Engineered Materials Characterization Report (EMCR) Update Draft for Viability Assessment (VA)

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EMCR UPDATE DRAFT FOR VA: ACTIVITY ID# WP20AM4

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Introduction and Documentation

This report is submitted to satisfy the requirements of YMP Activity ID No. WP20AM4, Review/Finalize EMCR Update Draft for VA. The documentation supporting this activity is attached and include:

1. J. C. Farmer, "Waste Package Degradation Expert Elicitation Panel: Input on the Corrosion of CRM Alloy C-22," Rev. 5, Lawrence Livermore National Laboratory, Livermore, CA, February 26, 1998, 20 pages.
2. J. C. Farmer, "Corrosion Resistant Materials Degradation," Presentation for NRC/DOE Appendix 7 Meeting on Waste Package Materials, Lawrence Livermore National Laboratory, February 11-12, 1998,
3. J. C. Farmer, R. D. McCright, A. K. Roy, G.E. Gdowski, F. T. Wang, J. C. Estill, K. J. King, S. R. Gordon, D. L. Fleming, D. Y. Lum, "Development of Corrosion Models for High-Level Waste Containers," Lawrence Livermore National Laboratory, UCRL-JC-128756, Proc. 6th International Conference on Nuclear Engineering, ICONE-6, May 10-15, 1998, American Society of Mechanical Engineers, 1998, 13 pages.
4. J. C. Farmer, R. D. McCright, "Crevice Corrosion and Pitting of High-Level Waste Containers: Integration of Deterministic and Probabilistic Models," Lawrence Livermore National Laboratory, UCRL-ID-127980, Part 1, October 13, 1997, 24 pages; Paper No. 160, Annual Meeting of the National Association of Corrosion Engineers (NACE), Corrosion 98, San Diego, CA March 22-27, 1998, NACE, Houston, TX, 1998, 24 pages.
5. J. C. Farmer, Crevice Corrosion and Pitting of High-Level Waste Containers: The Integration of Deterministic and Probabilistic Models (II), Lawrence Livermore National Laboratory, UCRL-ID-127980, Part 2, October 8, 1997, 64 pages (with 5 additional appendices).
6. J.- S. Huang, "Stress Corrosion Cracking in Canistered Waste Package Containers: Welds and Base Metals" and "Thermal Embrittlement of Carbon Steels in Canistered Disposal Containers," in Memorandum entitled "Stress Corrosion Cracking and Thermal Embrittlement in Waste Packages," Lawrence Livermore National Laboratory, Memorandum, September 25, 1997, 9 pages.

Anticipated Environments

The overall electrolyte concentration in the NFE environment is expected to be somewhere between 1X and saturated J-13 well water. This covers more than three orders-of-magnitude in chloride anion concentration. The pH of this solution is expected to be somewhere between 5 and 10. Exposed patches of the CRM could see this environment.

The pH in the crevice can be acidified due to the hydrolysis of dissolved polyvalent cations, such as Fe^{2+} . As discussed by Oldfield and Sutton, metal ions produced by anodic dissolution are assumed to undergo the following hydrolysis reactions [J. W. Oldfield, W. H. Sutton, "Crevice Corrosion of Stainless Steels: I. A Mathematical Model," British Corrosion Journal, Vol. 13, No. 1, 1978, pp. 13-22]:

These reactions have also been considered in a crevice corrosion model published by the NRC [J. C. Walton, S. K. Kalandros, "TWITCH – A Model for Transient Diffusion, Electromigration, and Chemical Reaction in One Dimension," Center for Nuclear Waste Regulatory Analyses, San Antonio, TX, CNWRA 92-019, 1992]. The range of pH expected under a worst-case scenario (no precipitation of $FeCO_3$; no leakage of dissolved metal or acid out of the crevice; no pH buffers; etc.) is illustrated by the data of Jones et al., as shown in Table 1 [D. A. Jones, B. E. Wilde, "Galvanic Reactions During Localized Corrosion on Stainless Steel," Corrosion Science, Vol. 18, 1978, pp. 631-643].

Table 1. Suppression of pH by Hydrolysis Reactions in $FeCl_2$, $NiCl_2$, and $CrCl_3$ (25 °C).

Salt	1 N	3 N	Saturated
$FeCl_2$	2.1	0.8	0.2
$NiCl_2$	3.0	2.7	2.7
$CrCl_3$	1.1	-0.3	-1.4

The lowest possible pH values expected with $FeCl_2$ solutions at 25°C is 0.2. The pH levels measured in $FeCl_3$ solutions by Francis Wang are shown in Table 2.

Table 2. Suppression of pH by Hydrolysis Reactions in $FeCl_3$ Solutions (25 °C).

$FeCl_3$ (wt. %)	pH
1	1.92
2	1.83
3	1.71
4	1.63
10	0.70

More realistic estimates must include transport of Fe^{2+} and other species out of the crevice, limitations on the rate of Cl^- transport into the crevice, pH buffer effects due to other ion, and precipitation of hydrolyzable Fe^{2+} by carbonate. Such effects will tend to make the pH higher than these extreme values based upon thermodynamic equilibrium. A transport model for crevice corrosion has been developed by two of members of this Expert Elicitation Panel and was used to predict a pH of roughly 2.8-3.2 during the attack of Alloy 625 [J. C. Farmer, R. D. McCright, "Crevice Corrosion and Pitting of High-Level Waste Containers: Integration of Deterministic and Probabilistic Models," Paper No. 160, Annual Meeting of the National Association of Corrosion Engineers (NACE), Corrosion 98, San Diego, CA March 22-27, 1998].

Figure 1. Prediction of transport-limited pH suppression in crevice during attack of Alloy 625. The potential assumed as a boundary condition at the crevice mouth (applied potential) was fixed at a level 100 mV more anodic than the critical pitting potential of Alloy 625.

During the Appendix 7 Meeting, the range of expected values given by the NRC Center are:

- A. NFE $5 < \text{pH} < 10$
- B. Crevice - Before Localized Corrosion of CRM: $3 < \text{pH} < 5$. Likely case, since this will occur near E_{corr} of A516. Due to hydrolysis of Fe alone. Depends upon transport and crevice geometry.
- C. Crevice - After Localized Corrosion of CRM: $-1 < \text{pH} < 3$. Requires potential above repassivation potential, and considered very unlikely. Due to hydrolysis of other dissolved metals, such as Cr and Mo. Depends on transport and crevice geometry.

It is believed that the electrochemical potential at the mouth of the crevice will be somewhere between the mixed potential of A516 Gr 12 and Alloy C-22, in either concentrated J-13 or concentrated (10 wt. % FeCl_3). See Table 3.

Table 3. Expected Electrochemical Potentials in Repository – Based on Measurements.

Case	A	B	C	D	E
T (°C)	90	90	90	90	90
NaCl (wt. %)	10	1	0	0	5
FeCl ₃ (wt. %)	0	0	0.6	3.1	0
pH	6.8	2.7	2.14	1.72	2.7
Radiolysis	No	No	No	No	No
Deaerated	No	Yes	Yes	Yes	No
E _{corr} (mV vs. SHE): A516 Gr 12					-520
E _{corr} (mV vs. SHE): C-22	-24	-29	+661	+714	
E _{pit} (mV vs. SHE): C-22	+442	+758	+905	+889	> +730
E _{pass} (mV vs. SHE): C-22	+550	+793	+857	+896	> +730
Above Threshold Potential	No	No	No	No	No

In the absence of FeCl₃, which is a product of the CAM corrosion, the greatest mixed potential expected is somewhere between -520 and -29 mV vs. SHE at 90°C. With FeCl₃ at 10 wt. %, potentials as high as +714 mV vs. SHE have been observed. Since the observed mixed potential never exceeded the pitting potential or the repassivation potential, localized attack is not expected. This interpretation is consistent with the interpretation of Cragnolino [G. A. Cragnolino, DOE/NRC Appendix 7 Meeting, Livermore, CA, February, 1998]. These observations do not account for the effects of gamma radiolysis and other effects.

