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

FY 2005 End of Year Report

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1. Research Objective

The overall goal of this program 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 pit propagation.

Since the inception of this program 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 metastable pitting i.e. the electrochemical noise data generated with the Hanford/SRS corrosion probe. Project focus for the FY'05 was on the alkaline pH / carbon steel tank systems used at Hanford and SRS. Also beginning in FY '05, INEEL tank chemistry and materials will be evaluate using methods established in this program as well as new approaches including the influence of the passive film. To accomplish these goals a full-time Graduate Research Assistant has joined the program at LANL. This student is pursuing their PhD (WSU). These planned activities are also discussed below

2. Research Progress and Implications

Specific milestones for the project during FY '05 were 1) identify specific relationships between metastable pitting activity (electrochemical noise, EN) and pitting damage on electrode surfaces, 2) identify the influence of ionizing radiation on electrochemical parameters such as pitting potential and metastable pitting 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.[1,2] 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)[3] which combines the Type I (Gumbel), II (Frechet), III (Weibull) distributions. 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

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[1] GL. Edgemon, "Tank 241-AZ-101 Prototype Corrosion Probe: Two Year Status Report," Lockhead Martin Hanford Corportation, report #HNF-3416, September, 1998.

[2] S. Reid, G.E.C. Bell, G.L. Edgemon, "The use of Skew and Kurtosis and Neural Networks for Determining Corrosion Mechanisms from EN Data,", Corrosion/98, paper #176, NACE, Houston, 1998.

[3] P.J. Laycock, R.A. Cottis, P.A. Scarf, Journal of the Electrochemical Society, **137**, 64, 1990.

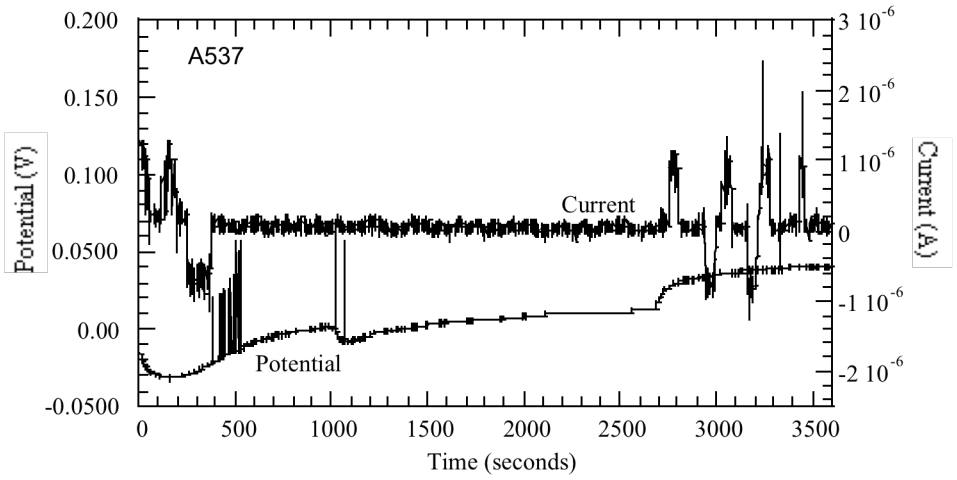

Figure 2-1 Current/Potential time record for carbon steel A537 in a simulated alkaline waste solution at 40º C. Data were collected using three identical electrodes. In this set-up a zero resistance ammeter is placed between two of the electrodes and the third is used as a pseudo-reference electrode.

