

Project Title: The Influence of Radiation on Pit Solution Chemistry as it Pertains to the Transition from Metastable to Stable Pitting in Steels, EM-50, EMSP TTP # 81989
DOE Report Number: unavailable (submitted for LAUR)
Publication Date: June 10, 2002.

Lead Principal Investigator:

R. Scott Lillard
Los Alamos National Laboratory
LANL MS G755
P.O. Box 1663
Los Alamos, NM 87545-1663
505-667-6325
Lillard@lanl.gov

Co-Investigator: (repeatable)

Robert J. Hanrahan
University of Florida
406 nsb
P. O. Box 117200
Gainesville, FL 32611-7200
352-392-1442
hanrahan@chem.ufl.edu

Graduate Students / Post Doctoral Research Associates

Dr. Basia Muga, Post Doctoral Research Associate, Dept. of Chemistry, University of Florida

Research Objective

The goal of this research is to develop new methods to mitigate corrosion in DOE HLW tanks. To accomplish this, we will characterize the parameters that influence the transition from metastable pitting (also referred to as electrochemical noise) to stable pitting. These parameters include 1) the development of the critical pitting solution chemistry, 2) metastable pit morphologies and dynamics. Once we have evaluated these parameters, we will then examine the influence of gamma irradiation on pit stability. Ultimately we will have identified the role of both radiolytic reactions and inherent pit reactions in the transition from metastable to stable pitting. Having identified these reactions only then it will be possible to develop more specific and effective corrosion mitigation strategies.

Research Progress and Implications

EM-50, EMSP TTP # 81989 is a new start up that began in October 1, 2001. This report summarizes the progress between Oct. 1 and June 1, 2002.

This research has begun to identify the fundamental species and reactions that occur at incipient pitting sites so that new methods for mitigating corrosion in DOE HLW tanks at SRS and Hanford may be found. This has been accomplished by identifying regions of metastable pitting activity (i.e. electrochemical noise, EN) for tank steels in simulated Hanford/SRS waste solutions (see details below). Although these waste analogues are nominally passivating for carbon steels, the presence of EN in these solutions as well as Hanford/SRS waste tanks suggests

that pit initiation does not necessarily owe to a deviation from the specified chemistry limits. Further, it suggests that, a transition to stable pitting under "passivating" chemistries may be possible. Such transitions may be facilitated by radiation solution chemistries that develop in the incipient pit. For example, water radiolysis of solutions containing iron corrosion products results in the oxidation of Fe⁺⁺ to Fe⁺⁺⁺. The addition of this oxidation reaction (which does not ordinarily occur in basic solutions) is significant as the hydrolysis of Fe⁺⁺⁺ within an incipient pit will result in a lower local pH than can be achieved by Fe⁺⁺. In turn, this results in higher dissolution rates at the incipient pit site. Thus, one might anticipate that the susceptibility to pitting corrosion in irradiated solutions increases with radiation flux. To demonstrate this, we have equipped a gamma irradiation cell (Co⁶⁰) with the capability of taking real-time electrochemical data. We hope to demonstrate that metastable pitting activity (and dissolution reactions in general) increases with gamma flux. Further, by analyzing the composition of the electrolyte (in real time or immediately after irradiation) we hope to identify species that participate in the formation of the incipient pit solution (such as Fe⁺⁺⁺ as described above).

These findings have a significant impact on tank operations which have traditionally focused on the addition of hydroxyl or nitrite to mitigate corrosion. By identifying the species that form at incipient pit sites (such as that are responsible for EN) as a result of both radiolytic reactions and inherent pit reactions it is possible to develop a species specific corrosion mitigation strategy. In terms of the Fe(II) to Fe(III) reaction given as an example here, it may be possible to add small quantities of an Fe(II) chelating agent to preferentially bind this species such that it is not available for reactions with radiolysis products. Thus, avoiding a decrease in incipient pit pH that may occur in a radiation environment.

Planned Activities

The following tasks for the remainder of FY 02 and FY 03 have been identified.

task	begin date	anticipated completion
Potentiodynamic data during irradiation	July 2002	October 2002
Metastable pitting studies		
Video microscopy of pit dynamics	July 2002	January 2003
Statistical analysis of events	ongoing	March 2003
Metastable pitting during irradiation	October 2002	June 2003
Pit solution analysis	April 2003	FY 04

Information Access

One Page Adobe Acrobat File attached.

