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The Effect of Gamma Radiation on Reference Electrodes and Platinum and Carbon Steel Bare Metal Electrodes in a Simulated Waste Solution

M. J. Danielson

September 1993

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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**The Effect of Gamma Radiation on Reference
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Metal Electrodes in a Simulated Waste Solution**

Final Report

M. J. Danielson

September 1993

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**Pacific Northwest Laboratory
Richland, Washington 99352**

MASTER

Summary

Electrochemical potential measurements of materials in waste tanks are important in determining if the materials have a propensity for stress corrosion cracking and pitting. Potential measurement requires a reference electrode, but the effect of radiation on the potential generated by the reference electrode has been an unknown quantity. To determine the significance of the radiation effect, Pacific Northwest Laboratory conducted studies of five types of electrodes under gamma radiation at room temperature. The subjects were two types of silver/silver chloride reference electrodes (Fisher and Lazaran), a mercury/calomel reference electrode, a platinum "flag," and a piece of A-537 carbon steel; the electrodes were exposed to a simulated caustic tank environment. The Fisher silver/silver chloride and mercury/calomel reference electrodes showed essentially no radiation effects up to a flux of $2.1\text{E}6$ R/h and fluence of $9.4\text{E}8$ R, indicating they would be useful reference electrodes for in-tank studies. The Lazaran[®] silver/silver chloride electrode showed serious potential deviations at fluences of $2\text{E}8$ R, but it would be the electrode of choice in many situations because it is simple to maintain. Radiation affected the open circuit potential of both the platinum and carbon steel electrodes. This effect indicates that corrosion studies without radiation may not duplicate the corrosion processes expected in a waste tank. Mixed-potential theory was used to explain the radiation effects.

Acknowledgments

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1.0 Introduction

The purpose of this study conducted by Pacific Northwest Laboratory (PNL) is to determine the effects of radiation on reference electrodes. Additionally, bare platinum and carbon steel electrodes were tested to examine the effects of both gamma radiation and waste chemistry on their open circuit potential. Earlier results were reported by Danielson;^(a) final results and discussion are presented here. Future work to extend the life of waste tanks and associated piping at the Hanford Site will require the insertion of remote electrochemical probes, including electrochemical potential measurements to predict the type and rate of corrosion degradation processes.

The purpose of the reference electrode used in this study is to generate a constant electrochemical potential within the solution. The value of this potential is known on the Standard Hydrogen Electrode thermodynamic scale; potentials of other electrodes are measured **relative** to it. From a materials performance standpoint, a potential measurement is used to determine when a material is in a potential regime that causes it to become vulnerable to stress corrosion cracking or pitting--the two failure processes that have been observed to date in nuclear waste tanks.

The two most commonly used reference electrode half cells are based on mercury/calomel and silver/silver chloride. The half cell electrochemical reactions are shown below:

These electrodes consist of the metal in contact with its slightly soluble metal chloride salt. Fixing the aqueous chloride ion concentration fixes the electrochemical potential when the system is truly at equilibrium. In a practical sense, equilibrium means 1) that the reaction rates for the right and left directions of equation 1 or 2 are equal, 2) that these rates are much larger than for any accidentally introduced contaminant that is electrochemically active, and 3) that the rate is high enough that the small electron current required to drive a voltmeter does not alter the equilibrium potential. Reference electrodes require the creation of a micro-environment for the chloride-containing solution (usually KCl) in contact with the metal/metal salt. Contact of this electrode solution with the external world occurs through a leaky, ion-conducting bridge (porous membrane). Dilution of the chloride solution or contamination with an incompatible external environment can cause large shifts in the generated reference electrode potential.

(a) Danielson, M. J. 1993. Corrosion Probe Test Apparatus -- The Effect of Gamma Radiation Upon Reference Electrodes. Letter Report, TWRSP-93-029, Pacific Northwest Laboratory, Richland, Washington.