From transport modeling of corrosion in the CAM-CRM crevice, it is known that the electrochemical potential inside the crevice is less anodic (less severe) than the potential established or applied at the mouth of the crevice [J. C. Farmer, R. D. McCright, "Crevice Corrosion and Pitting of High-Level Waste Containers: Integration of Deterministic and Probabilistic Models," Paper No. 160, Annual Meeting of the National Association of Corrosion Engineers (NACE), Corrosion 98, San Diego, CA March 22-27, 1998]. This is due to ohmic drop along the length of the crevice. Consequently, any estimate of corrosion rate based on the electrochemical potential at the crevice mouth, coupled with the assumption of suppressed pH and elevated chloride inside the crevice, should be conservative.

In summary, the environmental conditions determined to be of greatest interest by consensus of the entire Expert Elicitation Panel are summarized as follows: (a) T = 25, 50, and 100°C; (b) pH = 2.5 & 3-10; (c) E_{applied} = 340 & 640 mV vs. SHE.

Passive Corrosion Rates of Alloy C-22 in Relevant Environments

Reasonable values for the penetration rate of Alloy C-22 due to dissolution through the passive film appear to be between 0.009 microns per year in a simulated, acidified, concentrated, J-13 well water, and 13 microns per year in a simulated crevice solution. Passive corrosion is consistent with opinions voiced by representative of the NRC. They state that no significant localized corrosion (localized penetration of the passive film) occurs at potentials well below the repassivation potential, E_{pass}. In the absence of radiolysis, the measured corrosion potential (mixed potential), E_{corr}, in such environments appears to be well below E_{pass}. This is a general view held by other investigators in the field of corrosion science. The observed penetration rates for Alloy C-22 in relevant environments are summarized in Figure 3, and are indicative of passive corrosion.

Figure 2. Electrochemical potential inside crevice is less severe than that applied in the mouth.

Figure 3. Observed Passive Corrosion Rates for Alloy C-22: Measured Weight Loss of Samples Exposed in Long Term Corrosion Test Facility (LTCTF); Corrosion Current Measurements at Open Circuit Potential (Roy, LLNL); and Measured Weight Loss of Samples Exposed to Simulated Crevice Solutions (Asphahani, Hanes International).

These observations are well represented by the regression equation (correlation) given to the EEP earlier. Data from the LTCTF was combined with the rates calculated from Roy's linear sweep polarization measurements, as well as the rates published by Asphahani. The combined data set was then used as the basis of an overall correlation of penetration rates with temperature, pH, equivalent NaCl concentration, and FeCl₃ [J. C. Farmer et al., "Development of Models for High-Level Waste Containers," Proc. 6th Intl. Conf. On Nuclear Engineering, ICON-6, May 10-15, 1998, San Diego, California, ASME, 1998, 13 p.]. The following linear equation was found to be adequate for the correlation of Alloy C-22 penetration rates:

$$\ln\left(\frac{\Delta p}{\Delta t}\right) = b_0 + b_1\left(\frac{1000}{T + 273}\right) + b_2(pH) + b_3(C_{NaCl}) + b_4(C_{FeCl_3})$$

where $\Delta p/\Delta t$ is the apparent penetration rate ($\mu\text{m y}^{-1}$); T is the temperature ($^{\circ}\text{C}$); C_{NaCl} is the equivalent concentration of NaCl (wt. %); and C_{FeCl_3} is the concentration of FeCl₃ (wt. %). Within the bounds of thirty-eight (38) experimental observations for Alloy C-22, the coefficients were determined to be:

$$b_0 = +13.409$$

$$b_1 = -5.5587$$

$$b_2 = -0.87409$$

$$b_3 = +0.56965$$

$$b_4 = +0.60801$$

More specifically, the correlation for Alloy C-22 is:

$$\ln\left(\frac{\Delta p}{\Delta t}\right) = 13.409 - \left(\frac{5558.7}{T + 273}\right) - 0.87409(pH) + 0.56965(C_{NaCl}) + 0.60801(C_{FeCl_3})$$

The "standard error of estimate" ($s_{y/1234}$) and the "sample multiple variable regression coefficient" ($r_{y/1234}$) are defined by Crow, Davis and Maxfield [E. L. Crow, F. A. Davis, M. W. Maxfield, Statistics Manual, Dover Publications, Inc., New York, NY, 1960, pp. 147-19]. The "standard error of estimate" is a measure of the scatter of the observed penetration rates about the regression plane. About 95% of the points in a large sample are expected to lie within $\pm 2s_{y/1234}$ of the plane, measured in the y direction. Values for the above correlation are:

$$s_{y/1234} = 1.5092$$

$$r_{y/1234} = 0.65628$$

The "multiple variable regression coefficient" indicates a reasonably good fit to the data set, given the large number of independent variables. As discussed in the literature, uncertainty in a given model parameter, β_j , can be determined from the standard error of estimate, as shown by Eqns. 7 and 8 [E. L. Crow, F. A. Davis, M. W. Maxfield, Statistics Manual, Dover Publications, Inc., New York, NY, 1960, pp. 147-19]:

$$s_{b_j} = s_{y/1234} \sqrt{ne_{jj}}$$

$$\beta_j = b_j \pm (t_{a/2, n-k-1}) \times s_{b_j}$$

This simple correlation has been tested within the bounds of anticipated conditions. The predictions appear to be reasonable for combinations of input parameters representative of the: Near Field Environment (NFE); SDW; SCW; SAW; SCMW; the unusually harsh, simulated crevice corrosion test of Asphahani (10 wt. % FeCl₃); and the conditions predicted during preliminary tests of the LLNL crevice transport model [J. C. Farmer, R. D. McCright, "Crevice Corrosion and Pitting of High-Level Waste Containers: Integration of Deterministic and Probabilistic Models," Paper No. 160, Annual Meeting of the National Association of Corrosion Engineers (NACE), Corrosion 98, San Diego, CA March 22-27, 1998]. The worst case within the bounds of the regression analysis is the simulated crevice condition used by Asphahani (10 wt. % FeCl₃). In the repository, the concentration of FeCl₃ is expected to be limited to much lower values by the presence of carbonate, which precipitates iron. **It must be noted that combinations of input parameters that are clearly beyond the range of the data included in the correlation cannot be used to generate reasonable predictions. Therefore, this correlation should not be used for saturated solutions of J-13 and/or FeCl₃. With in the limits of the experimental data, predictions are believed to be good representations of the observations.**

For completeness, the above correlation also included observations of passive corrosion rate inferred from Ajit Roy's cyclic polarization measurements. It is well known that the corrosion (or penetration) rate of an alloy, dp/dt , can also be calculated from the corrosion current density, i_{corr} , as follows:

$$\frac{dp}{dt} = \frac{i_{corr}}{\rho_{alloy} n_{alloy} F}$$

where ρ_{alloy} is the density of the alloy, assumed to be approximately 8.4 g cm⁻³, and F is Faraday's constant. The number of gram equivalents per gram of alloy, n_{alloy} , is calculated with the following equation:

$$n_{alloy} = \sum_j \left(\frac{f_j n_j}{a_j} \right)$$

where f_j is the mass fraction of the j-th alloying element in the material, n_j are the number of electrons involved in the anodic dissolution process, which is assumed to be congruent, and a_j is the atomic weight of the j-th alloying element. These equations have been used to calculate penetration rates for Alloy C-22 from apparent corrosion currents determined during cyclic polarization measurements. In principle, such electrochemically-determined rates should be consistent with those observed in the LTCTF, though experience indicates that such electrochemically-determined rates are conservative (higher than those actually observed).