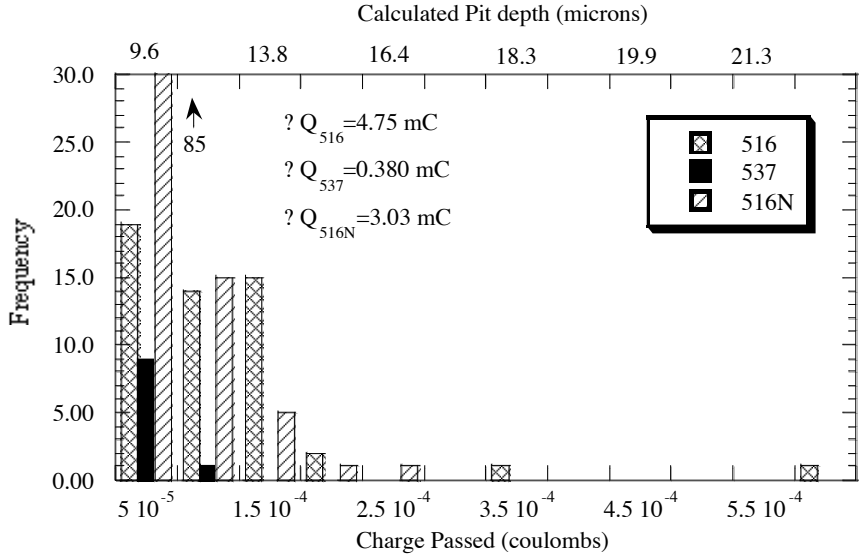

Figure 2-2 Charge passed distribution for electrochemical noise experiments on several carbon steels in an alkaline simulated waste solution at 40ºC.

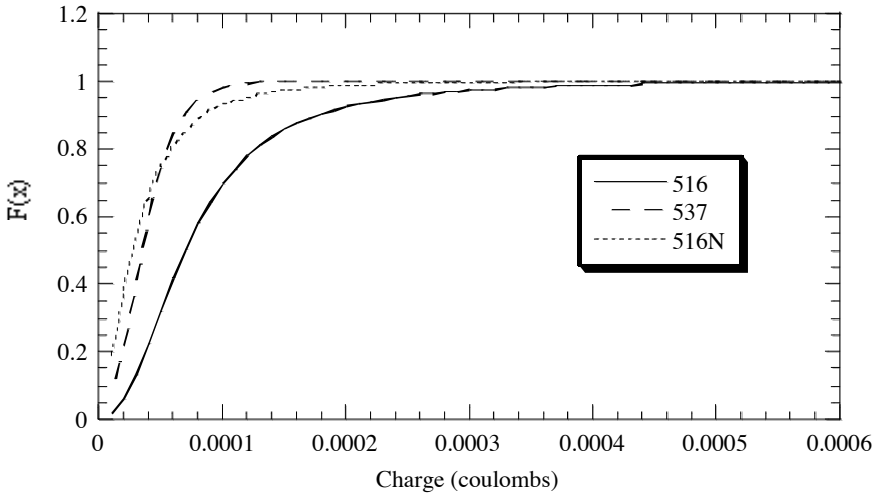

Figure 2-3 The cdf for A516, A537, and A516N as a function of charge passed in electrochemical noise experiments (from data presented in Fig. 2-1).

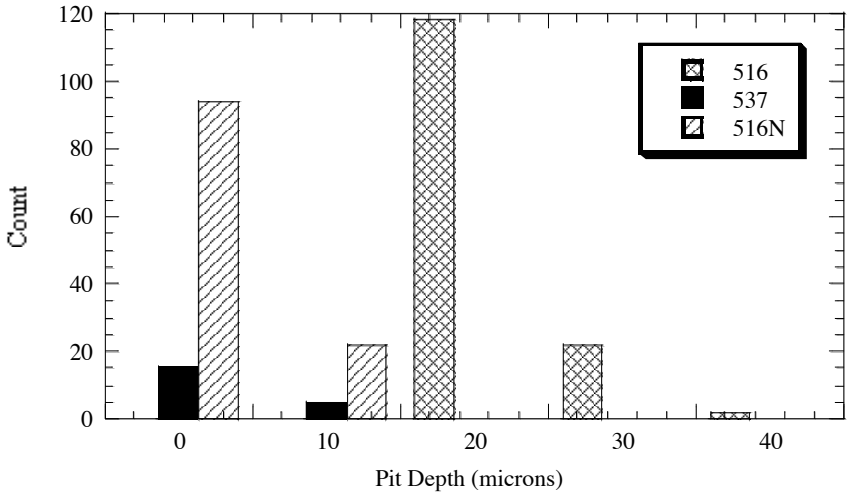

Figure 2-4 Pit depth distribution for mild steels exposed to simulated waste solution in electrochemical noise experiments. Data were collected after EN experiments (Fig. 2-2).

