**Yearly Progress Report**

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

**Covering Period:** June 1, 2002 - May 31, 2003

**Recipient:** University of Florida
Chemistry Department
P.O. Box 117200
Gainesville, FL 32611

**Award Number:** DE-FG07-01ER63299

**Subcontractors:** none

**Other Partners:** Dr. R. Scott Lillard
Los Alamos National Laboratory
LANL MS G755
P.O. Box 1663
Los Alamos, NM 87545-1663

**Contact:** Prof. Robert J. Hanrahan
(352) 392-1442
hanrahan@chem.ufl.edu
**Project Team:** Dr. Barbara G. Muga

**Project Objective:** Investigate the influence of gamma radiation on the hydrolysis of electrolyte and metal electrode surface, and the role which radiation plays in the corrosion process, in particular, the onset of metastable and stable pitting events.

**Background:** High level radioactive waste has been stored in underground tanks at various DOE sites for over 50 years. The tank material, mostly carbon steels, are subjected to a severe corrosion environment. Studies to understand this corrosion process are needed to mitigate the effect of corrosion.

**Status:**

In June, exploratory experiments were begun using newly installed Versastat unit. Fast scans of open circuit potential (OCP) *vs.* miniature saturated calomel electrode (MSCE) and potentiodynamic (PD) recordings were obtained (without a radiation field) to establish reproducible conditions. In July, despite more delays and disruption due to building renovations, an exploratory series of PD and potentiostatic (PS) scans, without and with a radiation field of 1 Mrad/hr, were made. Except where otherwise mentioned all experiments were run at room temperature ~22 C. Using a 3 electrode cell (working electrode: A537Cl1 carbon steel; counter electrode: Pt wire or Pt mesh; reference electrode: MSCE; electrolyte: 0.19 M NaOH/0.11 M NaCl solution) we found that the OCP is fairly consistent, but the repassivation potential (RP) is dependent on scan rate and Versastat vertex potential during a PD scan. At a fast (5 mV/sec) PD scan rate (Fig. 1), the RP dependence on vertex potential (Fig. 2) is likely due to a buildup of passivating film at higher potentials, indicating the importance of undergoing pre-treatment prior to PD and PS scans. On the other hand a slow (0.05 mV/sec) scan rate allows time for pitting to occur and results in lower RP values (Fig. 3), suggesting that equilibrating time is an important factor.

For PS scans, the effect of radiation (1 Mrad or 10 Kgrey per hour) was explored by recording paired cycles alternately with and without a radiation field. Fig. 4 and Fig. 5 show typical responses. Generally higher current levels and pitting activity were seen (as expected) during PS tests with applied radiation.

Suspecting that solution conductivity may be at least partly responsible for observed effect (conductivity should increase due to gamma ray induced ionization) a like series of experiments were run using Pt wire or mesh as a working electrode. Two consistent results were observed:

1) The application of a radiation field always results in an increased current during a PS cycle with a limiting exponential growth-like rise; removal of the radiation field always results in an exponential decay-like decrease in current as shown in Fig. 6.

2) The forward minimum current potential, OCP and return minimum current potential, RP, values are closer to each other when a radiation field is present as shown in Figs. 7 and 8. Apparently, the radiation field accelerates equilibration of surface (passivating) films.

Inconsistent and intermittent observations included an oscillatory current background (with varying amplitude and period) during many PS scans. Much effort was expended on controlling and eliminating these background oscillations which were reduced but never entirely eliminated. Continuation of these exploratory experiments in a radiation field led to some general observations as follows:

1) The slower the potentiodynamic (PD) scan rate, the greater probability that a current excursion will occur. This is expected for metastable pitting and is true without and with a radiation field, but more so in a radiation environment.

2) The slower the PD scan rate, the smaller is the difference, $\Delta E$, between the open circuit potential (OCP) and the repassivation potential (RP).

3) In a radiation field and for fast PD scans (a) $\Delta E$ (i.e. OCP - RP) is larger, (b) RP is significantly less negative (larger *re* MSCE) and (c) OCP is slightly less negative compared to responses without radiation.

4) Long term OCP recording in a radiation field requires extended time for equilibration to occur. During this time OCP values rise to a maximum, go through a broad minimum and only after well over 3 hours does it begin to approach a stable value for A537Cl1 carbon steel. But A516gr70 carbon steel gave an irregular response before reaching a final (equilibrium) value.

