGSCC – transgranular SCC, IGSCC – intergranular SCC

** CF – corrosion fatigue, SD – slip dissolution

Table 2: General Characteristics of Near-neutral pH and High-pH SCC of Pipeline Steels (adapted from NEB 1996).

Characteristic	Near-neutral pH SCC	High-pH SCC
Crack path and morphology	Transgranular (possible intergranular initiation), with evidence for extensive corrosion of the crack walls	Intergranular, with tight, narrow cracks
Electrolyte	Dilute HCO_3^- solution (of the order of a 1-10 mM), with a pH in the range 5.5 to 7.5	Concentrated $\text{CO}_3^{2-}/\text{HCO}_3^-$ solution (0.1 to $>1.0 \text{ mol}\cdot\text{dm}^{-3}$), with a pH > 9.3
Potential	Potentials corresponding to E_{CORR} in anaerobic environments (-0.685 to $-0.715 \text{ V}_{\text{SCE}}$)	Occurs in a specific range of potentials which is temperature dependent (-0.525 to $-0.675 \text{ V}_{\text{SCE}}$ at room temperature)
Temperature	No apparent effect of temperature	Crack growth rate increases exponentially with temperature with an activation energy of $\sim 40 \text{ kJ/mol}$
Loading conditions	Requires cyclic loading, crack growth rate is a function of maximum stress, range of stress during cyclic loading, and loading frequency	Cyclic loading promotes film rupture, cracking dependent on crack-tip strain exceeding critical strain for slip/film rupture
Mechanism	Corrosion fatigue, but nature of corrosion component uncertain	Slip dissolution

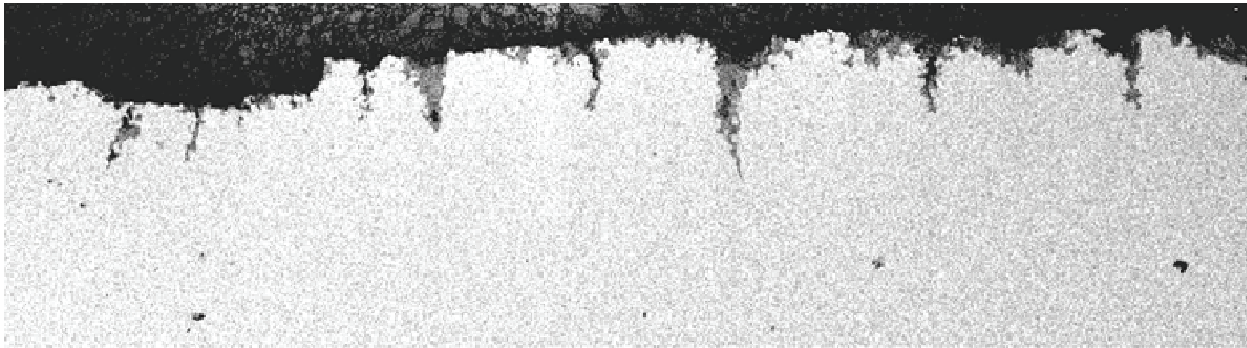
2.1.1.1 Near-neutral pH SCC

Near-neutral pH SCC (NNpHSCC) was first recognized as a distinct form of cracking in the 1980's after cases of gas pipeline rupture in Northern Ontario and Alberta (NEB 1996). Extensive field analyses indicated distinct differences between the characteristics of the crack path and morphology and the associated environmental conditions for this form of cracking and those associated with the classical form of pipeline SCC first observed in the United States in the 1960's and now referred to as high-pH SCC (Section 2.1.1.2). Cracks tend to occur in colonies of interlinked (or coalesced) cracks (Figure 2(a)), with the size of the colony determined to some degree by the area of disbonded coating that usually protects the pipe surface from the groundwater environment. Cracking is transgranular, but extensive corrosion of the crack walls is typically observed (Figure 2(b)), indicative of a relatively corrosive environment within the crack.

Near-neutral pH SCC occurs under relatively benign environmental conditions, comprising $1\text{-}10 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3} \text{ HCO}_3^-$, $1\text{-}5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3} \text{ Cl}^-$, $\sim 1 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3} \text{ SO}_4^{2-}$, with Na^+/K^+ or $\text{Ca}^{2+}/\text{Mg}^{2+}$ as the dominant cations depending on location (King et al. 2000). The key environmental parameter is CO_2 , which both determines the dissolved HCO_3^- concentration and buffers the pH. The pH of solutions associated with NNpHSCC exhibit a pH in the range 5.5-7.5, which corresponds to the pK_a for the dissociation of carbonic acid (H_2CO_3)



(a) Surface appearance of near-neutral pH SCC cracks on a cleaned pipeline surface



(b) Cross section through a near-neutral pH SCC crack colony. The image represents a section 3.8 mm long by 1.0 mm wide.

Figure 2: Metallographic Images of Near-neutral pH Stress Corrosion Cracks on a Pipeline Steel.



The speciation of the $\text{H}_2\text{CO}_3/\text{HCO}_3^-/\text{CO}_3^{2-}$ system as a function of pH is illustrated in Figure 3. Although dissolved CO_2 is known to be necessary for this form of cracking, the precise role of the bicarbonate ion (or undissociated carbonic acid) is uncertain.

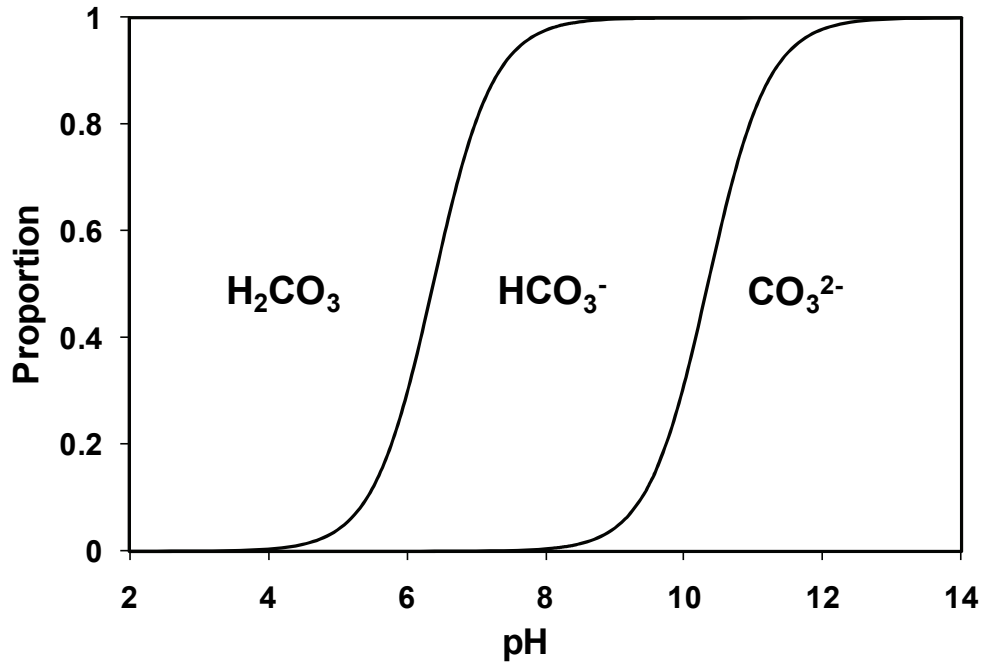


Figure 3: Aqueous Speciation of the Carbonic Acid/Bicarbonate/Carbonate System.

Carbon steel corrodes under active conditions in NNpHSCC environments, which is confirmed by both voltammetric measurements (King et al. 2000) and the fact that the E-pH range for cracking only marginally overlaps the stability field of Fe_3O_4 (Figure 1). Rather than magnetite formation, the observation of cracks in the field is often associated with the presence of "pasty white" iron carbonate ($FeCO_3$). The pasty consistency reported from field observations is due to the amorphous nature of the precipitate and the small particle size, which implies that the nucleation of $FeCO_3$ is favoured over the growth of pre-existing crystallites.

In contrast with the high-pH form of cracking (see below), there is apparently no effect of temperature on NNpHSCC. At one time this was believed to be due to the fact that the solubility of CO_2 increases with decreasing temperature, offsetting any increase in rate with increasing temperature, but this hypothesis is no longer considered correct. It is more likely that the nature of the rate-controlling process, possibly involving hydrogen or mechanical loading, is insensitive to temperature.

A wide range of pipeline steels have been shown to be susceptible to NNpHSCC (Parkins 2000). Pipeline steels produced in the 1950's to 1990's tended to have a ferrite-pearlite microstructure with a strong through-wall banded structure produced by hot rolling. Cracking has been observed in steels with yield strengths of 240 MPa to 483 MPa (35-70 ksi) (NEB 1996). Within the specifications for pipeline steels, there is no obvious dependence on the chemical composition of the steel, although the presence of MnS and other non-metallic inclusions is believed to be detrimental (NEB 1996, Parkins 2000), as for H-related cracking (King 2009).