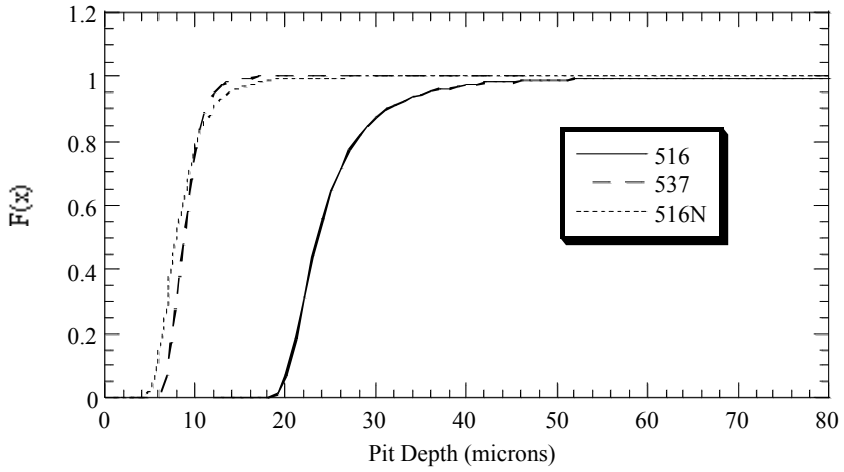

Figure 2-5 The CDF for A516, A537, and A516N as a function of pit depth in electrochemical noise experiments. Data from experiment described in Fig. 2-4.

$2x10^{-4}$ 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 pit depths on the samples after the experiment (Figure 2-4). These data were then fit using the GEV method. 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 chemistry changes (pH, inhibitor additions, dilutions, etc.) on tank pitting susceptibility in real time.

With respect to the influence of ionizing radiation, to correlate changes in solution chemistry at incipient pit sites with radiation dose we identified two separate tasks: 1) what is the influence of ionizing radiation on electrochemical parameters such as pitting potential and metastable pitting (EN) activity and 2) 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. We have also tabulated charge passed during EN events and pit depths for both irradiated and non-irradiated samples (2-6a and b.) The fit to the GEV CDF for pit depth is shown in Figure 2-7. Relative differences in pitting susceptibility between irradiated and no-irradiated samples are clearly evident in this figure.

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.

To explain the observed difference between irradiated and non-irradiated samples we have analyzed 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 2-8 and a front view, after assembly, is shown in Figure 2-9. In our initial experiments we show that detectable quantities of Fe^{2+}, Fe^{3+}, and Cl^- could be identified after a series of potentiostatic (PS) holds were made (Table 2-2). These species were identified using a specially developed crevice washing technique and ion chromatography of this solution. Iron(III) is of interest as it may help to lower incipient pit pH increasing the probability of it transition to a stable propagating pit. Initially, only Cl^- concentrations appear to be greater within the artificial pit of the irradiated samples. Similar to a decrease in pH, increased Cl^- concentration will also promote the autocatalytic reactions at an incipient pit The ultimate 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.