5) In a radiation field and at slow scan rate, PD scans produce strange variations such as (a) multiple OCP values, (b) current excursions (pitting) at lower voltages, (c) return OCP (RP) values lower than forward OCP values (as expected) and (d) possibly no RP value at all before terminal voltage is reached. These responses, of an exploratory nature, are understood in term of pitting and crevice induced corrosion but seem to be more intense, frequent and erratic in a radiation environment.

We repeated many earlier experiments to establish procedures for obtaining reproducible PD and PS scan results as it appears that pre-treatment of the working electrode is a critical factor. Again we established that, for a given applied voltage the onset of corrosion, as evidenced by increased current during PS scans, appears sooner in a radiation environment. We also showed that under radiation, the passivation region may exhibit a negative slope - 'back bend'- as the vertex is approached at fast (5mV/sec) scan rates. We followed up on earlier observations of long-term behavior of OCP in a radiation field. Figs. 9-11 show the typical OCP variation in time with and without radiation of 1 Mrad/hour at room temperature for A537Cl1 carbon steel. Under radiation, an initial rise in OCP is followed by a decrease leading to a broad minimum before final equilibration is reached. Without radiation the OCP drifts upward from its initial value (Fig. 11). Electrolyte composition change may be a factor in this slow path to final equilibration.

In January 2003 we re-established the pronounced 'back bend' of the passivation region and lower OCP value in a radiation environment. We redirected efforts to the calibration of spectrophotometric analysis of corrosion products, mainly $Fe^{3+}$, $Fe^{2+}$, and to a re-measurement of the Co-60 irradiation field by Fricke dosimetry. The design and drawing of an elevated temperature housing (oven) within the Co-

irradiator was begun. The confined space and requirement for remote insertion of the Co-60 source represent a challenge.

During February, the group met with Dr. Scott Lillard of LANL and reviewed existing data and future plans. Ideas were discussed for the extraction of small pitting-solution volumes for subsequent chemical analysis. It is expected that these pitting solution extracts will have measurable $Fe^{3+}/Fe^{2+}$ ratios and an increased $Cl^{1-}$ concentration relative to bulk electrolyte. The challenge is securing and analyzing minute volumes from the pitting region.

Duplicate experiments were run using A516gr70 carbon steel coupons and glyptal as masking agent to define exposure area, and, by selected masking, we demonstrated that "weaker" areas of coupon corrode at lower potentials, "stronger" surfaces (not corroding at lower potentials) require higher potentials to induce pitting. A series of experiments were run in which carbon steel coupons were polished on all surfaces and then immersed in electrolyte. Radiation tended to produce more erratic results which were hampered by waterline and bottom tip corrosion, not previously a problem when mask-defined flat surfaces were entirely immersed.

By May, the assembly and temperature calibration of the Co-irradiator oven was completed allowing experiments to be conducted at elevated temperatures. Temperature calibration was established using a thermistor digital temperature probe calibrated against a Hg thermometer which in turn was calibrated at 0 C (ice water) and 100 C (boiling water) at atmospheric pressure. The temperature signal was shown to be stable in the radiation field.

Four pairs of A516gr70 carbon steel coupons were polished to mirror-like surfaces with a final polishing pad charged with 14,000 Mesh diamond compound. After ultrasonic cleaning a glyptal covering of coupon tip was made and allowed to dry overnight. Coupons were stored in a dessicator until used.

Alternate PD runs at 40 C with and without radiation field were made with results shown in Figs. 12 and 13. Overall, the PD scan results are more consistent from run-to-run at 40 C than previously observed at room temperature, ~22 C. The passivation region is more limited and repeatable at 40 C. It appears as if, at elevated temperature, the passivation film is more uniform in its ability to stabilize or limit corrosion. Moreover, at elevated, much higher potentials are realized without a clearly defined pitting potential appearing.

The OCP values (rising potential at minimum current) are more consistent in the radiation field at 40 C and are similar to 22 C data. OCP values at 40 C were lower (by ~0.1 V) in a radiation field than without. The repassivation potentials, RP's, were about the same (~0.8 V *re* MSCE). A cautionary note: for the elevated temperature data, corrosion at bottom tip (where much of non-flat surface occurs) was precluded by a film of glyptal.