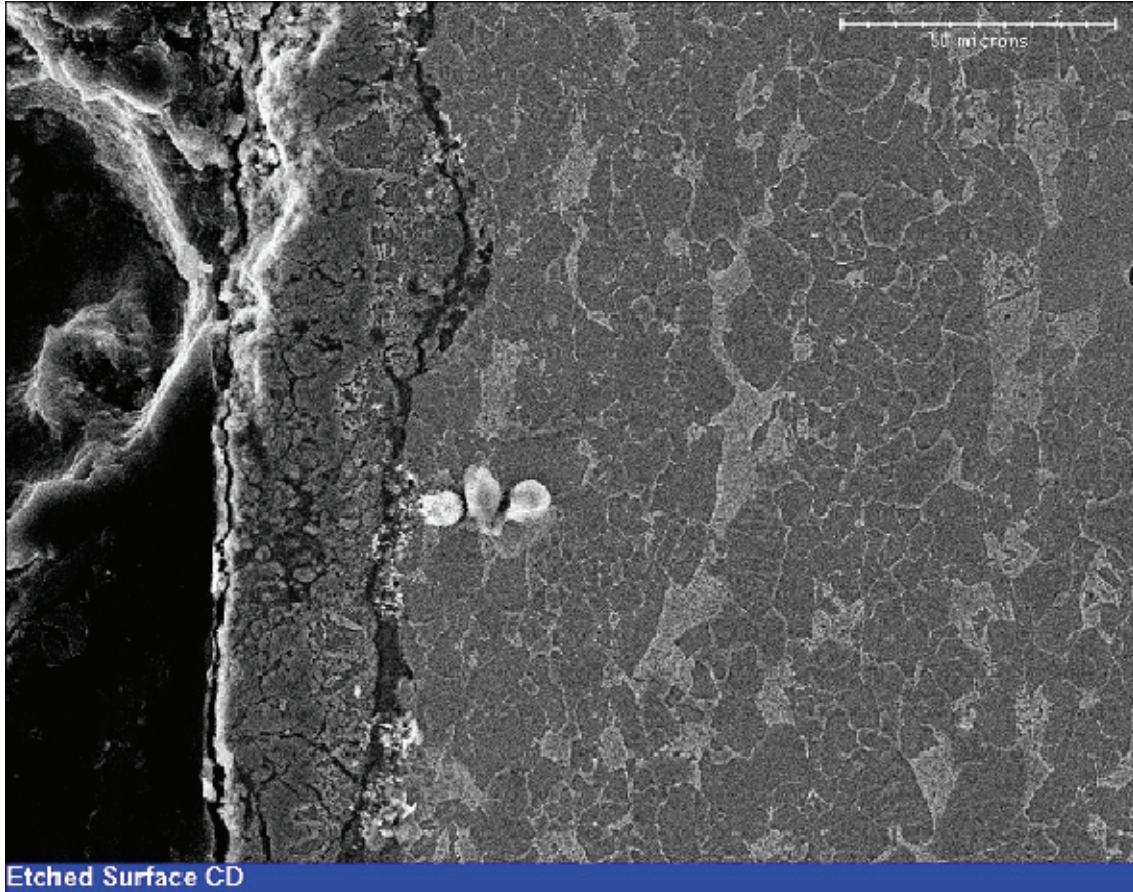


Figure 4: Cross-section Through a Millscale Layer on the Surface of a Pipeline Steel.

The presence of millscale on the pipe surface has been found to enhance the susceptibility to both crack initiation and crack propagation. Millscale is formed during the manufacturing process and consists of a layer of magnetite, maghemite, and scale and mineral impurities some tens of micrometres thick. Millscale is electrochemically active and can polarise the underlying steel surface at the base of pores or cracks in the film, thus promoting localised dissolution and crack initiation (Qin et al. 2004). Millscale also appears to affect crack propagation, possibly by maintaining a sharp crack tip by inducing a slight cathodic polarisation (by some tens of millivolts) of the crack tip (Been et al. 2008).

There are two main sources of tensile stress, namely; the hoop stress resulting from the pressure of the gas inside the pipe and residual stress from the pipe manufacturing process. Gas transmission pipelines typically operate at a pressure equivalent to 72% to 80% of the specified minimum yield stress (SMYS) of the material, with liquid pipelines and local distribution systems operating at lower %SMYS. Pipeline failures due to NNpHSCC have been observed at operating pressures equivalent to stress levels as low as 40-50% SMYS (NEB 1996), although high residual stresses may have contributed significantly to cracking at these low levels of applied stress.

Pipelines are subject to cyclic loading and, in the majority of studies, cracking can only be induced in the laboratory under dynamic loading conditions. Crack propagation is now thought to involve a form of corrosion fatigue, in which the crack growth (either per unit time da/dt or per loading cycle da/dN) is a function of the maximum stress intensity factor K_{max} , the magnitude of the loading cycle (expressed as the change in stress intensity factor ΔK), and the loading frequency f . Figure 5 shows a compilation of crack growth rates fitted to a modified corrosion fatigue model based on a driving force involving $\Delta K^2 K_{max} f^{0.1}$ (Chen et al. 2008).

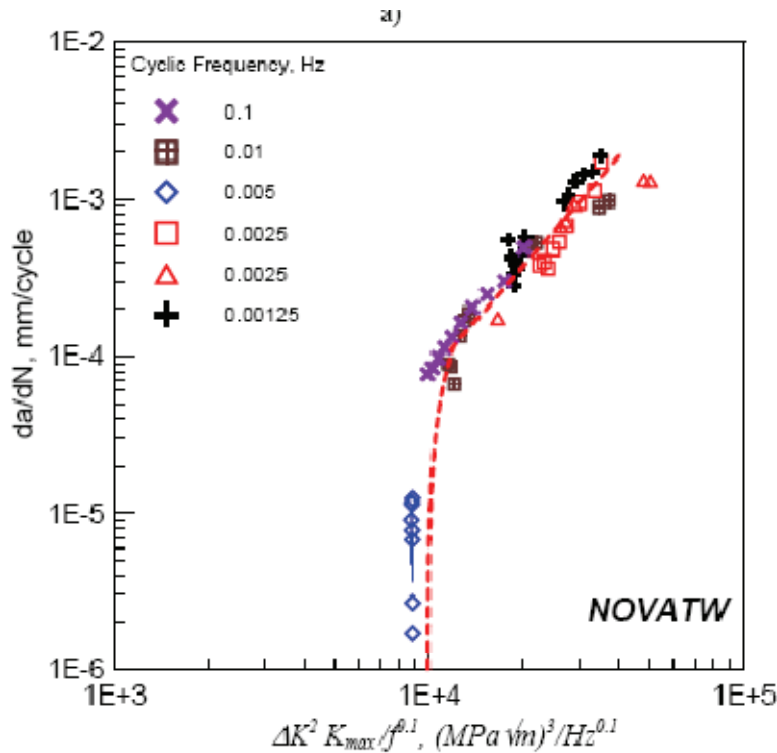


Figure 5: Crack Growth Rates Fitted to a Modified Corrosion Fatigue Model (Chen et al. 2008).

Although current thinking is that the mechanism of NNpH SCC can be described by a corrosion fatigue process, there are several reports in the literature of crack growth under static or near-static conditions (King 2010). Crack growth in these cases may be due to dynamic strain resulting from creep, pipeline steels being susceptible to creep at room-temperature (Chen et al. 2009a).

It is also uncertain what corrosion process is responsible for the enhanced crack growth observed in near-neutral pH solutions. Because cracking occurs at the open-circuit potential, it is difficult to distinguish between anodic and cathodic contributions to cracking without polarizing the sample away from E_{CORR} and, potentially, altering the mechanism. Various authors have proposed a role of hydrogen, of anodic dissolution, and of hydrogen-assisted dissolution (King 2010). Although not definitive, it appears most likely, however, that it is hydrogen and its transport to the crack tip that is responsible for the environmental enhancement of crack growth (Been et al. 2008, Chen et al. 2009b).

2.1.1.2 High-pH SCC

High-pH SCC of pipeline steels was first encountered in the 1960's resulting in a number of in-service and hydrostatic test failures. Visually, cracks have a similar surface appearance to NNpH SCC cracks (Figure 2(a)), but in cross-section appear to be tighter and devoid of precipitated corrosion product. Cracking is intergranular in nature. High-pH SCC has been investigated extensively by Parkins and co-workers (Leis and Parkins 1998; Parkins 2000; Parkins and Fessler 1978; Parkins and Singh 1990; Parkins and Zhou 1997a,b).

High-pH SCC is associated with concentrated bicarbonate/carbonate solutions with a pH close to the pK_a for the HCO_3^-/CO_3^{2-} couple of pH 10.34 (at 25°C) (Figure 3). The total carbonate concentration is of the order of 0.1-1 mol·dm⁻³ and the majority of laboratory testing has been performed in a so-called 1N-1N solution comprising 0.5 mol·dm⁻³ Na₂CO₃ plus 1 mol·dm⁻³ NaHCO₃ (Parkins 2000).

There are believed to be two major mechanisms by which such concentrated HCO_3^-/CO_3^{2-} are formed. The most common mechanism involves the concentration of the electrolyte under a porous coating on a cathodically protected pipeline. The increase in pH resulting from the action of the cathodic protection system is counteracted by the transport of CO₂ from the surrounding (soil) environment, which dissolves in the electrolyte layer on the surface of the protected structure and leads to the formation of a concentrated HCO_3^-/CO_3^{2-} solution. The second mechanism involves the evaporative concentration of a dilute HCO_3^-/CO_3^{2-} solution on the hot pipe surface. In either mechanism, the predominant cation(s) must be Na⁺ (and/or K⁺) because the limited solubility of calcium and magnesium does not permit the development of sufficiently concentrated solutions (Beavers and Worthingham 2002). Furthermore, the presence of CO₂ is also important.

