**The Influence of Radiation on Pit Solution Chemistry as it Pertains to the
Transition from Metastable to Stable Pitting in Steels**

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1. Research Objectives

The overall goal of this proposed research is to develop more effective and innovative methods for solving corrosion problems in waste storage tanks. We will accomplish this goal by establishing a science base for understanding the influence of irradiation and solution chemistry on metastable pit initiation and stabilization. This base will allow the formulation of more effective corrosion mitigation strategies in current tanks, the development of materials selection criteria for the deployment of future remediation technologies, and broaden the understanding of data currently being collected by in-tank corrosion probes currently in use at the sites.

2. Research Progress and Implications

This project began in FY '02. Since then substantial contributions have been made toward understanding the influence of γ radiation on corrosion electrochemistry in waste storage tanks as well as understanding the fundamental processes that produce the EN data generated with the Hanford/SRS corrosion probe.

Project focus for the FY '02-'04 was on the alkaline pH / carbon steel tank systems used at Hanford and SRS. Specific milestones for the project during FY '02- '04 were 1) identify specific relationships between metastable pitting activity (EN) and pitting damage on electrode surfaces, 2) identify the influence of ionizing radiation on electrochemical parameters such as pitting potential and metastable pitting (EN) activity, 3) characterize the influence of ionizing radiation on the local solution chemistry that develops at incipient pit sites. In this section we will summarize the progress made on each of these milestones.

Prior to this project, many methods (noise resistance, localization index, pitting function skew/kurtosis, etc.) had been proposed for correlating EN data with pitting activity.^{20,21} However, none was universal accepted and, more importantly, no clear relationship between pitting damage (i.e. pit depth) and any of these methods had been established. In our work, we have demonstrated that there is statistical relationship between charge passed per EN event and physical damage on the electrode surface. In this method we integrate the charge passed per event from the current time record in the EN data (Figure 2-1). Below a given threshold in charge the event is disregarded. Above this threshold the event is tabulated. The resulting probability distribution function (Figure 2-2) is then analyzed using extreme value statistics. Here, we used the generalized version (GEV) which combines the Type I (Gumbel), II (Frechet), III (Weibull) distributions.²² The fit to the GEV cumulative distribution function (CDF) is shown in Figure 2-3. Relative differences in materials pitting susceptibility are associated with different probabilities to achieve a specific charge passed. For example, 90% of the events on A537 are 8×10^{-5} C while on A516 the 90% threshold occurs at 2×10^{-4} C. Therefore, one would predict from this method that the physical damage on the electrode surface would be greater on A 516 as compared to A537. This prediction was verified by measuring actual pit depths on the samples after the experiment (Figure 2-4) and fitting the subsequent data to the GEV. As seen in Figure 2-5 the, CDF for pit depths measure on the samples after the exposure, the probability of finding a deeper pit on A516 is greater than it is of finding one on A537. As it relates to the EN probe being used at Hanford and SRS, there is a one-to-one correlation between our method for analyzing the current time data collected with these probes and pitting damage on the electrode surface. Thus, using our method it will be possible to determine from EN data the impact of

Figure 2-1 Current/Potential time record for carbon steel A537 in a simulated alkaline waste solution at 40° C. Data were collected using three identical electrodes. In this set-up a zero resistance ammeter is placed between two of the electrodes and the third is used as a pseudo-reference electrode.

Figure 2-2 Charge passed distribution for electrochemical noise experiments on several carbon steels in an alkaline simulated waste solution at 40°C.

Figure 2-3 The cdf for A516, A537, and A516N as a function of charge passed in electrochemical noise experiments (from data presented in Fig. 2-2).

Figure 2-4 Pit depth distribution for mild steels exposed to simulated waste solution in electrochemical noise experiments. Data were collected after EN experiments in Fig. 2-2.

Figure 2-5 The cdf for A516, A537, and A516N as a function of pit depth in electrochemical noise experiments. Data from experiment described in Fig. 2-3.

chemistry changes (pH, inhibitor additions, dilutions, etc.) on tank pitting susceptibility in real time.