**Future Work**: In further work, a new sample holder capable of holding larger corrosion cells is under assembly. This will provide a large electrolyte volume to be used but will result in a less uniform and less intense radiation field at the coupon position. It will allow us to use larger working electrode units and we will be able to compare our miniature coupons with larger size coupons fabricated at LANL. Much of the previous work will be repeated with these newer coupons which are encapsulated in clear Epofix epoxy resin.

**Equipment Purchase:** One of the original research goals of the University of Florida group was to contribute to the knowledge base concerning tank corrosion by carrying out chemical analysis of metal ions in solution (especially $Fe^{2+}$ plus other ions) produced by corrosion of the alloy steel of the tanks. Unfortunately, analysis of ferrous ion is especially difficult due to the necessity of adding post-column reagents prior to an optical absorbance detector. After checking with the three major manufactures in this field (Dionex, Waters and Metrohm) we found that none could offer a complete instrument for the funds available.

In our original proposal we had anticipated spending $9850 for ion chromatography equipment during the first budget period (September 15, 2001 - March 14, 2003) and an additional $9600 for chromatographic accessories during the second 18-month period (March 15, 2003 - September 14, 2004). By combining funds for the entire 3-year period it will now be possible to purchase a suitable instrument. In addition, Prof. Hanrahan became emeritus as of May 6, and he will now be able to contribute to experimental work in this area.

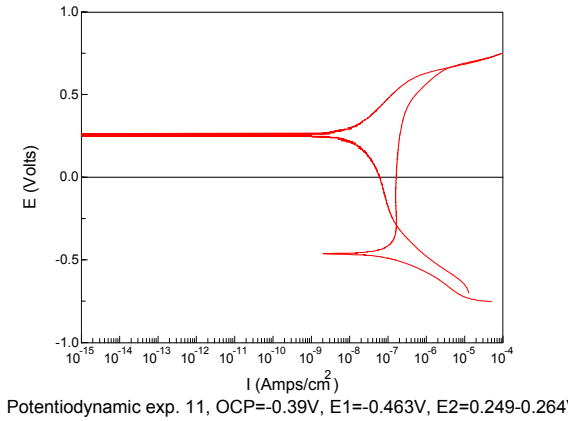


Fig. 1. Potentiodynamic scan of corrosion cell (A537Cl1 coupon), vertex potl. = 0.75 V *re* MSCE, scan rate = 5 mV/sec, no radiation.

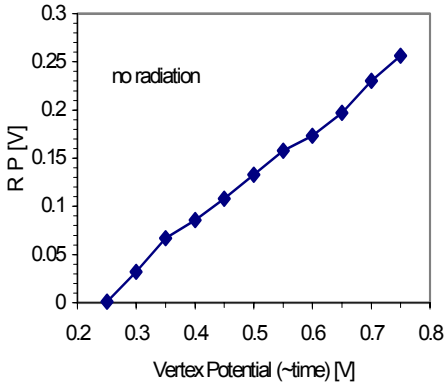


Fig. 2. Repassivation potl. (RP) vs. vertex potl. (~time). All scan rates = 5 mV/sec, no radiation.

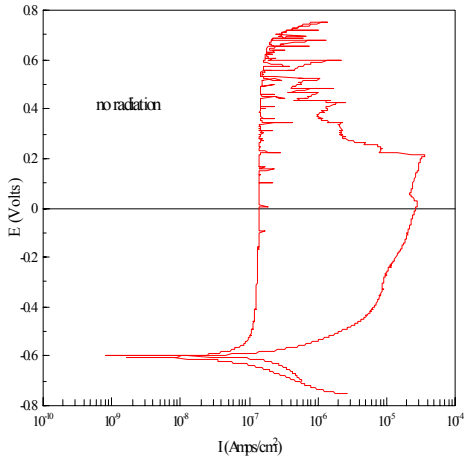


Fig. 3. Potentiodynamic scan of corrosion cell (A537Cl1 coupon), scan rate = 0.05 mV/sec, no radiation.

