# A PRELIMINARY ASSESSMENT OF PITTING CORROSION MODELS

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# ABSTRACT

This is an intermediate milestone report issued as part of the Engineered Barrier System Performance Assessment Code (EBSPAC) program. The report assesses the models relevant to localized corrosion of waste package materials, with emphasis on pitting corrosion of Fe-Cr-Ni-Mo alloys. Both stochastic and deterministic models for pitting are evaluated. It is concluded that while stochastic models are important in estimating the variability in the performance of waste packages, deterministic models are necessary in order to predict the long-term resistance of waste package materials to localized corrosion. The use of repassivation potential for predicting long-term performance and the need for modeling this potential are addressed.

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# 1 INTRODUCTION

In order to demonstrate compliance with Code of Federal Regulations 10 CFR 60.112 and 10 CFR 60.113, it is necessary to develop models that simulate key processes governing the performance of the Engineered Barrier System (EBS). To determine if the U.S. Department of Energy (DOE) has demonstrated compliance with the regulatory requirements set forth in 10 CFR 60.112 and 10 CFR 60.113, the U.S. Nuclear Regulatory Commission (NRC) needs to develop methodologies suitable for independent assessment of EBS performance. The EBS performance assessment methodology contains two parts: (i) use of an integrated of simplified code, referred to as Source Term Code (SOTEC), that can be integrated into the overall repository performance assessment code without a great penalty in terms of computational time, and (ii) use of detailed auxiliary models, referred to as Engineered Barrier System Performance Assessment Codes (EBSPAC), to provide technical bases for SOTEC. As part of the EBSPAC activities, models for localized corrosion (pitting and crevice corrosion) have been reviewed with the purpose of selecting the models most useful for long-term prediction. This report provides a status of the review activity pertaining to models for pitting corrosion of Fe-Cr-Ni-Mo alloys. The other alloy system currently under consideration by DOE, the copper-based alloys, is not examined in this report. This is both because the localized corrosion behavior of the Cu-base alloys is quite different from that of Fe-Cr-Ni-Mo alloys, and because of a paucity of quantitative models for the localized corrosion of Cu-based alloys. Another alloy system that may become a design alternative is titanium. Some of the approaches used for the Fe-Cr-Ni-Mo alloys have been applied to Ti-based alloys, but significant differences in the mechanisms of localized corrosion do exist between these two alloy systems. The localized corrosion models for Ti alloys will be considered in the future, if necessary.

Localized corrosion is considered to be one of the important failure modes determining the performance of high-level waste container materials, especially those alloys that corrode at a low uniform corrosion rate (passive alloys). The importance of localized corrosion can be recognized when one compares the corrosion rate of a passive alloy (approximately 1 $\mu$m/year as uniform wall thinning) with that of an alloy undergoing active pitting (approximately 10,000 $\mu$m/year as a growing pit). Crevice corrosion is usually encountered more frequently in industrial structures than pitting. Indeed, in experimental investigations of pitting, precautions have to be taken to avoid crevice corrosion. However, crevices may act to provide a severe micro-environment within which either active general corrosion (total destabilization of a passive film) or pitting may take place. Hence, to understand crevice corrosion initiation and repassivation, pit initiation inside the crevice may need to be understood. Additionally, the same type of mass-transport controlled governing equations can be written for an active pit as for a crevice. For these reasons, the various approaches used to model pit initiation, growth, and repassivation are reviewed in this report.