OPTIONAL ADDITIONAL INFORMATION

Electrochemical Noise - Experimental Data

High-level radioactive waste has been stored in underground storage tanks at various DOE sites for nearly 60 years. At Hanford, approximately 227,000 m³ of waste has accumulated in 177 tanks (1-2). The tanks at Hanford are fabricated from the following mild steels: ASTM A537-Class 1, ASTM A515-Grade 60, and ASTM A516-Grade 60. The single shell tanks were not stress relieved following fabrication as were the inner tanks of the double-shell tanks. Waste

tank steels at Savannah River Plant include ASTM A516 Grade 70 (as-fabricated and normalized), ASTM A537 Class 1, and ASTM A285 Grade B.

During the lifetime of these tanks, a corrosion mitigation strategy based on experiments in surrogate waste solutions has been developed. Recently, Edgemon *et al.* used a high pH, simulated waste solution to acquire electrochemical noise (EN) data on mild steels (3). The researchers found that uniform corrosion and stress corrosion cracking can be distinguished from one another when using appropriate electrode geometries. Uniform corrosion is characterized by random changes in the current and potential corresponding to fluctuations between anodically and cathodically controlled behavior. Crack growth is characterized by sharp periodic, drops in potential which occur simultaneously with positive current spikes. Subsequent to that work, EN monitors have been placed in both Hanford and SRS tanks. Congdon *et al* describes pitting corrosion in carbon steel used to store dilute waste at the Savannah River Plant (4). Hydroxide depletion by carbon dioxide absorption in the wetted film above the waterline leads to pitting. Aggressive anions in the waste include nitrate, sulfate, chloride, and fluoride. A minimum effective nitrite concentration corresponding to the aggressive anion concentration was noted for passivating the steel. No pitting was observed on the steel tested in solutions with nitrite levels exceeding this minimum concentration.

The research being conducted under this grant differs significantly from the work just described, in that, we are examining the development of the solution chemistry at incipient pit sites (such as those that occur during EN), and the influence of radiolytic reactions on pit solution chemistry. To accomplish this we have begun to study the conditions (composition, temperature, potential) that produce EN in Hanford and SRS tanks. We will also evaluate INEEL tank materials (austenitic stainless steels) and chemistries (acid chloride) in FY 03 and 04. The materials investigated thus far include: ASTM A537-Class 1, ASTM A516-Grade 70, and ASTM A516-Grade 70 normalized (n). These alloys range in composition from: 0.24-0.31 wt% C, 0.6-1.6% Mn, 0.035% P, 0.04% S, and 0.15-0.30% Si (Table 1 and 2). ASTM A516-70 was examine in the as received and normalized conditions (1 hrs. at 900° C). For electrochemical evaluation the samples have been mounted and prepared metallographically (grinding/polishing). These alloys have been studied in a tank supernatant liquid analog solution, the composition of this analog is out lined in Table 3.

Table 1 Composition (wt%) of steels used in Hanford and SRS waste tank construction

	C	Mn	Si	Cr	Ni	P	S	Mo	Al	Cu	V	Nb
A537	0.23	1.25	0.28	0.11	0.11	0.006	0.005	0.020	0.032	0.080	0.003	0.002
A516g60	0.21	1.14	0.23	0.03	0.01	0.016	0.018	0.010	-----	0.030	-----	-----
A516g70	0.23	1.11	0.26	0.02	0.01	0.007	0.010	0.004	0.036	0.010	0.019	0.003
A515g60	0.21	0.46	0.46	0.04	0.02	0.020	0.013	0.006	-----	0.015	0.001	0.001
A285gC	0.11	0.86	0.86	0.02	0.02	0.006	0.006	0.010	-----	0.100	-----	-----

Table 2 Mechanical properties of Hanford and SRS steels.

	Yield Strength (ksi)	Tensile Strength (ksi)	% elongation
A537	67.3	89.5	23
A516g60	51.8	77	37
A516g70	52.5	74.7	40
A515g60	57.0	73.3	23
A285gC	50	64	26

Table 3 Composition of solution used to simulate Hanford / SRS tank supernatant liquid.