The magnitude of the observed rates shown in Figure 3 appear to be consistent with those quoted in the article by Smailos, Schwarzkopf, and Koster [E. Smailos, W. Schwarzkopf, R. Koster, "Corrosion Behaviour of Container Materials for the Disposal of High-Level Wastes in Rock Salt Formations," Nuclear Science and Technology, Commission of the European Communities, DUR 10400, 1986], though the correlation cannot be used at such high salt concentration since data from experiments with saturated solutions were not included in the correlation. Penetration rates for Alloy C-4 in a

concentrated brine at 90, 170 and 200°C are given. The authors state: "Hastelloy C-4 has also resisted pitting corrosion and stress corrosion cracking, in the absence of irradiation, and its corrosion rate has been low at all testing temperatures (< 1 microns/yr), but it has been attacked by crevice corrosion." The authors go on to state that when it is exposed to gamma irradiation at $\sim 10^5$ rad/hr, pitting corrosion was observed. This pitting corrosion is believed by several investigators in the field to be due to the formation of oxidants such as H_2O_2 , which shift the corrosion potential in the anodic direction, closer to the pitting and repassivation potential. At LLNL in the mid 1980's, Glass performed definitive radiolysis experiments showing that the corrosion potential of 316L stainless steel in 0.018 M NaCl at 30°C shifted from approximately -100 mV vs. SCE to approximately +100 mV vs. SCE when exposed to gamma irradiation (3.3×10^6 rad/hr) from a Co-60 source [R. S. Glass et al., Gamma Radiation Effects on Corrosion: I. Electrochemical Mechanisms for the Aqueous Corrosion Processes of Austenitic Stainless Steels Relevant to Nuclear Waste Disposal in Tuff, Corrosion Science, Vol. 26, No. 8, 1986, p. 577-590; J. C. Farmer et al., "Corrosion Models for Performance Assessment of High-Level Radioactive-Waste Containers," Nuclear Engineering & Design, Vol. 129, 1991, pp. 57-88]. The level of radiation expected at the outer surface of the CRM at the instant of CAM penetration is estimated to be orders-of-magnitude less than these exposures (10^5 - 10^6 rad/hr). At the Appendix 7 Meeting held at LLNL in February, 1998, the NRC said that they are ignoring the effects of radiolysis on corrosion, and believe that they are well justified in doing so. Note that radiolysis could form other oxidants, such as chlorine free radicals, ozone, and perhaps even unanticipated species such as peroxydisulfate, which has a very anodic redox potential. However, at low levels of radiation, the effects are not expected to be great. In regard to the C-4 penetration rate data, it must be noted that at high temperature, the expected rates for C-22 would be expected to be lower, as shown in Table 4. In regard to this table, two rates attract particular attention: Alloy C, 5 wt. % $FeCl_3$, 50°C, 0.075 mm crevice; Alloy C-276, $H_2SO_4/HCl/FeCl_3/CuCl_2$, 50°C.

Table 4. Published Penetration Rates (microns/yr) for Similar Alloys.

Exposure	T (°C)	C	C-4	C-276	C-22	Source
10 wt. % $FeCl_3$	25		7.6	5.1	2.5	Haynes, 1987
10 wt. % $FeCl_3$	50		12.7	2.5	2.5	Haynes, 1987
10 wt. % $FeCl_3$	75		508	12.7	12.7	Haynes, 1987
5 wt. % $FeCl_3$	50	20				Jackson & van Rooyen, 1972
5 wt. % $CuCl_2$	50	10				Jackson & van Rooyen, 1972
5 wt. % NaOCl	50	6				Jackson & van Rooyen, 1972
5 wt. % $FeCl_3$ + 5 wt. % HCl	25	20				Jackson & van Rooyen, 1972
5 wt. % $FeCl_3$ ***	50	5200				Jackson & van Rooyen, 1972
10 wt. % $FeCl_3$	25			5.08		Asphahani, 1980
10 wt. % $FeCl_3$	50			5.08		Asphahani, 1980
Sea Water, Surface**	25			Nil		Hack, 1983
Sea Water, 2370-6780 ft**				Nil		Reinhart, 1969 (~24 samples)
7 vol. % H_2SO_4 + 3 vol. % HCl + 1 wt. % $FeCl_3$ + 1 wt. % $CuCl_2$	25			7.62		Asphahani, 1980
7 vol. % H_2SO_4 + 3 vol. % HCl + 1 wt. % $FeCl_3$ + 1 wt. % $CuCl_2$	50			610		Asphahani, 1980

Nomenclature: **Crevice sample *** Tight crevice – 0.075 mm

Such high rates have not been observed with Alloy C-22 samples, configured in tight crevice geometries, and exposed to acidified (pH~2.7), concentrated (1000X) J-13 well water at 90°C. In cases where such high rates have been observed with lesser alloys such as C-4, the observed penetration rates for C-22 have remained low [Haynes, 1987, 10 wt. % FeCl₃]. This raises three important questions: (a) can the NRC repassivation potential criteria be applied to Alloys C, C-4 and C-276 in cases where large penetration rates are predicted; (b) are measured penetration rates for Alloys C, C-4, and C-276 in mixed strong acids really indicative of the rates expected for C-22 in relevant repository environments; (c) are the FeCl₃ environments reasonable simulations of a crevice; and (d) is the gradient in electric potential, or electric field, sufficient to induce complete separation of alkali metal cations and halide/oxy anions, thereby producing such an environment.? In regard to the last question, predictions based upon electric double layer theory indicate that electric fields of 10⁹ V/cm at the electrode-electrolyte interface (across the compact double layer) may be possible. The field in the diffuse double layer is much less. The extreme field strengths in the compact double layer are believed to be sufficient to induce complete charge separation. However, since such gradients do not exist in the bulk electrolyte found in crevices, pits and cracks, what physical process could be responsible for creating concentrated mixtures of H₂SO₄ and HCl? What plausible scenario can we provide to create environments where such high penetration rates have been observed?

Values for 1000X J-13 are based upon the above correlation, since the chloride concentration is within the range of data included in the correlation [J. C. Farmer et al., "Development of Corrosion Models for High-Level Waste Containers," Proc. 6th International Conference on Nuclear Engineering, ICONE-6, San Diego, CA, May 10-15, 1998, ASME, 1998, 13 p.]. In the case of saturated J-13, estimates are based upon the article by Smailos, Schwarzkopf, and Koster [E. Smailos, W. Schwarzkopf, R. Koster, "Corrosion Behaviour of Container Materials for the Disposal of High-Level Wastes in Rock Salt Formations," Nuclear Science and Technology, Commission of the European Communities, EUR 10400, 1986], as interpreted by another member of the Expert Elicitation Panel [D. Shoesmith, "Passive Corrosion of the CRM," electronic mail message, February 13, 1998]. The data quoted by Shoesmith is for "Q-Brine" and "Z-Brine" electrolytes, as shown Table 5a.

