

2. To: (Receiving Organization) Distribution	3. From: (Originating Organization) Equipment Engineering	4. Related EDT No.: N/A
5. Proj./Prog./Dept./Div.: RPP Corrosion Probe	6. Design Authority/Design Agent/Cog. Engr.: EC Norman Resp.	7. Purchase Order No.: N/A
8. Originator Remarks: This document satisfies the requirements of Milestone A.2-1 of FY 2000 TTP # RLO-9-WT-41		9. Equip./Component No.: N/A
11. Receiver Remarks:		10. System/Bldg./Facility: N/A
11A. Design Baseline Document? <input type="checkbox"/> Yes <input checked="" type="checkbox"/> No		12. Major Assm. Dwg. No.: N/A
		13. Permit/Permit Application No.: N/A
		14. Required Response Date: N/A

15. DATA TRANSMITTED					(F)	(G)	(H)	(I)
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	Approval Designator	Reason for Transmittal	Originator Disposition	Receiver Disposition
1	RPP-5694		0	A Plan to Develop, and Technical & Administrative Demonstrates EN Based Requirements Necessary for Corrosion Monitoring Proceduralized Use of EN Systems in Hanford Site Waste Tanks Systems at Hanford	N/A	1	1	
				ECN 8/22/00				

16. KEY		
Approval Designator (F)	Reason for Transmittal (G)	Disposition (H) & (I)
E, S, Q, D OR N/A (See WHC-CM-3-5, Sec. 12.7)	1. Approval 2. Release 3. Information 4. Review 5. Post-Review 6. Dist. (Receipt Acknow. Required)	1. Approved 2. Approved w/comment 3. Disapproved w/comment 4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)											
(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN
		Design Authority				1	1	EA Fredenburg	<i>EA Fredenburg</i>	8/22/00	
		Design Agent				1	1	NW Kirch	<i>NW Kirch</i>	8/25/00	R2-11
1	1	Resp. Cog. Engr. EC Norman	<i>EC Norman</i>	8/22/00							
1	1	Resp. Cog. Mgr. AH Friberg	<i>AH Friberg</i>	8/24/00							
		QA									
		Safety									
		Env.									

18. EC Norman EC Norman Signature of EDT Originator 8/22/00 Date	19. GP Purcell Authorized Representative for Receiving Organization 8/22/00 Date	20. AH Friberg Design Authority/Cognizant Manager Resp. 8/25/00 Date	21. DOE APPROVAL (if required) Ctrl No. _____ <input type="checkbox"/> Approved <input type="checkbox"/> Approved w/comments <input type="checkbox"/> Disapproved w/comments
---	--	--	--

A Plan to Develop and Demonstrate Electrochemical Noise Based Corrosion Monitoring Systems in Hanford Site Waste Tanks

E. C. Norman

CH2M HILL Hanford Group, Inc.

Richland, WA 99352

U.S. Department of Energy Contract DE-AC06-96RL13200

EDT/ECN: 629683

UC: 2030

Org Code: 74700

Charge Code: 112671

B&R Code: EW4010000

Total Pages: 23

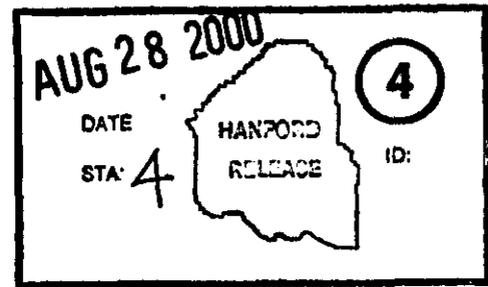
Key Words: corrosion monitoring/control, electrochemical noise, probe

Abstract: This document describes changes that need to be made to the site's authorization basis and technical concerns that need to be resolved before proceduralized use of EN based corrosion monitoring systems is fully possible at the Hanford Site. This report meets the requirements of TTP-RL09-WT-41 Milestone A.2-1.

TRADEMARK DISCLAIMER. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

Printed in the United States of America. To obtain copies of this document, contact: Document Control Services, P.O. Box 950, Mailstop H6-08, Richland WA 99352, Phone (509) 372-2420; Fax (509) 376-4989.

 8/29/00
Release Approval Date



Release Stamp

Approved For Public Release

**A Plan to Develop and Demonstrate Electrochemical Noise Based
Corrosion Monitoring Systems in Hanford Site Waste Tanks**

**G. L. Edgemon
Hiline Engineering and Fabrication, Inc.
2105 Aviator Drive
Richland, Washington 99352**

Table of Contents

Table of Contents 2
Introduction 3
Existing Hanford Waste Composition Specifications 4
EN Based Corrosion Monitoring 5
Current Technical Issues 6
 Modifications to Field Equipment 6
 Additional Laboratory Work 12
Impact on Tank Farm AB 16
Impact on Tank Farm OSDs 17
Summary and Conclusions 17
Recommendations for Future Work 19
References 20

Introduction

Underground storage tanks made of mild steel are used to contain radioactive waste generated by plutonium production formerly conducted at the Hanford Site. Tanks are of a single-shell design or double-shell design. Corrosion of the walls of these tanks is a major issue. Corrosion-related failure of single-shell waste tank walls could lead to the leakage of radioactive contaminants to the soil and groundwater. Corrosion of the walls of double-shell tanks could lead to leakage of waste into the annulus between shells. Leakage of waste to the annulus would demand the expensive and time consuming process of transferring waste from the failed tank to an intact tank.