# 2 PHENOMENOLOGY OF PITTING AND TYPES OF PITTING CORROSION MODELS

## 2.1 CRITICAL POTENTIALS

It is a well known experimental finding that pitting and crevice corrosion are initiated when the electrode potential rises above a critical potential. This critical potential, referred to as $E_p$, for pitting, and $E_c$, for crevice corrosion, depends on the test technique, solution composition, temperature, and alloy composition. While these potentials were once considered to be single-valued functions of the environmental and alloy factors, later investigations (Shibata, 1977) showed that they are distributed values because of the random nature of pit initiation process. The pit initiation process has been further classified into unstable (or metastable) and stable pitting. The stochastic processes related to pit initiation have been characterized in terms of birth and death (repassivation) of unstable pits, eventually leading to formation of stable pits. Here, the terminology in the literature is confusing: Shibata and co-workers generally follow the terminology initiated by Shibata and Takeyama (1977) and call the repassivation process as the "birth" process (rebirth of uncorroded specimens) and the initiation of pits as the "death" process (death of the specimen's capabilities). All other investigators, following the terminology by Evans (1961), call the "birth" process as the birth of pits (generation or initiation) and the "death" process as the death of pits (repassivation). In this and subsequent reviews, the terms pit "generation" and "repassivation" will be used when referring to stochastic models. Once pitting has been nucleated, pit growth rates can be calculated using deterministic models that incorporate charge transfer and transport processes. Growth of stable pits has also been treated in terms of extreme value statistics to determine the probability of the occurrence of the deepest pit in a given area (Laycock, Cottis, and Scarf, 1990). However, the extreme value statistical treatment of pit growth assume a deterministic growth law. During stable pit growth, if the potential decreases below a critical potential, pits repassivate. This critical potential is called the repassivation potential, $E_{rp}$. There has been a considerable controversy in the fundamental mechanisms governing $E_{rp}$ and in the significance of $E_{rp}$ for long-term prediction.

## 2.2 PIT INITIATION MODELS

### 2.2.1 Stochastic Models

Many experimental findings have indicated that the pit initiation process is a stochastic event (Shibata and Takeyama, 1977, 1981; Shibata and Takamiya, 1986; Williams, Westcott, and Fleischman, 1985a, 1985b; Mola et al., 1990). This means that statistical distributions describe the critical pit initiation potential and the pit initiation time at any given potential. Shibata and Takeyama (1977) were one of the earliest to propose a model for pitting potential based initially on the assumption of a pit generation rate, $\lambda$, independent of time, but dependent on applied potential. However, their model was really a curve fitting approach using an exponential distribution to fit their experimental data of pit initiation times (survival probability) at various applied potentials. Based on their data, they found that the pit generation rate had three values depending on the survival time. At short survival times, $\lambda$ was proportional to $(E - E_{crit})$, where E is the applied potential and $E_{crit}$ is a critical potential below which no pit initiation events were observed within the experimental time scale. At intermediate and long survival times (It must be emphasized that these experiments were only conducted up to a total time of 70 seconds), the pit generation rate was exponentially dependent on potential. The assumption of an

exponential distribution of survival probability was never justified and a more general Weibull distribution could have fit the data just as well without the need to introduce three pit generation rates. Shibata and Takeyama (1981) modified their original approach to include a pit generation rate, $\lambda$, and a repassivation rate, $\mu$, but retaining the exponential distribution. Again based on experimental data, they suggested that $\lambda$ increased exponentially with applied potential, while $\mu$ was independent of applied potential. Together these two parameters defined the observed pitting potential, $E_p$, and its observed dependence on potential scan rate. Shibata and Takamiya (1986) showed that $\lambda$ decreased with a decrease in chloride concentration, but the effect of chloride concentration on $\mu$ was relatively small. Williams, Westcott, and Fleischman (1985a, 1985b) developed a stochastic model for pit initiation based on their earlier investigations of the electrocrystallization process. They assumed that small, random fluctuations in current density or concentration of species ($H^+$, $Cl^-$) at the metal-electrolyte interface can cause nucleation of metastable pits. These fluctuations were assumed to occur over a scale corresponding to the surface roughness of the metallic surface. These metastable pits do not all survive, some repassivate. However, the metastable pits that survived beyond a critical age, $\tau_c$, were assumed to result in stable pits that can then grow. Based on these assumptions, they derived the probability, P(0), that no stable pits form at any given time $t$