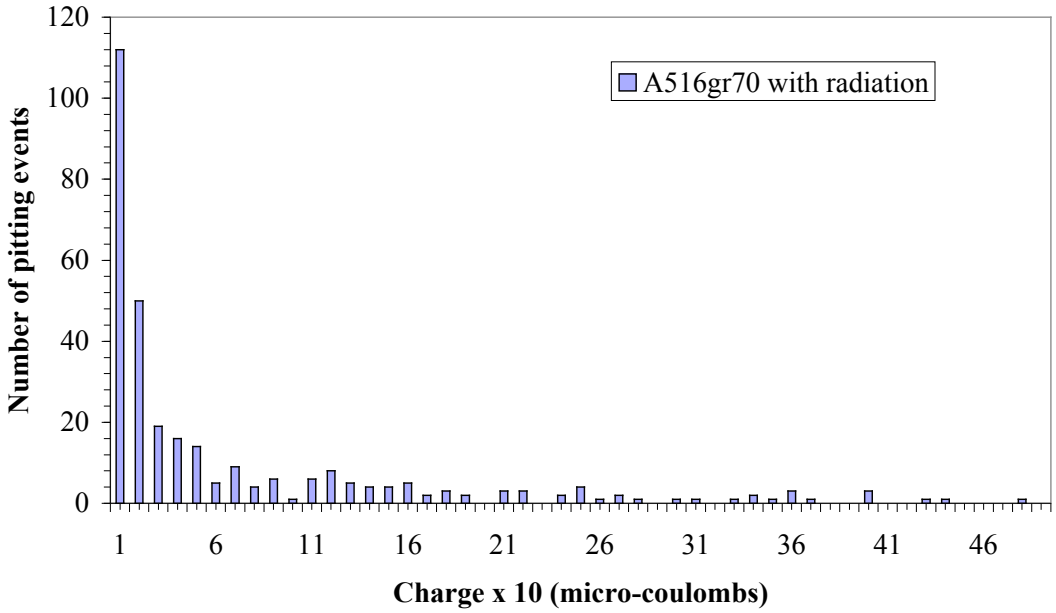

Figure 2-6a Histogram of charge passed during metastable pitting events for carbon steel A516 in an alkaline simulated waste solution during γ radiation. Data represents the accumulated values of SDP and LDP events observed during potentiostatic holds from six separate metal coupon experiments.

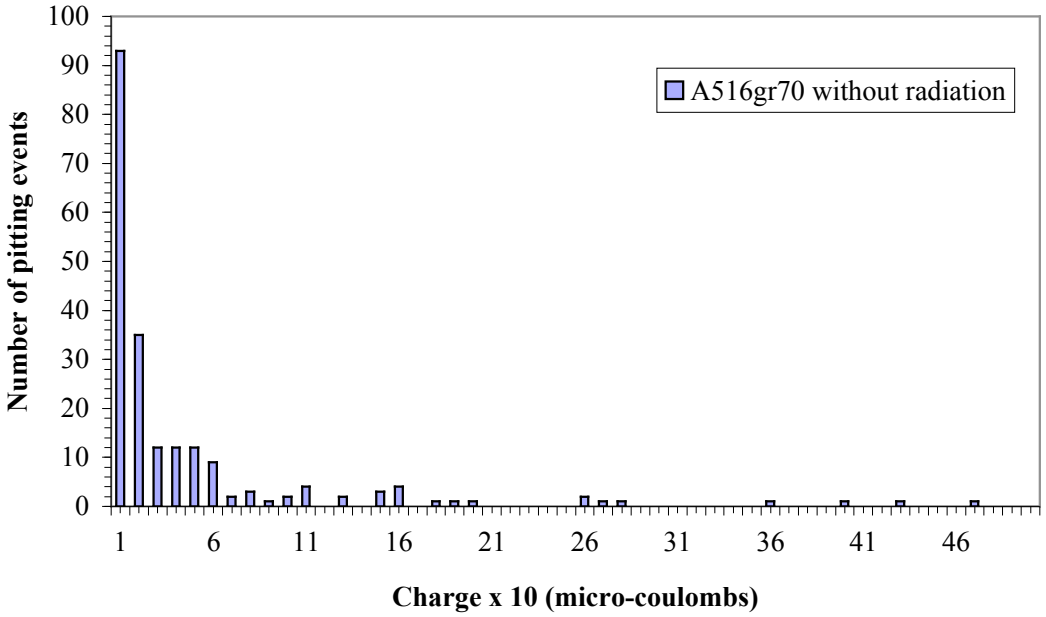

Figure 2-6b Histogram of charge passed during metastable pitting events for carbon steel A516 in an alkaline simulated waste solution in the absence of radiation. Data represents the accumulated values of SDP and LDP events observed during potentiostatic holds from six separate metal coupon experiments.