Radiation creates high-energy, transient redox species that may cause the reference electrode potential to drift from the thermodynamic value when they recombine upon the electrode surface, making the results of a potential measurement of questionable value. The primary products from gamma irradiation of water in the pH range 5 to 9 are presented in Table 1.1 (Spinks and Woods 1976).

The hydroxyl radical, hydrogen peroxide, and perhydroxyl radical are oxidizing species, while the hydrated electron, hydrogen atom, and hydrogen molecule are reducing species. As indicated in Table 1.1, the hydroxyl radical and the hydrated electron are the principal species formed in pure water. However, the actual concentrations of these extremely reactive species are very low and are modified by chemical reaction with scavenger species (such as oxygen, nitrate, nitrite, chloride). It is estimated (Burns, Marsh, and Walters 1983) that the steady state concentration of hydrogen peroxide and perhydroxyl radical at a gamma flux of $2E5$ R/h is in the range of $1E-6$ moles/L. The oxidized and reduced species can recombine on a metallic surface, using the metal as the electron transfer vehicle. If the magnitude of the kinetic rate constants for the recombination of the redox species is similar to those that fix the reference electrode or corrosion potential, then a shift in the open circuit electrode potential can be expected. This potential shift can be explained in quantitative terms by applying mixed-potential theory (Fontana and Greene 1978).

A recent paper (Taylor 1991) studying the effects of gamma radiation on the silver/silver chloride reference electrode at elevated temperature and pressure indicates that an offset of 100 mV is possible. This uncertainty is significant considering the observation (Beavers, Thompson, and Parkins 1985) that the potential regime for caustic cracking in carbon steels is approximately 100 mV wide in 10% NaOH. In an early effort to understand corrosion processes in waste tanks, measurements were taken of the electrochemical potential of carbon steels in actual waste tanks (Ondrejcin, Rideout, and Donovan 1979; Bickford, Congdon, and Oblath 1988; Olson, N.^(a)), and that information was combined with laboratory studies. Unfortunately, there is always the uncertainty of an error in the potential measurement due to the effects of radiation.

Table 1.1. Primary Products from Gamma Irradiation of Pure Water

Product	G, species number/100eV
OH (hydroxyl radical)	2.72
e_{aq}^- (hydrated electron)	2.63
H_3O^+ (hydronium ion)	2.63
H_2O_2 (hydrogen peroxide)	0.68
H (hydrogen atom)	0.55
H_2 (hydrogen molecule)	0.45
HO_2 (perhydroxyl radical)	0.026

(a) Olson, N. PNL Monitoring of Hanford Tank 241-AN107 (from approximately 1987 through 1989).

Very little is known of the interaction of radiation-induced species in solution and electrochemical potentials measured on bare metal electrodes that are inert (platinum) or corroding. Burns, Marsh, and Walters (1983) reported the effect of gamma radiation on stainless steel and mild steel pressure vessels containing high-purity water environments in the presence of air, argon, and hydrogen. In the oxygenated case, radiation increased the corrosion rates for stainless and mild steels. In the presence of air, the free corrosion potential of the stainless steel became more anodic when irradiated. Modeling was performed to predict the surface concentration of radiolytic species that controlled the surface reactions and corrosion behavior. Glass et al. (1986) showed that 304L and 316L in oxygenated J13 ground water undergo significant anodic polarizations under gamma irradiation ($3.3\text{E}6 \text{ R/h}$). Potential shifts of 0.150 to 0.250 V have been observed. Radiation-enhanced pitting was a concern, but the pitting potential for 316L is considerably above the open circuit potential observed while under radiation. The potential shifts are associated with radiation-produced H_2O_2 , and the open circuit potentials are slow to recover after removal from the radiation.

2.0 Experimental

Figure 2.1 is an illustration of the experimental apparatus and electrodes that were subjected to various gamma fluxes at the PNL gamma facility. The following five types of electrodes were inserted into a simulated waste chemistry of 3.0 m NaOH, 0.5 m NaNO₂, and 1.0 m NaNO₃ at room temperature.

