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Mr. K. C. Chang
Mail Stop 623-SS
U. S. Nuclear Regulatory Commission
Washington, DC 20555

Dear Kien:

Services Rendered on High Level Waste Repository Performance Assessment Development: 4-18-87/5-1-87

During this period I have carried out a number of efforts that I will describe briefly in this report. The critique of the Aerospace Methodology Demonstration Report was considered in detail and a formal rebuttal prepared. A brief rebuttal of some of the main points was provided to you in the form a memorandum. The detailed rebuttal was provided to Ken Stephens for incorporation in the letter that he sent to you.

I have reviewed the Aerospace Methodology Demonstration Report with the view of making those changes that would be required in order to incorporate, as an appendix, the report on the procedures developed to include discrete and external events in the methodology. The draft report has been annotated so that these changes can be included in the final version.

The development of an approach to pitting corrosion that can be used in the methodology has occupied the majority of my time. The reported studies that have been carried out by Bertocci and his coworkers[1] at NBS, by Viswanathan and coworkers[2] at BNL, and by Marsh and coworkers[3] at AERE, Harwell have been very valuable in providing additional insight into the features that a useful approach should be able to reproduce. The salient features that

1 Ugo Bertocci et al, "A Statistical Analysis of the Fluctuations of the Passive Current", National Bureau of Standards. Undated Report

2 M. Viswanathan et al, "Dissolution of Iron Within Artificial Pits" BNL 38075 Informal Report August 1985

3 G. P. Marsh et al, "Evaluation of the Localised Corrosion of Carbon Steel Overpacks for Nuclear Waste Disposal in Granite Environments" in Scientific Basis for Nuclear Waste Management IX, Lars O. Werme, ed Materials Research Society Symposia Proceedings 50 (1986) 421-428

are apparent are that for pitting that exhibits the characteristic of having a large depth to diameter ratio, the rate of growth of the pit depth should have a square root of time dependence. This comes about because the controlling process in this case is diffusion of some critical product out of the pit. Marsh and coworkers show this phenomenon very clearly in the case of low carbon steel in a carbonate solution. Their experiments were carried out for up to 10,000 hours. Similarly Viswanathan and coworkers examine the pitting of an iron 16% chromium steel in two different concentrated salt solutions and observe a similar behavior. They assumed a model based on one-dimensional diffusion, and their experimental results showed the expected time behavior. The studies of Bertocci and coworkers were designed to provide information that could lead to a stochastic model of the onset of pitting based on the observation of current spikes in an electrochemical experiment. Such spikes are thought to be indicative of protective film breakdown and repassivation. It is conjectured that a continuously growing pit will eventually occur or that the surface will become completely passive with no current flowing. The observations and analyses indicated that the processes were very complex and that no simple statistical explanation of the observed current spikes was valid.

I have made use of these observations to modify the original Aerospace Statistical approach to pitting. The modification is very approximate at this point, but may have some usefulness. The assumptions of the approach are that the maximum rate of pit growth is determined by the diffusion of a product from the bottom of the pit, that the number of pits having the maximum rate of growth is very small compared to the total number of pits, and that failure of a container is defined by a specific number of pits penetrating the container. A further implicit assumption of the approach is that several different mechanisms make contributions to the pitting process that are essentialy stochastic. As a result the distribution of growth rates (or pit depths measured at a specific point in time) can be described as an exponential function. This latter assumption follows from the data of Marsh and coworkers.

Applying diffusion as a rate controlling mechanism to the simplest approximation of the original statistical approach leads to the following form:

$$t = \frac{D^2 \rho \ \ln(m/l) \ \exp[k/(T-T_o)]}{2 \ C_s \ W \ D^*}$$

Where; D = thickness of the container (centimeters)
m = the total number of pits assuming an exponential distribution
l = the number of pits resulting in container failure
k = a constant
T = temperature (degrees Kelvin)
ρ = density of the container (g/cm^2)
W = atomic weight of container material (g/mole)
D^*= diffusion coefficient at 20 C (cm^2/s)
C_s= saturation concentration of diffusing species ($moles/cm^3$)

This formulation is not very satisfying because the time dependent temperature is not deirectly accounted for. Also the saturation concentration of the diffusing species is likely to be temperature dependent as well. Futhermore, the procedure that was use to arrive at the equation assumed a constant lambda when in fact it should be a function of the maximum rate which is dependent on the depth of the pit and the temperature dependent diffusion coefficient. A much better approximation is being developed.

In actual calculations the rate equation would be integrated numerically until the container fails at time "t_{fail}". In this way both temperature dependent parameters could be treated appropriately. Several of these parameters would be random variables in a Monte Carlo calculation, but that would be the subject of a more extensive treatment. Here I will confine the analysis to carrying out a sample calculation for the case of constant temperature, a low carbon steel container and assuming that the diffusing species is H_2. This result is based on the pit depth distribution function given by Marsh and coworkers for data taken at 10,000 hours. The result is that failure would occur in about 336 years if the criterion for failure is the presence of 2000 penetrating pits. This result is compatible with the results calculated in the Demonstration Report. In the latter case the maximum rate of penetration was assumed to be constant, whereas this result accounts for the decrease in rate as the pit becomes deeper. Also the present result is based on much better experimental data as well as a mechanism that has both a theoretical and experimental basis. Although the result should not be taken too seriously, it does illustrate the value of accounting for the mechanism that is expected to control a particular process.

Marsh and his coworkers carried out an analysis of their results that led to the prediction that in order to achieve a container lifetime of 1000 years the container thickness would have to be 20 cm. This result was achieved by applying extreme value statistics to the pit depth distributions that they measured at different times up to 10,000 hours. This provided them an estimate for the probable maximum pit depth. These depths when plotted as a function of time led to the equation:

$$D = 8.35\ t^{0.46}$$

where D is the maximum pit depth in millimeters and t is time in years. This procedure amounts to equating failure to the penetration of a single pit anywhere in the container. This is an unreasonably severe criterion. Furthermore Marsh and coworkers do not include the possibility that there is some maximum possible rate based on a definite mechanism. The equation itself, which has a high correlation coefficient, is in excellent agreement with the diffusion limited process. Marsh and coworkers attempted to model the process using equilibrium thermodynamics. Their model predicted a constant rate that was a factor of 10^4 greater that the early time rate (maximum rate) measured in their experiments. Including a statistical method of accounting for the requirement that there is some minimum number of pits that must penetrate and applying a mechanistic approach to the expected rate, as has been done approximately here, seems to be more appropriate. For an 8 cm thick container their equation would predict failure in 136 years.

There are other processes that may have a significant impact on the pitting mechanism. In particular, the absorption of H_2 by iron could modify the rate by providing a second mechanism by which it could be removed. Also the solubility of H_2 in water obeys Henry's law and, consequently, in the Basalt environment the saturated concentration would be higher by an order of magnitude and this in turn would lead to a reduction of the failure time calculated above. As Marsh and coworkers point out the presence of iron hydroxide in the pit would reduce the flux of corrosion products from the pit and would reduce the pit growth rate. Finally if the conductivity of the solution in the pit falls to a sufficiently low value, growth could be halted in favor of production of a new pit at the surface. None of these processes have been studied quantitatively.

I anticipate completing a draft report that addresses both uniform and localized corrosion within the next two weeks. This report will not be inclusive but will consider both iron and copper in basalt and copper and stainless steel in tuff.

I am enclosing three (3) copies of the Voucher for Professional Services for your approval. I am also including a Claim for Reimbursement for Expenditures on Official Business.

If you have any questions please call me at any time.

Sincerely;

Robert

Robert B. Moler