

## A Probabilistic Model for Stress Corrosion Cracking of Stainless Steel SNF Interim Storage Canisters

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### Abstract

In the U.S., spent nuclear fuel (SNF) is stored in dry storage cask systems for long-term interim storage. The systems commonly used consist of welded stainless steel containers enclosed in ventilated cement or steel overpacks. These containers may be required to perform their waste isolation function for many decades, and failure by chloride-induced stress corrosion cracking (SCC) due to deliquescence of deposited salts is a major concern, particularly for near-marine storage sites.

This paper presents a probabilistic performance assessment model to evaluate the probability of canister failure (through-wall penetration) by SCC. The model first assesses whether environmental conditions for SCC—the presence of an aqueous film—are present at canister weld locations (where tensile stresses are likely to occur) on the canister surface. Geometry-specific storage system thermal models and weather data sets representative of U.S. SNF storage sites are implemented to evaluate location-specific canister surface temperature and relative humidity (RH). As the canister cools and aqueous conditions become possible, the occurrence of corrosion is evaluated. Corrosion is modeled as a two-step process: first, pitting is initiated, and the extent and depth of pitting is a function of the chloride surface load and the environmental conditions (temperature and RH). Second, as corrosion penetration increases, the pit eventually transitions to a SCC crack, with crack initiation becoming more likely with increasing pit depth.

Once pits convert to cracks, a crack growth model is implemented. The SCC growth model includes rate dependencies on both temperature and crack tip stress intensity factor, and crack growth only occurs in time steps when aqueous conditions are predicted. The model suggests that SCC is likely to occur over potential SNF interim storage intervals; however, this result is based on many modeling assumptions. Sensitivity analyses provide information on the model assumptions and parameter values that have the greatest impact on predicted storage canister performance, and provide guidance for further research to reduce uncertainties.

## 1. Introduction

Following initial cooling in pools, spent nuclear fuel (SNF) is transferred to dry storage casks for longer-term storage at the reactor sites. The storage cask systems are commonly welded stainless steel containers enclosed in ventilated concrete or steel overpacks. These cask systems are intended as interim storage until a permanent disposal site is developed, and until recently, were licensed for up to 20 years, and renewals also up to 20 years. In 2011, 10 CFR 72.42(a) was modified to allow for initial license periods of up to 40 years, and also, license extensions of up to 40 years. However, the United States does not currently have a disposal pathway for SNF, and these containers may be required to perform their waste isolation function for many decades beyond their original design criteria. Of primary concern with respect to the long-term performance of the storage casks is the potential for canister failure due to localized corrosion. For most dry cask storage systems, passive ventilation is utilized to cool the casks within the overpacks, and large volumes of outside air are drawn through the system. Dust and aerosols within the air are deposited on the steel canisters, and as the casks cool over time, salts in the dust will deliquesce to form brine on the storage container surface. Under these conditions, chloride-induced stress corrosion cracking (SCC) of welded zones is of concern, as it is a well-documented mode of attack for austenitic stainless steels in marine environments (Kain 1990), and many independent spent fuel storage installations (ISFSIs) are located in coastal areas. Recent canister inspections have shown that chloride salts can be present on the surface of in-service canisters in near-marine settings (Bryan and Enos 2014; EPRI 2014). Here, the available information on the canister surface environment and experimental and observational experience with stress corrosion cracking of stainless steels is utilized to develop a probabilistically-based model for evaluating the potential for SNF interim storage canister failure by through-wall SCC.

