Development of a Robust Reference Electrode in Aggressive Chemical and Radiation Environments in the Hanford Waste Tanks– 26213

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ABSTRACT

The Hanford site stores more than 200 million liters of radioactive and chemically hazardous wastes from the production of weapons materials. The wastes are stored in 177 underground carbon-steel storage tanks, separated between 149 single shell tanks (SSTs) and 28 double shell tanks (DSTs). The DSTs provide critical retrieval and interim storage before the waste is vitrified in the Waste Treatment and Isolation Plant (WTP). The tanks will need to remain in-service far beyond the initial 40-year design life, and effective corrosion control practices must remain in force to extend the tanks' lifespans. This effort includes direct measurements of corrosion rate (e.g., ultrasonic measurements and corrosion coupons) and electrochemical processes (e.g., linear polarization measurements and open circuit potential measurements). The Hanford site began monitoring the corrosion potential in select DSTs in 2008. Of the 45 reference electrodes that have been installed, 29 have failed and 6 others provided unreliable results.

DOE-EM is supporting a 3-year program to develop a chemical and radiation resistant reference electrode for application in the Hanford tanks. The first year of the program focused on understanding the failure mechanism for the reference electrodes and identification of candidate construction materials that would mitigate degradation of the electrodes in the waste environment. During the second year of the program, the objectives were to: 1) test candidate materials under simulated waste conditions, 2) design components that will extend the service life of the electrode, 3) fabricate materials for prototype reference electrodes, and 4) assemble prototype reference electrodes for accelerated testing.

The reference electrode is constructed of four principal parts: 1) junction, 2) casing, 3) inner chamber backfill materials, and 4) the sensing wire. Principally, improvements of the junction, casing, and inner chamber backfill materials are being pursued. The junction material at the interface between the waste and the inner chamber of the reference electrode was identified as a critical component in the failure of the reference electrodes. Nine candidate replacement junction materials were tested under simulated waste conditions to evaluate permeation rate. These materials included a variety of polymeric and ceramic materials, some of which were 3-D printed. Thus far, porous polyvinylidene fluoride materials have performed satisfactorily and are being considered for prototype development. The commercial electrode casing materials in general have performed well. Additionally, 3-D printing of chemically and mechanically stable materials is being investigated as a means for further improvement in fabrication consistency.

SRNL has also investigated altering the reference electrode design to extend the service life. The new design of the interior of the reference electrode casing creates a longer, more tortuous path between the junction material and the electrode sensing wire. A finite element model was used to optimize the design without adversely impacting the circuit resistance of the electrode during the measurements, thus preserving the measurement accuracy while enhancing the service life.

The inner chamber back fill materials are also critical to the performance of the reference electrode. Materials that are resistant to intruding tank waste and provide a conductive path to the sensing wire were investigated. Gel and powder materials that are interspersed with a conductive chloride bearing material were tested for their influence on diffusion and electrode resistance.

All the investigated materials and components will be assembled, with collaboration from commercial vendors, to fabricate the initial prototypes. Accelerated testing of the prototypes will be initiated in Year 2 of the program and will be completed in Year 3. A recommendation on the materials of construction and the design of the new robust reference electrode will be presented to the Hanford tank farm facility.

INTRODUCTION

The Hanford site stores approximately 200 million liters of radioactive and chemically hazardous wastes. Of the 177 underground, carbon-steel storage tanks that contain the waste, 149 are single shell tanks (SSTs) and 28 are double shell tanks (DSTs) [1]. The double shell tanks provide interim storage before the waste is to be vitrified in the Waste Treatment and Isolation Plant (WTP). DSTs have been in service for 38 to 56 years, and current plans indicate that the WTP waste retrieval operations will be completed in 2075 [2]. Therefore, the tanks must remain in service beyond their 40-year design life. Thus, effective corrosion control practices must exist and remain [1].

One approach to assessing tank corrosion and stress corrosion cracking (SCC), is the use of electrochemical techniques to measure the open-circuit potential (OCP) or corrosion potential (E_{corr}) of the tank. The OCP provides a metric for assessment of the corrosion behavior (e.g., passivity, localized attack, etc.) of materials in a specified environment. For the DSTs, two corrosion mechanisms of concern are localized corrosion and stress corrosion cracking (SCC), the onset of each indicated by when the OCP of the tank steel exceeds the repassivation potential for localized corrosion (E_{rp}) or the critical cracking potential for SCC (CCP), as shown in Figure 1. This is a conservative approach as it ignores the gestation time for corrosion initiation and stable growth cannot be measured. The OCP, E_{rp}, and CCP are usually measured using laboratory tests in tank waste simulants or real wastes extracted from the tanks. However, the OCP also can be measured directly in the tank. The benefit of in-tank OCP measurements is that the effects of tank wall steel inclusions and of long-term contact with waste are more accurately represented than in laboratory tests. While OCP measurements are simple in practice, interpreting the data is complicated because of the presence of concurrent anodic and cathodic reactions that occur along the tank steel surface.

