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Joseph Farmer
Daniel McCright

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Joseph Farmer & Daniel McCright
University of California, Lawrence Livermore National Laboratory
P.O. Box 808; 7000 East Avenue; Mail Stop L-352
Livermore, California 94550
Voice 510-423-6574; Fax 510-423-2086; E-mail farmer4@llnl.gov

Introduction

A key component of the Engineered Barrier System (EBS) being designed for containment of spent-fuel and high-level waste at the proposed geological repository at Yucca Mountain, Nevada is a two-layer canister. In this particular design, the inner barrier is made of a corrosion resistant material (CRM) such as Alloy 625 or C-22, while the outer barrier is made of a corrosion-allowance material (CAM) such as carbon steel or Monel 400. Initially, the containers will be hot and dry due to the heat generated by radioactive decay. However, the temperature will eventually drop to levels where both humid air and aqueous phase corrosion will be possible. As the outer barrier is penetrated, uniform corrosion of the CRM will be possible in exfoliated areas. The possibility for crevice formation between the CAM and CRM will also exist. In the case of either Alloy 625 or C-22, a crevice will have to form before significant penetration of the CRM can occur. Crevice corrosion of the CRMs has been well documented. Lillard and Scully have induced crevice corrosion in Alloy 625 during exposure to artificial sea water [1]. Jones and Wilde have prepared simulated crevice solutions of $FeCl_2$, $NiCl_2$ and $CrCl_3$, and measured substantial pH suppression [2]. Asphahani measured the dissolution rates of

Alloys 625 and C-22 in such artificial crevice solutions at various temperatures [3,4]. Others have observed no significant localized attack in less severe environments [5].

Uniform Corrosion

The corrosion current densities of Alloys 625 and C-22 have been determined as functions of temperature, pH, concentrations of NaCl and $FeCl_3$, and extent of aeration. The penetration rates were then calculated from values of the corrosion current densities, and analyzed by multiple variable linear regression, thereby establishing empirical expressions for the penetration rate.

Crevice Corrosion

Dissolution of the CAM wall will produce iron ions, whereas dissolution of the CRM wall will produce nickel and chromium ions. As discussed by Oldfield and Sutton, metal ions produced by anodic dissolution are assumed to undergo hydrolysis reactions, thereby suppressing the pH of the crevice solution [6]. The hydrolysis equilibrium constants can be found in the literature [6,7]. If solubility limits are exceeded, $Fe(OH)_2$, $Ni(OH)_2$, $Cr(OH)_3$ and $Mo(OH)_3$ precipitates are assumed to form.

Fluxes of ions in the crevice are calculated with the Nernst-Planck equation, which governs electromigration, diffusion, and convective transport [8]. The current density is then defined in terms of these fluxes. In cases with strong supporting electrolyte, the electromigration term can be ignored. Transient concentrations can be determined from the gradient of the flux. The concentration of dissolved iron is assumed to include Fe^{2+}, Fe^{3+}, $Fe(OH)^{+}$ and $Fe(OH)^{2+}$. Similar assumptions are made for other dissolved metals. The partial differential equations (PDEs) that describe the transport of such reactive species in the crevice can be solved numerically. Both the Crank-Nicholson and the 'explicit' methods have been used [9,10]. The assumed boundary conditions (BCs) imply that the concentrations of dissolved metals are zero at the crevice mouth (NFE), and that crevices are symmetric about a mirror plane where the flux is zero. The BCs for H^+ and dissolved O_2 are slightly different in that non-zero concentrations are assigned at the crevice mouth. The PDEs that define transient concentrations in the crevice require determination of the potential gradient, as well as the (apparent) homogeneous rates. First, the axial current density along the length of the crevice is calculated by integrating the wall current density. The electrode potential along the length of the crevice can then be calculated from the axial current density. This technique is similar to that employed in other models [11-13].

Pitting

A probabilistic model has been developed for pitting of the CRM in the harsh crevice environment. This model divides the container surface into a two-dimensional (2D) array of hypothetical cells, where probabilities for the transition from one pitting state to another can be assigned [14,15]. As described by Shibata [16,17], nucleation or death of a pit embryo is determined by comparing random numbers to an environment-dependent birth or death probability, respectively. After a pit embryo reaches a critical age, it is assumed to become a stable pit. This approach has already been explored for modeling pit initiation and growth on high-level waste containers by Henshall [18-20]. However, the Henshall model requires additional work to enable it to deal with important environmental parameters, such as pH. The probabilistic model presented here involves competitive adsorption of Cl^- and OH^-, which is consistent with the discussion by Strehblow [21]. This approach introduces the needed dependence on pH. 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. In the case of pit propagation in carbon steel, Marsh gives a criteria based upon the passive current density [22]. An equivalent deterministic model has been formulated which can also be used to predict the transients in vacancy, embryo, and stable pit density [14,15]. This model. gives results comparable to the probabilistic pitting model.