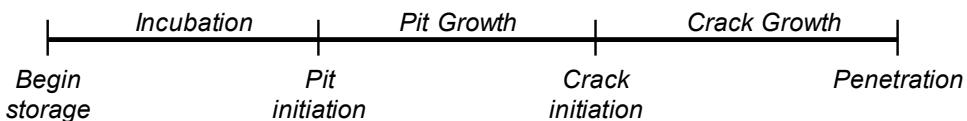
### 1.1 Criteria for SCC

In order for SCC to occur, three criteria must be met: the metal must be susceptible to SCC, an aggressive environment must exist, and sufficient tensile stress must be present to support SCC. In general, these criteria are expected to be met, at least at some ISFSI sites, during the period of interim storage, especially if the development of a repository for final disposal is delayed. The welded interim storage canisters are made of austenitic stainless steels which are susceptible to SCC, especially in the heat affected zones (HAZ) of welds. Field studies have found chloride salts on the canister surfaces at some sites; if temperatures drop sufficiently for salt deliquescence, a corrosive aqueous environment could potentially occur. Finally, recent weld residual stress (WRS) modeling conducted by the Nuclear Regulatory Commission (NRC 2013) indicates that through-wall tensile stresses of sufficient magnitude to support SCC are likely to exist in weld HAZ; these predictions have been confirmed by recent measurements of WRS on a full-diameter mockup funded by the US DOE (Enos and Bryan 2016).

### 1.2 General description of the probabilistic SCC model.

The general progression of conditions leading to canister penetration by SCC is shown in Figure 1.

Each of these periods and events are incorporated into the model described here. After placement into storage, the evolution of the canister surface environment (temperature, RH, and salt load) is tracked through time. First, there is an incubation period for pitting, corresponding to the interval of time required for a given canister surface location to cool to the point that the RH is sufficiently high for salts to deliquesce and corrosion becomes possible. This limiting RH value for corrosion is known as  $RH_L$ . The incubation period is calculated using an environmental model that combines a canister surface temperature model with ambient weather data to calculate whether the  $RH_L$  has been exceeded in each time step. Once the  $RH_L$  is reached, a maximum pit size model is used to evaluate the deepest pit that can be on the surface, as a function of the canister surface environment. Over time, as the canister cools and the deposited salt load increases, the maximum pit size increases. Pits are required precursors for stress corrosion cracks, and the likelihood of SCC initiation from a pit increases as the pit deepens (Turnbull et al., 2006). A pit-to-crack transition model is used to evaluate when a crack initiates. The crack growth rate is then calculated as a function of temperature and through-wall stress profile, and applied to the crack for any time-steps when aqueous conditions are predicted to occur (a time-of-wetness model). For each simulation in the probabilistic model, this calculation is done at all locations on the canister surface that correspond to weld locations. Each realization is run for either 100 years or until crack penetration is predicted. The probabilistic results are determined from 100 total realizations, each with a different sampled set of parameter values.



**Figure 1. General Timeline for SCC Initiation and Penetration of an Interim Storage Canister.**

## 2. Environment Model

The environment at any given location on the storage canister surface will be aggressive if two criteria are met: a corrosive chemical species is present, and aqueous conditions exist. The greatest concern of SCC is at near-marine sites, so the assumption is made in this model that the deposited salts are chloride-rich sea-salts. Deposition of chloride-rich salts is assumed to begin immediately upon emplacement, and the deposited surface load is increases over time. Some amount of chloride is always assumed to be present; therefore, in this model, corrosion can occur, or progress, at any location the canister surface where the time-step-specific RH is greater than the  $RH_L$ .

The location-specific RH values can be calculated from the canister surface temperature at any given location; and the absolute humidity (AH), or water content, of the inflowing air. To determine