Corrosion monitoring is currently provided at the Hanford Site through a waste chemistry sampling and analysis program. In this process, tank waste is sampled, analyzed and compared to corrosion control specifications derived from laboratory exposure of coupons in simulated waste. Tank wall corrosion is inferred by matching measured tank chemistries to the results of the laboratory simulant testing. This method is expensive, time consuming, and does not yield real-time data. A project to improve the Hanford Site's corrosion monitoring strategy was started in 1995.

A small number of techniques have previously been tried at Hanford and elsewhere within the DOE complex to determine the corrosivity of nuclear waste stored in underground tanks [1]. Coupon exposure programs, linear polarization resistance (LPR), and electrical resistance techniques have all been tried with limited degrees of success. These techniques are most effective for monitoring uniform corrosion, but are not well suited for early detection of localized forms of corrosion such as pitting and stress corrosion cracking (SCC). Pitting and SCC have been identified as the most likely modes of corrosion failure for Hanford Double Shell Tanks (DST's) [2-3].

Over the last 20 years, a new corrosion monitoring system has shown promise in detecting localized corrosion and measuring uniform corrosion rates in process industries [4-20]. The system measures electrochemical noise (EN) generated by corrosion. The term EN is used to describe low frequency fluctuations in current and voltage associated with corrosion. In their most basic form, EN-based corrosion monitoring systems monitor and record fluctuations in current and voltage over time from electrodes immersed in an environment of interest. Laboratory studies and field applications have shown that different types of corrosion create different patterns of current and voltage fluctuations (i.e., EN). By monitoring the EN produced by corrosion on electrodes immersed in Hanford waste tanks, waste tank corrosion conditions can be observed in real-time.

A two-year laboratory study was started at Hanford in 1995 to provide a technical basis for using EN-based systems to monitor corrosion in Hanford's nuclear waste tanks [21]. Based on this study, a prototype system was constructed and deployed in DST 241-AZ-101 in August 1996 [22]. Based on the successful demonstration of this prototype, a full-scale system was designed and installed into DST 241-AN-107 in September 1997 [23]. A second-generation full-scale system similar to the 241-AN-107 system was designed, fabricated and installed in 241-AN-102 in August 1998 [24]. The third-generation system with numerous design improvements was

deployed in DST 241-AN-105 in fiscal year 2000 [25]. A fourth-generation system is scheduled to be deployed in a DST early in fiscal year 2001.

The new corrosion monitoring systems are the cornerstone of an effort to augment the existing corrosion monitoring program at Hanford (waste chemistry sampling/analysis) by incorporating real-time corrosion data. Real-time EN based corrosion monitoring should eventually be an integral part of Hanford's tank integrity program as it would help to ensure safe, efficient, long term waste storage until retrieval and final disposal can be accomplished. This document describes changes that need to be made to the site's authorization basis and technical concerns that need to be resolved before proceduralized use of EN based corrosion monitoring systems is fully possible at the Hanford Site.

Existing Hanford Waste Composition Specifications

Initial corrosion control specifications for DSTs at Hanford were developed from the results of an extensive SCC testing program at the Savannah River Site (SRS) [26]. It was found that corrosion of low carbon steels was dependent on hydroxide, nitrite, and nitrate concentrations. Addition of minor constituents such as carbonate, phosphate, sulfate, silicate, fluoride, and chloride in low concentrations did not have a significant impact on corrosion behavior of test materials. Thus, SRS corrosion specifications focused on the waste concentrations of hydroxide, nitrate, and nitrite. Because the tank materials used at SRS are similar to the DST steels at Hanford, corrosion specifications developed from the SRS tests were applied to tank farm operations at Hanford. Since the SRS testing program focused on SCC, which generally occurs at temperatures above normal Hanford tank temperatures, and on waste types that did not adequately describe all of the Hanford waste tanks, the new corrosion specifications were considered as an interim measure of corrosion control until further testing could be performed to augment the SRS results.

In 1980, the Hanford Waste Tank Corrosion Studies were initiated to provide the necessary corrosion data to define safe operating conditions for the Hanford DSTs [26]. Rockwell Hanford personnel supplied tank chemistry information to Pacific Northwest Laboratories who performed tests on several thousand coupons in various environments and statistically interpreted the data. Corrosion was again found to be largely controlled by waste concentrations of hydroxide, nitrate, and nitrite. Current Hanford corrosion specifications are based on these studies [27].

Regular time intervals for tank waste chemistry sampling for corrosion monitoring are not defined in the current Tank Farm Authorization Basis (AB) or the Operational Specification Documents (OSDs) [27-29]. OSD T-151-00007 specifies only that tank contents must comply with the given waste composition limits. Tank inputs must be controlled so that tank contents comply with composition limits following a transfer. Verification of compliance with composition limits is not necessary for transfers from catch tanks containing waste previously verified to comply with DST composition limits, or condensate from DSTs. For all other transfers, it must be verified that the composition limits in the receiving tank will not be exceeded prior to transferring additional waste into a tank.