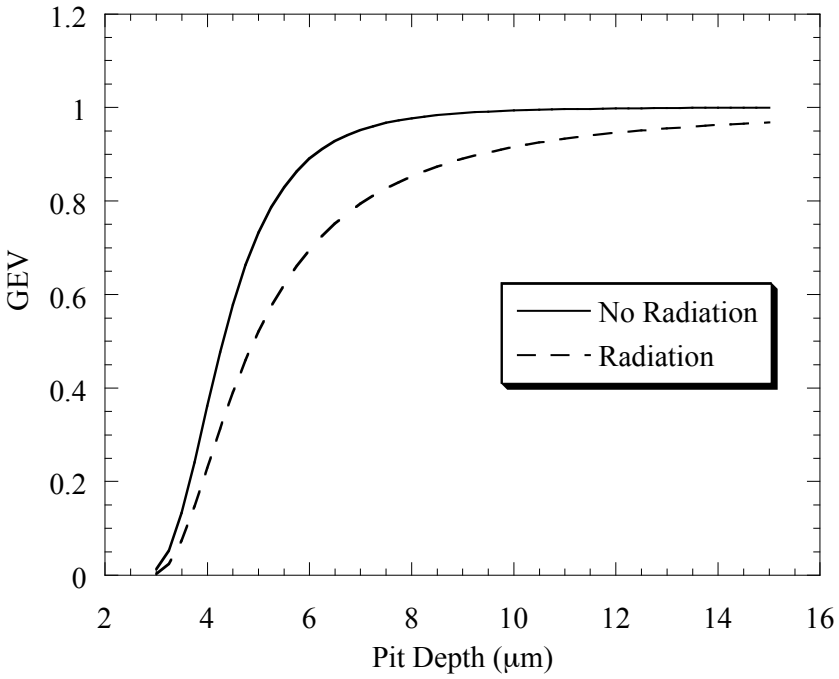

Figure 2-7 The CDF for pit depths from irradiated and non-irradiated carbon steel A516 samples in simulated alkaline waste tank solution.

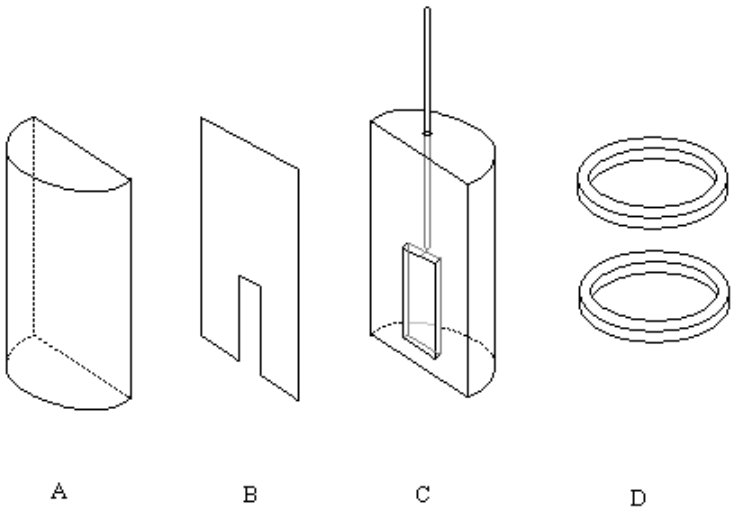

Figure 2-8 "Artificial Pit" assembly: slit dimension approximately 0.22 cm^2, electroplating tape thickness is 0.0064 cm. A – plastic hemi-cylindrical cover; B – electroplating tape with lower slit applied to coupon; C – plastic hemi-cylinder with embedded coupon and insulated electrical wire attachment through top; D – Teflon rings for clamping hemi-cylinders together.