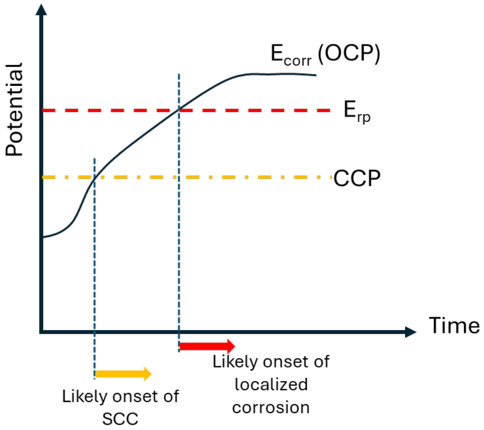

Figure 1. Diagram of the onset of localized corrosion or SCC when the OCP exceeds the repassivation potential or the critical cracking potential.

Since 2008, the structural integrity program at Hanford has used reference electrodes to monitor the tank material OCP [1, 3]. One of the underlying challenges with reference electrodes in the waste chemistry environment is long term stability. Failures have been noted within 2-3 years of service due to ingress of contaminants from the tank waste, specifically hydroxide ions, into the internal components of the reference electrode via the junction material, thus, altering the potential readings [4].

The junction material lies at the interface between the waste and the inner chamber of the reference electrode and allows ionic transport between the internal and external solutions for the purposes of potential measurements. Some key considerations for the material include the minimization of the junction potential, a steady flow rate, and chemical inertness [5]. The liquid junction potential occurs when different ions with varying mobilities come into contact, leading to a potential difference at the junction that is detrimental to measurement accuracy. A stable potential also requires a steady, gradual flow of the reference electrode's electrolyte into the test solution. The junction material must also not react with the test solution. Therefore, finding a material that can allow the ionic transport while simultaneously preventing the intrusion of contaminants from the waste, such as hydroxide ions, will increase the longevity of the reference electrodes.

MATERIALS AND TESTING

The materials listed in Table 1 have undergone laboratory testing to determine their efficiency and stability as junction material. An H-cell set up was used to monitor the pH changes across the candidate materials. More specifically, the set up included tap water on one side of the H-cell and 3 M sodium hydroxide on the other, as shown in Figure 2. The candidate junction materials were placed in the middle compartment of the cell so that sodium hydroxide would permeate through the frit. Silicon gaskets were placed on each side to prevent leaks. The pH was measured using a standard calibrated pH probe. Sodium hydroxide was chosen for testing because it has been found to cause failures of previous reference electrodes. Therefore, a material with tendency to minimize hydroxide permeation will limit the number of failures.

Table 1. Materials matrix for reference electrode junction

Nafion
NASICON
Polyvinylidene fluoride
Alumina

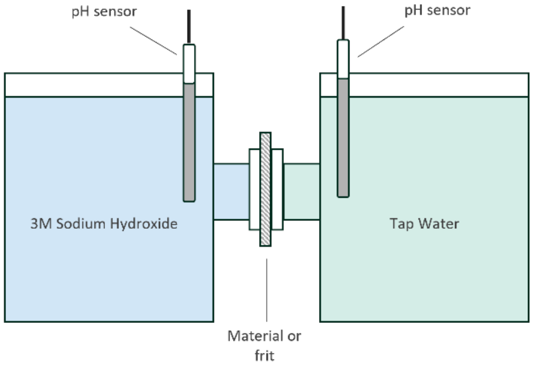

Figure 2. Schematic of H-cell set up using sodium hydroxide and tap water.

RESULTS AND DISCUSSION

H-Cell Experimentation

Nine materials were tested over a span of eight days, with pH change for the tap water tracked and monitored for each. The pH change in the tap water was measured relative to its starting pH to determine the extent of ion transport. The side with tap water was of interest because of the natural diffusion of dissolved sodium hydroxide from an area of high concentration to low. Because an ideal material is expected to minimizes the permeation of contaminants, smaller pH changes were more desirable. The H-cell test results at room temperature are shown in Figure 3. NASICON material is not included in this graph because less than 24 hours into the experiment it disintegrated and thus was not tested for further use.