Time allowed for recovery from out of specification waste chemistry discoveries is not defined in the current Tank Farm AB or OSDs. If a tank content composition limit is violated, waste transfers in progress are stopped and the Tank Farm Operations Shift Manager is notified. The Shift Manager then notifies the managers of Tank Farm Operations and Tank Farm Engineering. Additional notifications are made per WHC-IP-0842, Volume II, Section 5.10 and a recovery plan is developed. Recovery plans include actions to be taken to return tank chemistry to the proper operating specifications. No time limit is specified in the current Tank Farm AB or OSDs for performance and completion of the recovery plan. Tanks 241-AY-101, 241-AN-102 and 241-AN-107 continue to be operated even though they have remained out of corrosion control waste chemistry specification limits for long periods of time (up to several years).

EN Based Corrosion Monitoring

Due to difficulties in consistently maintaining the Hanford Site waste chemistry corrosion control specification in some of the Hanford DSTs and recent revelations concerning the corrosivity of potential waste chemistries that could be encountered during the DST sludge washing process, the use of EN based corrosion monitoring systems has been proposed as a way to improve the safety and efficiency of the existing Hanford Site corrosion control program [30].

For many years, EN has been observed in plant and field applications during corrosion and other electrochemical reactions, and the phenomenon is well established. Typically, EN consists of low frequency (< 1 Hz) and small amplitude signals that are spontaneously generated by electrochemical reactions occurring at corroding or other surfaces. Laboratory studies and recent reports have reported that EN analysis is well suited for monitoring and identifying the onset of localized corrosion, and for measuring uniform corrosion rates [4-20].

Like most EN based corrosion-monitoring systems, the Hanford tank corrosion monitoring systems are designed to measure instantaneous fluctuations in corrosion current and potential between sets of three nominally identical mild steel electrodes (a working, a counter, and a pseudo-reference electrode) immersed in the waste. The fluctuations in current and potential are caused by corrosion of the electrodes. It has been shown that each type of corrosion phenomenon presents a unique relationship between corrosion current and potential transients in the temporal data [4-23].

In addition to eight channels of corrosion monitoring, the latest Hanford systems also incorporate other instrumentation such as thermocouples, a high liquid level detector, ports for pressure/gas sampling, and strain gauges to monitor the effects of tank operations on the downhole instrumentation [22-25]. In tank portions of the probes have been subjected to site seismic and structural analyses for general service equipment [31, 32]. These features add functionality to the probe, provide for a better understanding of the relationship between corrosion and other tank operating parameters, and optimize the use of the riser that houses the probe in the tank.

Following installation of the in-tank and ex-tank portions of the system, data can be collected from the eight channels of corrosion monitoring electrodes. User configurable software is typically set up to simultaneously collect current and voltage measurements (i.e., EN) from all eight channels at a rate of one measurement per second. Data is recorded continuously unless

interrupted by system fault or manually stopped by the operator. Periodically, data are downloaded for analysis. Data are subjected to a number of statistical analyses and compared with historical data from other Hanford systems, laboratory test data on Hanford waste simulants, and EN data from other process chemical industries [21]. Following this process, conclusions are drawn about corrosion occurring in the waste tank, system operation, and potential system troubles.

Interpretation of EN based corrosion monitoring data is currently the responsibility of a corrosion engineer. Since corrosion probes are not covered in the current Tank Farm AB or OSDs, corrosion probe data are not officially used to influence tank farm operations. Changes in the Tank Farm AB or OSDs are necessary to facilitate a controlled use of corrosion monitoring data in tank farm operation decisions.

Current Technical Issues

Several technical issues demand resolution before proceduralized use of corrosion monitoring at Hanford is possible. These issues include the need for modifications to field equipment to overcome electrostatic interference in the data cable and the need for additional laboratory testing to resolve technical concerns that have arisen during field operation.

Modifications to Field Equipment

A prerequisite for using EN based corrosion monitoring systems under rigid procedures and controls at Hanford is to build a sufficiently large high-quality tank corrosion database to facilitate interpretation of new data as the number of monitored tanks is increased. Four systems have been installed at Hanford to date. The first three systems met with limited success. The fourth system is working properly and returning high-quality data. A fifth system based on the fourth system design is scheduled for installation in early FY 2001. Despite the collection of over 580 million points of tank corrosion data from these systems, a high quality database of sufficient size is still lacking due to performance problems with the systems. All systems installed to date during the development effort have been hampered by system configuration and hardware issues in collecting high quality data. These problems can be corrected, but will demand a significant engineering effort.

The 241-AZ-101 system was the first EN system installed at Hanford and demonstrated that these systems could withstand a waste tank environment. The 241-AZ-101 system was installed in August 1996. Although a great deal of data were collected from a single channel immersed in the waste, the instrument sensitivity was deemed to be too low and monitoring was discontinued in 1999. Electrochemical *current* noise data collected from this tank were of high quality, but the corresponding voltage noise data was not acceptable [22, 33, 34].