$$Ln[P(0)] = -\lambda a(t-\tau_c)\exp(-\mu\tau_c) \qquad (2\text{-}1)$$

where $\lambda$ is the frequency of nucleation of metastable pits per unit area (different from that of Shibata's), $\mu$ is the probability of repassivation, $\tau_c$ is the critical age beyond which the metastable pits become stable pits, and $a$ the specimen area. Henshall (1992) essentially used the same approach, but with a Monte-Carlo technique to predict the evolution of stable pits on type 304 stainless steel. Williams, Westcott, and Fleischman (1985b) also provided mechanistic rationale for their stochastic theory. They considered pit nucleation events to be related to the creation of micro-crevice cells between the protuberances on the surface of the metal. They hypothesize that while the passive current density is small on an average, there can be wide fluctuations within the very small areas corresponding to the surface roughness that can cause formation of a highly acidic micro-environment and initiate active corrosion in these small areas. These fluctuations in local current densities were assumed to decrease with a decrease in applied potential and hence the presence of a critical pitting potential was rationalized. More recently, Stewart and Williams (1992) suggested that the stochastic event in the pit initiation process on commercial austenitic stainless steels is the supply of sulfur from the dissolved MnS inclusions to the micropit surrounding the inclusion and hence, the rate of generation of stable pits depends on the size and distribution of sulfide inclusions.

Unfortunately, for predictive purposes, one is still left with a need to assume values for a critical potential below which no nucleation of metastable pits takes place and a critical age beyond which these pits become stable. More importantly, the pit generation rate and repassivation probability can be derived only from experimental measurements over time scales much smaller than the required time periods for containment. There seems to be no fundamentally justifiable scheme by which $\lambda$ and $\mu$, derived from short-term laboratory experiments (1000 seconds or less) in concentrated chloride solutions, can be extrapolated to long time periods in predicted repository environments. From the perspective of long-term prediction and design for long-term performance, one then has to resort to deterministic (mechanistic) models that attempt to predict the critical pitting potentials as functions of various environmental factors. It must be noted that deterministic models can also be used to derive distribution of pit initiation times or potentials by assuming distributed values of more fundamental parameters (Macdonald and Urquidi-Macdonald, 1992).

## 2.2.2 Mechanistic Models

Mechanisms of pitting corrosion have been investigated from the 1920s (Evans, 1927) and are continuing to evolve. Many of the models have been attempts to provide qualitative explanations of observed phenomenology. Some of the models, at least in the form they were originally proposed, have been discarded in light of new data. A comprehensive review of various mechanistic models will be provided in a subsequent report. The reader is referred to other sources for more information (Szklarska-Smialowska, 1986). However, the current mechanistic theories can be divided into two major categories: i) those that assume that pitting is initiated in a passive film by the creation and movement of defects (Okada, 1984; Lin, Chao, and Macdonald, 1981), and ii) those that assume that microscopic defects, such as inclusions, exist prior to the initiation of pits and these defects modify the local environment such that the passive film is destabilized, either by a critical concentration of $H^+$ (Galvele, 1976; 1981; Gravano and Galvele, 1984) or by a critical combination of $Cl^-$ and thiosulfate (Alkire and Lott, 1989). The latter two models are applicable to pitting repassivation also. However, destabilizing of passive films by a critical concentration of anionic species implies that a more fundamental process is responsible for the destabilization. Hence the metal chloride nuclei model by Okada (1984) and the point defect model by Lin, Chao, and Macdonald (1981) are still of interest from this perspective. The latter is of particular interest because it appears to be useful in predicting not only the effects of environmental variables, but also the role of alloying elements. For example, in the Lin, Chao, and Macdonald model, the critical pitting potential is derived from the consideration of the effect of chloride ions on the movement of cationic species in the passive film. The fundamental assumption of the model is that the passive film growth takes place by the transport of anionic species from the solution-passive film interface inward to the metal and cationic species in the opposite direction. Movement of cationic species away from the metal-passive film interface towards the solution phase generates point defects in the form of cation vacancies in the film-metal interface. Under ideal circumstances, the cation vacancies will diffuse into the metal and be absorbed. However, when the rate of movement of cations away from the metal is greater than the rate of movement of cation vacancies into the metal, concentration of cation vacancies build up at the metal-film interface, which, upon attaining a critical size, become pit nuclei. The role of chloride was seen as enhancing the transport of cations away from the metal-film interface to the solution-film interface. Based on this hypothesis, Lin, Chao, and Macdonald (1981) derived the relationship between the critical potential for pit nucleation and bulk chloride concentration as