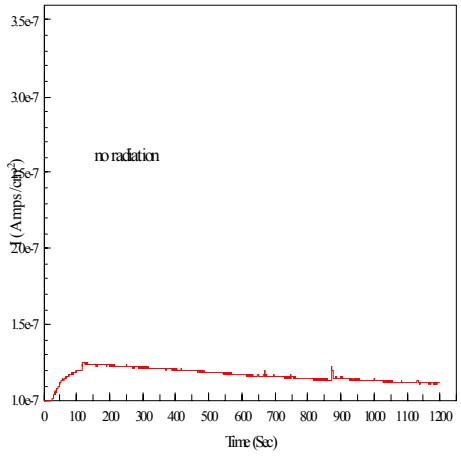


Fig. 4. Potentiostatic test of corrosion cell (A537Cl1 coupon), no radiation, applied potl. = 0.1 *re* MSCE. Compare with Fig. 5.

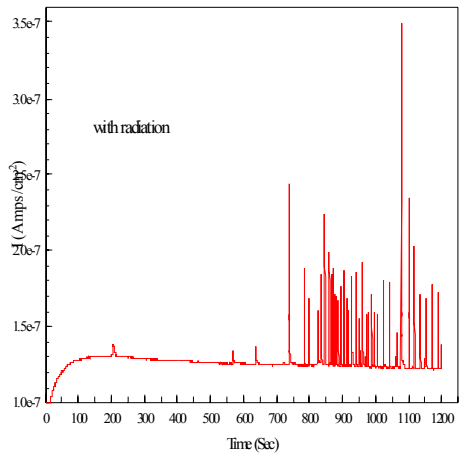


Fig. 5. Potentiostatic test of corrosion cell (A537Cl1 coupon), with radiation, applied potl. = 0.1 V *re* MSCE. Compare with Fig. 4.

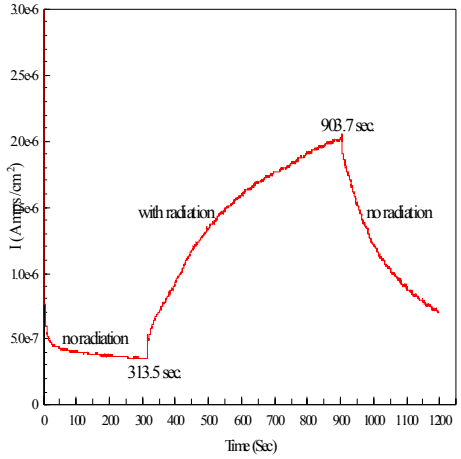


Fig. 6. Potentiostatic test of corrosion cell (two Pt mesh), applied potl. = 0.1 V *re* MSCE.

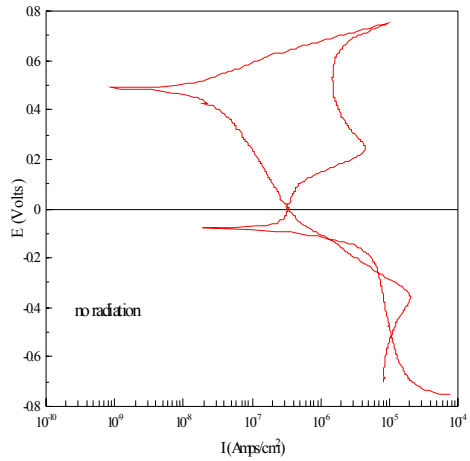


Fig. 7. Potentiodynamic scan of corrosion cell (Pt wire and Pt mesh), no radiation, scan rate = 5 mV/sec.

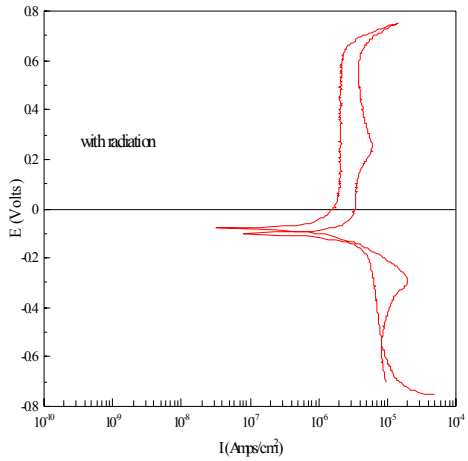


Fig. 8. Potentiodynamic scan of corrosion cell (Pt wire and Pt mesh) exposed to radiation, scan rate = 5 mV/sec.