Cracking is found to occur only within a narrow range of potentials (Parkins 2000). Figure 6 compares the potential range for cracking in 0.5 mol·dm⁻³ Na₂CO₃ plus 1 mol·dm⁻³ NaHCO₃ solution at 75°C with the results of fast and slow potential scans. Voltammetric scans of different scan rates are used to identify potential regions of marginal passivity, a feature characteristic of certain mechanisms of SCC (see below). Cracking in this environment occurs between approximately -0.7 V_{SCE} and -0.6 V_{SCE}, a range that could encompass the corrosion potential depending upon the concentration of oxidant.

Both the stress level and the strain rate are found to affect the observed cracking behaviour. Failures of high-pressure gas pipelines have been observed at stresses between 46% and 76% of SMYS (King 2010), which would represent an actual load of as little as 40% of the actual yield stress. Cyclic loading is found to promote crack initiation, with the threshold stress decreasing with increasing load range (i.e., decreasing R value, where R is the ratio of the minimum to maximum stress of the cycle). Crack propagation is promoted by the (crack-tip) strain rate ($\dot{\epsilon}_{CT}$), with the crack growth rate increasing with increasing $\dot{\epsilon}_{CT}$ (Parkins 2000). At high strain rates (greater than 10⁻⁴ s⁻¹), however, the crack growth rate becomes independent of $\dot{\epsilon}_{CT}$ (Leis and Parkins 1998). At low strain rates (less than, say 10⁻⁸-10⁻⁹ s⁻¹), the crack growth rate drops precipitously, approaching zero (Leis and Parkins 1998).

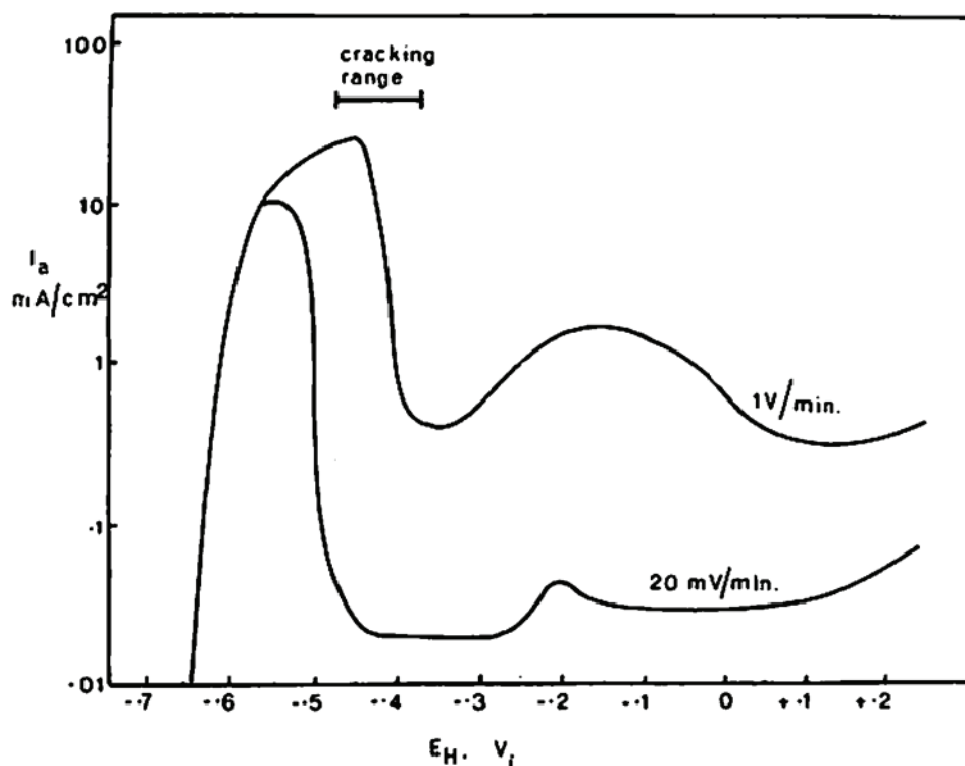


Figure 6: Results of Fast and Slow Voltammograms on Carbon Steel in $0.5 \text{ mol}\cdot\text{dm}^{-3} \text{ Na}_2\text{CO}_3$ Plus $1 \text{ mol}\cdot\text{dm}^{-3} \text{ NaHCO}_3$ at 75°C and the Associated Range of Potentials for Stress Corrosion Cracking (Parkins 1977). The plot shows the anodic current density (I_a in $\text{mA}\cdot\text{cm}^{-2}$) as a function of potential (E_H in V_{SHE}) for potential scan rates of $1 \text{ mV}\cdot\text{min}^{-1}$ and $20 \text{ mV}\cdot\text{min}^{-1}$.

A characteristic of cracks in the laboratory, and likely those in the field, is that the crack growth rate decreases with time. Continued crack propagation, in both the lengthwise and depthwise directions, is supported by crack coalescence in which the tips of adjacent cracks interact and coalesce into a single crack. Crack coalescence is also a feature of NNpHSCC and evidence for it can be seen in Figure 2(a).

There is no clear evidence for the role of steel chemistry or microstructure in high-pH SCC. There is evidence that the finer microstructures characteristic of modern thermo-mechanically controlled-processed (TMCP) steels are less susceptible than banded ferrite-pearlite microstructures characteristic of older steels (King 2010). Manganese sulphide inclusions (MnS) have long been associated with enhanced crack initiation (and, possibly, propagation) and the levels of sulphur are now closely controlled. The millscale layer on pipe surfaces has also been found to be detrimental, either by promoting crack initiation (Qin et al. 2004) or by poisoning the electrochemical potential into the appropriate range for cracking.

High-pH SCC follows a slip-dissolution mechanism in which crack advance occurs by dissolution of steel exposed as a protective surface film ruptures as a result of slip at the crack tip. As discussed in more detail below, this mechanism accounts for the observed effects of strain rate and temperature on crack growth.

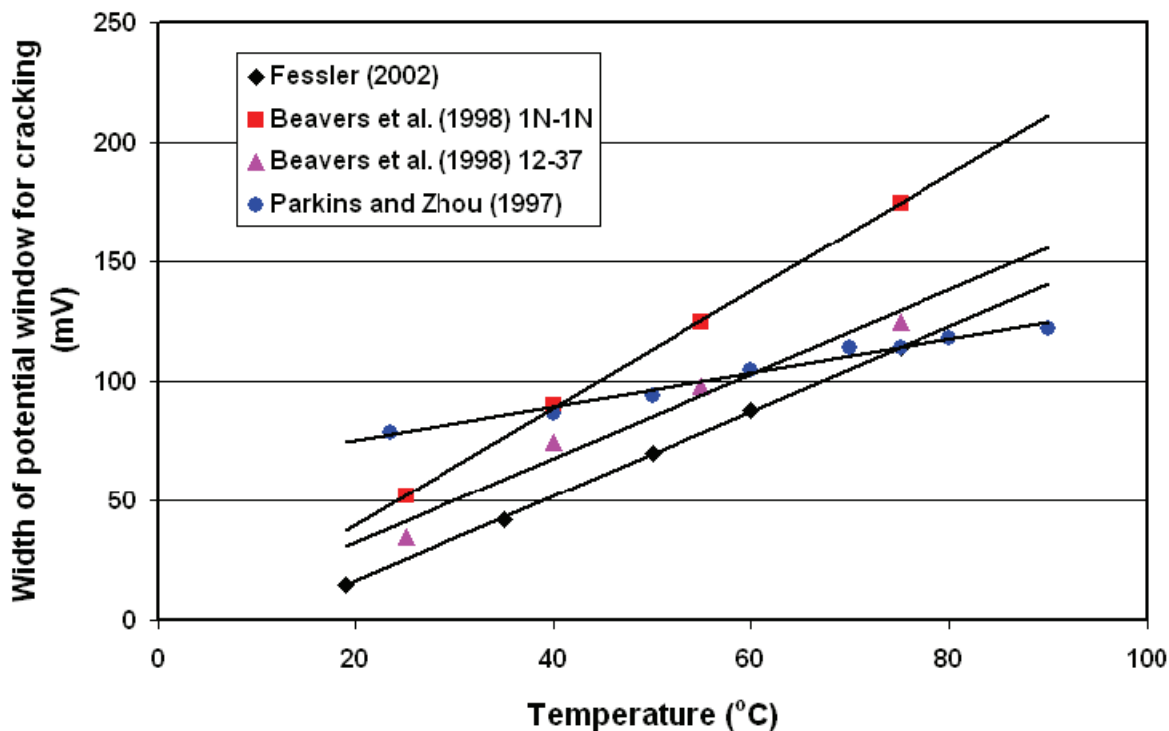


Figure 7: Width of the Potential Range for High-pH SCC Crack Propagation as a Function of Temperature (King et al. 2003).

The severity of high-pH SCC increases with increasing temperature. Temperature plays a number of roles in the cracking process, including:

- the evaporative generation of the environment,
- the increased rate of dissolution at the crack tip following film rupture,
- the width of the potential range for cracking (Figure 7), and
- shifting the potential range for cracking to more-negative potentials with increasing temperature.

The importance of the effect of temperature is evidenced by the distribution of high-pH SCC failures on gas pipelines. The vast majority of failures have occurred within 10 miles (16 km) of the outlet of the compressor station where the gas and, hence, the pipe temperature is hottest. Indeed, the predominant effect of temperature is further evidenced by the fact that the frequency of this form of cracking has been greatly diminished by the installation of coolers at compressor stations to lower the exit gas temperature (King et al. 2003). This predominant effect of temperature clearly has implications for the possibility of this form of cracking in the repository (Section 3.1.2).