Constituent	Concentration (M)
NaNO ₂	1.8
NaNO ₃	3.6
Na ₂ HPO ₄ *7H ₂ O	0.05
Na ₂ SO ₄	0.14
NaAlO ₂	0.57
NaF	0.076
NaCl	0.11
NaOH	0.19

A typical potentiodynamic polarization curve for A516 steel (as received) in the simulated tank solution is shown in Fig.1. Similar curves were recorded for A537 and A516(n) in this solution (Fig. 2 and 3). The forward and reverse scan directions are indicated by the arrows. This curve is characterized by an open circuit potential (OCP) of approximate -0.55 V SCE, a passive region between the OCP and 0.45 V, and a solution oxidation potential (nitrite to nitrate) at approximately 0.46 V. The lack of a pitting potential and a hysteresis in the reverse scan of the potentiodynamic polarization curves generated in the simulated tank solution might indicate to the investigator that the material is not susceptible to pitting in this solution. However, the passive region of this polarization curve is associated with several small peaks in the current, the largest of these peaks occurring at approximately 0.375 V SCE. These peaks in current are a result of metastable corrosion pits. These pits grow for a period of time and then repassivate. The evolution of metastable pitting events (also referred to as electrochemical noise, EN) can be more clearly seen in potentiostatic holds, Fig. 4. During a potentiostatic hold, the current is recorded as a function of time, in this case, data were recorded for a total of 1200 s at each potential at an acquisition rate of 10 Hz (10 pts./s). Pitting events are seen as peaks in the current such as those at times of 531 and 533 seconds. The event at 533 s resulted in the most physical damage on the surface as indicated by the peak current and duration associated with this event. Thus, for deviations in passivating tank solution chemistries, such as those that may occur during irradiation as a result of water radiolysis, there is the potential for stable pitting even though the tank solution chemistry is fully passivating.

There are clear differences in the statistical population of the EN events as a function of material and solution compositions. In these early stages of our investigation we have only begun to identify these relationships. Examples are shown in Figs. 5 and 6 for the simulated tank solution and an NaOH/Cl solution where stable pitting is observed. Surprisingly, for the simulated tank solution which is not associated with a pitting potential and stable pitting, the frequency and magnitude of events is greater as compared to the NaOH/Cl solution which contains an equivalent Cl⁻ concentration and pH but does not contain nitrite. It is also observed that the normalized material in any given solution exhibits few events of lesser magnitude.

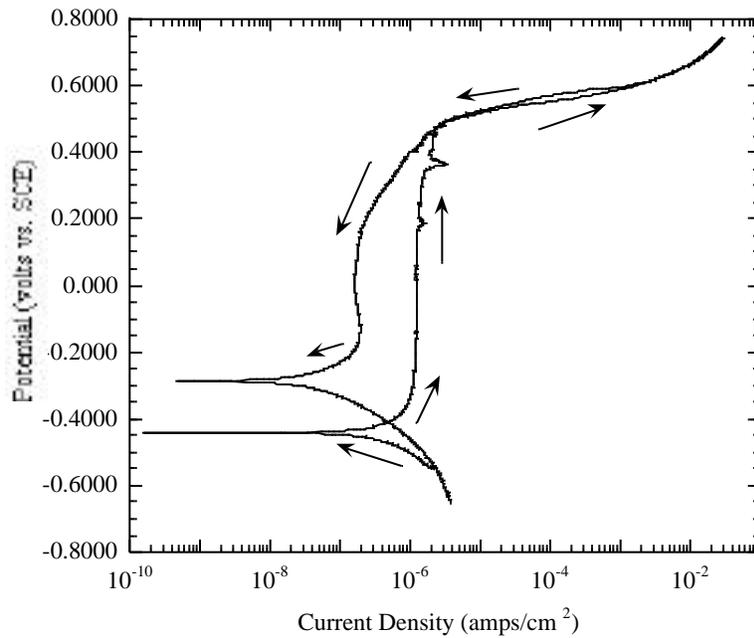


Fig. 1. Potentiodynamic polarization curve for A516 in simulated waste solution at 40° C (ambient aeration).