Tank 241-AN-107 was instrumented with a larger, more robust system in September 1997 [23]. Electronics were upgraded to correct the voltage sensitivity problem seen in the 241-AZ-101 system. No funding was provided the following year for the necessary level of data analysis to validate system performance. In September 1998, data from the 241-AN-107 system were finally analyzed. It was found that data quality was low due to external electrostatic noise

pickup along the long data cable that leads from the in-tank probe to the data collection hardware housed outside the tank farm [35]. No funding was provided to troubleshoot or repair the 241-AN-107 system until FY 2000.

In late FY 1998, a system was installed into 241-AN-102 [24]. Instrumentation used on the 241-AN-102 system was expected to correct the data cable noise pickup that plagued the 241-AN-107 system. However, analysis of the 241-AN-102 data revealed problems similar to those experienced with the 241-AN-107 system. Although the new system software greatly speeds the data analysis process, external noise and interference in the data has rendered the existing 241-AN-102 data too questionable for use [36].

As indicated by the performance of the 241-AN-102 and 241-AN-107 systems, several technical issues related to data collection need to be resolved before EN based corrosion monitoring systems are considered for Hanford DSTs. The primary concern with data collection involves interference with the analog signal as it passes from the electrodes immersed in tank waste up to the corrosion monitoring hardware.

On the 241-AN-102 system, Belden 1061A data cable is used to transmit data from the in-tank probe to the data collection hardware. The data cable extends from the top of the corrosion probe approximately 300 feet into the 241-AN-274 caustic addition building where it passes through MTL Model 755 AC intrinsic safety barriers before final termination in the corrosion monitoring hardware. A schematic of the 241-AN-102 system is shown in Figure 1.

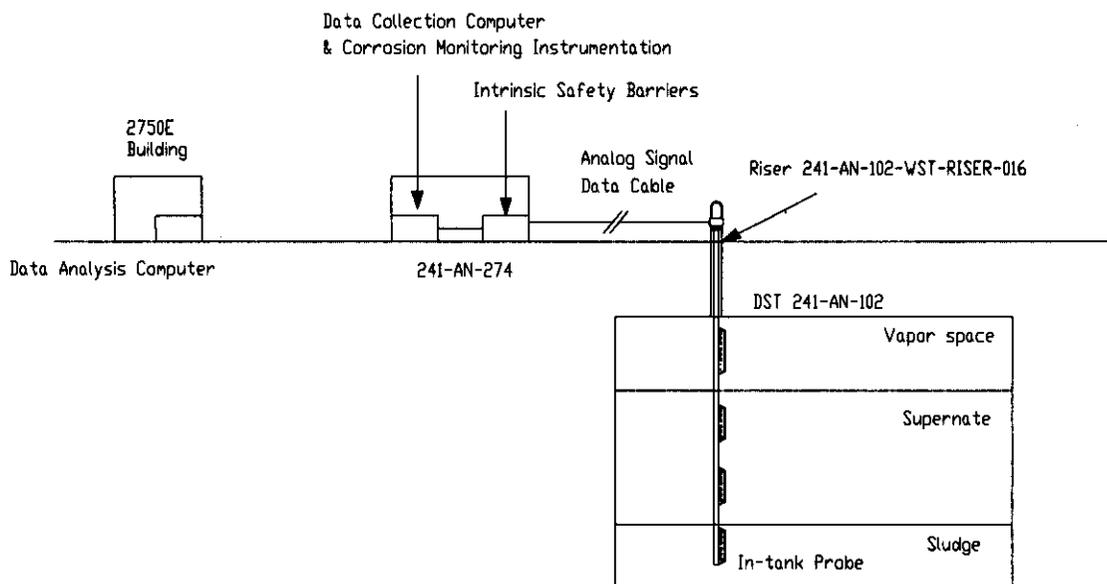


Figure 1: Schematic of field installation of the 241-AN-102 corrosion monitoring system

On the 241-AN-107 system, Belden 1220B data cable is used to transmit data from the in-tank probe to the data collection hardware. The data cable extends from the top of the corrosion probe into Model MTL 755 AC intrinsic safety barriers then runs approximately 500 feet into the 241-AN-271 instrument building where it terminates at the corrosion monitoring hardware. A schematic of the 241-AN-107 system is shown in Figure 2.