2.1.2 Nitrate

High concentrations of nitrate ions, particularly as boiling solutions, induce the SCC of C-steel under open-circuit conditions. Although such conditions may not seem relevant to the repository environment, if nitrate ions are present initially then evaporative concentration of thin electrolyte films during the early thermal transient could conceivably lead to such environments.

Intergranular cracking occurs over a wide range of potentials (Figure 8). Susceptibility to cracking, as measured by the threshold stress, decreases with increasing NO_3^- concentration and is lower in ammonium-containing solutions than in solutions of the alkali metal salts (Li^+ , Na^+ , K^+) or Ca^{2+} (Parkins 1977). Cracking is a strong function of temperature, with the crack growth rate increasing with increasing temperature with an activation energy of between 50 and 120 kJ/mol. Chloride ions inhibit the aggressiveness of the nitrate ion in $\text{Ca}(\text{NO}_3)_2$ solutions but, interestingly, not in NH_4NO_3 solution (Figure 9). Carbonate, bicarbonate, and phosphate also inhibit SCC in nitrate solutions (Parkins 1977). The inhibitive effect of Cl^- may be associated with competition for adsorption sites and/or soluble Fe(II) complexes with NH_4^+ ions, which it has been suggested are formed within the crack by the cathodic reduction of NO_3^- to ammonia. A critical $[\text{Cl}^-]:[\text{NO}_3^-]$ ratio of 0.1 above which cracking does not occur can be inferred from the data in Figure 9.

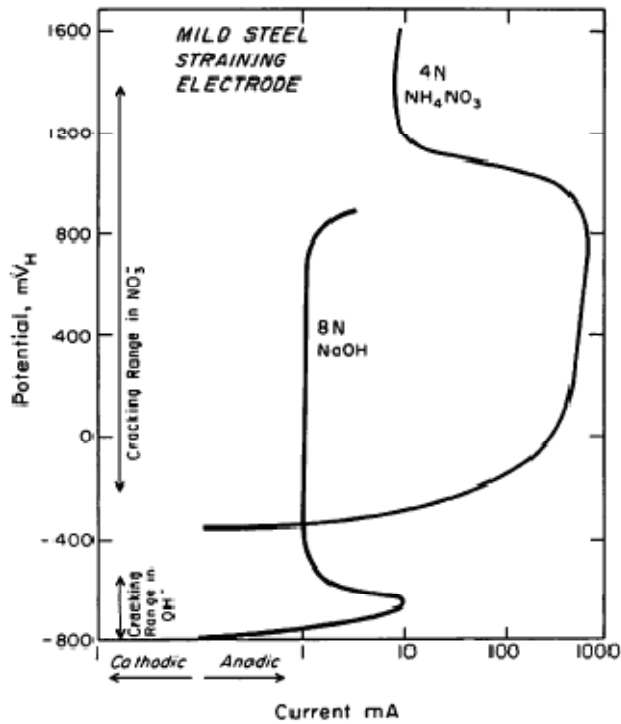


Figure 8: Comparison of the Voltammetric Behaviour and Range of Potentials for Cracking in Caustic and Concentrated Nitrate Solutions (Staehele 1977).

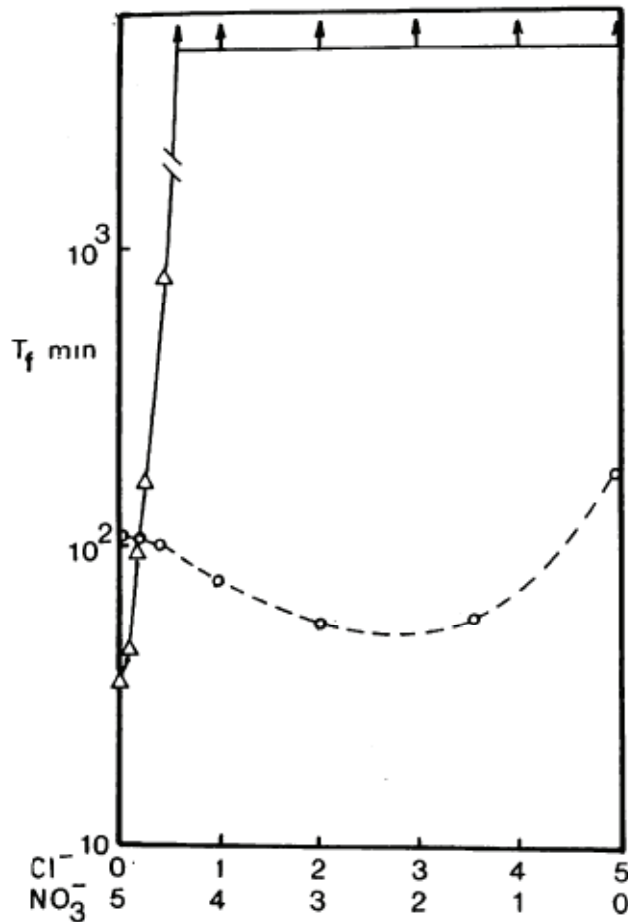


Figure 9: The Inhibitive Effect of Replacing Nitrate Ions by Chloride in 5N Solutions of Ca²⁺ (Δ) But Not in NH₄⁺ Solutions (O) (Parkins 1977). The plot shows the time-to-failure (in minutes) of tensile samples exposed to solutions of constant Ca²⁺ concentration but of varying [Cl⁻]:[NO₃⁻] ratios.

The characteristics of the cracking process are consistent with a slip dissolution mechanism involving crack advance by dissolution following the rupture of a passive film at the crack tip.

2.1.3 Caustic

Caustic cracking of C-steel was the first reported instance of SCC of ferritic steels and one of the first ever recognised cases of the environmentally assisted cracking of metals (Parkins 1977).

Caustic cracking exhibits many of the same characteristics as SCC in concentrated HCO₃⁻/CO₃²⁻ and nitrate environments, being intergranular in nature and a strong function of temperature and potential. Figure 10 shows the potential dependence of the time to failure of C-steel in 35%

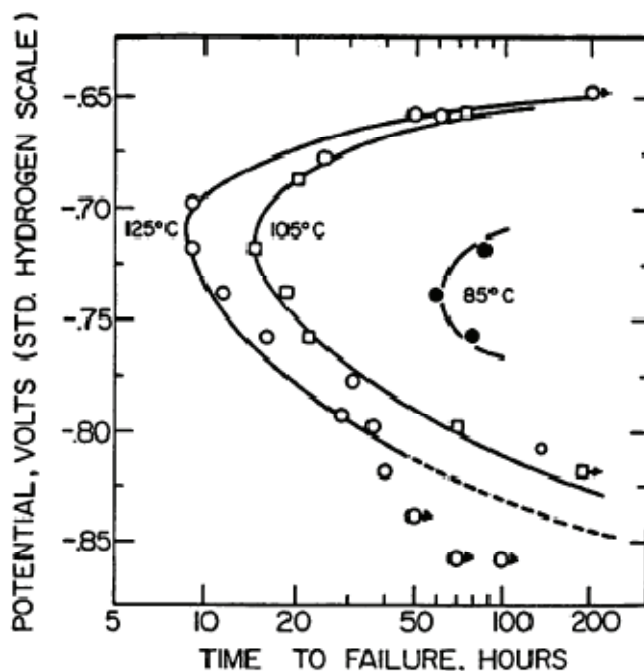


Figure 10: Dependence of the Time-to-Failure of C-steel on Potential in 35% NaOH Solution at Three Temperatures (Uhlrig 1977).

NaOH solution for three different temperatures (Uhlrig 1977). There is a significant increase in the range of potentials over which cracking occurs with increasing temperature. The activation energy for crack growth is ~ 75 kJ/mol. The width of the potential window for cracking also increases with increasing caustic concentration. Cracking has been reported in NaOH solutions at concentrations between 4 and 75 wt.%, equivalent to molar concentrations of 1-20 mol-dm⁻³. Clearly the surface would be strongly passivated at such alkaline pH with the formation of a protective Fe₃O₄ layer.

Cracking occurs in highly stressed regions and typically requires some degree of plastic deformation (Ciaraldi 1992).

2.1.4 Miscellaneous Environments

There are a number of other environments in which the SCC of C-steel has been identified but which are unlikely to be formed in the repository. These environments are discussed briefly here for the sake of completeness.

2.1.4.1 High-temperature Water

Stress corrosion cracking of low-alloy steels has been reported in the nuclear industry in high-purity water at high temperature. Temperatures in the range 200-250°C appear to be optimum, although cracking has been reported at temperatures up to 320°C (Ciaraldi 1992). Low levels of

dissolved O₂, to control the potential in the cracking range, and dynamic strain have been reported to be important factors. Cracking is thought to be the result of a slip-dissolution mechanism.

2.1.4.2 Carbon Monoxide-Carbon Dioxide

Cracking of C-steel has been observed in environments containing a mixture of carbon monoxide and carbon dioxide (Brown et al 1977, Kowaka and Nagata 1977). This system is interesting in that cracking is transgranular, as opposed to intergranular in the majority of the other systems described above.

Cracking is dependent on potential but occurs over a relatively narrow range of values (-0.475 to -0.575 V_{SCE}, Brown et al. 1977). The severity increases with increasing CO partial pressure, with both the threshold stress decreasing and the crack growth rate increasing with p_{CO}. The threshold stress can be as little as 25% of the yield stress. Unlike the intergranular forms of SCC in carbonate, nitrate, and caustic solutions, cracking is more severe at lower temperatures with SCC observed at temperatures of 40 and 70°C but not at 100 and 150°C (Kowaka and Nagata 1977). Because of the presence of CO₂, the steel dissolves actively, although the addition of CO inhibits dissolution. Cracking occurs under freely corroding conditions.