1. Fisher® Scientific (Pittsburgh, PA), silver/silver chloride (saturated KCl), Model 13-620-53. This design was chosen because it minimized the amount of polymeric materials that would be sensitive to radiation damage. Both the inner and outer envelopes were glass. The salt bridge was a porous ceramic plug.
2. Fisher® Scientific (Pittsburgh, PA), mercury/calomel (saturated KCl), Model 13-620-52. Construction was identical to item 1.
3. Rosemount (Cedar Grove, NJ), Lazaran® II, silver/silver chloride (saturated KCl), Model 524-10759953. The electrode body was constructed of a microporous Kynar® (polyvinylidene fluoride) electrode body and salt bridge.
4. Platinum flag (Beckman, Fullerton, CA), 1.2 cm² area. Glass electrode body.
5. Specimen of A-537 carbon steel, 7.1 cm² area. A-537 was used to construct some of the double-shell tanks at the Hanford Site.

The calomel electrode was chosen for study because this type was used earlier at Savannah River for in-tank potential measurements. The Lazaran® electrode has been used at the Hanford Site for in-tank measurements of Tank 241-AN107. The Fisher silver/silver chloride electrode was included since it is a commonly used electrode design noted to be robust.

The potentials of these five electrodes were measured relative to a referee reference electrode of silver/silver chloride (4.0 m KCl electrolyte), which was kept outside the gamma source to ensure that there were no radiation effects on its electrochemical potential. Since the distance to the gamma source was approximately 14 ft (4.3 m) below ground level, the salt bridge of the referee electrode was made 22 ft (6.7 m) long. Polyethylene was used for the majority of the structural components because of its radiation resistance.

Potentials were measured between the referee reference electrode and the five test electrodes using five specially constructed 10¹² ohm input impedance, isolation amplifiers (Analog Devices AD204JN). These amplifiers in the unity gain configuration have a high common mode rejection of noise and freedom from ground loops. Data were recorded with a Strawberry Tree (Sunnyvale, CA) MINI-16 data acquisition system and an IBM-AT computer. Both room temperature and electrode container temperature were recorded. The shielding water in the gamma pit was unheated, so the experimental apparatus lowered into the gamma pit was a few degrees C below room temperature.

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Figure 2.1. Electrode Apparatus

Experiments were performed at the following gamma fluxes: 1.5E2, 3.0E3, 1.3E4, 1.1E5, and 2.1E6 R/h. At the end of the reference electrode tests (included platinum and carbon steel electrodes), the total fluence had accumulated to 9.35E8 R. At both the beginning and end of this test series, the potential of the referee reference electrode was measured against the PNL laboratory standard calomel reference electrode. The potential was -0.0452 V at the start and -0.0437 V at the end, within 0.002 V of the theoretical value, indicating that the referee reference electrode was functioning correctly. Table 2.1 shows the experimental flux and fluence data for the first series of tests.

After the reference electrode tests were completed, the bare platinum and carbon steel electrodes were tested in 3.0 m NaOH. The purpose of this second test series was to evaluate the effect of nitrite and nitrate on the open circuit potential while under gamma irradiation.

Table 2.1. Experimental Flux and Fluence Data

Flux R/h	Time, h	Fluence, R	Cumulative Fluence, R
1.58E2	92	1.47E4	1.47E4
3.08E3	72	2.22E5	2.36E5
1.33E4	72	9.58E5	1.19E6
1.13E5	93.3	1.06E7	1.17E7
2.13E6	97.3	2.07E8	2.19E8
2.13E6	336	7.16E8	9.35E8

3.0 Discussion

3.1 Reference Electrode Behavior

The electrochemical potential of each candidate reference electrode versus the referee reference electrode as a function of time is presented in Figures 3.1 through 3.4. Because the electrodes behaved similarly, only data for the highest flux are shown in these figures. A typical temperature-time plot is shown in Figure 3.5. The experimental potential data appear as a heavy, dark line, while the theoretical potential value is shown as a thin, horizontal arrow.

