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UNCERTAINTIES IN CONTAINER FAILURE TIME PREDICTIONS

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ABSTRACT

Stochastic variations in the local chemical environment of a geologic waste repository can cause corresponding variations in container corrosion rates and failure times, and thus in radionuclide release rates. This paper addresses how well the future variations in repository chemistries must be known in order to predict container failure times that are bounded by a finite time period within the repository lifetime. Preliminary results indicate that a 5000 year scatter in predicted container failure times requires that repository chemistries be known to within $\pm 10\%$ over the repository lifetime. These are small uncertainties compared to current estimates.

INTRODUCTION

Predictions of waste container failure time distributions are important because they affect predictions of radionuclide release rates to the environment. It is also important to understand how well such failure times can be predicted using existing data bases, so that the corresponding uncertainties in release rates can subsequently be assessed. The purpose of the present paper is to provide initial estimates of the expected scatter in container failure time predictions. These estimates were obtained using a computational approach analogous to a sensitivity study. The primary assumptions and the general methodology of this approach are outlined below. More detailed descriptions and the results of this analysis appear in subsequent sections.

This paper addresses a limited and idealized subset of the possible container failure scenarios: the continuous wet corrosion process. The connotation of "continuous" disregards cyclic dryouts, etc., and corrosion is assumed to proceed without interruption after the containers cool to the boiling point of water. The connotation of "wet" includes full or partial immersion, or a liquid film on the container surface. Also, only corrosion of an outer metallic container is addressed, and inner barriers such as fuel rod cladding are not treated. Although these assumptions simplify a very complicated problem, still more restrictions are necessary to ensure clarity and mathematical tractability in this initial study, as follows.

This treatment is limited to cases of stress-free uniform (general) or localized (pitting) corrosion phenomena. This restriction permits use of a generic (power law) mathematical form for the corrosion model, rather than relying on any specific model or correlation from the literature. Such a specific corrosion model would most likely limit the analysis to a particular material and chemistry, whereas greater generality is sought in this study. The price for such generality is that only relative corrosion rates can be computed, rather than absolute values. However, this is adequate for a sensitivity study because only the variations in corrosion rates (caused by stochastic variations in thermal- and chemistry-related model parameters) are sought. These variations in corrosion rates cause scatter in the predicted container failure times. Assessment of the magnitude of this scatter is the subject of this paper.

In the following sections, the generic corrosion model is first described, followed by the methodology employed in this study, and the results.

CORROSION MODEL

With the above limitations and restrictions in mind, a generic power-law corrosion model was defined by considering several specific models as case studies, and extracting the common mathematical features as follows. The first model considered was the pitting corrosion equation of Stahl and Miller [1], as described by Liebetrau, et al [2] for high-level stainless-steel containers:

$$dh/dt = \frac{M.W.}{\rho} \left[\frac{z_+}{z_-} + 1 \right] D \frac{C_+(0)}{h} \left\{ \exp \left(\frac{z_- F}{RT} \Delta \phi \right) - 1 \right\} \quad (1)$$

where h is the pit depth, t is time, D is the diffusivity of the metal cation in the pit, $C_+(0)$ is the concentration of the cation at the pit opening, T is temperature, and the other parameters are defined in [2]. Grouping terms in Equation (1) gives a simpler mathematical form:

$$dh/dt = C_1 C_+(0) f(T) / h \quad (2)$$

where C_1 is a constant and $f(T)$ is an Arrhenius-type function combining the temperature dependence of the diffusivity (D) and the last term in Equation (1). Holding all parameters except h constant in time, integration of Equation (2) gives a parabolic equation for h as a function of time:

$$h = C f_1(C_+(0)) f_2(T) t^{1/2} \quad (3)$$

where C is a constant, f_1 depends on the square root of the concentration $C_+(0)$, and f_2 has the Arrhenius form

$$f_2(T) = \exp[\Delta G/2RT] \quad (4)$$

In [2], the concentration $C_+(0)$ was assumed to be linearly dependent on the Eh and the concentration of aggressive species such as Cl^- :

$$C_+(0) = \alpha (1 + Eh) + \beta [Cl^-] \quad (5)$$

where α and β are constants.

The second model considered was the pitting corrosion model of Beck and Alkire [3] for hemispherical pits of radius r , as described by Farmer and McCright [4]:

$$r = [r_1^2 + 2DC_s M t/p]^{1/2} \quad (6)$$

where D is the diffusivity of the metal salt in the electrolyte, C_s is the saturation concentration of the metal salt in the electrolyte, t is time, and the other parameters are defined in [4]. Letting $r = h$, taking the initial pit radius r_1 to be zero, and recognizing that D has an Arrhenius form, Equation (6) can be seen to have the same mathematical form as Equation (3).

The third series of models considered were those commonly employed for uniform (or general) corrosion [5]. These models have the mathematical form

$$h^n = K_n t \quad (7)$$

where h is the corrosion depth, $n = 1, 2$, or 3 for linear, parabolic, or cubic corrosion behavior, and

$$K_n = A_n \exp(\Delta G_n / RT) \quad (8)$$

where A_n is a constant. If A_n can depend on the concentration of an aggressive species, Equation (7) can also be said to exhibit a mathematical form similar to Equation (3).