Although the cracking potentials are sufficiently negative for hydrogen evolution in the acidic solution to occur, the mechanism is not thought to involve hydrogen because it can be suppressed by cathodic polarisation (Brown et al. 1977). Instead, Brown et al. (1977) suggested that the adsorption of CO inhibits dissolution, in effect passivating the surface. Disruption of the adsorbed layer by stress at emergent slip planes would then allow crack advance by dissolution, in a slip-dissolution-type mechanism. Alternatively, the adsorption of CO could cause decohesion of Fe-Fe bonds, thus promoting crack growth.

2.1.4.3 Ferric Chloride

Ferric chloride species have been reported to induce the SCC of ferritic alloys (Strauss and Bloom 1960). Such species could be formed during the early aerobic and transition phases in the evolution of the repository environment. Cracking was transgranular in nature and occurred in plastically deformed regions of the sample. However, these studies were conducted at a temperature of 316°C and there is no evidence for a similar effect at lower temperatures representative of those expected in a DGR.

2.1.4.4 Phosphate

Parkins et al. (1978) report the intergranular SCC of C-steel in phosphate solutions as a function of pH. Cracking exhibits a similar dependence on potential as other forms of intergranular cracking in caustic, carbonate, and nitrate environments, but the crack growth rate decreases with increasing temperature. Phosphate is unlikely to occur in significant concentrations in repository environments. Furthermore, cracking only occurs in acidic solutions and the crack velocity decreases with increasing pH, approaching zero at pH 7 (Beavers et al. 1985). Since the near-field repository environment will be buffered by the presence of bentonite, SCC due to phosphate need not be considered further.

2.2 MECHANISMS OF SCC OF CARBON STEEL

2.2.1 Slip Dissolution

The slip-dissolution (SD) model is, in its various forms, one of the earliest mechanisms proposed to account for the SCC of materials. In its most basic form, the SD model states that crack advance occurs by dissolution of the underlying metal following the rupture of a protective surface film. Early proponents of the SD model include Vermilyea (1977) and Parkins (1977), with much subsequent work published by Ford and Andresen (e.g., Ford and Andresen 2002) and Shoji and co-workers (e.g., Lu and Shoji 2006) on the cracking in light water reactor environments. More recently Hall (2009a) has criticized the Ford-Andresen model and has developed his own version of the slip dissolution model that accounts for cracking under constant and variable loading conditions (Hall 2009b). Newman and Healy (2007) have also reviewed the basis for the SD model and considered the sensitivity of the predicted crack growth rates to various parameters.

Figure 11 shows a schematic illustration of the SD model (Parkins 1993). The SD model is often associated with intergranular forms of cracking as the grain boundary can act as a preferential dissolution pathway due to the accumulation of impurities. However, there is no reason why slip could not occur along emergent slip planes within the grain, leading to transgranular cracking.

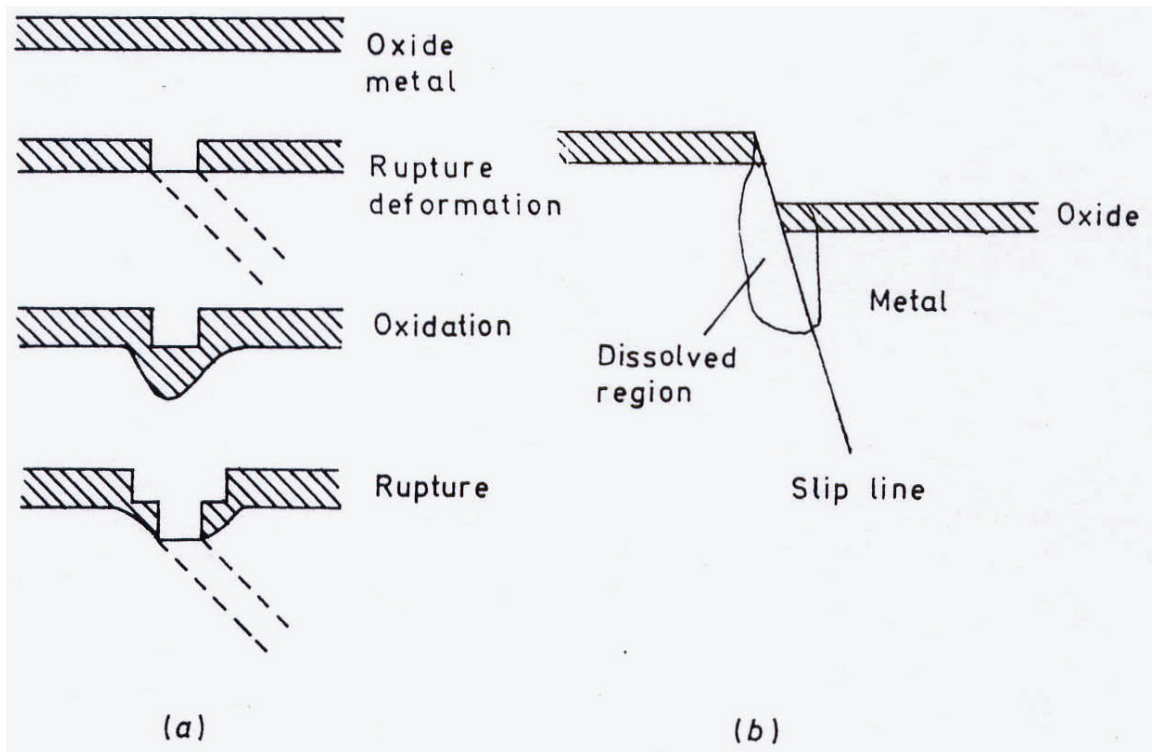


Figure 11: Schematic Illustration of the Film-rupture or Slip Dissolution Model for Stress Corrosion Cracking (Parkins 1993).

The characteristics of cracking described by the SD model can be understood in terms of the balance between various processes. Thus, cracking tends to occur in systems which exhibit marginal passivity, since if the system is too passive then film rupture is more difficult and the subsequent crack advance by dissolution will be limited. Furthermore, cracking is a balance between the extent of dissolution, as determined by the relative rates of dissolution and passivation, and the mechanical factors that control film rupture.

As a result of these competing processes, systems that follow a SD mechanism are characterized by:

- a crack growth rate that depends on the (crack-tip) strain rate, with an absence of cracking at both high (due to predominantly ductile fracture) and low (due to stable film growth) strain rates,
- cracking in a range of potentials corresponding to conditions that promote "marginal" passivity,
- a temperature dependence that mirrors the temperature dependence of the dissolution and/or film growth processes,
- environmental effects that can be similarly explained in terms of their effects on dissolution or film growth, and
- material characteristics that affect either the stress-strain properties (and, thus, the extent of plastic deformation and/or creep) or the film formation/dissolution properties.

Crack growth kinetics can be theoretically predicted based on the characteristics of the dissolution and film formation behaviour of the steel and the mechanical loading conditions. Cracking can be either continuous if the crack-tip strain rate exceeds the rate of re-passivation or discontinuous if the rate of passivation exceeds the rate at which film rupture occurs. For continuous crack growth, the crack velocity (v) is related to the anodic current density at the crack tip (i_{CT})

$$v = i_{CT} \frac{M}{zF\rho} \quad (1)$$

where M is the atomic mass, z is the valency of dissolved metal, F is the Faraday constant, and ρ is the density. If the crack-tip strain rate ($\dot{\epsilon}_{CT}$) is slow, the crack tip periodically repassivates and the crack advances discontinuously at a rate given by

$$v = \frac{Q_F}{\epsilon_C} \dot{\epsilon}_{CT} \frac{M}{zF\rho} \quad (2)$$

where Q_F is the charge density corresponding to crack advance and ϵ_C is the critical strain for film rupture.

2.2.2 Stress-assisted Intergranular Corrosion

The stress-assisted intergranular corrosion mechanism is similar to the tarnish-rupture mechanism for copper alloys and involves the rupture of a brittle film at the grain boundary (Figure 12). A brittle film grows preferentially along the grain boundary which then ruptures under the influence of tensile stress. Further growth of the film along the grain boundary and its subsequent rupture lead to repeated crack advances and leaves characteristic crack arrest markings on the fracture surface. Although stress-assisted intergranular corrosion shares

certain characteristics with the slip dissolution model, the two mechanisms are distinguished by the fact that, in the former, crack growth is limited to the thickness of the oxide (film) at the grain boundary whereas in the latter crack growth is due to dissolution following film rupture.

The stress-assisted intergranular corrosion mechanism was promoted in the 1970-1980's but has fallen out of favour in recent years. Clearly, this model can only explain intergranular cracking.