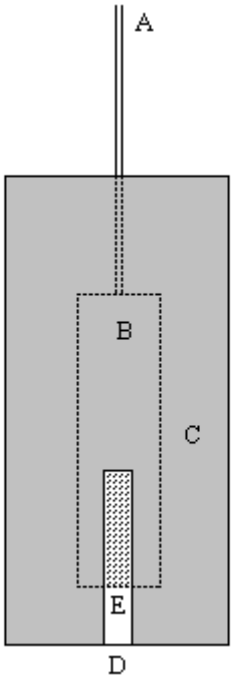

Figure 2- 9 Front view of working "Artificial Pit" electrode. Coupon embedded in hemi-cylindrical epoxy mold with electroplating tape over-lay (dark portion) showing slit and exposed (dotted area) coupon area. A - electrical wire attachment; B – embedded coupon; C- corrosion tape overlay/ mask; D – electrolyte solution access; E – exposed coupon area (dotted area).

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 ± 1.1 x 10^{-7}	2.3 ± 1.6 x 10^{-7}
I_{pass} (A/cm^2)	1.7 ± 0.3 x 10^{-6}	5.9 ± 2.6 x 10^{-7}
E_{pit} (V)	0.44 ± 0.12	0.46 ± 0.06
E_{rp} (V)	-0.73 ± 0.20	-0.70 ± 0.16
SDP/LDP	5.1	2.5

Table 2-2 Summary of artificial pit solution analyses.

Sample No.	Pit Volume (mL)	Con. Fe^{3+} (ppm)	Fe^{3+} (ng) in pit volume	Con. Cl^- (ppm)	Cl^- (μg) in pit volume	Fe^{3+}/Cl^-	Number of pitting events
			With radiation				
1	0.00208	0.139	57.4	8.57	2.93	19.5x10^{-3}	206
2	0.00188	0.331	132.0	32.3	6.95	19.0x10^{-3}	71
3	0.00201	0.163	73.2	17.4	3.30	22.2x10^{-3}	7
			Without radiation				
4	0.00182	0.846	439.0	10.7	6.01	73.0x10^{-3}	0
5	0.00179	2.16	912.0	4.49	1.59	573.0x10^{-3}	470
6	0.00211	0.0357	17.9	5.11	2.45	7.31x10^{-3}	21

Note: Columns for Fe^{3+} and Cl^- concentrations are recorded data for the rinse solution volumes.

3. Planned Activities

In this work we will investigate the influence of oxide rupture and formation on the transition from meta-stable to stable pitting in simulated high-level radioactive wastes. In-situ straining electrode experiments will be used to characterize continuous oxide film breakdown and repassivation transient current response of 316L stainless steel (SS) in a simulated acid chloride waste. Experiments will be conducted in the milli to micro second time regime during electrode straining. The study of discrete transient current events will establish the effect of film repassivation on the elusive pitting stability phenomena through fast time scale data acquisition for modeling active mechanisms responsible for incipient pit nucleation growth processes.

Milestones for Program and Students PhD

- Design the experimental setup and determine the experimental parameters to acquire the rapid transient current response due oxide film rupture in a simulated waste-water-storage environment (Summer ’05)
- Initial transient current data due to oxide rupture via an electrode straining technique will be collected (Summer '05 -Winter '05)
- Present Ph.D. proposal to WSU (Fall ’05 or Spring ‘06)
- Poster presentation at NACE conference (Spring ‘06)
- Continued collection of data (thru Spring '07)
- Preparation of manuscript for submission (Fall ’06)
- Defend Ph.D. (Summer ’07)

4. Information Access

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," accepted *Corrosion*, 2003.
3) C.A. McCall, R.S. Lillard, "Pitting Corrosion of Stainless Steel 316L in Simulated Acid-Chloride High Level Radioactive Waste," accepted *Corrosion Engineering Science and Technology*, 2004.
4) B. Galuszka-Muga, R.J. Hanhrahan, M.A. Hill, R.S. Lillard, , "The Influence of Gamma Radiation on Pitting Corrosion of Carbon Steels Alkaline High Level Radioactive Waste Tanks," submitted, *CEST, 2005.*