$$E_p = \frac{4.606RT}{\chi F\alpha}\log\frac{J_m}{J^0 u^{-x/2}} - \frac{2.303RT}{\alpha F}\log a_{Cl^-} \qquad (2\text{-}2)$$

where $\chi$ is the charge of the cation, F the Faraday constant, $\alpha$ is the charge transfer coefficient, $J_m$ is the rate of submergence of the cation vacancies into the metal, $J^0$ is the migrational flux of cations, u is a pre-exponential term associated with the chloride-oxygen vacancy at the solution-film interface, T the temperature, and $a_{Cl^-}$ is the activity of chloride ion in the solution. It can be seen from Eq. 2-2, that this model can explain the typical dependence of pitting potential on chloride concentration.

Additionally, in a recent paper (Urquidi-Macdonald and Macdonald, 1987), the distributed values of pitting potential and incubation time were derived using the point defect model. This was derived by assuming that there is a distribution of defects within the passive film such that the diffusivity of cations is distributed, although this need not be the only factor in the model that may be assumed to be distributed. Hence the point defect model should be examined in detail in terms of the effect of temperature and chloride concentration on the distribution of pitting potential and incubation time.

## 2.3 PIT REPASSIVATION MODELS

The pit repassivation potential, $E_{rp}$, is typically not as widely scattered as the pit initiation potential. However, because there has long been a controversy as to the existence of a minimum repassivation potential, not much effort has been placed in modeling repassivation potential. Recently, there has been an increased interest in pitting repassivation potential (Sridhar and Cragnolino, 1992; Thompson and Syrett, 1992) in terms of utilizing it as a lower bound parameter for life prediction. Tsujikawa, Sone and Hisamatsu (1987) modeled some of their experimental results on repassivation potentials of pits and crevices and suggested that the repassivation potential is related to the effect of external potential on solution composition inside the pits or crevices. However, their model cannot be used to directly obtain repassivation potentials. Nevertheless, this will be a useful concept to explore using a more rigorous transport treatment (Walton, 1992).

# 3 SUMMARY

Pit initiation and repassivation models are being reviewed as part of the auxiliary model development effort in the EBSPAC program. A preliminary assessment of the models has been presented in this report. The pit initiation models can be classified into stochastic and mechanistic models. Stochastic models have been proposed recently for use in life prediction of high-level waste containers. However, the stochastic models that have been advanced in the literature derive the parameters from short-term experiments (less than 1000 seconds). There is currently no method by which the stochastic model parameters such as pit generation and repassivation rates can be extended to long time periods. Hence, mechanistic models are necessary to justify the use of specific functional relationships. Additionally, all the stochastic models depend on a minimum potential below which no pitting occurs. There is currently no rigorous mechanistic model by which to derive this potential. However, some mechanistic models offer the possibility for deriving the critical potentials as functions of environment and material factors. The point defect model, in particular, needs to be examined further. In the case of repassivation potential, there currently is no rigorous model that can justify the use of repassivation potential as a lower bound parameter for long-term prediction. This needs to be investigated using a transport model recently developed at the CNWRA (Walton, 1992).

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