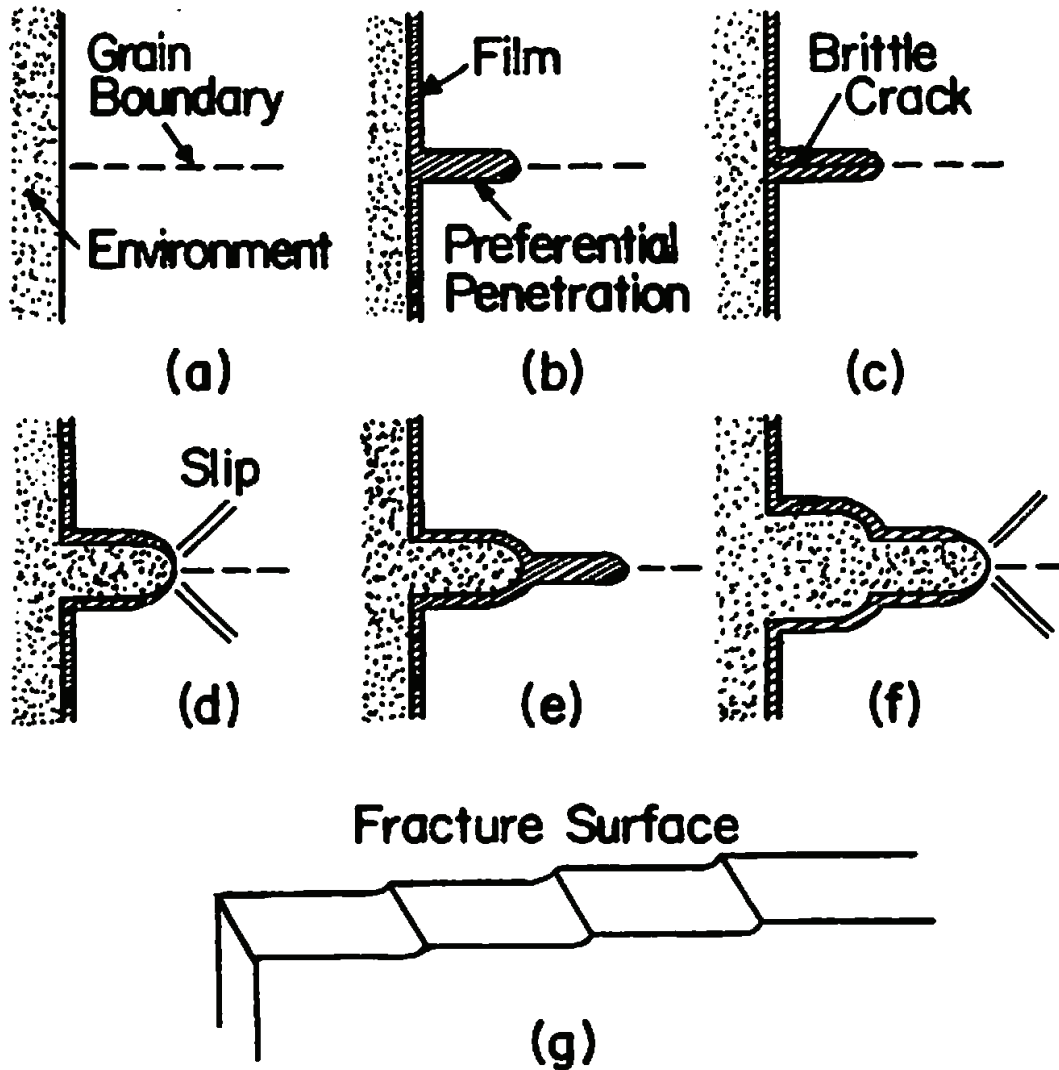


Figure 12: Schematic Illustration of the Stress-assisted Intergranular Corrosion Mechanism (Pugh 1977).

2.2.3 Film-induced Cleavage

The film-induced cleavage mechanism has been popularized over the past 20-30 years by Sieradzki and Newman (1985, 1987), although it traces its routes back to the work of Edeleanu and Forty (1960) and Pugh and co-workers (Beavers and Pugh 1980, Pugh 1985). The model was developed to account for transgranular cracking resulting in cleavage-like cracking. A brittle crack, in the otherwise ductile underlying material, is triggered by the fracture of thin surface layer. The initiating surface layer must possess suitable properties and is often associated with a nanoporous layer produced by dealloying. Alternatively, a porous surface layer can be produced by rapid dissolution producing etch pits (Sieradzki and Kim 1992) or, conceivably, by a thin surface oxide film, although the latter type of initiating layer has not been widely studied. Regardless, the initiating layer must be sufficiently continuous with the substrate that the initiating crack continues to propagate into the underlying metal. Such layers are typically formed under conditions of rapid dissolution and, hence, would tend not to form for the more-limited dissolution rates to be expected in repository environments.

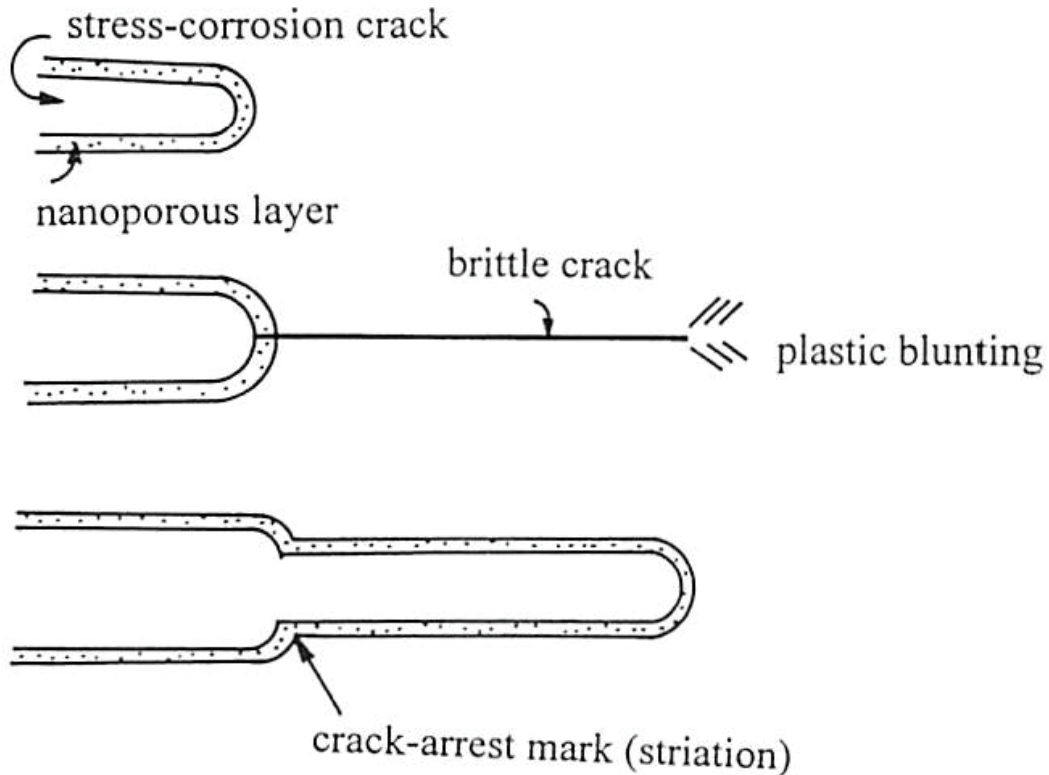


Figure 13: Schematic Illustration of the Film-induced Cleavage Model (Newman 2002).

The crack growth rate can be expressed in terms similar to that for the SD model. Crack growth results primarily from the jump of the crack a distance H beyond the initiating surface layer of thickness h . If the surface layer fractures at a frequency $\varepsilon/\varepsilon_{CT}$ then the crack velocity is given by (for $H \gg h$)

$$v = \frac{\varepsilon \dot{\varepsilon}_{CT}}{\varepsilon_C} H(h) \quad (3)$$

where, in general, the distance H is a function of the thickness of the initiating layer.

To date, the film-induced cleavage model has not been invoked to explain the SCC of C-steels.

2.2.4 Surface Mobility Model

The surface mobility (SM) model was developed by Galvele and co-workers (Farina et al. 2005; Galvele 1987, 1993, 1996, 2000; Serebrinsky and Galvele 2004; Serebrinsky et al. 1999), but has found limited application outside of this group. Crack growth is presumed to occur by the capture of vacancies (or emission of atoms) at a stressed crack tip. The process is enhanced by surface diffusion.

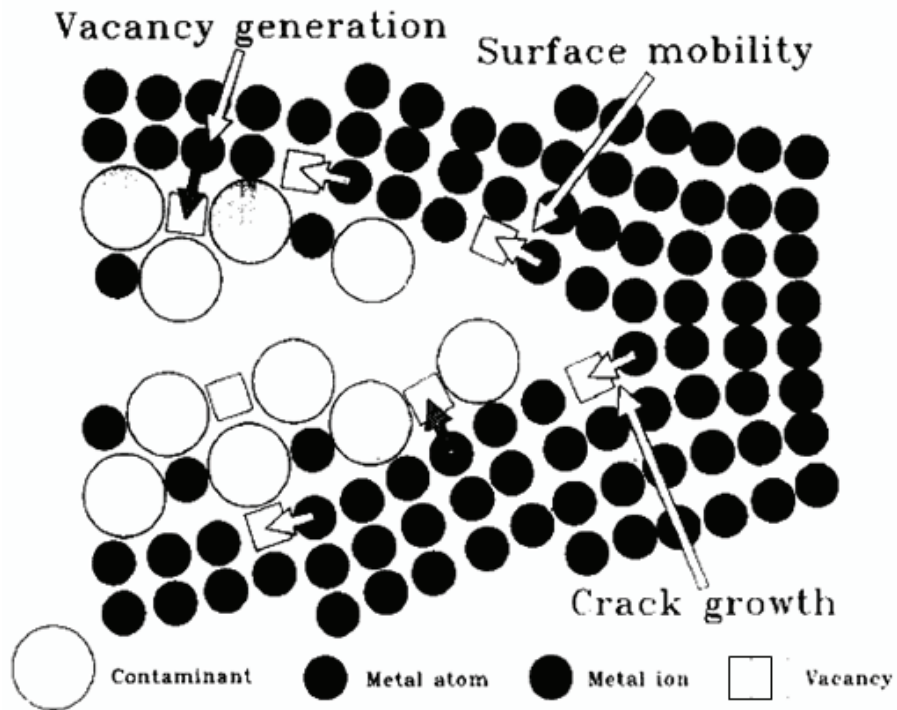


Figure 14: Schematic Illustration of the Surface Mobility Model (Galvele 1987).