Both the flux and fluence had minimal effects on the electrochemical potential generated by the mercury/calomel and silver/silver chloride electrodes. Potentials remained stable within 0.002 V, making these electrode designs acceptable from the standpoint of stability and reproducibility of potential, even up to a flux of $2.1\text{E}6$ R/h and fluence of $9.4\text{E}8$ R. The principal disadvantage of these electrodes is that they leaked 1 to 2 mL/week of KCl electrolyte from their reservoirs through the porous ceramic tips. Consequently, without periodic electrolyte replenishment, the electrodes would dry out or allow significant contamination to enter in less than one month, resulting in drift of the generated reference potential.

Figure 3.1. Electrical Response of Silver/Silver Chloride Reference Electrode at $2.1\text{E}6$ R/h

Figure 3.2. Electrical Response of Mercury/Calomel Reference Electrode at $2.1E6$ R/h

Figure 3.3. Electrical Response of Lazaran Reference Electrode at $2.1E6$ R/h

Figure 3.4. Electrical Response of Lazaran Reference Electrode (second exposure to a flux of $2.1\text{E}6 \text{ R/h}$)

Figure 3.5. Temperature of the Laboratory and Gamma Pit

Figures 3.6 and 3.7 are photographs of the mercury/calomel and silver/silver chloride electrodes, respectively, new and after receiving a fluence of $9.4\text{E}8$ R. Cotton is used in these electrodes to hold the metal salt in contact with the internal electrical lead. During testing, radiation destroyed the cotton and allowed the internal metal salts, along with mercury in the calomel electrode, to fall to the bottom of the electrode compartment, as shown in the photographs. This occurrence does not affect the electrode potential. Furthermore, Fisher personnel are willing to build electrodes using glass fibers to hold the metal salts in position, and they can provide electrodes with electrolyte leakage rates below $5\text{ }\mu\text{L/h}$.

The Lazaran[®] reference electrode is a fully sealed design that does not permit replenishment of the electrolyte. The porous electrode body is constructed from a fluorinated polymer that would be expected to undergo significant radiation damage. According to Figure 3.3, potential deviations were starting to occur at a flux of $2.1\text{E}5$ R/h and a fluence of approximately $2\text{E}8$ R. The potential deviation is less than 0.005 V, indicating that up to this fluence, the electrode behavior remained useful. As seen in Figure 3.4, continued irradiation at $2.1\text{E}6$ R/h resulted in significant potential deviations (>0.050 V), and the electrode completely failed at a fluence of $9.4\text{E}8$ R.

Figure 3.8 is a photograph of a new Lazaran[®] electrode and another electrode that received a fluence of $9.4\text{E}8$ R. The surface of the irradiated unit is covered with blisters approximately 0.010 in. (0.025 cm) in diameter, with a crack running across each blister. The electrode body is hypothesized to have accumulated structural damage that allowed external contaminants to enter the electrode compartment. Fluence is thought to be more important than flux to the degradation process. Based on the simplicity of the design and its low maintenance, this reference electrode is the design recommended for the lower flux levels believed to exist in most of the waste tank environments.

3.2 Bare Metal Electrode Behavior

The effect of radiation on the open circuit or free corrosion potential of bare platinum and carbon steel electrodes was studied in two chemistries. Iron is passivated but corrodes slowly at a rate usually less than 0.5 mils/year (Divine et al. 1985) in a caustic environment, while platinum is totally inert. Nitrate and nitrite are important components in the waste solution whose effect on the open circuit potential under gamma radiation is unknown, but these components are known as both potent corrosion inhibitors and accelerators. Figures 3.9 and 3.10 show the potential as a function of flux in solutions of $3.0\text{ m NaOH} + 0.5\text{ m NaNO}_2 + 1.0\text{ m NaNO}_3$ and 3.0 m NaOH , respectively. In the nitrate and nitrite-containing solutions, the potential of the platinum electrode is a monotone function of flux, becoming increasingly positive (anodic) as the flux increases. A maximum potential anodic shift of 0.18 V was observed for the platinum electrode. The results for the carbon steel electrode are mixed, but the potential also becomes more positive with increased flux. At 158 R/h, a potential shift of over 0.12 V was observed for the carbon steel electrode, but this shift was not maintained at the next higher flux. After removal of the electrodes from the radiation field, recovery of the potential to the nonirradiated value was slow, requiring hours to days. Figures 3.11 and 3.12 show the potential-time response at a flux of $2.1\text{E}6$ R/h. A polarization of 0.1 V is significant in terms of its effect on stress corrosion cracking and pitting processes.