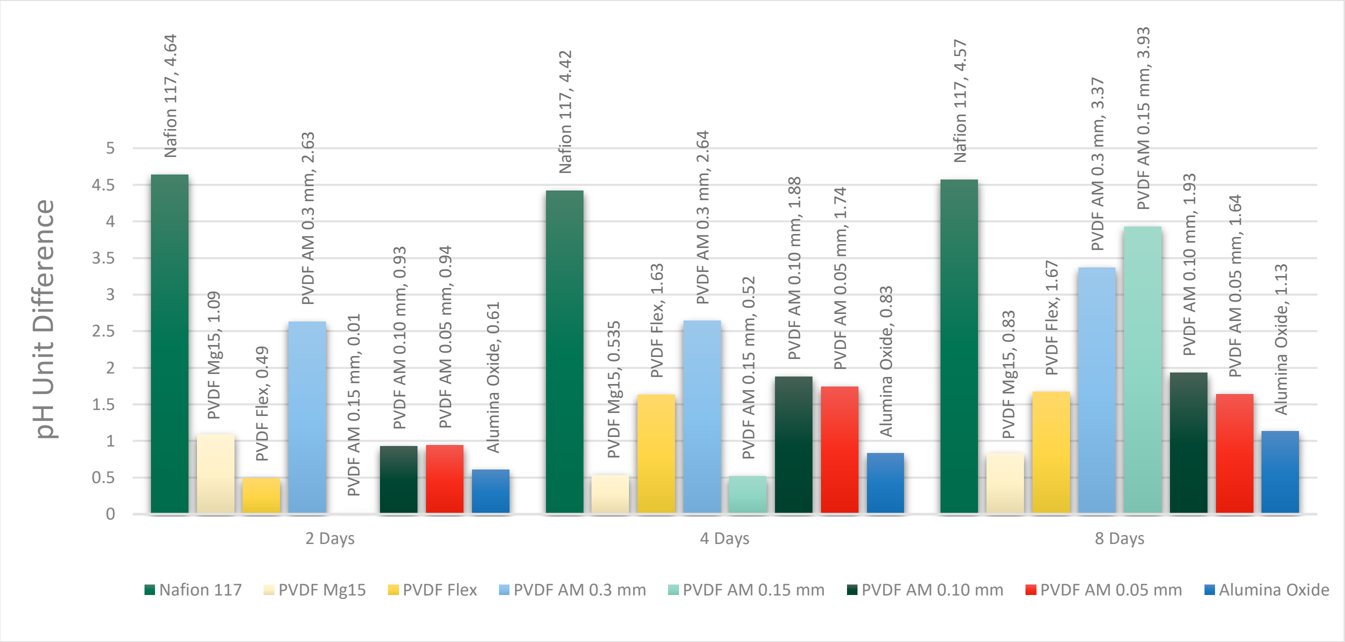

Figure 3. pH unit difference over time with various materials.

Nafion 117 performed poorly in the highly caustic environment, having the highest pH difference of the materials tested. Future testing of this material will not be considered further. In contrast, alumina oxide showed small consistent pH changes over time, more specifically, on day eight only showed a 1.13 pH unit difference. Polyvinylidene fluoride (PVDF) MG15, a vendor-supplied, low-porous homopolymer, shows consistently small perturbations when measuring the pH. PVDF Flex, also supplied by a vendor, is a flexible copolymer with larger pore sizes also exhibited small perturbations, albeit somewhat larger than MG15.

Additional additive manufactured (AM) PVDF materials with various layer heights were tested. In AM, the layer height is the thickness of each individual layer of material, affecting the material quality, strength and porosity. Thinner layers provide higher resolution and smoother surface finish, while thicker layers print faster but have the potential for poorer adhesion. Larger layer heights also typically cause an increase in porosity [6]. Here, the difference of the layer heights can be observed in correlation with the pH difference in the H-cell measurements. The smaller layer heights of 0.10 mm and 0.05 mm consistently demonstrate a lower pH difference and ion diffusion; after 8 days, the pH increase was less than 2. In comparison, the larger layer heights of 0.15 mm and 0.3 mm were associated with a pH change between 3 and 4 by day 8.