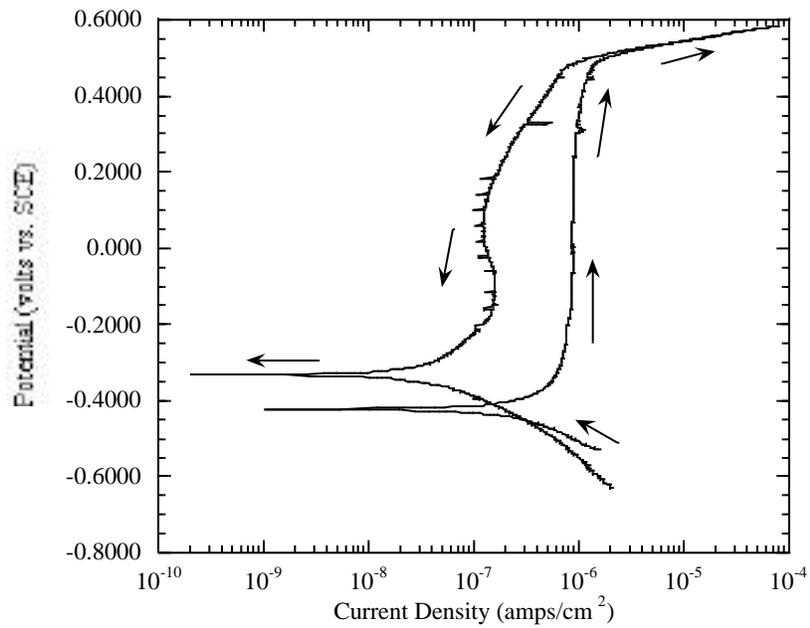


Fig. 2. Potentiodynamic polarization curve for A537 in simulated waste solution at 40° C (ambient aeration).

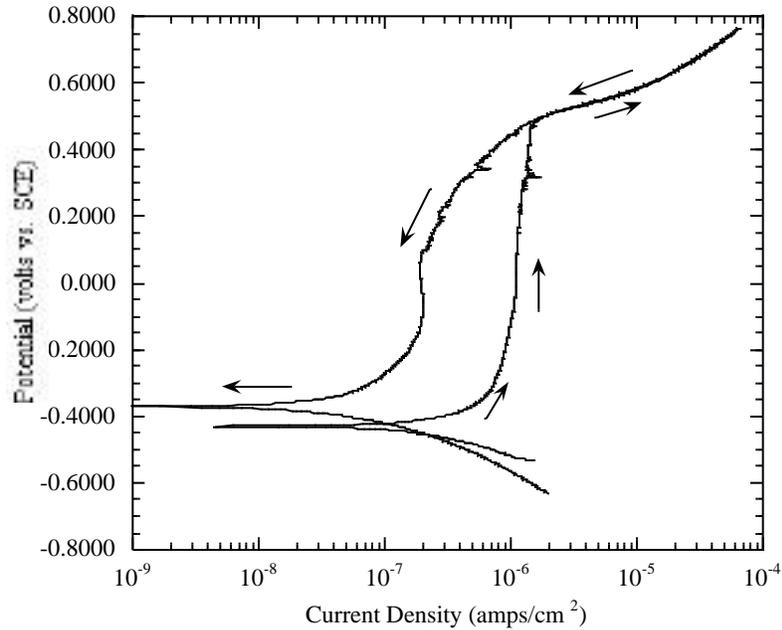


Fig. 3. Potentiodynamic polarization curve for A516(n) in simulated waste solution at 40° C (ambient aeration).