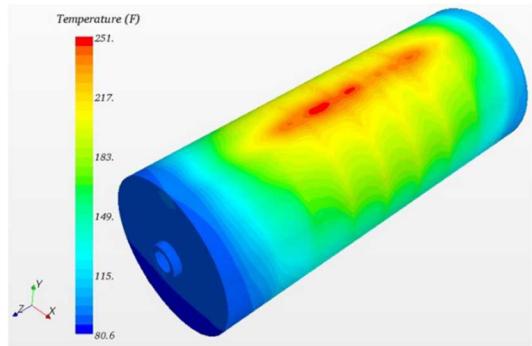
location-specific canister surface temperatures through time, maps of canister surface temperatures were calculated using a specific set of values for horizontal and vertical storage system designs, using specific fuel loadings (number and geometry of assemblies); fuel burnup; heat load (corresponding to a given time out of reactor), and a single fixed ambient external temperature. The parameter values used are described elsewhere (Suffield et al., 2012). The thermal modeling provided temperature maps of the canister surface (for example, Figure 2) for each of 8 decay heat loads corresponding to different lengths of time out of the reactor, for a single ambient temperature of 15.6°C (60°F). For each time step in the 100-year simulation, the temperature predicted by the thermal model is modified for the actual ambient temperature, sampled from measured weather data corresponding to an existing ISFSI site.

Similarly to the ambient temperature, the predicted absolute humidity (AH) was sampled from a model based on measured weather data. Given the location-specific temperature and the AH of the incoming air, the RH at any point on the surface of the canister can be calculated, and is compared to the  $RH_L$  to determine if corrosion is possible.

### 3. Maximum pit size model

The maximum pit size that can form on the metal surface is calculated using an approach developed by Chen and Kelly (2010). This model describes the maximum pit depth as a function of several environmental parameters. In order for a pit to undergo stable growth, the cathode current ( $I_c$ ) available to support pit growth must exceed the anodic current ( $I_{pit}$ ) demand for the pit. The maximum pit size can then be calculated by calculating the maximum cathode current as a function of pit size, and comparing it to the predicted anodic current demand as a function of pit size. The ability of the cathode to supply current to the anode is controlled by the thickness and ionic strength of the brine layer on the metal surface. To calculate ( $I_c$ ) and ( $I_{pit}$ ), Chen and Kelly (2010) assume that the pit is hemispherical in shape with a radius of  $r_{pit}$ . The pit can grow stably when the value of  $I_{pit}/r_{pit}$  exceeds a critical value, called the pit stability criterion. By assuming a given value for the pit stability criterion,  $I_{pit}$  can be calculated as a function of the pit radius.

To calculate the maximum cathodic current available,  $I_{c,max}$ , the following equation is used.



(Suffield et al., 2012)

**Figure 2. Canister surface temperature map, for a horizontal storage canister with a decay heat load of ~7.6 kW.**

$$\ln I_{c,max} = \frac{4\pi k W_L \Delta E_{max}}{I_{c,max}} + \ln \left[ \frac{\pi e r_a^2 \int_{E_{corr}}^{E_{rp}} (I_c - I_p) dE}{\Delta E_{max}} \right] \quad (\text{Eq. 1})$$

where

$k$  = conductivity, Siemens/meter

$W_L$  = brine layer thickness, meters

$I_c$  = cathodic current density, Amps/m<sup>2</sup>

$I_p$  = passive current density, Amps/m<sup>2</sup> assumed to be  $10^{-4}$  A/m<sup>2</sup> in Chen and Kelly

$E_{rp}$  = repassivation potential = -0.4 V<sub>SCE</sub> in Chen and Kelly for 304 = potential at the mouth of the pit

$E_{corr}$  = -0.15 V<sub>SCE</sub> in Chen and Kelly =  $E_L$  = potential at the cathode edge