The comparison of the physical differences of the materials before and after testing also provide more insight in chemical inertness and lifespan. In Figure 4, the PVDF materials are shown after the testing, with the first row showing the side exposed to the tap water, and the second row showing the side exposed to the sodium hydroxide. The tap water sides generally show limited to no discoloration on any of the materials, but discoloration can be identified on the side exposed to the sodium hydroxide. The Flex, MG15 and lower layer height PVDF show slight discoloration, but the larger layer height material shows pronounced discoloration. The color change is likely caused by a chemical reaction, dehydrofluorination, that is known to degrade the polymer backbone over time [8]. No color change is observed for alumina.

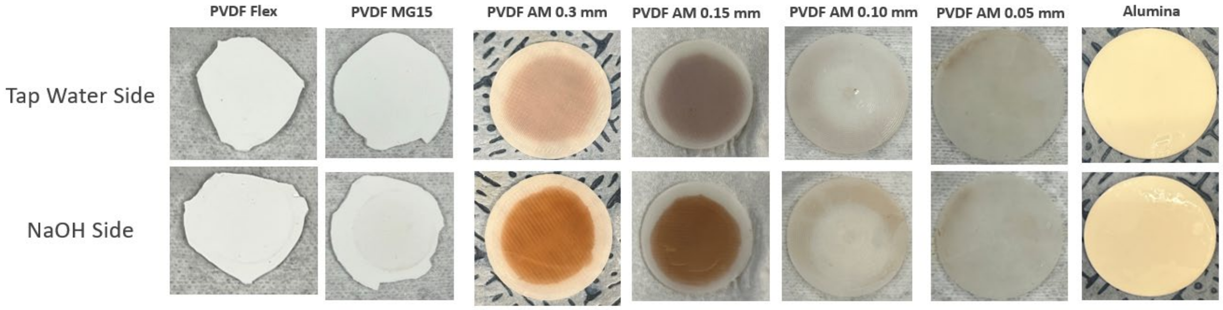

Figure 4. Material after H-cell testing.

Temperature conditions affect the mobility of hydroxide ions through the material, as well as the degree of dehydrofluroination, and additional analysis is required for material selection. Additional tests will be performed in the future at 30 and 70 °C, which are representative temperatures of the waste environment in the Hanford double shell tanks.

Design Enhancements

To address the problem of tank waste intrusion, the prototype body of the reference electrode involves modifying the reference electrode body such that the chemical path between the junction material and the Ag/AgCl sensing element is elongated. Implementation of an internal baffled tortuous path provides further hindrance by slowing the diffusion of contaminant ions (Figure 5). Alongside physical changes to the reference electrode, the properties of the fill solution will be selected to also impede contaminant ions.

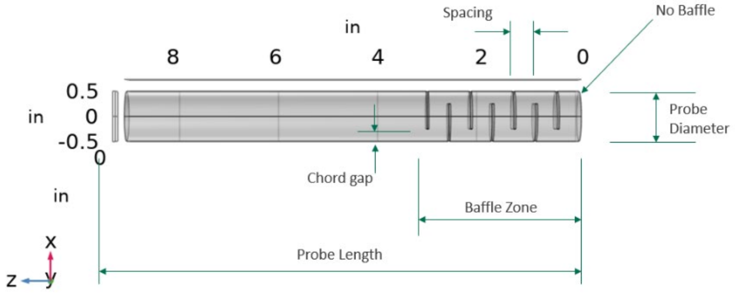

Figure 5. Tortuous path schematic.

A finite element model was used to investigate the effect of baffle size and number on the diffusion time from the electrode junction to the sensing wire. Figure 6 shows that when baffle size is 75% or greater of the reference electrode inner diameter, the diffusion time increases by a factor of three to four with 4-5 baffles. This increase in diffusion time is expected to correlate with an increased reference electrode lifetime, resulting in a lifespan of greater than 10 years.

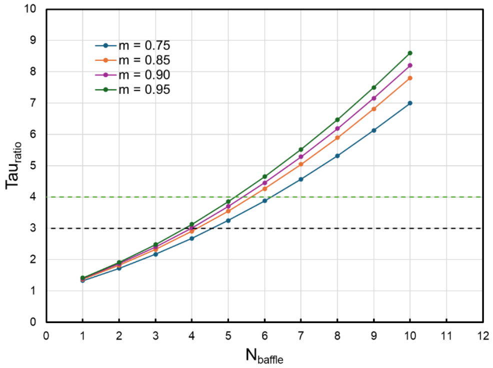

Figure 6. Time scale associated with the diffusion of a species vs. number of baffles, where m is the factor by which the baffle diameter is reduced with respect to the reference electrode inner diameter.

