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National Bureau of Standards
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Docket No.
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Wick
(Return to WM, 623-SS)

Mr. Everett A. Wick
Division of Waste Management
Office of Nuclear Materials Safety and Safeguards
U.S. Nuclear Regulatory Commission
Washington, DC 20555

Dear Mr. Wick:

Enclosed is our reply to your June 3, 1987 request for general technical assistance, rendered under Task 4 of FIN-A-4171-6, on the topic "Pitting Corrosion Modeling" by Robert B. Moler.

Technical content of this paper is lacking. In its present form, it is not an adequate summary of pitting modeling. The paper should begin with a more comprehensive review of the phenomena of pitting corrosion. All other sections except the final could benefit from including more references, more information and more basic considerations regarding pitting corrosion.

A summary or preferably an abstract is needed, so as to state the purpose of the document and to give conclusions. Other suggestions are given in the attached comments which were prepared by Dr. A. Fraker. These comments represent the views of Drs. U. Bertocci, A. Fraker, W. Liggett, and R. Ricker. These reviewers and I could interact with Mr. Moler, if you feel that this would serve your interests.

Sincerely,

Charles G. Interrante

Charles G. Interrante
Program Manager
Corrosion and Wear Group
Metallurgy Division

Enclosure

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Comments on "Pitting Corrosion Modeling" by Dr. Robert B. Moler, Consultant to the NRC

This paper on pitting corrosion modeling consists of sections including an introduction, an experimental studies review, theoretical considerations and the final section and main thrust of the paper, combined statistical and mechanistic approach to pitting.

The approach presented in the final section relies on two basic assumptions; that the mechanism controlling pit depth is one of diffusion and that the probability that a given pit has a given penetration rate is described by an exponential distribution of the rate. Other parameters considered are as follows: number of penetrations (ℓ) that define a container failure time (t_f), number of pits per unit area (n), depth of penetration (D), rate of growth (R), rate constant (K), saturation concentration (C_s), and lambda. Both the time t_n and lambda must be derived from the data.

Initiation of pitting is an electrochemical process in which breakdown occurs at discrete sites (voids, impurities, film weak spots, etc.) in a passive surface film. The onset of pitting may occur immediately on exposure, or after an incubation time.

The analysis of pit growth given in the introduction is not totally correct. Pit growth is controlled by a number of factors including the electrode potential difference between the bottom of the pit (anode) and the remaining surface of the material (cathode), the relation of the anode surface area to the cathode surface area, the diffusion of metal ions, the solution pH within the pit, all aspects of the solution concentration within the pit, etc. The solution pH and various aspects of the solution concentration within the pit will be dependent on diffusion, the nature of the corrosion products formed, the depth of the pit, etc.

Due to the factors influencing pit growth given in the above paragraph, the assumption that there is a maximum rate of pitting, which will remain constant over time, probably is not correct. There are too many variables to make this assumption.

The discussion of the work of Marsh and coworkers, which stated that pits overlapped and that the material was undergoing a form of "quasi" uniform corrosion, may benefit from some reference to ASTM G46-76. This "Standard Recommended Practice for Examination and Evaluation of Pitting Corrosion" is simple and gives one method of assessing pits, as the pitting factor, which is equal to the deepest metal penetration divided by the average metal penetration. A pitting factor of one indicates that the material is undergoing uniform corrosion, and as the pitting factor increases, the pits become deeper.

Some discussion was given of observations of Viswanathan, et.al. (Isaacs as consultant) who used a one-dimensional diffusion model of mass transfer; his model and experimental data differ by a factor of four. Another observation of Viswanathan was discussed, and this related to the formation of hydrogen in the pits. It was not clear why the production of hydrogen was thermodynamically impossible in the pit. This may not be a correct assumption. The concentrations of various ions, especially hydrogen, influence pit growth. The authors discussion on the role of hydrogen was not clear.

The work of Bertocci was discussed. This work deals with statistics of localized breakdown of a passive metal surface and uses electrical "noise" measurements (currents) which are analyzed both in the frequency and in the time domain. Frequency spectra are caused by a kind of shot noise. Current fluctions in the time domain indicate complicated statistical processes and cannot be described in terms of Poisson processes. Rapid current spikes are detected in the induction period prior to the onset of stable pits. These current measurements and statistical analyses are in the early stages and show potential for more accurately determining conditions for the iniation of pitting.

The approach given in the last section of the paper relies on a diffusion mechanism and the probability that a given pit has a given penetration rate up to a maximum rate which is described by an exponential distribution of that rate. This approach, as indicated in paragraphs 3, 4 and others above is oversimplified.