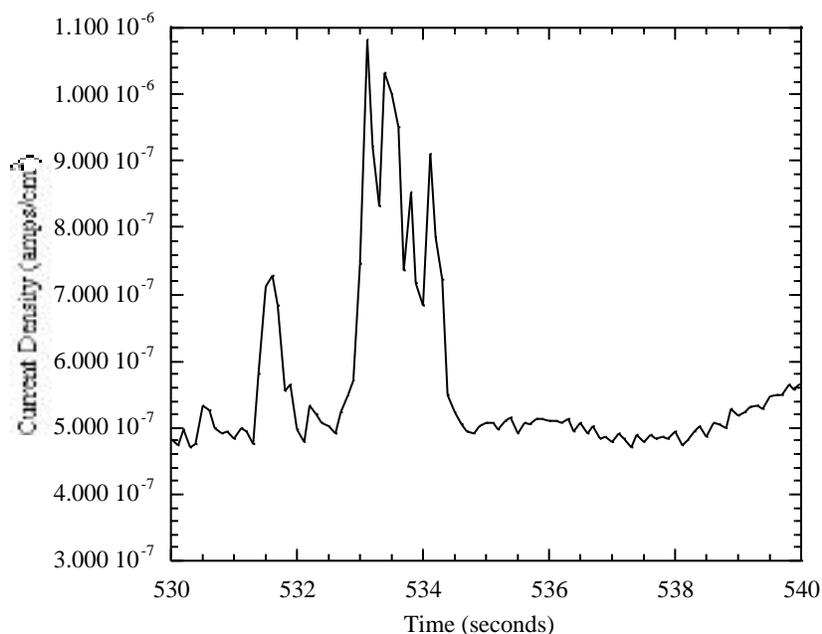


Fig. 4. Current time transient for A516 in NaOH/NaCl solution held at a potential of 0.154 V vs. SCE. The charge passed on the repassivation event is 4.31×10^{-7} Coulombs. The charge passed during the event at 533 s was 1.62×10^{-6} coulombs

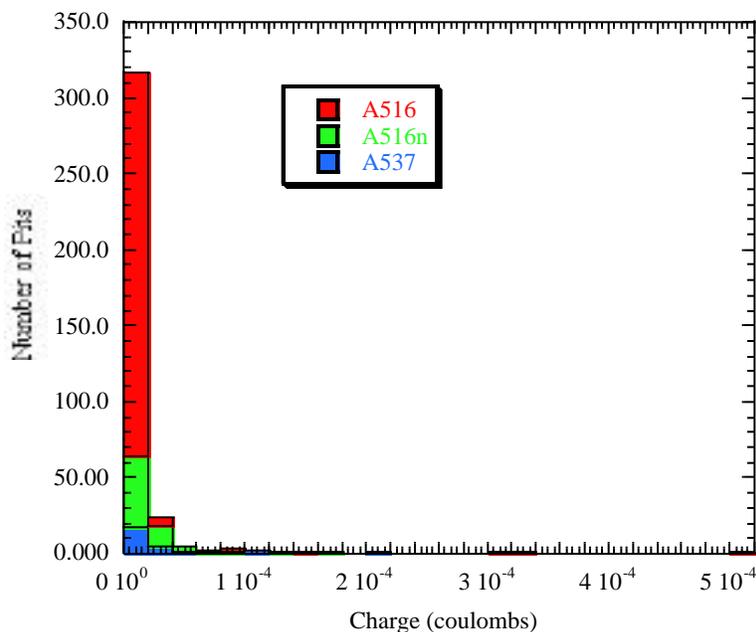


Fig. 5 Histogram of metastable pitting events (electrochemical noise) for samples in simulated waste solution at 40° C (ambient aeration).