From the above observations, a generic power-law corrosion model can be defined for this preliminary study:

$$h = C f_1([X]) f_2(T) t^b \quad (9)$$

where $0 < b < 1$. For this study, the reference case $b = 0.5$ was chosen to represent the assumed typical case of diffusion-controlled corrosion phenomena. Consequently, f_1 depends on the square root of the concentration of an aggressive species $[X]$, such as $[Cl^-]^{1/2}$. f_2 is given by Equation (4) with $\Delta G = 30000 \text{ cal/mol}^\circ K$ chosen as a typical value, and C is an arbitrary constant. C actually depends on the specific material and chemistry, and is not calibrated in this study. Consequently, only relative values of corrosion rates are possible, but are adequate for a sensitivity analysis, as discussed above. Equation (9) is not intended to serve as an exact corrosion model: it only captures some of the more important dependencies on concentration, temperature, and time. Further discussion concerning the application of Equation (9) to estimate the expected scatter in container failure time predictions appears in the next section.

SIMULATIONS

This section begins with a description of the approximations necessary to perform the simulations of container failure times, and concludes with an outline of the methodology employed for the calculations. Results are given in the following section.

The corrosion behavior expressed by the generic mathematical model in Equation (9) depends on three primary parameters: the temperature, the container material, and the repository chemistry. Each of these parameters depends on the time that the container resides in the repository. This includes the material itself because it can become sensitized to some forms of corrosive attack over long periods of time. The approximations used for temporal evolution of the temperatures and chemistries are described next.

The first parameter requiring approximation is the time (t_c) required for the containers to cool to $100^\circ C$, and thus to permit the onset of continuous wet corrosion. An estimate for the distribution of these times in a tuff repository was provided by Altenhofen and Eslinger [6]. The cumulative fraction of containers (F) that have cooled to $100^\circ C$ after emplacement forms an s-shaped distribution when plotted versus time, and was approximated by

$$F = Y / (1 + Y) \quad (10)$$

where $Y = \exp[-3.19 + 3.59 \times 10^{-3} t]$ and t is the time in years since the container was emplaced. F approaches 1.0 when t approaches 2000 years.

The Arrhenius function $f_2(T)$ also requires an approximation of container surface temperatures as a function of time, which was also available from [6]. These thermal histories are essentially a family of damped exponentials, as

expected for thermal decay. Two approximations were employed to represent certain basic features of this family. The first assumes that the container temperatures converge to a common value at about $t = 10,000$ years:

$$T(^{\circ}\text{C}) = 364 \Delta t^y \quad (11)$$

where $y = -0.1871$ and $\Delta t = t - t_0 + 1000$ is the time in years since the container surface cooled to 100°C . The second approximation treated the results of [6] as a family of parallel decaying exponentials:

$$T(^{\circ}\text{C}) = (t/t_0)^y \quad (12)$$

where $y = 2.125 \times 10^{-5} t_0 - 0.2084$. These two approximate thermal histories will be compared in the next section.

Simulations of corrosion and failure behavior using Equation (9) also require estimates of the temporal variations in the repository chemistry, for which little guidance is available. Estimates of spatial variations at the Yucca Mountain Site indicate that Eh can vary by $\pm 400\%$ and pH can vary by ± 1.5 points [7]. For the present study, it was assumed that these spatial variations were indicative of the bounding envelope of the temporal variations in aggressive species at the repository horizon. A starting value of $\pm 500\%$ was employed to bound the temporal variations in the parameter [X] in Equation (9). The temporal variations in [X] were modeled with fractional Brownian motion, a type of generalized random walk with correlations between the steps taken in the walk. These correlations between steps are characterized by a parameter called the Hurst exponent (H) in the equation

$$R/S = (\tau/2)^H \quad (13)$$

where R is the range of observations, S is the standard deviation, and τ is the time between observations [8]. For $H = 0.5$, the steps are independent and a classical random walk occurs. For $H < 0.5$ the not-so-random walk produces a "noisy" curve (anti-persistent), and for $H > 0.5$ the walk is called "persistent". Hurst [8] found that $H = 0.72$ for about 2000 years of observations on climatology, dendrochronology, and hydrology. This value of H was assumed to provide a representative approximation for the future variations in repository chemistries.

A sample of twenty realizations over 2^{10} years is shown in Figure 1. These curves were generated using the approximate method described in [8]. The scale on the vertical axis in Figure 1 corresponds to two standard deviations, so that about 95% of the observations would be expected to occur within variations of $\pm 200\%$. The magnitude of this $\pm 200\%$ envelope can be adjusted up or down by a simple multiplier. This permits modelling of the above $\pm 500\%$ spatial variation envelope, or of reduced variations at the horizon caused by geologic damping of surface climate changes. Note that this approximation only addresses the so-called "expected case" of the PACE 90 exercises, and does not treat unexpected cases such as volcanism, etc.