The expression for the crack velocity is given by

$$v = \frac{D_s}{L} \left[\exp \left(\frac{\sigma a^3}{kT} \right) - 1 \right] \quad (4)$$

where D_s is the surface (self) diffusivity, L is a diffusion length along the crack flank (typically 10^{-8} m), σ is the opening stress at the crack tip, and a is the atomic size (the approximate volume of a vacancy). Because all metals have an inherent self diffusivity, the crack velocity is never zero and the SM model predicts cracking in any environment. However, surface mobility is enhanced by adsorbed surface species and the formation of surface compounds so that cracking may be faster in certain environments.

The SM model has been criticized on a number of levels (Gutman 2003, 2004; Sieradzki and Friedersdorf 1994), with the main arguments (summarized by King and Newman 2010) being that:

- the crack growth rate expression (Equation (4)) is incorrectly based on a volume expression for the effect of stress on the vacancy concentration at the crack tip, rather than a surface basis as is appropriate for a crack, and
- the model does not account for capillary effects that would result in crack closure for the tight cracks assumed in the model.

In particular, if Equation (4) is re-formulated to account for the vacancy concentration on a free surface, the predicted crack growth rates are of the order of 10^{-20} m/s (King and Newman 2010), which are slow even over repository timescales.

2.2.5 Corrosion Fatigue

Corrosion fatigue describes the process by which the growth of fatigue cracks (i.e., cracks grown under cyclic load in the absence of an environment) is enhanced by the presence of an environment. Typically, the driving force for crack growth is described by the stress intensity factor range ΔK (Figure 15). Above a threshold value, the logarithm of the crack growth rate da/dN grows linearly with the logarithm of the driving force ΔK according to the Paris Law (Scott 1993). Any environmental enhancement results in an increase in da/dN above the Paris Law line. Once the crack becomes sufficiently deep that the stress intensity factor K exceeds the critical value K_C failure occurs due to fast crack growth.

As discussed in Section 2.1.1.1, the NNpHSCC of pipeline steels has been described in terms of a corrosion fatigue mechanism. Some researchers propose a conventional corrosion fatigue model involving ΔK as the driving force for crack growth. Chen and co-workers (Chen et al. 2008, 2009b) propose a modified corrosion fatigue model in which crack growth depends not only on ΔK but also on the maximum stress intensity factor K_{max} and the frequency of cyclic loading f in a combined driving force term $\Delta K^2 K_{max} f^{0.1}$. This model accounts for the observation that crack growth is both frequency dependent and depends on the maximum stress not just the stress range. The "corrosion" enhancement is believed to be due to the effects of hydrogen on the crack growth process (Chen et al. 2009b), which is consistent with both the environmental conditions under which NNpH SCC is observed and the cleavage-like transgranular nature of the fracture surface.

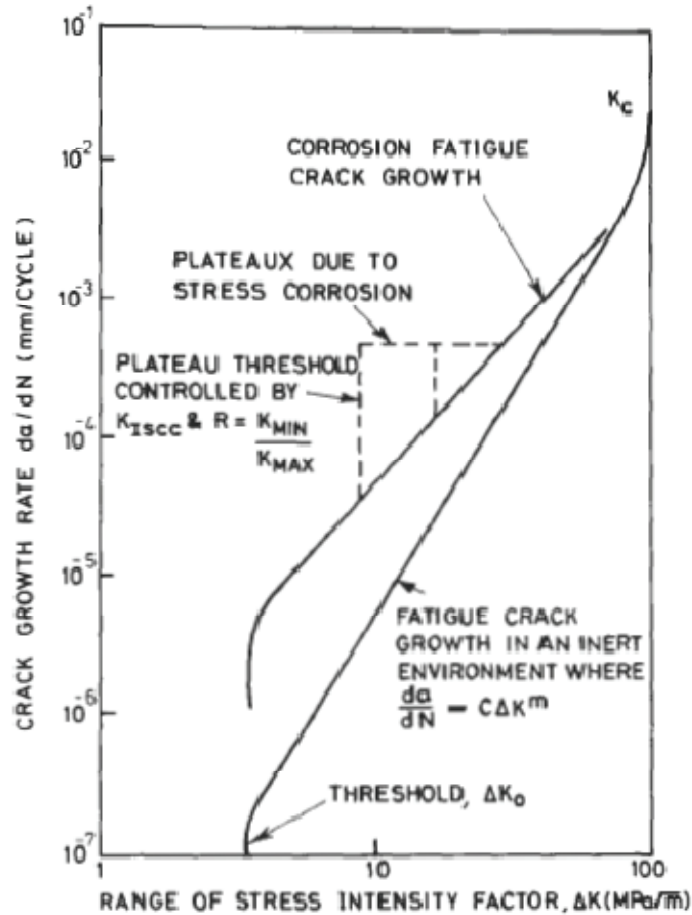


Figure 15: Basic Principles of Corrosion Fatigue (Scott 1993).

Although this mechanism may be appropriate for gas and liquid pipelines which are subject to cyclic loading, it is less clear that it is relevant for a statically loaded used-fuel container in a DGR.

3. IMPLICATIONS FOR CARBON STEEL USED FUEL CONTAINERS

3.1 EVIDENCE FOR SCC OF CARBON STEEL USED FUEL CONTAINERS

In this section, the implications of the evidence presented in Section 2 for the SCC of containers in the DGR is reviewed. Various methods for mitigating the possibility of cracking are discussed in Section 3.2.

The focus of this section is to determine whether conditions exist that would support SCC of C-steel containers in the DGR. In that regard, it is useful to consider the range of "threshold" conditions that have been reported for the various forms of cracking, for example, ranges of electrochemical potential for cracking, minimum solute concentrations or pH, or minimum stresses for crack initiation or stress intensity factors for crack growth (Table 1). Consideration of threshold conditions allows an assessment of whether the container will be susceptible in the DGR environment. The alternative strategy of arguing that cracks may initiate but that the rate of propagation is too slow to result in through-wall penetration is problematic when dealing with repository timescales.

3.1.1 Susceptibility of Material

Based on experience in the pipeline, chemical and pulp and paper industries, a wide range of carbon steels with differing chemistry and microstructure have been shown to be susceptible to SCC. Whilst it may be possible to develop a steel that is less susceptible to SCC, such development would require considerable effort and resources. Therefore, for the current purposes, it is assumed that the steel to be used for the container exhibits some susceptibility to cracking.

3.1.2 Nature of the Repository Environment

Carbon steel has been identified as a possible container material for a DGR in sedimentary rock (King 2007). Although C-steel could also be considered for use as a container material for a DGR in crystalline rock, the focus here is on environmental conditions for sedimentary rock.

The environmental conditions within a DGR in sedimentary rock have been summarized by King (2005b), a key component of which is the evolution of the environment from an initial aerobic unsaturated phase, through an intermediate anaerobic unsaturated period, to an eventual long-term anaerobic saturated phase.

3.1.2.1 Pre-saturation

Prior to complete saturation of the DGR, the repository environment will evolve from an initial warm (up to 100°C) aerobic phase to a period of cooler anaerobic conditions. During the initial warm aerobic phase it is possible that the container surface will be too dry to support electrochemical reactions or SCC. As the temperature cools and the relative humidity (RH) increases, deliquescence of salt deposits on the container will lead to localised wetting and the onset of corrosion. These deliquesced salt solutions will initially be saturated with respect to the salt, but will become progressively dilute as the RH increases. The extent of initial surface

wetting will depend on the surface coverage by salt contaminants, but it is unlikely that the surface will be covered by a continuous aqueous phase.

For SCC, the three most important environmental variables are the temperature, the nature and concentration of the aqueous phase, and the redox conditions (and, hence, E_{CORR}). It is currently not possible to predict the exact time dependence of these three variables for the UFC. Qualitatively, however, conditions will be most aggressive at the time of initial deliquescence of salt contaminants.

Of the various environments in which SCC of C-steel has been reported, those most likely to be present in the repository during the pre-saturation phase are concentrated solutions of carbonate, caustic, or nitrate. The formation of these environments, however, requires that carbonate, hydroxide, and/or nitrate salts be present on the surface. Furthermore, because of the limited solubility of $CaCO_3$ and $MgCO_3$, carbonate must be present as either the Na or K carbonate or bicarbonate salts. Both dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$) can be present in sedimentary rock and the latter is also present in Avonlea bentonite, but there is no indication of the presence of nahcolite ($NaHCO_3$), trona ($Na_3(CO_3)(HCO_3) \cdot 2H_2O$), or natron ($Na_2CO_3 \cdot 10H_2O$) in either. Nitrate minerals would not be expected to be naturally present in the rock or the bentonite sealing materials, but they could be introduced by blasting or other activities during construction. Sodium or potassium hydroxide are only likely to be present if a cementitious backfill was used. For the carbonate and nitrate, at least, the amount of salt present as surface contamination is likely to be limited. However, if they are present then the aqueous phase would be sufficiently concentrated to support cracking, at least for some time during the progressive deliquescence period.