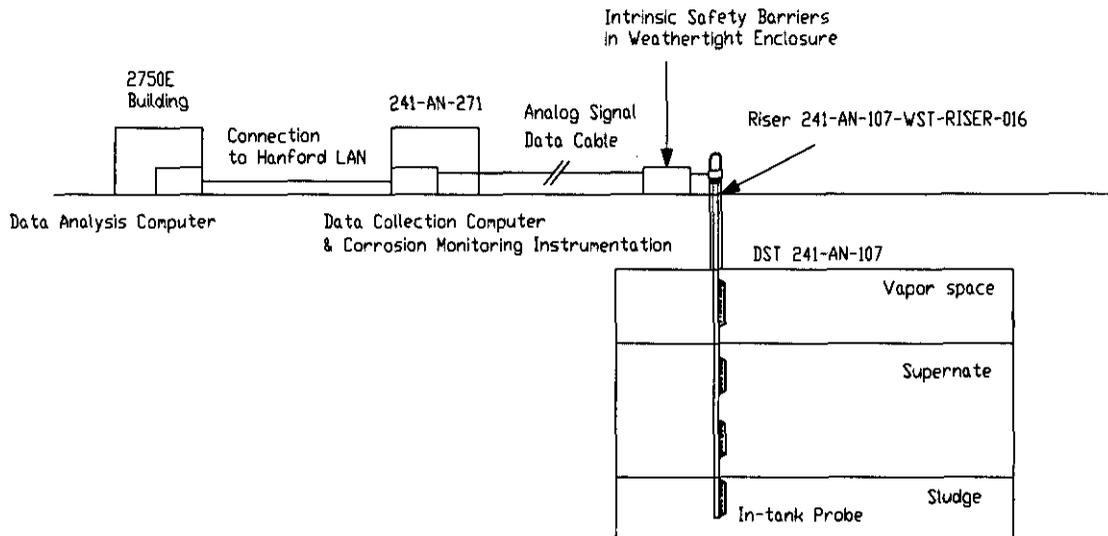


Figure 2: Schematic of field installation of the 241-AN-107 corrosion monitoring system

Both the Belden 1061A and 1220B data cables utilize bundles of unshielded twisted pair conductors with an overall grounded foil shield. The foil shield is grounded at the instrument ground on the 241-AN-102 system and at the tank on the 241-AN-107 system. Both systems perform poorly due to external electrostatic noise pickup and signal loss over the long cable length.

This problem was detected on both systems by comparing data collected over the same period of time on different channels as shown in Figure 3. Figure 3 shows mean current and mean potential data collected on two channels of the 241-AN-102 system over the same period of time. Channel 2 monitors C-ring electrodes located in the vapor space of the tank. Channel 6 monitors C-ring electrodes located in the supernate liquid near the bottom of the tank. In a normally operating system, peaks and valleys in the data indicate changes in corrosion behavior. Corrosion behavior on electrodes located in the vapor space of a tank should be distinctly different than the corrosion behavior of electrodes located in the liquid phase of the waste. At many points in this data set (and many other data sets) concurrent peaks were recorded on channels in the vapor space (Ch. 2) and channels in the supernate (Ch. 6). A particularly obvious

peak is located at ~12:00 p.m. on 12/1/98. In fact, the same types of peaks were recorded on all channels at the same time during this and other periods of collection. Since it is virtually impossible for corrosion events to simultaneously impact all channels many times each day, both in the vapor space and the liquid, it is clear that the cabling or other system component is picking up an external source of interference. This interference renders the data invalid. Similar problems are being recorded in the 241-AN-107 system.