Table 5a. Data for Passive Corrosion in Saturated Brines (Smailos et al.; Shoesmith).

Brine	pH	NaCl	KCl	MgCl ₂	MgSO ₄	H ₂ O	90°C Rate	170°C Rate	pH
		wt. %	wt. %	wt. %	wt. %	wt. %	µm/yr	µm/yr	Shoesmith
Q	4.9	1.4	4.7	26.8	1.4	65.7	0.02	0.15-0.66	~5

The rate of 10-14 microns/yr in Z-Brine at 90°C is interpreted as the "maximum possible" value by Shoesmith (taken here as rate at 99th percentile). According to page 10 of the Smailos Report: "After three years of exposure until now Hastelloy C-4 has remained resistant to pitting corrosion, and to stress corrosion cracking. At 90°C local crevice corrosion attacks occurred at single points at the metal/PTFE and metal/metal contact surfaces with maximum depths of 250 microns (metal/PTFE), and 20-70 microns (metal/metal), respectively." This translates into a maximum penetration rate of 15-51 microns/yr. It must be noted that the rates from the Smailos et al. Report had to be scaled for pH and temperature so that all conditions of interest in this elicitation could be covered. While the base rate used was taken from the "Z-Brine" data, the activation energy used to scale the rate for temperature had to be inferred from the "Q-Brine" data. A very reasonable value of the activation energy, E_a, was estimated to be approximately 12 kcal/mol. The estimate was made with the following equation, which is based upon an Arrhenius-type rate expression:

$$\frac{r_1}{r_2} = \exp \left[\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

At 170°C (T₁), the observed penetration rates were given as 0.66 and 0.15 microns/yr, which were averaged to give a single value of 0.4 microns/yr (r₁). At a lower temperature of 90°C (T₂), the observed rate was given as 0.02 microns/yr (r₂). Rates were scaled with the pH as implied by the correlation, since no better means of estimating the response is available. Therefore, the rates were assumed to obey the following empirical law:

$$\frac{r_1}{r_2} = \exp[0.87409(pH_2 - pH_1)]$$

Establishment of CDF's for 1000X and saturated J-13 cases require estimation distribution width about the mean. In regard to estimates based upon either the correlation and Shoesmith's interpretation of data published by Smailos et al., it was assumed that *logarithmic rates* were distributed normally about the *mean logarithmic rate*. To determine the CDF's for 1000X J-13, which was based upon the correlation, the following simplifying approximations were made:

$$y = \ln \left[\frac{\Delta p}{\Delta t} \right]$$

$$y_{5\%} \approx y_{predicted} - \delta y_{\alpha=0.05} \approx y_{predicted} - t_{\alpha=0.05} s_{y/123, k}$$

$$y_{95\%} \approx y_{predicted} + \delta y_{\alpha=0.05} \approx y_{predicted} + t_{\alpha=0.05} s_{y/123, k}$$

$$t_{\alpha=0.05} \approx 1.70$$

$$y_{1\%} \approx y_{predicted} - \delta y_{\alpha=0.01} \approx y_{predicted} - t_{\alpha=0.01} s_{y/123, k}$$

$$y_{99\%} \approx y_{predicted} + \delta y_{\alpha=0.01} \approx y_{predicted} + t_{\alpha=0.01} s_{y/123, k}$$

$$t_{\alpha=0.01} \approx 2.46$$

$$r_{5\%} = \left[\frac{\Delta p}{\Delta t} \right]_{5\%} \approx \exp \left[y_{predicted} - 1.70 \times s_{y/123, k} \right]$$

$$r_{95\%} = \left[\frac{\Delta p}{\Delta t} \right]_{95\%} \approx \exp \left[y_{predicted} + 1.70 \times s_{y/123, k} \right]$$

$$r_{1\%} = \left[\frac{\Delta p}{\Delta t} \right]_{1\%} \approx \exp \left[y_{predicted} - 2.46 \times s_{y/123, k} \right]$$

$$r_{99\%} = \left[\frac{\Delta p}{\Delta t} \right]_{99\%} \approx \exp \left[y_{predicted} + 2.46 \times s_{y/123, k} \right]$$

The CDF's based upon Smailos et al. assumed values at the 99th and 50th percentiles, and then assumed a log-normal distribution to estimate values at other percentiles. In this case, the standard deviation was estimated to be about 1.6228, the value of $u_{\alpha=0.05}$ was assumed to be 1.645 and the value of $u_{\alpha=0.01}$ was assumed to be 2.326. Based on the foregoing considerations, this member of the Expert Elicitation Panel proposes estimates for passive corrosion rates of the CRM represented by the CDF's summarized in Table 5b. Bold-face values correspond to rates taken from Table 5a.

Table 5b. Estimates of the CDF for Passive Penetration Rates – Dripping.