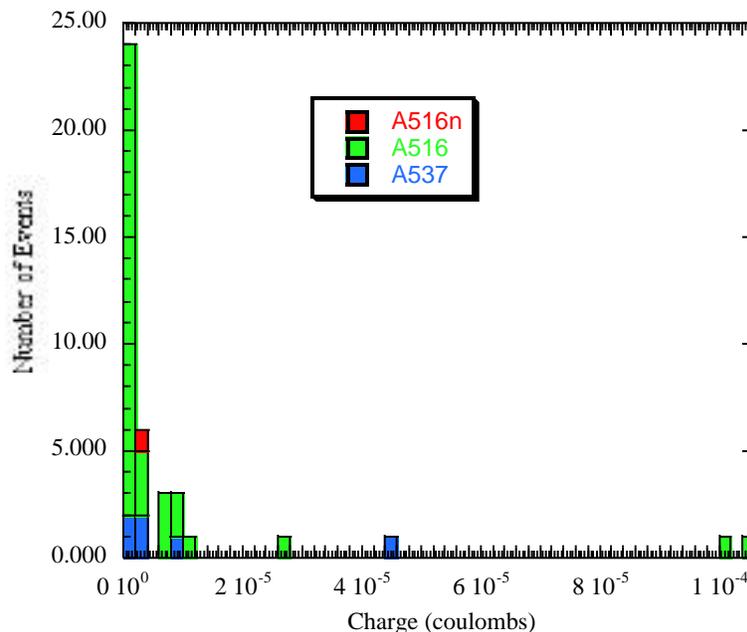


Fig. 6 Histogram of metastable pitting events (electrochemical noise) for samples in NaCl/NaOH solution at 40° C (ambient aeration). This solution contains an equivalent concentration of NaOH and Cl⁻ as the simulated tank solution but does not contain the other constituents (Table 3).

Development of a Gamma Irradiation Cell for Electrochemical Testing

A custom designed 600 curie Co-60 gamma irradiator (source replaced in 2000) for the steady-state radiolysis of solid, liquid or gaseous samples has been modified for our planned electrochemical experiments. This source provides a radiation intensity of 0.5 to 1.5 megarads/hour, depending upon geometry and sample size. An easily accessible working space of approximately 15 x 15 x 15 inches is available. The irradiator has been modified to accept an electrochemical cell and is now equipped with electrical feedthroughs for the PAR/EG&G potentiostat that will be used to conduct real-time experiments.

To overcome the potential of radiation damage that may be associated with the use of traditional reference electrodes a series of specially designed references have been developed. These electrodes have been tested by monitoring the OCP for nine pairs of possible reference electrodes in a radiation field of 1 Mrad (10 Kgrey) per hour. Relative voltages were recorded with a Fluke Model 8012A multimeter with a 10 M input impedance. As the PAR/EG&G potentiostat has an input impedance on the order of 10¹², fewer errors due to the impedance of the electrode (noise fluctuations for example) are anticipated in the actual electrochemical experiments. The OCP for the following pairs were recorded over an exposure period of 26 consecutive days, resulting in a cumulative total dosage of ~600 MRads (~6 Mgreys). EMF values were recorded also before and after radiation exposure. As with previous exploratory observations (see March report) relatively large, unexplained voltage drift patterns emerged for W/WO_x and Cu/Cu⁺⁺ electrode systems vs. SCE (saturated calomel). In general, the SCE vs. Ag/AgCl (satd) systems drifted as much as 20 mV over the exposure period and occasional swings of up to ~5 mV were observed over time periods of several minutes. Fig 7 is a plot of

one SCE vs. Ag/AgCl(satd) paired response showing the relative stability that can be expected over a short term of ~8 hours after beginning of radiation exposure. (Note: Y axes is expanded). Fig. 8 shows the response of the W/WO_x vs. SCE pair. An immediate response to the removal as well as to the insertion of the radiation source is evident. During the long term duration of exposure a wide variation occurred consistent with those observed in exploratory runs previously reported. Electrode cells will be disassembled for visual observation of radiation effects. Accumulated data are still being analyzed.