Figure 3.6. Mercury/Calomel Reference Electrode, New (left) and After Receiving a Fluence of 9.4×10^8 R (right)

Figure 3.7. Silver/Silver Chloride Reference Electrode, New (left) and After Receiving a Fluence of 9.48 R (right)

Figure 3.8. Lazaran^{4,22} Reference Electrode, New (right) and After Receiving a Fluence of 9.4E8 (left)

Figure 3.9. Potential vs Flux for the Carbon Steel and Platinum Electrodes (3.0 m NaOH, 0.5m NaNO₂, 1.0 m NaNO₃)

Figure 3.10. Potential vs Flux for the Carbon Steel and Platinum Electrodes (3.0 m NaOH)

Figure 3.11. Electrode Response of the Carbon Steel Electrode at $2.1\text{E}6$ R/h (3.0 m NaOH, 0.5 m NaNO_2 , 1.0 m NaNO_3)

Figure 3.12. Electrode Response of the Platinum Electrode at $2.1\text{E}6$ R/h (3.0 m NaOH, 0.5 m NaNO_2 , 1.0 m NaNO_3)

In contrast, tests (see Figure 3.10) conducted without the nitrate and nitrite indicated that an increasing flux results in the potential becoming increasingly negative (cathodic) for the platinum electrode. This effect was not clearly shown for the carbon steel electrode until a flux of $1\text{E}5$ R/h was reached. The technical literature indicates that oxygen-containing solutions become more anodic under irradiation, but these solutions were always near neutral in pH. There must be some major change in the G values at high pH so that the solution becomes net reducing.

Figure 3.13 is a photograph of the carbon steel electrode after it was subjected to a fluence of $9.4\text{E}8$ R in the $3.0\text{ m NaOH} + 0.5\text{ m NaNO}_2 + 1.0\text{ m NaNO}_3$ solution. Both the platinum and carbon steel electrodes were clean, shiny, and bright where exposed to the solution. About 1 cm above the solution level, the carbon steel specimen exhibited heavy rusting. The iron was free from general attack or uniform corrosion where the solution could wet the specimen. More ominously, the photograph shows pitting below the solution level.

3.3 Application of the Mixed-Potential Theory

The potentials generated by the mercury/calomel and silver/silver chloride reference electrodes were almost unaffected by the radiation flux, yet the open circuit potentials of the bare metal platinum and carbon steel electrodes were affected. The following interpretation of these experimental observations is somewhat speculative since certain essential data points remain to be determined. When two or more oxidation/reduction couples are present in a solution and are interacting with an electrode surface, mixed-potential theory provides a convenient method of predicting the result. Figure 3.14 is a schematic of various oxidation/reduction reactions that are possible with corroding metals, reference electrode half cells, and radiolytically formed species. Basically, mixed-potential theory requires a potential-dependent (E) electrochemical reaction (expressed as a current) for each oxidation and reduction process. The equations are coupled and solved through the current (I) continuity relationship:

$$\sum I_i = 0 \quad (3)$$

The electrode potential that results from satisfying the current continuity equation is the mixed potential or open circuit corrosion potential for a corroding electrode.