Data Source		Regression (Farmer)	Regression (Farmer)	Regression (Farmer)	Smailos (Shoemith)	Smailos (Shoemith)	Smailos (Shoemith)	Smailos (Shoemith)
Environment		1000X J-13	1000X J-13	1000X J-13	Z-Brinc	Z-Brinc	Z-Brinc	Z-Brinc
NaCl (wt. %)		1.2	1.2	1.2	Saturated	Saturated	Saturated	Saturated
T (°C)		25	50	100	90	25	50	100
Percentile (%)	pH	Microns/yr	microns/yr	microns/yr	microns/yr	microns/yr	microns/yr	microns/yr
50	1	4.36x10 ⁻³	1.85x10 ⁻²	1.86x10 ⁻¹	6.60x10 ⁻¹	1.71x10 ⁻²	8.29x10 ⁻²	1.03
50	2	1.82x10 ⁻³	7.71x10 ⁻³	7.74x10 ⁻²	2.75x10 ⁻¹	7.13x10 ⁻³	3.46x10 ⁻²	4.31x10 ⁻¹
50	3	7.59x10 ⁻⁴	3.22x10 ⁻³	3.23x10 ⁻²	1.15x10 ⁻¹	2.98x10 ⁻³	1.44x10 ⁻²	1.80x10 ⁻¹
50	5	1.32x10 ⁻⁴	5.60x10 ⁻⁴	5.62x10 ⁻³	2.00x10⁻²	5.18x10 ⁻⁴	2.51x10 ⁻³	3.13x10 ⁻²
50	7	2.30x10 ⁻⁵	9.75x10 ⁻⁵	9.79x10 ⁻⁴	3.48x10 ⁻³	9.02x10 ⁻⁵	4.38x10 ⁻⁴	5.46x10 ⁻³
50	10	1.67x10 ⁻⁶	7.08x10 ⁻⁶	7.11x10 ⁻⁵	2.53x10 ⁻⁴	6.55x10 ⁻⁶	3.18x10 ⁻⁵	3.96x10 ⁻⁴
Percentile (%)	pH	Microns/yr	microns/yr	microns/yr	microns/yr	microns/yr	microns/yr	microns/yr
5	1	3.35x10 ⁻⁴	1.42x10 ⁻³	1.43x10 ⁻²	4.57x10 ⁻²	1.18x10 ⁻³	5.75x10 ⁻³	7.16x10 ⁻²
5	2	1.40x10 ⁻⁴	5.93x10 ⁻⁴	5.95x10 ⁻³	1.91x10 ⁻²	4.94x10 ⁻⁴	2.40x10 ⁻³	2.99x10 ⁻²
5	3	5.84x10 ⁻⁵	2.47x10 ⁻⁴	2.48x10 ⁻³	7.96x10 ⁻³	2.06x10 ⁻⁴	1.00x10 ⁻³	1.25x10 ⁻²
5	5	1.02x10 ⁻⁵	4.31x10 ⁻⁵	4.32x10 ⁻⁴	1.39x10 ⁻³	3.59x10 ⁻⁵	1.74x10 ⁻⁴	2.17x10 ⁻³
5	7	1.77x10 ⁻⁶	7.49x10 ⁻⁶	7.53x10 ⁻⁵	2.41x10 ⁻⁴	6.25x10 ⁻⁶	3.03x10 ⁻⁵	3.78x10 ⁻⁴
5	10	1.29x10 ⁻⁷	5.44x10 ⁻⁷	5.47x10 ⁻⁶	1.75x10 ⁻⁵	4.54x10 ⁻⁷	2.20x10 ⁻⁶	2.75x10 ⁻⁵
Percentile (%)	pH	Microns/yr	microns/yr	microns/yr	microns/yr	microns/yr	microns/yr	microns/yr
95	1	5.67x10 ⁻²	2.40x10 ⁻¹	2.41	9.52	2.47x10 ⁻¹	1.20	14.9
95	2	2.37x10 ⁻²	1.00x10 ⁻¹	1.01	3.97	1.03x10 ⁻¹	4.99x10 ⁻¹	6.23
95	3	9.88x10 ⁻³	4.19x10 ⁻²	4.20x10 ⁻¹	1.66	4.30x10 ⁻²	2.08x10 ⁻¹	2.60
95	5	1.72x10 ⁻³	7.29x10 ⁻³	7.32x10 ⁻²	2.89x10 ⁻¹	7.48x10 ⁻³	3.63x10 ⁻²	4.52x10 ⁻¹
95	7	2.99x10 ⁻⁴	1.27x10 ⁻³	1.27x10 ⁻²	5.03x10 ⁻²	1.30x10 ⁻³	6.31x10 ⁻³	7.87x10 ⁻²
95	10	2.17x10 ⁻⁵	9.21x10 ⁻⁵	9.25x10 ⁻⁴	3.65x10 ⁻³	9.46x10 ⁻⁵	4.59x10 ⁻⁴	5.72x10 ⁻³
Percentile (%)	pH	Microns/yr	microns/yr	microns/yr	microns/yr	microns/yr	microns/yr	microns/yr
1	1	1.06x10 ⁻⁴	4.51x10 ⁻⁴	4.53x10 ⁻³	1.51x10 ⁻²	3.92x10 ⁻⁴	1.90x10 ⁻³	2.37x10 ⁻²
1	2	4.44x10 ⁻⁵	1.88x10 ⁻⁴	1.89x10 ⁻³	6.32x10 ⁻³	1.64x10 ⁻⁴	7.94x10 ⁻⁴	9.90x10 ⁻³
1	3	1.85x10 ⁻⁵	7.85x10 ⁻⁵	7.89x10 ⁻⁴	2.64x10 ⁻³	6.83x10 ⁻⁵	3.31x10 ⁻⁴	4.13x10 ⁻³
1	5	3.23x10 ⁻⁶	1.37x10 ⁻⁵	1.37x10 ⁻⁴	4.59x10 ⁻⁴	1.19x10 ⁻⁵	5.77x10 ⁻⁵	7.19x10 ⁻⁴
1	7	5.62x10 ⁻⁷	2.38x10 ⁻⁶	2.39x10 ⁻⁵	7.99x10 ⁻⁵	2.07x10 ⁻⁶	1.00x10 ⁻⁵	1.25x10 ⁻⁴
1	10	4.08x10 ⁻⁸	1.73x10 ⁻⁷	1.74x10 ⁻⁶	5.80x10 ⁻⁶	1.50x10 ⁻⁷	7.29x10 ⁻⁷	9.09x10 ⁻⁶
Percentile (%)	pH	Microns/yr	microns/yr	microns/yr	microns/yr	microns/yr	microns/yr	microns/yr
99	1	1.79x10 ⁻¹	7.57x10 ⁻¹	7.60	28.8	7.45x10 ⁻¹	3.61	45.1
99	2	7.45x10 ⁻²	3.16x10 ⁻¹	3.17	12.0	3.11x10 ⁻¹	1.51	18.8
99	3	3.11x10 ⁻²	1.32x10 ⁻¹	1.32	5.01	1.30x10 ⁻¹	6.29x10 ⁻¹	7.84
99	5	5.41x10 ⁻³	2.29x10 ⁻²	2.30x10 ⁻¹	8.72x10 ⁻¹	2.26x10 ⁻²	1.10x10 ⁻¹	1.37
99	7	9.43x10 ⁻⁴	3.99x10 ⁻³	4.01x10 ⁻²	1.52x10 ⁻¹	3.93x10 ⁻³	1.91x10 ⁻²	2.38x10 ⁻¹
99	10	6.85x10 ⁻⁵	2.90x10 ⁻⁴	2.91x10 ⁻³	1.10x10 ⁻²	2.86x10 ⁻⁴	1.39x10 ⁻³	1.73x10 ⁻²

Estimates for humid air corrosion assume rates comparable to those for aqueous-phase passive corrosion at neutral pH, which appears to be more or less consistent with the impressive “mirror finish” of an Alloy C sample after 56 years exposure to a coastal environment on the coast of North Carolina, summarized in Table 5c.

Table 5c. Estimates of the CDF for Passive Penetration Rates – Humid Air Corrosion.

T (°C)	25	50	100
Percentile (%)	microns/yr	microns/yr	microns/yr
1	5.62×10^{-7}	2.38×10^{-6}	2.39×10^{-5}
5	1.77×10^{-6}	7.49×10^{-6}	7.53×10^{-5}
50	2.30×10^{-5}	9.75×10^{-5}	9.79×10^{-4}
95	2.99×10^{-4}	1.27×10^{-3}	1.27×10^{-2}
99	9.43×10^{-4}	3.99×10^{-3}	4.01×10^{-2}

Probability of Initiating Localized Corrosion of CRM

The probability of localized corrosion, which is assumed to include both crevice corrosion and pit initiation, is based upon observations of the pitting and repassivation potential. First, all observed values are placed on a common potential scale, that of the standard hydrogen electrode (SHE). Correlations have been obtained for the electrochemical potentials of the AgCl and SCE reference electrodes as functions of temperature. The first correlation for Ag/AgCl/0.1M KCl was provided by David Shoesmith and was developed by AECL [King et al., “A High-Temperature, High-Pressure, Silver-Silver Chloride Reference Electrode: A User’s Guide,” AECL-9890, 1989].

$$E_{AgCl}(SHE) = 0.23755 - 5.3783 \times 10^{-4} T(^{\circ}C) - 2.3728 \times 10^{-6} T(^{\circ}C)^2 + 2.2671 \times 10^{-4} [T(^{\circ}C) + 273]$$

The second correlation for Hg/Hg₂Cl₂/satd. KCl was obtained from the well-known text by Bard & Faulkner [A. J. Bard, L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, New York, NY, 1980].

$$E_{SCE}(SHE) = 0.2412 - 6.61 \times 10^{-4} [T(^{\circ}C) - 25] - 1.75 \times 10^{-6} [T(^{\circ}C) - 25]^2 - 9.0 \times 10^{-10} [T(^{\circ}C) - 25]^3$$

Relevant temperature corrections can be calculated with each of these expressions, as given in Table 6 below:

Table 6. Correction of Reference Electrodes for Temperature Excursion from Ambient.