It is recognized that an increase in the distance and tortuosity of the diffusion path may have an adverse impact on the resistance, affecting the accuracy of the potential measurement. A second finite element model was performed to assess the effects of the baffle arrangement on the potential measurements. As shown in Figure 7, the error in the potential measurement with the same baffle configuration, as described above, is less than 0.1%. Thus, the baffles are anticipated to increase reference electrode lifetime without sacrificing accuracy.

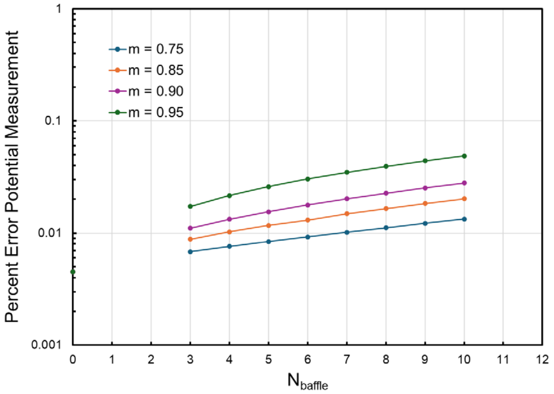

Figure 7. Percent error potential measurements vs. number of baffles, where m is the factor by which the baffle diameter is reduced with respect to the reference electrode inner diameter.

Prototypes implementing the baffle design are currently being produced and will be tested with standout materials from the H-cell junction testing. Additionally, various electrolyte fill solutions will be tested in these prototypes to further enhance the lifespan, stability and overall performance of the reference electrode. A chemical exposure durability test to waste simulants will be conducted on all reference electrode component materials (i.e., housing, junction, internal chamber fill and sensing wire). The simulants will be representative of the waste environment in the Hanford Double Shell Tanks (DST).

CONCLUSIONS

DOE-EM has undertaken a research program to develop reference electrodes that can withstand the waste tank environment for longer periods of time, increasing confidence in system performance. Materials testing is currently underway to determine the most efficient junction material for the reference electrode. Testing has been performed in an H-cell set up to provide information on the mobility of hydroxide ions through chosen materials. As hydroxide ions have been previously shown to be a cause of failure for the reference electrodes, the tests will assist in narrowing down material selection for a robust reference electrode. Future testing parameters will include elevated temperatures of 30°C and 70°C to mimic the tank environments. Alongside the junction materials, an alternative design concept to the reference electrode body that provides a tortuous path is presented. The finite element study concluded that with the tortuous path, the reference electrode should last more than 10 years.

REFERENCES

1. C. L. Girardot, RPP-7574, Rev. 8, "Double-Shell Tank Integrity Program Plan", August 10, 2021.
2. Parsons, *Final Report: Waste Treatment and Immobilization High Level Waste Treatment Analysis of Alternatives.* Richland: Office of River Protection, 2023.
3. M. M. Dahl and R. J. Crosswhite, RPP-RPT-51766, Rev. 41, *Corrosion Probe Monitoring Systems: January through March 2024 Quarterly Report*, May 2024.
4. K. Evans, et al., In-Tank Corrosion Probes: DNV laboratory evaluations of reference electrodes, Presentation at the Tank Integrity Expert Panel Corrosion Subgroup Meeting, Denver, CO, March 2023.
5. K. S. Sykes, J. Jiang, B. J. Wiersma, S. Chawla, N. Sridhar, K. Evans, and J. A. Beavers, "*Design and Materials of Reference Electrodes for Radioactive Waste Tank Service – A Literature Review,"* SRNL-STI-2024-00539, Rev. 0, November 2024.
6. J. Brackett, D. Cauthen, J. Condon, T. Smith, N. Gallego, V. Kunc, and C. Duty, *"The impact of infill percentage and layer height in small-scale material extrusion on porosity and tensile properties,"* Additive Manufacturing, 2022, **58**(15): 103063.
7. J.A. Choren, S.M. Heinrich, M.B. Silver-Thorn, "*Young's modulus and volume porosity relationships for additive manufacturing applications,"* J. Mater. Sci., 2013, **48**(15), 5101-5112.
8. J. Sharma, C. Totee, V. Kulshrestha, and B. Ameduri, *"Spectroscopic evidence and mechanistic insights on dehydrofluorination of PVDF in alkaline medium,"* European Polymer Journal. 2023, 201, 11280.

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