$e$  = Euler's number 2.71828

$r_a$  = pit radius, meters

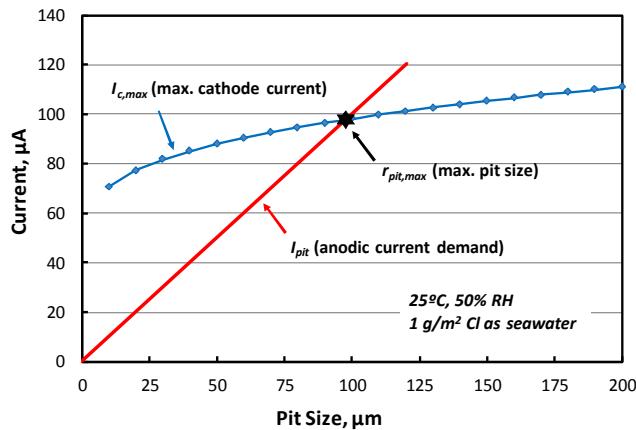
$r_L$  = radius of the cathode, meters

$\Delta E_{max} = E_{corr} - E_{rp}$

Derivation of the values for these parameters is described in Chen and Kelly (2010) and in subsequent papers by these authors (Woldemedhin et al. 2014; Srinivasan et al. 2015; Woldemedhin et al. 2015). Several of the parameters vary with the environmental conditions on the canister surface (temperature, RH, and salt load), including the conductivity  $k$ , the brine thickness  $W_L$ , and the integral term on the right hand side of the equation, which is derived from a cathodic polarization scan of the metal of interest (304 SS) in the brine of interest. Utilizing the environmental model described above, and assuming a salt deposition rate, a maximum pit size can be calculated at a given location on the canister surface at each time step as shown in Figure 3. The maximum cathode current for a given pit size is calculated using the equation above, and the anodic current from the pit stability criterion. The maximum possible pit size corresponds to size at which these two values are equivalent.

#### 4. Pit-to-crack transition model

Once the pit reaches a threshold value, a stress corrosion crack initiates. The threshold value is calculated using the Kondo criterion (Kondo, 1989); the crack tip stress intensity factor ( $K$ ) is calculated for a crack of equivalent depth as the pit, and a crack will initiate if the calculated  $K$



**Figure 3. Estimating maximum pit size using the Chen and Kelly approach.**

exceeds the threshold  $K$  for SCC,  $K_{ISCC}$ . In the probabilistic SCC model,  $K$  is calculated as a function of depth using data from tensile stress profiles for longitudinal and circumferential welds that were modeled by the NRC (2013), and the  $K_{ISCC}$  threshold value is sampled once per realization from a range of literature values.

Although this approach is simplified, this combination of the maximum pit depth model and the pit-to-crack transition model provides insights into the process of SCC crack initiation. Implicit in this model is that conditions that produce thicker brine layers, such as heavy salt loads, or moderate increases in RH, increase the size of possible pits that can form, and increase the likelihood of SCC initiation. Also, higher tensile stresses mean that the  $K$  value increases more rapidly with depth, and hence shallower pits can initiate SCC. These predictions match what has been observed experimentally (NRC 2014). Moreover, failure to evaluate salt load, RH and stress level independently may explain the variability in measured RH thresholds and chloride surface load thresholds for SCC initiation. The type of salt used can also have a huge impact. Below a RH of about 75% on the canister surface, a large fraction of the chloride in sea-salts may be present in the solid form. For instance, at 60% RH, sea-salts are only partially deliquesced—most chloride is present in as precipitated salts. For a chloride deposition load of 1 g/m<sup>2</sup>, the total brine present corresponds to a layer less than 1 micron thick. On the other hand, if the chloride is deposited as magnesium chloride, then at 60% RH, a 1 g/m<sup>2</sup> chloride load produces a brine layer over 300 microns thick. This thicker brine layer corresponds to a much larger cathode, a larger potential cathode current, and much deeper pits. Because of this difference, magnesium chloride is a poor analog for sea-salts, unless it is applied much more sparingly to the surface.

## 5. Crack growth rate model

Once a crack initiates, a crack growth rate is calculated every time step, and applied if the environmental model indicates that aqueous conditions are present. That is, the magnitude of the crack growth is a function of both the rate of growth and the time-of-wetness. SCC crack growth rates can be expressed in the following general form:

$$\frac{dx_{crack}}{dt} = \dot{x}_{crack} = \alpha_{crack} \cdot f(T) \cdot f(K) \cdot f(R_a) \cdot f([Cl^-]) \cdot f(pH) \cdot f(\sigma_{ys}) \dots \quad (\text{Eq. 2})$$

Where  $\alpha_{crack}$  is the crack growth amplitude factor (or, the crack growth rate at a fixed reference set of conditions), and that value can be modified by many other factors, including material property factors such as the stress intensity factor ( $K$ ), degree of sensitization ( $R_a$ ), and yield stress ( $\sigma_{ys}$ ); and environmental factors such as temperature ( $T$ ), chloride concentration ( $[Cl^-]$ ), the mass of chloride per unit surface area, and the solution pH.