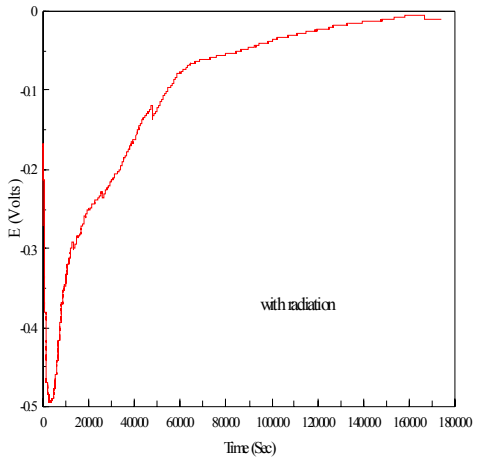


Fig. 9. OCP values recorded for electrolyte system following application of 1 Mrad radiation field. Electrodes inserted in electrolyte just prior to radiation exposure.

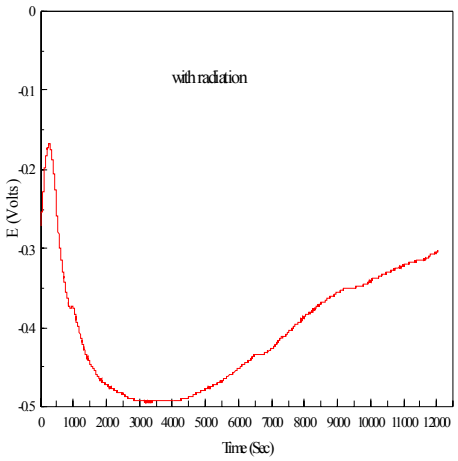


Fig. 10. Expanded view of Fig. 9. OCP response following initial application of radiation showing maximum/minimum response.

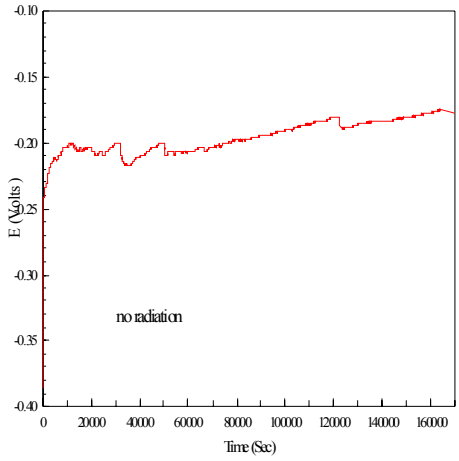


Fig. 11. OCP values for a pristine A537Cl1 coupon when placed in fresh electrolyte. No radiation applied during recording.

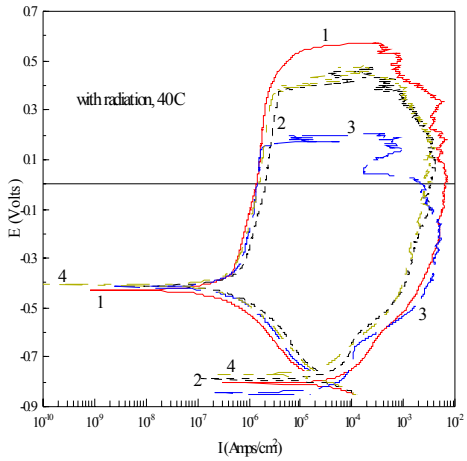


Fig. 12. Potentiodynamic scans for four A516gr70 coupons run in radiation field, scan rate = 0.05 mV/sec.

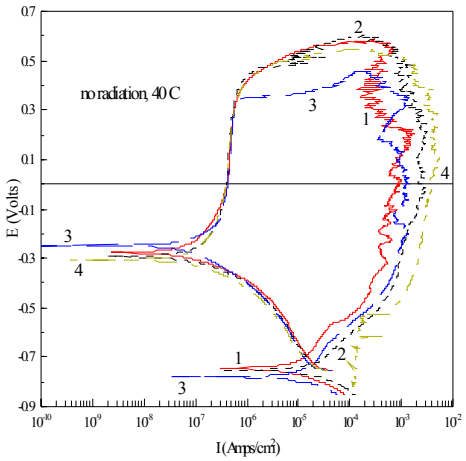


Fig. 13. Potentiodynamic scans for four A516gr70 coupons run without radiation, scan rate = 0.05 mV/sec.