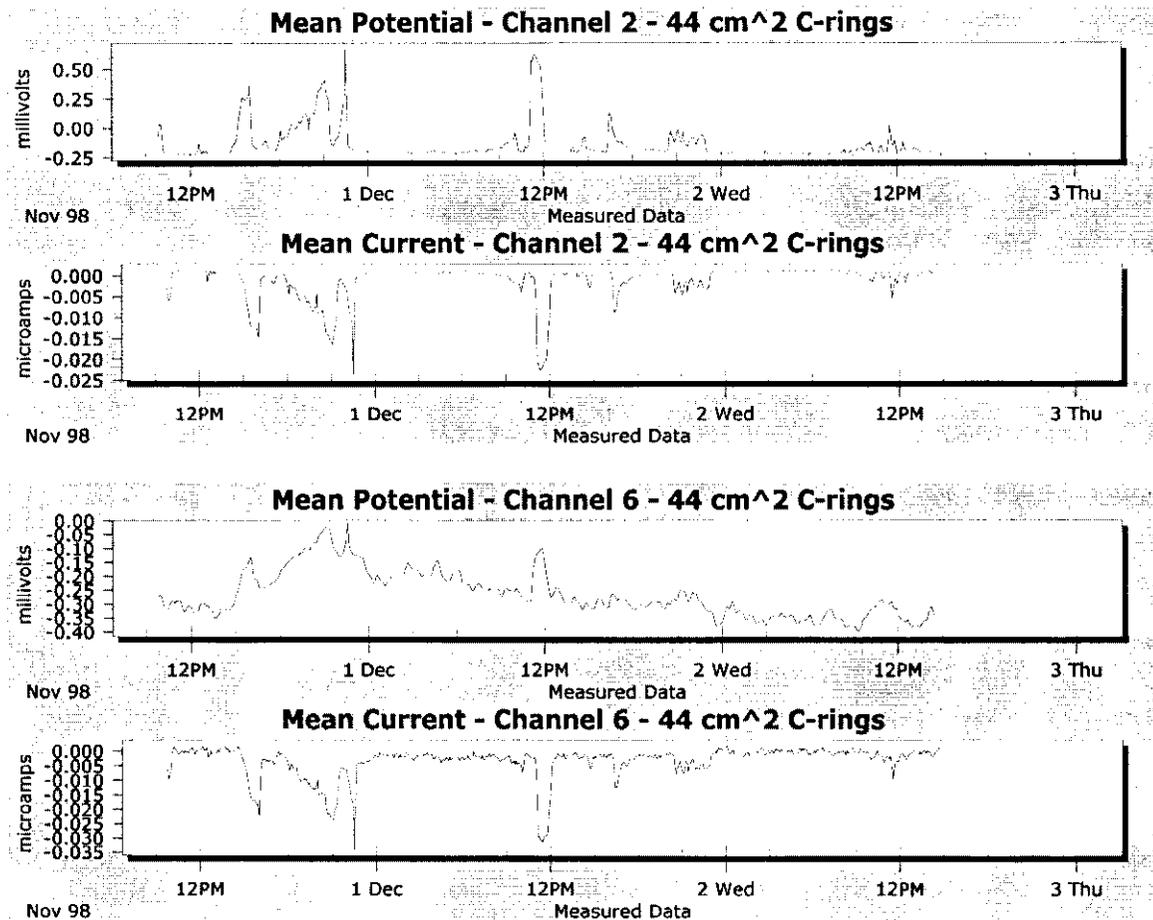


Figure 3: Mean current and mean potential data collected from electrodes in tank 241-AN-102 vapor space (Channel 2) and in the supernate (Channel 6). Concurrent spikes in the data indicate that the data cable is picking up interference from an external source of noise.

In January 2000 a new system was installed in 241-AN-105. The system was redesigned to correct the data collection problems being experienced with the 241-AN-102 and 241-AN-107 systems. A schematic of the 241-AN-105 system is shown in Figure 4. In the 241-AN-105 system, Belden 8178 data cable is used to transmit data from the in-tank probe to the data collection hardware. The data cable extends from the top of the corrosion probe approximately 10 feet into the MTL Model 755 AC intrinsic safety barriers and corrosion monitoring hardware. The data signal is digitalized by the corrosion monitoring equipment and transmitted through

Belden 9842 cable approximately 500 feet into a data analysis computer housed in the 241-AN-271 instrument building.

Like the 241-AN-102 and 241-AN-107 systems, the overall foil shield on the data cable carrying the analog signal (Belden 8178) is grounded to provide a level of protection from electrostatic interference. However, each twisted pair in the cable is connected to a driven foil shield that is held at the same potential as the conductors by a circuit in the corrosion monitoring equipment.

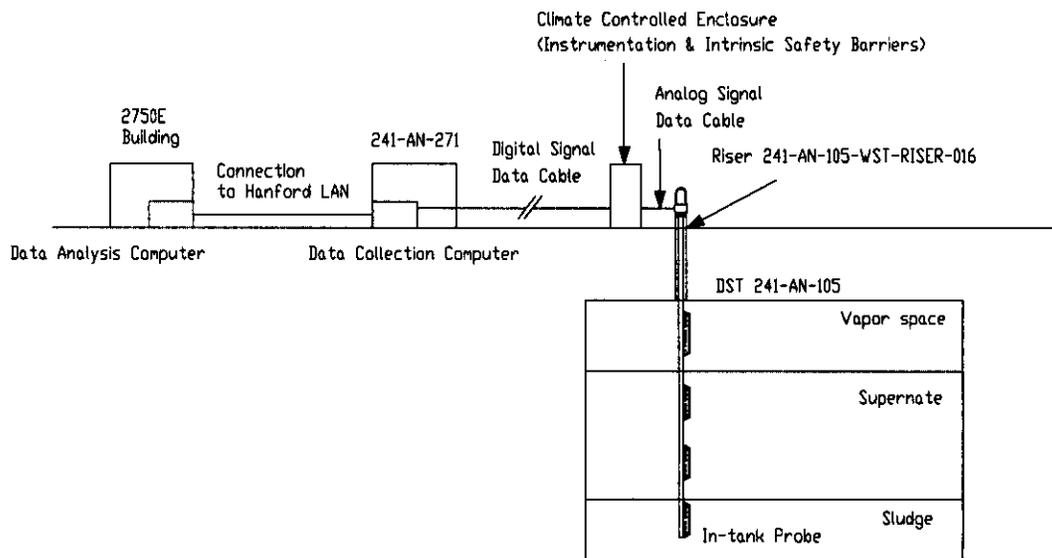


Figure 4: Schematic of field installation of the 241-AN-105 corrosion monitoring system

A wiring schematic for the data cable is shown in Figure 5. The use of driven shields in conjunction with a much shorter analog data cable was expected to eliminate data interference problems. Instead, crosstalk between shields became an issue with the Belden 8178 cable. Driven shields were disconnected in April 2000 and the 241-AN-105 system is now returning good data. Good data is being returned despite the disconnection of the driven shields due to the reduction in analog data cable length from up to 500 feet on previous systems to 60 feet (10 feet above ground) on the 241-AN-105 system. Figure 6 shows a week of data collected prior to the disconnection of the driven shields. Figure 7 shows the improvement in signal quality after the removal of the driven shields.

Data collection has never been terminated on the 241-AN-105 system. Although data have been periodically corrupted by signal interference, it has been determined that the probe can still be used to monitor for SCC since the initiation or growth of a crack in an electrode produces a signal many times greater than the interference signal levels. Even though the signal was corrupted for several months by the cable crosstalk, SCC would have produced a measurable change in signal visible despite the interference caused by crosstalk.