The iron corrosion reaction illustrates the process. The anodic process is the oxidation of Fe to Fe^{+2} while the cathodic reaction is the evolution of hydrogen. The current at which the two rate processes are equal is known as the corrosion current or exchange current, and the associated potential is the open circuit corrosion potential. If oxidizing radiolytic species are present (such as H_2O_2), an additional cathodic reaction (reduction of H_2O_2) can occur on the electrode surface. The potential moves into the anodic direction, since under mixed-potential theory, the new corrosion potential will always lie between open circuit potentials of the separated or unconnected oxidation/reduction systems. The potential-current density plot of Figure 3.14 also indicates that the corrosion rate increases, which is

Figure 3.13. Carbon Steel Electrode (A-537) After Receiving a Fluence of $9.4E8$ R

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Figure 3.14. Schematic Current-Potential Plot for Mixed-Potential Mechanism

consistent with experimental evidence. For a significant interaction of two different oxidation/reduction systems, the currents associated with the oxidation and reduction must be of similar magnitudes. In the case of iron corrosion, a corrosion rate of 0.5 mil/year corresponds to a current of about $1\text{E-}6\text{ A/cm}^2$. The reduction of $1\text{E-}6\text{ M H}_2\text{O}_2$ under diffusion control could support a limiting current of approximately $2\text{E-}7\text{ A/cm}^2$, indicating that mixed-potential theory is a plausible mechanism for explaining the anodic polarization of the carbon steel electrode in nitrate and nitrite-containing electrolyte.

The platinum electrode is not corroding but is responding to some ill-defined redox process involving the nitrate and nitrite. Under radiolysis, oxidizing species are formed that interact with the redox couple on platinum, and the potential moves in an anodic direction. To further increase the oxidizing effectiveness of the radiolytic environment, nitrate will react with hydrated electrons to decrease the net concentration of reducing species (Van Konynenburg 1986):

The cathodic movement of the potential in the 3.0 M NaOH solution in the absence of nitrate and nitrite is more difficult to explain. Reaction 4 will not be taking place; consequently, the net concentration of reducing species should be higher. The G values shown in Table 1.1 are for pure water in a pH range of 5 to 9. The G values are hypothesized to increase for the reducing species when the pH is very caustic; thus, the solution becomes net reducing in the absence of nitrate and nitrite.

Both the mercury/calomel (Ives and Janz 1961) and silver/silver chloride electrode systems are considered to be very reversible, meaning that their exchange current (i_0) is very high. The exchange current is a measure of the electrochemical reaction rate when the system is at equilibrium. The author has not been able to find experimental data to verify the magnitude of the exchange currents of each metal with its sparingly soluble chloride salt. Experimental data (Vetter 1967) for mercury in equilibrium with the mercurous ion and silver in equilibrium with the silver ion include measurements of exchange currents in the range of 5 A/cm^2 . Referring back to Figure 3.14, the redox currents for the illustrated silver/silver chloride electrode are several orders of magnitude higher than those for the radiolytically formed redox species. Though the reference electrode reactions interact with the new redox couples, their adjustment in open circuit potential has to deviate very little from the equilibrium value. Consequently, gamma radiation has very little effect on their generated potentials.

4.0 Conclusion

The following conclusions are based on the studies conducted of five types of electrodes exposed to gamma radiation at room temperature.

1. Both the Fisher mercury/calomel and Fisher silver/silver chloride reference electrodes generate constant reference voltages (within about 0.002 V) in radiation fields up to 2.1×10^6 R/h and a total fluence of 9.4×10^8 R. Electrochemical probe packages for insertion into radioactive environments can use reference electrodes based on these compositions. The Fisher® Scientific models should be ordered with a low electrolyte leakage rate salt bridge.
2. The Lazaran® silver/silver chloride reference electrode is satisfactory to somewhat lower radiation fluences (2×10^8 R). However, its low maintenance design, which never requires electrolyte additions, makes it the most attractive design for lower-fluence applications.
3. The radiolysis of oxygenated, simulated waste solutions results in the polarization of both platinum and carbon steel electrodes from their open circuit potentials, relative to the nonirradiated condition. Depending on the presence or absence of nitrate and nitrite, the polarization can be either anodic or cathodic. This potential dependence may have a significant impact on the propensity for stress corrosion cracking and pitting. Future laboratory testing that simulates waste tank conditions must be sensitive to this issue.
4. Mixed-potential theory offers a reasonable explanation of the radiation effects on the reference electrodes and the bare metal electrodes.

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