Although the use of the above thermal histories $T(t)$ for simulations with Equation (9) is an obvious substitution, further description is required concerning the use of the chemical histories $[X(t)]$ shown in Figure 1. $[X(t)]$ was substituted directly into the f_1 term in Equation (9). It was also assumed that $[X(t)]$ could affect the exponent b in Equation (9), which caused variations around the reference value $b = 0.5$. This assumption admits the possibility that changes in aggressive species can change the basic corrosion behavior from parabolic to linear or cubic, which can occur because of intermittent ruptures of protective corrosion films, for example. Another

possibility is the change in pitting corrosion rates for stainless steels as $[Cl^-]$ increases [9]. It should be noted that this approach was also assumed

Figure 1. Twenty fractional Brownian realizations of repository chemistry variations

to incorporate the temporal changes in the container material itself due to sensitization, etc.

A brief outline of the simulation procedure will conclude this section, as follows. The distribution of cooling times (t_0) to reach $100^\circ C$ was divided into twenty segments, each segment representing a subset of containers with a thermal history given by either Equation (11) or (12). In each realization of the chemical history $[X(t)]$, each subset of containers was given a portion of $[X(t)]$ which began at the respective t_0 for that subset. Thus each subset had a slightly different chemical and thermal history, as would occur in reality. The corrosion increment was computed on an annual basis for each subset using a differential form of Equation (9):

$$\Delta h = C [X(t)]^{1/2} f_2(T(t)) (t_j^b - t_i^b) \quad (14)$$

where f_2 is given by Equation (4) and i and j represent two successive time steps. Corrosion increments were accumulated until the sum of the Δh for each container subset reached unity (corresponding to a 1 cm container thickness if diffusivities are given in cm^2/yr). After all subsets "failed" in this manner, the resulting distribution of failure times for this temporal realization was plotted, generally giving a distorted s-shaped curve. A total of twenty realizations were used to approximate the expected scatter in the failure time distributions. Results are described below for various levels of uncertainties (variations) in $[X(t)]$.

RESULTS

It was no surprise that large variations in $[X(t)]$ resulted in a large scatter in predicted failure time distributions. With the bounding envelope (at two standard deviations) for $[X(t)]$ variations set at $\pm 500\%$, the scatter in failure times was greater than the repository design lifetime of 10,000 years. The failure distribution curves for all twenty realizations of $[X(t)]$ did not fit on the same plot until the $[X(t)]$ envelope of variations was reduced to $\pm 10\%$, which resulted in a characteristic scatter of about 5000 years at $F = 0.5$. This is shown in Figure 2 for the thermal history given by Equation (11). Note that b also varied by $\pm 10\%$ in this figure. The obvious conclusion is that future repository chemical histories and corrosion mechanisms must be known to better than $\pm 10\%$ if container failure times are to be bounded within a time span smaller than half the repository design lifetime. This will require substantially more characterization of $[X(t)]$ since current estimates give uncertainties of about $\pm 500\%$. It may also be of interest to note that varying b and $[X(t)]$ by $\pm 5\%$ reduced the scatter only by a relatively small amount to 4000 years.

The primary contributor to the scatter in Figure 2 was the variations in b . Reducing these variations in b to $\pm 1\%$ while maintaining $\pm 10\%$ for $[X(t)]$ in f_1 gave a 1000 year scatter in predicted failure times at $F = 0.5$, while $b \pm 0\%$ gave a 630 year scatter. Although the scatter is substantially reduced, such small variations in b would seem to require that the chemistry-dependent corrosion mechanisms which determine the value of b must be known rather well.

Figure 2. Container failure time distributions for $\pm 10\%$ variations in repository chemistry $[X(t)]$, and b . Dashed curve is time to reach 100°C [6]. Thermal history from Equation (11).

Figure 3 shows the results for varying b and $[X(t)]$ by $\pm 10\%$, using Equation (12) for the thermal history. Although the scatter at $F = 0.5$ is comparable to Figure 2, it is noteworthy that this thermal history appears to give a maximum in the fraction of containers failed at 10,000 years, i.e., $F = 0.8$. This result would seem to indicate that improved estimates of thermal histories may eventually establish an upper bound for the number of failed containers, and thus for the amount of radionuclides that can be released to the environment. Such improved estimates are the subject of continuing investigations.

Figure 3. Container failure time distributions for $\pm 10\%$ variations in repository chemistry $[X(t)]$, and b . Dashed curve is time to reach 100°C [6]. Thermal history from Equation (12).

CONCLUSIONS

The above analysis has indicated that much more must be known about repository temperatures $T(t)$ and chemistries $[X(t)]$, and about container corrosion mechanisms (b) and material evolution (sensitization), if the container failure times are to be predicted with uncertainties that are less than about ± 2500 years. Although this work can be viewed as an initial version of a tool for assessing the difficulties of failure predictions, the reader should note that this was only a preliminary analysis, and many approximations were employed. There is much opportunity for improvements of the above estimated uncertainty in the future.

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