T (°C)	E _{Ag/AgCl/0.1M KCl} (V vs. SHE)	E _{SCE} (V vs. SHE)
25	0.2902	0.2412
60	0.2722	0.2344
90	0.2629	0.1906
95	0.2485	0.1861

In the case of the Ag/AgCl/0.1M KCl electrode, the potential must also be corrected for electrolyte concentration, so that it is applicable for the standard AgCl electrode with saturated KCl. First, the solubility of KCl as a function of temperature is obtained from the CRC Handbook [CRC Handbook, Chemical Rubber Company, 61st Edition, 1980-81, p. B-132].

$$T = 20^{\circ}\text{C} : C_{\text{saturated KCl}} = 23.8 \text{ grams per } 100 \text{ cc}$$

$$T = 100^{\circ}\text{C} : C_{\text{saturated KCl}} = 56.7 \text{ grams per } 100 \text{ cc}$$

The saturation concentrations at other temperatures is estimated by simple linear interpolation, as shown in Table 7:

Table 7. Saturation Concentration of KCl by Linear Interpolation.

T (°C)	C _{saturated KCl} (g per 100 cc)	C _{saturated KCl} (mol/kg)
20	23.8	3.192
25	25.86	3.468
60	40.25	5.398
90	52.59	7.053
95	54.64	7.329
100	56.7	7.605

Note that a formula weight of KCl is assumed to be approximately 74.56, and ignores any hydration effects. Obviously, we have ignored activity coefficients. The Debye-Huckel equation could be used to estimate the activity coefficients, however, it only applies rigorously to infinitely dilute solutions. Other activity coefficient models for higher electrolyte concentrations are controversial, due to a general lack of knowledge of the sphere of hydration surrounding individual ions, a general inability to account for Coulombic and dipole interactions between each pair of individual ions, and other equally important effects. A simplification of the Nernst equation, which also ignores activity coefficients, can be used to make a first order correction of the potential of the Ag/AgCl/KCl reference electrode for KCl concentration. The Nernst equation can be written as:

$$E = E^0 + \frac{RT}{nF} \ln \frac{C_O}{C_R}$$

where the convention is assumed to be:

Application of this simplified Nernst equation to the Ag/AgCl/KCl reference electrode yields:

$$E_{\text{Ag/AgCl/satd KCl}} - E_{\text{Ag/AgCl/0.1M KCl}} = -\frac{RT}{F} \ln \frac{C_{\text{satd. KCl}}}{C_{0.1\text{M KCl}}}$$

where the assumed reaction is:

Given Faraday's constant of 9.64846×10^4 C/equiv, the value of RT/F at 25°C is 0.02569 V, and can be scaled to different temperatures (Table 8).

Table 8. Correction of Electrode Potential for Concentration.

T (°C)	RT/F (V)	E _{Ag/AgCl/0.1M KCl} (V vs. SHE)	C _{saturated KCl} (mol/kg)	Concentration Correction (V)	E _{Ag/AgCl/satd KCl} (V vs. SHE)	E _{SCE} (V vs. SHE)
25	0.02569	0.2902	3.468	-0.0911	0.1991	0.2412
60	0.02871	0.2722	5.398	-0.1145	0.1577	0.2344
90	0.03129	0.2629	7.053	-0.1332	0.1297	0.1906
95	0.03172	0.2485	7.329	-0.1362	0.1123	0.1861

Application of these corrections to measured corrosion, pitting, and repassivation potentials is summarized in Tables 9a and 9b. Note that the interpretation of cyclic polarization (CP) curves is very subjective. Where more than one inflection point might be interpreted as the potential of interest, the most conservative value was chosen (least anodic repassivation potential, for example). These data are summarized in Figure 4.

Figure 4. Observations of repassivation potential as a function of chloride concentration, temperature, and pH.

The probability of initiating localized corrosion are based on the stochastic probability theory of pit initiation, as discussed by Baroux [B. Baroux, "Further Insights on the Pitting Corrosion of Stainless Steels," Chapter 9, Corrosion Mechanisms in Theory and Practice, P. Marcus, J. Oudar, Eds., Marcel Dekker, Inc., New York, NY, pp. 265-309]. First, the expression for the survival probability is:

$$\delta P_s = 1 - \bar{\omega} \times \delta S$$

where δP is the survival probability (probability of no pitting) of an infinitesimal area δS on a sample of area S . The survival probability of the entire surface S is then:

$$P_s = \left[1 - \bar{\omega} \times \delta S \right]^{\frac{S}{\delta S}}$$

Table 9a. Corrosion and Threshold Potentials (vs. SHE) Measured by LLNL & NRC.

Source	ID	T	T	NaCl	FeCl ₃	Cl ⁻	pH	E _{corr}	E _{pit} - low	E _{pit} - high	E _{pass}
		C	K	Wt. %	Wt. %	mol/kg		V vs. Ref.	V vs. Ref.	V vs. Ref.	V vs. Ref.
LLNL	090996C1	90	363	10.00	0	1.552	6.83	-0.154	0.312	0.312	0.42
LLNL	103397C1	90	363	1.00	0	0.155	2.69	-0.159	0.628	0.733	0.663
LLNL	102497C2	90	363	1.00	0	0.155	2.67	-0.162	0.628	0.785	0.611
LLNL	102797C1	90	363	5.00	0	0.776	2.69	-0.202	0.423	0.654	0.158
LLNL	081997C1	90	363	1.00	0	0.155	2.69	-0.145	0.59	0.687	0.638
LLNL	082697C2	60	333	5.00	0	0.776	6.53	-0.105	0.393	0.448	0.407
LLNL	110497C2	90	363	0.00	0.61	0.113	2.14	0.531	0.775	0.829	0.727
LLNL	103097C1	90	363	0.00	3.05	0.564	1.72	0.584	0.759	0.766	0.655
LLNL	103197C2	90	363	0.00	3.05	0.564	1.72	0.439	0.838	0.872	0.688
NRC	C22-1	95	368	25.78	0	4.000	8.2				0.916
NRC	C22-2	95	368	25.78	0	4.000	8.2				0.911
NRC	C22-3	95	368	25.78	0	4.000	8.2				0.9
NRC	C22-4	60	333	25.78	0	4.000	8.2				0.911
NRC	C22-5	95	368	6.44	0	1.000	8.2				0.829
NRC	C22-6	60	333	6.44	0	1.000	8.2				0.986
NRC	C22-7	95	368	0.18	0	0.028	8.2				0.854

Table 9b. Corrosion and Threshold Potentials (vs. SHE) Measured by LLNL & NRC.