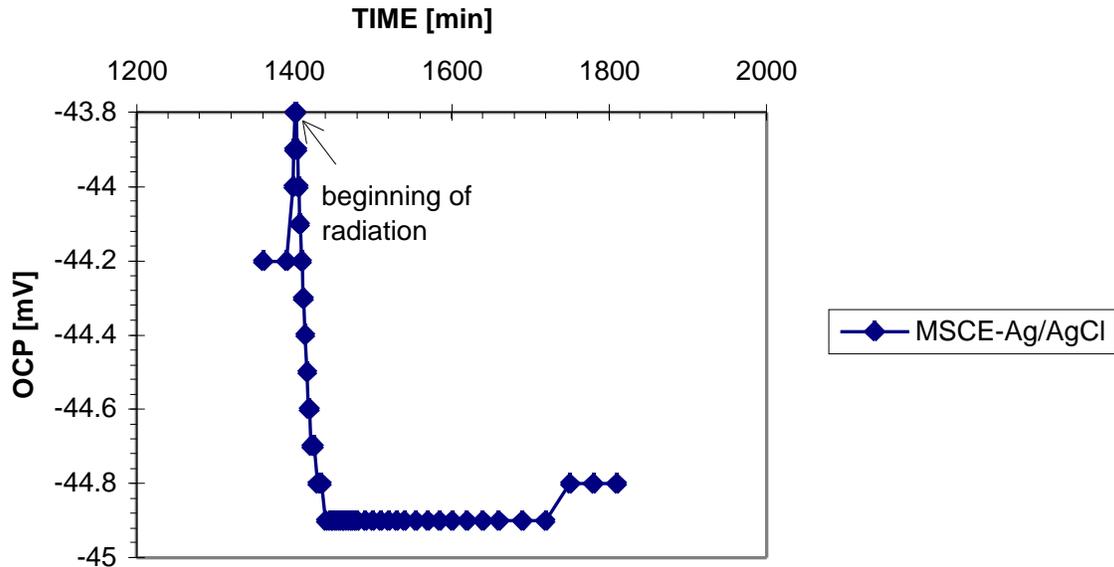


Fig. 7. SCE vs. Ag/AgCl (saturated) over 8 hours)

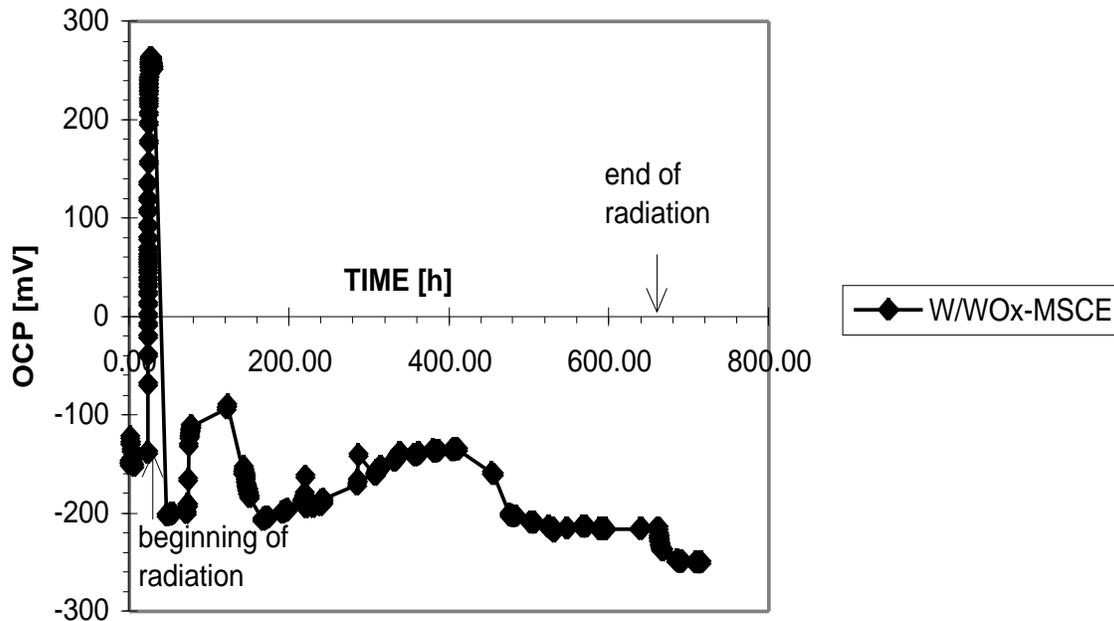


Fig. 8. W/Wox (saturated KCl) vs. SCE.

References

1. R.E. Gephart and R.E. Lundgren, "Hanford Tank Clean up: A Guide to Understanding Technical Issues," PNNL-10773, July 1996, p. 31.
2. "Expert Panel Recommendation for Hanford Double-Shell Tank Life Extension," C.W. Stewart, ed., PNNL-13571, June 2001.
3. G.L. Edgemon, M.J. Danielson, and G.E.C. Bell, "Detection of stress corrosion cracking and general corrosion of mild steel in simulated defense nuclear waste solutions using electrochemical noise analysis," *Journal of Nuclear Materials* **245** (1997) 201-209.
4. J.W. Congdon, "Inhibition of nuclear waste solutions containing multiple aggressive anions," *Materials Performance* **27** (#5), (1988) 34-38.

OPTIONAL PROPRIETARY INFORMATION

Not applicable.