Plans are being made to reconfigure the 241-AN-102 and 241-AN-107 systems to match the 241-AN-105 system. Since C-rings on the 241-AN-102 and 241-AN-107 systems could have cracked during system down time, these systems can no longer be used for SCC detection. However, provided that the electrodes and gaskets are intact, it should be possible to monitor for other forms of corrosion (pitting and uniform corrosion). System data will be evaluated closely at startup in an effort to determine the condition of the in-tank probe. If in-tank probes have failed (as identified by the production of unknown signals or lack of corrosion signals), in-tank probes will be replaced. Driven shields will again be used on these systems. However, a separate length of Belden 8162 cable will be used on each channel. Testing has indicated that the additional separation between channels provided by Belden 8162 cable eliminates the crosstalk problems associated with the Belden 8178 cable. An additional system scheduled for installation in FY 2001 will also be configured to match the 241-AN-105 system configuration. Once all four new systems come on-line, the EN database should grow rapidly.

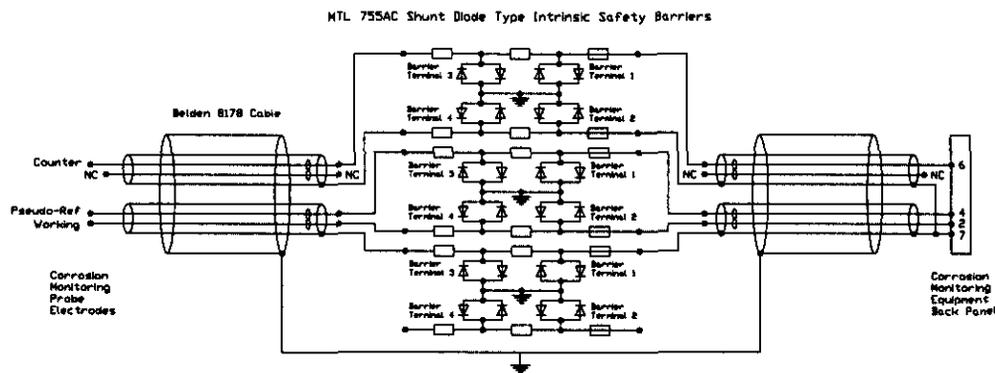


Figure 5: Wiring diagram for 241-AN-105 data cable showing two driven shields per channel

Figure 6: Raw current and potential noise data collected from electrodes in tank 241-AN-105 vapor space (Channel 1) and in the supernate (Channel 3) prior to disconnection of driven shields. Concurrent spikes on multiple channels are indicative of periodic cross-talk between channels.

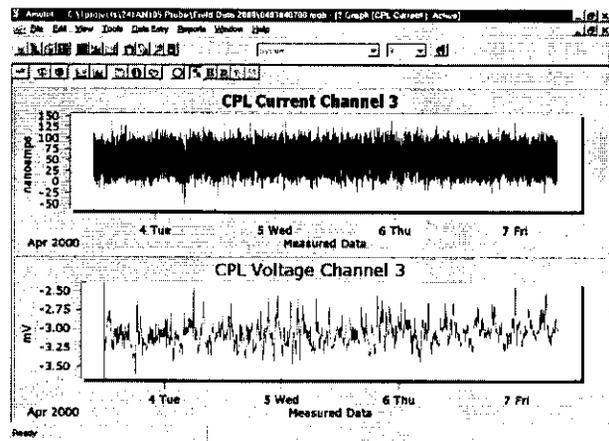


Figure 7: Raw current and potential noise data collected from electrodes in tank 241-AN-105 vapor space (Channel 1) and in the supernate (Channel 3) following the disconnection of driven shields. Channels began behaving independently of each other as they should following this field repair.

Additional Laboratory Work

In addition to the technical challenges associated with data collection in the field, several issues relating to baseline system data have surfaced since the start of field data collection. One of the largest areas of concern is the need for additional laboratory testing on carbon steel undergoing localized corrosion in realistically out-of-spec simulated waste solutions. Additional concerns exist over the effects of electrode fouling, initial surface condition of electrodes, electrode size and the potential for crevice corrosion between the electrodes and the gaskets that insulate the electrodes from the probe body. Additional laboratory testing would help to answer these questions.

Funding and time were not available to answer all the questions concerning probe operation in 1995. Enough work was done in 1995 to demonstrate that a system could work in nuclear waste tanks [21]. It was assumed at the conclusion of testing that additional tests would be conducted at a later date if operating concerns surfaced following installation of the prototype probe in 241-AZ-101. The 1980s PNNL corrosion tests validated the current corrosion control composition specifications through a five year multi-million dollar program. The EN testing has been very limited in comparison. Additional laboratory testing should utilize industry accepted corrosion test methods alongside EN tests for comparison purposes.

Very little work has been performed in the area of optimizing the surface area and the design of the electrodes used on the Hanford corrosion probes. Laboratory testing at PNNL and ORNL on carbon steels in Hanford waste simulants indicated that some electrode designs were better than others at generating recordable EN signals for SCC and pitting [21]. These electrode designs have been incorporated into the current Hanford probe specification/design. No work has been done to see if the electrode surface area or design is optimal for Hanford tank conditions. Additional laboratory testing should be performed to see if electrode design could be improved to improve sensitivity.