ID	Reference	Correction	E _{corr}	E _{pit} - low	E _{pit} - high	E _{pass}	Comments
		V	V vs. SHE	V vs. SHE	V vs. SHE	V vs. SHE	
090996C1	Ag/AgCl/KCl	0.1297	-0.0243	0.4417	0.4417	0.5497	inconsistent
103397C1	Ag/AgCl/KCl	0.1297	-0.0293	0.7577	0.8627	0.7927	
102497C2	Ag/AgCl/KCl	0.1297	-0.0323	0.7577	0.9147	0.7407	
102797C1	Ag/AgCl/KCl	0.1297	-0.0723	0.5527	0.7837	0.2877	inconsistent
081997C1	Ag/AgCl/KCl	0.1297	-0.0153	0.7197	0.8167	0.7677	
082697C2	Ag/AgCl/KCl	0.1577	0.0527	0.5507	0.6057	0.5647	inconsistent
110497C2	Ag/AgCl/KCl	0.1297	0.6607	0.9047	0.9587	0.8567	
103097C1	Ag/AgCl/KCl	0.1297	0.7137	0.8887	0.8957	0.7847	
103197C2	Ag/AgCl/KCl	0.1297	0.5687	0.9677	1.0017	0.8177	
C22-1	SCE	0.1861				1.1021	
C22-2	SCE	0.1861				1.0971	
C22-3	SCE	0.1861				1.0861	
C22-4	SCE	0.2344				1.1454	
C22-5	SCE	0.1861				1.0151	
C22-6	SCE	0.2344				1.2204	
C22-7	SCE	0.1861				1.0401	

The pit generation rate, PGR, is then defined in terms of the time derivative of the elementary pitting probability:

$$\frac{d\bar{\omega}}{dt} = g = PGR$$

$$\bar{\omega} = \int_0^t (PGR) dt$$

We then make the following simplification by assuming that PGR is independent of time and that $\delta S \sim S$. While it would be better to avoid such gross over simplification, it does provide some degree of insight into the expected dependence of the survival probability, and the probability of pit initiation, on electrochemical potential. This insight is needed to address the question regarding probability of pitting.

$$P_s \approx 1 - PGR \times t \times S$$

The probability of pitting (localized corrosion, LC) is then assumed to be:

$$P_{LC} \approx PGR \times t \times S$$

It is observed empirically that:

$$\ln(PGR) \approx \beta (E - E_{pit})$$

Therefore:

$$\ln\left(\frac{P_{LC,1}}{P_{LC,2}}\right) \approx \ln\left(\frac{PGR_1}{PGR_2}\right) \approx \beta (E_1 - E_2)$$

We can estimate the empirical constant β as:

$$\beta = \frac{\ln(P_{LC,1}/P_{LC,2})}{(E_1 - E_2)}$$

Now, for illustration, consider a hypothetical case where the repassivation potential is assumed to be the point at which there is a 5% chance of initiating localized corrosion. Furthermore, assume that the average repassivation potential is 800 mV vs. SHE, and that the observed scatter around the average ± 50 mV. The probability of initiating localized corrosion at 800 mV vs. SHE is assumed to be 5%, and the probability of initiating localized corrosion at 800-50 mV vs. SHE is assumed to be 1%. In this case,

$$\beta = \frac{\ln(5/1)}{(800 \text{ mV} - 750 \text{ mV})} \approx 0.032 \text{ mV}^{-1}$$

The CDF based upon these simplification and assumptions are summarized in Table 10a, where the recommended case is Case 3. It should be noted that the maximum probability of pitting is believed to be less than a 15% (99th percentile, pH 2.5, 640 mV), with typical values of 0.01-2.12% (Table 10b).

Penetration Rates Due to Localized Corrosion

The expert assessments to date have provided two alternative ways to model localized corrosion of the inner barrier: a) “exponential” pit growth law, and b) “logarithmic” pit growth law: Exponential crevice growth law is expressed as follows:

$$p = B \times t^n$$

where p is the crevice depth, B is a constant, t is time, and n is an exponent. Distributions for the constants B and n have been provided. A crevice corrosion model suggested recently by LLNL belongs to this type ($n = \frac{1}{2}$ corresponding to a diffusion-controlled penetration rate). Logarithmic crevice growth law is expressed as follows:

$$p = k \times \exp\left[\frac{Q}{T}\right] \times \log[t] - x_0$$

where k, Q and x_0 are constants, T is temperature, and t is time. Distributions for the constants k, Q and x_0 have been provided.

While the logarithmic expression has some very attractive features, it has a severe inconsistency at zero time (undefined logarithm, $\log(0)$). Therefore, this member of the Panel prefers the exponential form. The penetration rates for localized corrosion shown in Tables 12 are based on Asphahani's data for Alloys C-22 and C-276, which are summarized in Tables 4 and 11, respectively. These data can also be found in Tables 22 and 23 of Gdowski's degradation mode survey, respectively [G. E. Gdowski, “Survey of Degradation Modes of Four Nickel-Chromium-Molybdenum Alloys,” UCRL-ID-108330, March, 1991, pp. 30-31]. Specific points used to generate Table 12 are in bold-face type. In the case of localized corrosion at 340 mV vs. SHE, it was assumed that the penetration rates were similar to those observed for Alloy C-22 in simulated crevice solutions (accelerated passive corrosion in 10 wt. % FeCl_3). In the case of localized corrosion at 640 mV vs. SHE, it was assumed that the penetration rates were similar to those observed for Alloy 625 (active crevice in 10 wt. % FeCl_3 and active pitting corrosion in “green death” solution). The apparent activation energy is assumed to be 20 kcal/mol, which is close to that observed for many chemical reactions. Note the rapid wall penetration predicted at high applied potential (640 mV vs. NHE) and low pH (2.5).

In regard to pit penetration rates, it must be noted that the current elicitation does not deal with the issue of “stiffling” which leads to the death or a propagating pit. It must be noted that the pit can “die” if the depth becomes so great that the current density at the base of the pit falls below the passive current density. The importance of such “stiffling” has also been pointed out by Scully [J. R. Scully, “Appendix D, Elicitation Interview Summaries,” Waste Package Degradation Expert Elicitation Project Final Report, K. J. Coppersmith, R. C. Perman, M. Pendleton, J. L. Younker, Civilian Radioactive Waste Management System Management and Operating Contractor, Geomatrix Consultants, San Francisco, CA, August 15, 1997, pp. JS 1-30]. In the case of pit propagation in carbon steel, Marsh gives the following criteria based upon the passive current density, i_{pass} [G. P. Marsh, K. J. Taylor, Z. Sooi, “The Kinetics of Pitting Corrosion of Carbon Steel,” SKB Technical

Report 88-09, Swedish Nuclear Fuel and Waste Management Company (SKB), Box 5864, S-102 48, Stockholm, 1988, 39 p.]:

$$\frac{i_{pass}}{4F} \leq D \left. \frac{\partial C(x,t)}{\partial x} \right|_{x=0}$$

It was noted that careful measurements of i_{pass} are required for any theoretical analysis. The critical concentration gradient across the pit is estimated to be:

$$\left. \frac{\Delta C}{\Delta x} \right|_{critical} \geq \frac{i_{pass}}{4FD}$$

A typical passive current density for Alloy C-22 determined with cyclic polarization is $\sim 10^{-6}$ A/cm². Given a typical liquid-phase diffusivity of $\sim 10^{-5}$ cm²/sec, and Faraday's constant of 9.64846×10^4 C/equiv ($\sim 10^5$ C/equiv), the critical concentration gradient across the pit is estimated to be $\sim 10^{-6}$ equiv/cm⁴. Since the maximum possible pit depth is 2 cm (wall thickness), a critical saturation concentration at the base of the pit is calculated to be $\sim 2 \times 10^{-6}$ equiv/cm³ ($\sim 6.67 \times 10^{-4}$ mol/kg for trivalent dissolved metal such as chromium). If any dissolved species at the base of the pit has a solubility less than this limiting value, the pit will die before wall penetration is achieved. From the Pourbaix diagram of chromium (calculated by Marcel Pourbaix), it can be seen that the estimated concentration of Cr₂O₃ is 10^{-11} to 10^{-12} mol/kg at saturation, whereas the estimated concentration of the more soluble Cr(OH)₃ is 10^{-6} to 10^{-7} mol/kg at saturation. Clearly, in either case, the pit will stifle (die) before a pit depth of 2 cm is achieved. Predicted pit depths greater than 2 cm are not realistic.