The effects of  $K$  and  $T$  are included in the model presented here; the other factors are not considered explicitly, but are included implicitly in the experimental data sets used to parameterize the SCC

growth rate. The experimental data sets include base metal, weld, HAZ, and sensitized samples, and both 304 and 304L, capturing the effects of different  $R_a$  and  $\sigma_{ys}$  values. For a model accounting only for the effects of  $K$  and  $T$ , a power law dependence is assumed for  $K$ , while an Arrhenius relationship is assumed for the temperature dependence (Wu and Modarres, 2012):

$$\frac{dx_{crack}}{dt} = \alpha_{crack} \cdot \exp \left[ -\frac{Q}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \cdot (K - K_{th})^{\beta_{crack}} \quad (\text{Eq. 3})$$

where:

$dx_{crack}/dt$  is the crack growth rate

$\alpha_{crack}$  is the crack growth amplitude

$Q$  is the activation energy for g=crack growth

$R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ )

$T$  is the temperature (K) of interest

$T_{ref}$  is a reference temperature (K) at which  $\alpha$  was derived. To be consistent with the PNNL thermal model, a reference temperature of  $15.55^\circ\text{C}$  ( $60^\circ\text{F}$ ) is used as the reference temperature.

$K$  is the crack tip stress intensity factor

$K_{th}$  is the threshold stress for SCC

$\beta_{crack}$  is the stress intensity factor exponent.

The above equation is implemented in this report. For a cracked structure under remote or local loads, the stress intensity factor ( $K$ ) is a measure of the stress field ahead of the crack. The stress intensity factor  $K = \sigma_{\text{applied}} Y \sqrt{\pi x_{crack}}$ , where  $\sigma_{\text{applied}}$  is the tensile stress from the weld residual stress profile and  $Y$  is a shape parameter, equal to 1 for an infinite flat plate. The threshold stress intensity factor for SCC,  $K_{th}$ , was sampled from a range of literature values for each realization. The stress corrosion cracking growth rate model is parameterized by fitting experimental rates determined for atmospheric SCC under ambient and high temperature conditions for 304 and 304L stainless steels, from several literature sources.

## 6. Results and Conclusions

The model for SCC prediction presented here has not been completely parameterized. Specifically, more data are needed to parameterize the maximum pit size model, including cathodic polarization curves for brine compositions typical of deliquesced sea-salts. The model has not yet been used to estimate canister penetration times. However, in developing the model, the importance of certain parameters has become clear. Parameters controlling the incubation time are for SCC include the RH and the salt load on the canister surface, which will determine when a pit can grow to sufficient size to initiate from a crack. Once a crack initiates, the sampled crack growth rate is the most important parameter affecting predicted breakthrough times, largely because of the high scatter in the available data used to parameterize the model.

Although the model still lacks some parameterization, the model conceptualization offers insights

into the factors controlling canister penetration by SCC, and highlights research needs to reduce the scatter. Simplified, the basic approach has been developed and applied to an example case. The study illustrates the need for additional experimental efforts to allow quantitative evaluation of important processes (e.g., pit initiation and growth under atmospheric conditions), and to reduce uncertainties in important parameters such as SCC growth rate, limiting RH for corrosion, and weld residual stress profiles. Additional model development and parameterization is required prior to applying it to SNF canisters at actual ISFSI sites.

## Acknowledgments

Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. This document is SAND2016-XXXX.

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