Semi-Empirical Models

The simplest model for predicting crevice corrosion of the inner barrier is semi-empirical. Data published by Asphahani [3,4] and compiled by Gdowski [23] has been used to establish such correlations for Alloys 625 and C-22 in simulated crevice solutions with 10 wt. % $FeCl_3$. Penetrations have been predicted for Alloys 625 and C-22 at several temperature levels between 20 and 100°C. After 10,000 years the predicted penetration of Alloy C-22 does not exceed the thickness of the inner barrier wall (2 cm).

Results

Concentration profiles inside the CAM-CRM crevice have been calculated, first during corrosive attack of the CAM wall, then during corrosive attack of the CRM wall. A peak is predicted in the iron concentration near the crevice mouth due to the combined effects of a potential that decays with increasing crevice depth, and the assumed BC of zero concentration at the crevice mouth. Calculations for corrosive attack of the CRM wall have also been performed. The predicted concentrations of dissolved metals rise sharply from zero at the crevice mouth to peak values inside the crevice. At large distances into the crevice, the predicted concentrations fall from the peak values to plateaus. Since H^+ is generated by the hydrolysis of dissolved metals, and since it is transported in a similar fashion, its predicted concentration profiles (not shown) track those of the dissolved metals. In general, the pH is found to approach an asymptotic value (pH~3). Such representative values can be used as input for predictive pitting models.

In simulations, the number of vacancies (unpitted area) decreases with time, while the number of stable pits increases. Initially, the number of pit embryos increases rapidly. The embryo density evenutally reaches a maximum and begins to fall at the point where the rate of embryo conversion to stable pits exceeds the rate of embryo births. The overall pit generation rate is proportional to the embryo density, and passes through a maximum. The effect of pH suppression and imposed potential on pitting of the CRM has also been simulated. The predicted rate of pit generation is enhanced by pH suppression, which is consistent with experimental observation. These models predict that the corrosion potential of the CAM provides some protection for the CRM within the crevice.

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References

1. Lillard, Scully, J. Electrochem. Soc. 141, 11 (1994) 3006-3015.
2. Jones, Wilde, Corr. Sci. 18 (1978) 631-643.
3. Haynes H-2002B (1987).
4. Asphahani, Matls. Perform. 19, 12 (1980) 33-43.
5. Hack, Matls. Perform. 22, 6 (1983) 24-30.
6. Oldfield, Sutton, Brit. Corr. J. 13, 1 (1978) 13-22.

7. Cotton, Wilkinson, Advanced Inorganic Chemistry, 5th Ed., John Wiley & Sons (1988) 679-755.

8. Newman, Electrochemical Systems, 2nd Ed., Prentice Hall (1991).

9. Jenson, Jeffreys, Mathematical Methods in Chemical Engineering, Academic Press (1963) 410-422.

10. McCracken, Dorn, Numerical Methods and Fortran Programming with Applications in Science and Engineering, John Wiley and Sons (1964) 377-385.

11. Gartland, Corrosion 97, Paper No. 417, NACE (1997) 17 p.

12. Xu, Pickering, J. Electrochem. Soc. 140, 3 (1993) 658-668.

13. Nystrom, Lee, Sagues, Pickering, J. Electrochem. Soc. 141, 2 (1994) 358-361.

14. Farmer, McCright, U. California, LLNL, UCRL-JC-127980, Part 1 (1997).

15. Farmer, UCRL-JC-127980, Part 2 (1997).

16. Shibata, Takeyama, Corr. 33, 7 (1977) 243-251.

17. Shibata, Corr. 52, 11 (1996) 813.

18. Henshall, J. Nucl. Matls., 195 (1992) 109-125.

19. Henshall, Matls. Res. Soc. Symp. 353 (1995) 679-686.

20. Henshall, UCRL-ID-125300 (1996).

21. Strehblow, in Corrosion Mechanisms in Theory and Practice, Marcus, Oudar, Eds., Marcel Decker (1995) 201-237.

22. Marsh, Taylor, Sooi, Technical Report 88-09, SKB, Stockholm (1988).

23. Gdowski, UCRL-ID-108330 (1991).

Technical Information Department • **Lawrence Livermore National Laboratory**
University of California • Livermore, California 94551