With respect to the influence of ionizing radiation, to achieve our ultimate goal of correlating changes in solution chemistry at incipient pit sites with radiation dose we identified two separate tasks: what is the influence of ionizing radiation on electrochemical parameters such as pitting potential and metastable pitting (EN) activity and how does it influence local solution chemistry that develops at incipient pit sites. Potentiodynamic polarization curves generated on carbon steels in simulated tank solutions at the UF radiation chemistry facility show marked differences in the electrochemical noise with and without radiation. Specifically a decrease in the pitting potential for carbon steels in a simulated waste solution is observed during γ irradiation (Table 2-1). Consistent with this observation, a decrease in repassivation potential is also observed for polarization curves run during irradiation. Further, an increase in surface damage from long duration metastable pitting events (EN) is measured during irradiation (Table 2-1 SDP/LDP¹ and Figures 2-6a and 2-6b). The implication of these results is that radiation promotes the transition from metastable to stable pitting. Within the context of local solution chemistry at corrosion initiation sites, one would conclude that γ radiation influences dissolution kinetics within the metastable pits, for example by changing the metal hydrolysis reactions. A systematic study of the radiolytic effects on the hydrolysis and transport reactions inside the metastable pit might provide explanations for these observations. Thus far no investigation of the influence of γ -radiation on the transition from metastable to stable pitting or pit solution development and hydrolysis reactions has been undertaken.

¹ SDP: short duration pulse, an EN event lasting < 20 s. LDP: long duration pulse, an EN event lasting > 20 s.

Figure 2-6a Histogram of charge passed during metastable pitting events for carbon steel A516 in an alkaline simulated waste solution during γ radiation. Data represents the accumulated values of SDP and LDP events observed during potentiostatic holds from six separate metal coupon experiments.

Figure 2-6b Histogram of charge passed during metastable pitting events for carbon steel A516 in an alkaline simulated waste solution in the absence of radiation. Data represents the accumulated values of SDP and LDP events observed during potentiostatic holds from six separate metal coupon experiments.

In the final year of this program (FY '04) we have begun to analyze the influence of γ radiation on pit solution chemistry. We are doing this with an artificial pit assembly and ion chromatography with the aim of detecting and quantifying metal ions in corrosion products of carbon steels. We have designed an artificial pit working electrode in which the starting pit volume is about 1.4 micro-liter. An exploded view of this assembly is shown in Figure 2-7 and a front view, after assembly, is shown in Figure 2-8. In an exploratory experiment we showed that detectable quantities of Fe^{3+} and Mn^{2+} could be identified after a series of potentiostatic (PS) holds were made. Component parts of this assembly have been cast and fabricated. The artificial pit electrode will serve as the working electrode in the usual three-electrode experimental set-up. A primary objective of these experiments is to test the effect on pitting of limited (confined) electrolyte volume at the carbon steel surface for different applied potentials (AP), with and without a radiation field at 40°C.

Table 2-1 Summary of potentiodynamic polarization data taken at the UF Radiation Chemistry Lab. Data with and without γ radiation are presented. Each data set represents the average of six separate experiments.

	In Radiation Field	Without Radiation Field
OCP (V)	-0.41 ± 0.90	-0.30 ± 0.03
I_{corr} (A/cm ²)	$5.2 \pm 1.1 \times 10^{-7}$	$2.3 \pm 1.6 \times 10^{-7}$
I_{pass} (A/cm ²)	$1.7 \pm 0.3 \times 10^{-6}$	$5.9 \pm 2.6 \times 10^{-7}$
E_{pit} (V)	0.44 ± 0.12	0.46 ± 0.06
E_{tp} (V)	-0.73 ± 0.20	-0.70 ± 0.16
SDP/LDP	5.1	2.5

Figure 2-7 “Artificial Pit” assembly: slit dimension approximately 0.22 cm^2 , electroplating tape thickness is 0.0064 cm . A – plastic hemi-cylindrical cover; B – electroplating tape with lower slit applied to coupon; C – plastic hemi-cylinder with embedded coupon and insulated electrical wire attachment through top; D – Teflon rings for clamping hemi-cylinders together.