If a concentrated carbonate (or nitrate) phase is present then the temperature and potential must also be in the appropriate range for cracking. High-pH SCC in concentrated carbonate solutions is favoured by higher temperatures, but has been observed on pipelines at temperatures as low as 20-30°C. Cracking also depends on the potential, with a permissive range of approximately $-0.65 \pm 0.1 V_{SCE}$. It seems likely, therefore, that the potential and temperature would be within the respective ranges for cracking at some stage during the evolution of the environment, but it is not currently possible to estimate when and how long SCC might be possible. Similar arguments also apply to SCC in nitrate solutions, with possibly a longer duration of cracking in this case because of the larger potential range.

Although it is difficult to exclude the possible formation of a concentrated aqueous phase during the initial thermal transient, any such phase is likely to be present as isolated droplets of liquid with limited volume. This, in turn, will limit the spatial distribution of any possible cracks.

As the environment evolves further, any surface aqueous phase will become more dilute. More importantly from a cracking perspective, however, the environment will become anaerobic. The potential is then likely to fall outside the respective potential windows for cracking and SCC will become less likely.

3.1.2.2 Post-saturation

Because of the low hydraulic conductivity of the sedimentary rock, saturation of the DGR could take many thousands, or even tens of thousands, of years (King 2005b). Anaerobic conditions will have become established prior to saturation of the repository. Deep ground waters in sedimentary formations are expected to be saline and would, therefore, be more likely to

support general corrosion rather than SCC. However, there could be a (short) period of time when the container is in contact with anaerobic, dilute bentonite pore water before the development of a saline pore fluid. These conditions could support near-neutral pH SCC (Section 2.1.1.1). As discussed in more detail below, however, this form of cracking requires a cyclic stress unlike the static load to which the container will be subject.

3.1.3 Stress and Stress Intensity Considerations

3.1.3.1 Crack Initiation

The loading conditions for crack initiation are characterized by a threshold stress σ_{th} . For the concentrated carbonate high-pH SCC environment, the threshold stress under static loading conditions is of the order of the yield stress. The threshold is reduced under cyclic loading, but this is unlikely to reduce the value of σ_{th} for the container. In boiling nitrate solutions, however, the threshold stress of annealed C-steel can be low as 10-20% of the yield stress.

3.1.3.2 Crack Growth

Growth of an initiated crack or of a non-repaired surface-breaking weld flaw depends on the stress intensity factor K_I or the crack-tip strain rate $\dot{\epsilon}_{CT}$. In concentrated carbonate solutions, Parkins (2000) has reported a threshold stress intensity factor K_{ISCC} of $\sim 21 \text{ MPa}\cdot\text{m}^{1/2}$. To put this value in context, consider a single edge crack in a semi-infinite plate, for which the stress intensity factor is given by (Murakami 1987)

$$K_I = 1.1215\sigma_t\sqrt{(\pi a)} \quad (5)$$

where σ_t is the tensile stress and a is the crack depth. If the tensile stress on the container is equal to the yield stress (say, 500 MPa), a crack 0.5 mm deep would exceed the value of K_{ISCC} . However, if the load is only 50% of the yield stress then the crack would have to be more than 2 mm deep to propagate. Such small crack-like defects are possible on the container surface.

Continued crack propagation via the slip-dissolution mechanism requires that the strain rate be sufficient to rupture the passive film at the crack tip. In concentrated carbonate solutions, Parkins (2000) has demonstrated that the crack velocity decreases at strain rates less than 10^{-8} - 10^{-7} s^{-1} and that it drops to zero for crack-tip displacement rates less than 10^{-10} - $10^{-9} \text{ mm}\cdot\text{s}^{-1}$. Loading rates on the container are likely to be extremely slow and it is possible that the strain rate will be below the threshold for cracking, although estimation of the actual strain rate is beyond the scope of the current report.

3.2 MITIGATION OF SCC

Based on the above discussion, the probability that the environmental conditions within the DGR will support SCC appears low. Nevertheless, it is prudent to consider methods for further mitigating the probability of cracking. Here, these mitigation procedures are discussed in terms of material-related, environmental, and container design factors.

3.2.1 Material Selection

Although, as noted above, many grades of C-steel have been found to be susceptible to SCC in one or more environments, there are a number of material-related factors that can mitigate the probability of SCC, including:

- the use of fine-textured TMCP steel
- use of a higher strength material to reduce the probability of plastic deformation and crack initiation, although higher-strength steels are more susceptible to hydrogen induced cracking
- for concentrated carbonate solutions, use of steels with increased Ti, Mo, Cr, and Ni contents, which have been shown to inhibit cracking
- removal of millscale

3.2.2 Environmental Considerations

Although some species, such as chromates, permanganates, and molybdates, have been shown to inhibit corrosion and cracking of C-steels (Beavers et al. 1985), it is impractical to add SCC inhibitors to the repository environment. However, environmental modifications that could be used to mitigate SCC include:

- reducing the maximum container temperature, although this has implications for container loading and/or spacing and obvious economic consequences
- shortening the aerobic phase through the addition of O₂ scavengers
- ensuring minimal surface contamination of the container by deliquescent salts

3.2.3 Container Design

Proper container design provides several opportunities for mitigating the probability of SCC, including:

- avoiding stress raisers and crack-like flaws in the weld region and the body of the container
- minimizing applied stresses and the possibility of creep through the use of alloys with increased strength and/or use of thicker wall sections
- reduction of surface tensile residual stresses using a suitable post-weld stress-relief process

3.3 OVERALL ASSESSMENT OF PROBABILITY OF SCC

Overall, the probability of through-wall penetration of a C-steel used fuel container by SCC is low. The low probability of SCC is a result of several factors, including:

- the general absence in the DGR of environmental conditions that have been shown to support SCC of C-steels
- the limited volume of concentrated electrolytes that would be formed by the deliquescence of surface salt contaminants during the thermal transient, such solutions being known to induce SCC
- the absence of cyclic loading to support near-neutral pH SCC
- proper design of the container, including the use of a sufficient wall thickness to limit the level of stress and creep, the avoidance of notches and other stress concentrators, the selection of a material with low inherent susceptibility to SCC, and the reduction of tensile residual stresses.

The most likely period for SCC appears to be during the initial thermal transient when the container surface is first wetted due to the deliquescence of surface salt contaminants. Deliquescence of carbonate, nitrate, or hydroxide salts will result in the concentrated solutions commonly associated with the SCC of C-steel. The environment will also be relatively aerobic during this period, which is an important consideration since cracking in these environments involves dissolution and is potential dependent. However, the volume of these deliquesced electrolytes will be small and their concentration will decrease as the temperature in the DGR decreases and the relative humidity increases. Cracking will only be possible for a limited period of time and, if possible at all, is only likely to take the form of shallow surface cracks limited in area by the spatial dimensions of the deliquesced droplets. Such surface cracking, even if it does occur, will not lead to container through-wall penetration.

Cracking becomes less likely as the environment evolves from the initial warm aerobic phase to the long-term cool, anoxic conditions. There may be a period of susceptibility to near-neutral pH SCC (Section 2.1.1.1) after the repository has become anoxic, but only if the container is contacted by a dilute carbonate solution prior to the ingress of the saline ground water. However, even if such a dilute carbonate solution is present, SCC is unlikely because this form of cracking requires a cyclic load.

A review of the mechanistic aspects of the SCC of C-steel supports this assessment of the likely cracking behaviour of the container. Of the models proposed to account for the SCC of C-steel and of metals in general, the most likely mechanism for C-steel containers is the slip dissolution model. This mechanism involves anodic dissolution and implicitly will be restricted to the limited period of aerobic conditions. Corrosion fatigue involving a hydrogen mechanism, which could operate under the long-term anaerobic conditions, requires a cyclic load and is, therefore, unlikely to occur. The film-induced cleavage model has not been previously shown to account for the SCC of C-steel and is generally applicable in environments that support higher dissolution rates than are likely in the DGR. Furthermore, there is no evidence that the types of surface film that will form on the container are suitable for initiating a cleavage-like crack in the steel substrate, the basic hypothesis of the film-induced cleavage model. Finally, the surface mobility model has also not been invoked to explain the SCC of C-steels and its mechanistic and mathematical basis has been questioned.

4. CONCLUSIONS

Carbon steel is susceptible to SCC in a number of environments, some of which could be present or be generated in the repository. The most likely period for SCC is the initial thermal transient when the container surface is first wetted due to the deliquescence of surface salt contaminants. Deliquescence of carbonate, nitrate, or hydroxide salts will result in the concentrated solutions commonly associated with the SCC of C-steel. The environment will also be relatively aerobic during this period, which is an important consideration since cracking in these environments involves dissolution and is potential dependent.

Cracking becomes less likely as the environment evolves from the initial warm aerobic phase to the long-term period of cool, anoxic conditions. There may be a period of susceptibility to near-neutral pH SCC after the repository has become anoxic, but cracking is unlikely because this form of SCC requires a cyclic load.

Overall, the probability of through-wall penetration of a C-steel used fuel container by SCC is low. The low probability of SCC is a result of several factors, including:

- the general absence in the repository of environmental conditions that have been shown to support SCC of C-steels
- the limited volume of concentrated electrolytes that would be formed by the deliquescence of surface salt contaminants during the thermal pulse, such solutions being known to induce SCC
- the absence of cyclic loading to support near-neutral pH SCC
- proper design of the container, including the use of a sufficient wall thickness to limit the level of stress and creep, the avoidance of notches and other stress concentrators, the selection of a material with low inherent susceptibility to SCC, and the reduction of tensile residual stresses.

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