Table 10a. Estimated CDF Probabilities for Initiation of Localized Corrosion.

Case 1: P = 5% at E_{pass} & P = 1% at $E_{pass,low}$	Environment A	Environment B	Environment C
pH	2.5	2.5	5 to 7
E (mV vs. SHE)	340	640	340
β at 25°C	8.05×10^{-3}	8.05×10^{-3}	8.05×10^{-3}
β at 50°C	8.05×10^{-3}	8.05×10^{-3}	8.05×10^{-3}
β at 100°C	8.05×10^{-3}	8.05×10^{-3}	8.05×10^{-3}
P at 25°C	0.0368	0.4123	0.0074
P at 50°C	0.0824	0.9221	0.0165
P at 100°C	0.1843	2.0625	0.0368
Case 2: P = 50% at E_{pass} & P = 5% at $E_{pass,low}$	Environment A	Environment B	Environment C
pH	2.5	2.5	5 to 7
E (mV vs. SHE)	340	640	340
β at 25°C	1.15×10^{-2}	1.15×10^{-2}	1.15×10^{-2}
β at 50°C	1.15×10^{-2}	1.15×10^{-2}	1.15×10^{-2}
β at 100°C	1.15×10^{-2}	1.15×10^{-2}	1.15×10^{-2}
P at 25°C	0.0449	1.4148	0.0045
P at 50°C	0.1419	4.4684	0.0142
P at 100°C	0.4480	14.1120	0.0449
Case 3: P = 50% at E_{pass} & P = 1% at $E_{pass,low}$	Environment A	Environment B	Environment C
pH	2.5	2.5	5 to 7
E (mV vs. SHE)	340	640	340
β at 25°C	7.82×10^{-3}	7.82×10^{-3}	7.82×10^{-3}
β at 50°C	7.82×10^{-3}	7.82×10^{-3}	7.82×10^{-3}
β at 100°C	7.82×10^{-3}	7.82×10^{-3}	7.82×10^{-3}
P at 25°C	0.0424	0.4427	0.0089
P at 50°C	0.0927	0.9678	0.0194
P at 100°C	0.2026	2.1154	0.0424

Table 10b. Estimated CDF Probabilities (%) for Initiation of Localized Corrosion – Based on 10a.

Percentile (%)	A/25°C	A/50°C	A/100°C	B/25°C	B/50°C	B/100°C	C/25°C	C/50°C	C/100°C
1 (Case 1)	0.0368	0.0824	0.1843	0.4123	0.9221	2.0625	0.0074	0.0165	0.0368
5	0.0396	0.0876	0.1935	0.4275	0.9450	2.0890	0.0082	0.0180	0.0396
50 (Case 3)	0.0424	0.0927	0.2026	0.4427	0.9678	2.1154	0.0089	0.0194	0.0424
95	0.0437	0.1173	0.3253	1.1501	2.7181	8.1137	0.0067	0.0168	0.0437
99 (Case 2)	0.0449	0.1419	0.4480	1.4148	4.4684	14.1120	0.0045	0.0142	0.0449

Table 11. Observed Localized Corrosion Penetration Rates for Alloy 625.

Crevice Corrosion	Crevice Corrosion	Pitting Corrosion	Pitting Corrosion
25°C	50°C	25°C	102°C
10 wt. % FeCl ₃	10 wt. % FeCl ₃	7 vol. % H ₂ SO ₄ + 3 vol. % HCl + 1 wt. % FeCl ₃ + 1 wt. % CuCl ₂	7 vol. % H ₂ SO ₄ + 3 vol. % HCl + 1 wt. % FeCl ₃ + 1 wt. % CuCl ₂
38.1 microns/yr	3,150 microns/yr	7.62 microns/yr	48,060 microns/yr

Table 12. Estimates of the CDF's for Penetration Rate Parameters for Localized Corrosion.

pH=2.5							
E=340 mV							
Percentile	n	k (for n=1)	Ea	Q	Depth (1 yr; 25°C; n=1)	Depth (1 yr; 75°C; n=1)	Depth (1000 yr; 60°C; n=1)
%	none	microns/yr	cal/mol	K	microns	microns	cm
0	0	5.07×10^{12}	5000	2500	0.01	1.7	0.0461
1	0.1	7.99×10^{12}	10000	5000	0.02	2.6	0.0726
5	0.3	1.26×10^{13}	15000	7500	0.03	4.2	0.1148
50	0.5	3.83×10^{13}	20000	10000	0.10	12.7	0.3481
95	0.7	1.16×10^{14}	25000	12500	0.31	38.5	1.0550
99	0.9	9.37×10^{14}	30000	15000	2.50	310.4	8.5056
100	1	7.08×10^{15}	35000	17500	18.89	2345.1	64.2713
pH=2.5							
E=640 mV							
Percentile	n	k (for n=1)	Ea	Q	Depth (1 yr; 50°C; n=1)	Depth (1 yr; 102°C; n=1)	Depth (1000 yr; 60°C; n=1)
%	none	microns/yr	cal/mol	K	microns	microns	cm
0	0	2.42×10^{15}	5000	2500	87	6360	22
1	0.1	3.82×10^{15}	10000	5000	137	10018	35
5	0.3	6.04×10^{15}	15000	7500	217	15855	55
50	0.5	1.83×10^{16}	20000	10000	657	48060	166
95	0.7	5.55×10^{16}	25000	12500	1990	145677	504
99	0.9	8.79×10^{16}	30000	15000	3150	230555	798
100	1	6.64×10^{17}	35000	17500	23803	1742155	6031
pH=3-10							
E=340 mV							
Percentile	n	k (for n=1)	Ea	Q	Depth (1 yr; 25°C; n=1)	Depth (1 yr; 75°C; n=1)	Depth (1000 yr; 60°C; n=1)
%	none	microns/yr	cal/mol	K	microns	microns	cm
0	0	5.07×10^{12}	5000	2500	0.01	1.7	0.0461
1	0.1	7.99×10^{12}	10000	5000	0.02	2.6	0.0726
5	0.3	1.26×10^{13}	15000	7500	0.03	4.2	0.1148
50	0.5	3.83×10^{13}	20000	10000	0.10	12.7	0.3481
95	0.7	1.16×10^{14}	25000	12500	0.31	38.5	1.0550
99	0.9	9.37×10^{14}	30000	15000	2.50	310.4	8.5056
100	1	7.08×10^{15}	35000	17500	18.89	2345.1	64.2713

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