Figure 2- 8 Front view of working “Artificial Pit” electrode. Coupon embedded in hemi-cylindrical epoxy mold with electroplating tape over-lay (dark portion) showing slit and exposed (dotted area) coupon area. A - electrical wire attachment; B – embedded coupon; C- corrosion tape overlay/ mask; D – electrolyte solution access; E – exposed coupon area (dotted area).

4. Planned Activities - Subject to renewal.

If renewed, the largest thrust area of program will be solution chemistry analysis. That is, the influence of γ -radiation on hydrolysis reactions and *in situ* metal oxidation. As we have discussed above, considerable progress has already been done in this area. Future work will focus on the speciation and concentration of pit solution constituents (such as Cr^{+3} , Fe^{+2} , H_3O^+ etc...) as a function of γ -irradiation. To accomplish this the cell described above will be used to create the critical pitting solution such that ion chromatography may be used to quantify the species in solution. In these experiments, the artificial pit electrode will be anodically dissolved such that a critical pitting solution will develop between the two slides similar to that created in a natural pit. This arrangement will also provide an environment for electrochemical testing and a sufficiently small volume for spectroscopic examination of the pitting solution following irradiation. The data from these experiments will be used in conjunction with the metastable pitting data and model predictions of pit solution development to determine the species that are both critical to the incipient pit chemistry and which also participate in the water radiolysis scavenger reactions.

With respect to the metastable pitting studies, work thus far has focused on the behavior of carbon steels in alkaline waste environments. If renewed, in the next stage we will examine metastable pitting (EN) associated with austenitic stainless steels in simulated acid-chloride waste solutions. Initial studies indicate that there are relationships between metastable pitting activity and parameters such as solution composition and applied potential. For SS 316L in a $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{NaCl}$ solution each current time record is associated with a low frequency (0.4 Hz) noise signal, however, above 0.75 V SCE an additional high frequency component (> 1 Hz) is also observed. Thus, we hope to answer why does this transition occur? Is this associated with an instability in the passive film or, rather, a change in solution chemistry at the incipient pit site? What is the influence of radiation on this transition?

5. Information Access

During the 2.5 yrs of funding we have received from DOE-EMSP we have published one manuscript on water radiolysis reactions and submitted an additional two manuscripts for publication all in peer reviewed journals. Currently we are in the process of preparing a fourth publication:

- 1) R.S. Lillard, "The Influence of Water Radiolysis Products on Passive Film Formation and Reduction in a Mixed Radiation Environment," *Corrosion Engineering Science and Technology*, vol. 38, no. 3, pg. 173, 2003.
- 2) M.A. Hill, R.S. Lillard, "Accelerated Methods for Predicting Carbon Steel Lifetimes in Alkaline High Level Radioactive Waste Tanks," submitted to *Corrosion*, 2003.
- 3) C.A. McCall, R.S. Lillard, "Pitting Corrosion of Stainless Steel 316L in Simulated Acid-Chloride High Level Radioactive Waste," submitted to *Corrosion Engineering Science and Technology*, 2004.
- 4) B. Galuszka-Muga, R.J. Hanhraham, M.A. Hill, R.S. Lillard, , "The Influence of Gamma Radiation on Pitting Corrosion of Carbon Steels Alkaline High Level Radioactive Waste Tanks," in preparation.

6. *Optional Additional Information - Student Funding*

Post doctoral students funded under this program include:

- 1) Dr. Carol A. McCall, Materials Corrosion and Environmental Effects Lab, Materials Science and Technology Division, Los Alamos National Laboratory.
- 2) Dr. Basia, Galuszka-Muga, Radiation Chemistry Laboratory, Dept. of Chemistry, University of Florida.