In addition to the optimization of electrode design, the lack of representative SCC data generated during proof-of-principle testing in 1995 is still of great concern. During the proof-of-principle testing, no electrodes were successfully cracked and monitored in realistic simulated off-normal waste chemistries [21]. Numerous attempts were made to induce SCC by placing a variety of stressed electrodes in a variety of waste chemistries. With each test stress levels were increased and environments were made more aggressive. The testing program proved that stressed carbon steel electrodes were relatively resistant to SCC in realistically off-normal waste chemistries that could occur in the Hanford waste tanks. Since no SCC was induced in realistic off-normal waste environments, no SCC EN data was collected from such environments. These data would be useful when evaluating data collected from in-tank probes now in service.

The only solution that repeatedly caused SCC propagation in the stressed electrodes was concentrated ammonium nitrate with no pH adjustment at near boiling temperature. This environment is obviously not an optimal representation of actual off-normal Hanford tank waste. Although the mechanism for SCC propagation in carbon steels immersed in nitrate solutions is the same no matter what cation is attached to the nitrate anion, it is unclear if the magnitude of the EN signal generated during SCC would be constant with varying cations and pH level. Most of Hanford's tank waste contains sodium nitrate instead of ammonium nitrate. Additionally, the pH of wastes transferred to tanks was first adjusted upward to values around 12 or higher through the addition of sodium hydroxide in order to passivate the tank walls and minimize corrosion. Typical EN signals from localized corrosion become smaller in magnitude as the tested system becomes more passive. Due to the lack of laboratory data on passive carbon steel/tank waste solutions, it is simply assumed that SCC signals generated in more passive tank waste systems will be of the same geometry as those created by SCC in boiling ammonium nitrate, but smaller in magnitude. This assumption has not been confirmed through laboratory testing.

An additional area of concern relates to the formation of crevices between the corrosion probe electrodes and the sealing gaskets that prevent waste intrusion behind the electrode and potentially into the probe body. Gaskets used on the specimen holders utilized in the laboratory testing and the gaskets utilized on 241-AZ-101, 241-AN-102, and 241-AN-107 probes were all 3/8" diameter square cut O-ring gaskets made from peroxide cured EPDM. Figure 8 shows the configuration of the original gasket/sealing surface design.

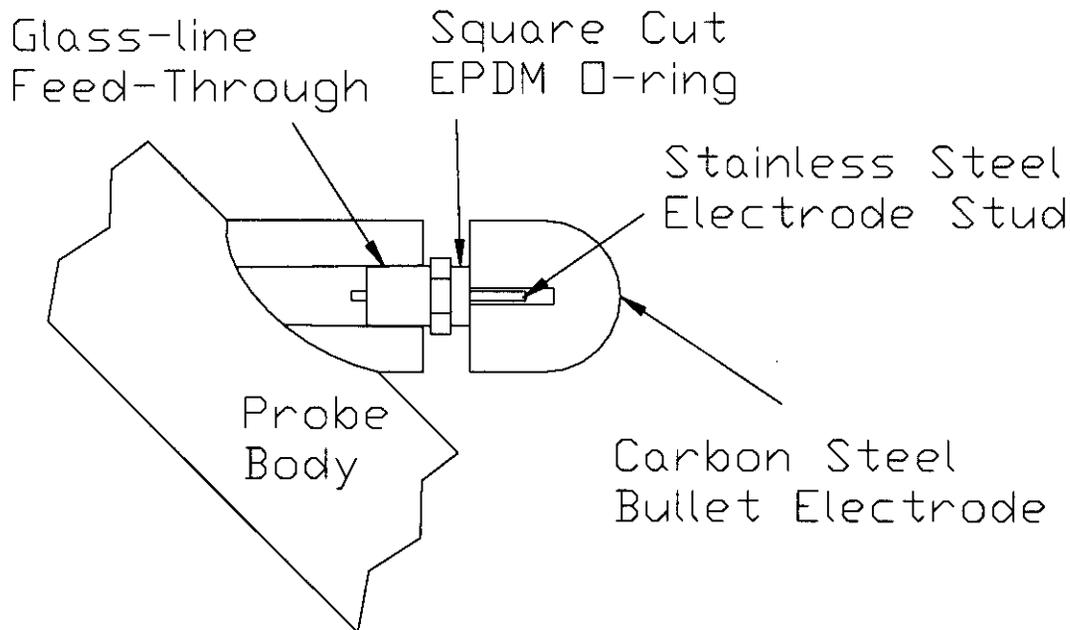


Figure 8: Square cut O-ring gasket design for sealing surface used on first corrosion probes

These gaskets were used on the in-tank corrosion probes based on the results of literature review and gasket performance during the laboratory testing. However, it is not clear how these gaskets behave over long periods of time. EPDM, when exposed to radiation, embrittles over time and can lose its ability to seal as a gasket. Although EPDM is commonly used in applications demanding radiation resistant polymers, exactly how long the gasket will maintain its seal in Hanford tank waste is unknown. Additionally, it is unknown what the effects on EN data will be when a gasket fails. If a gasket fails, it is expected that there will be a visible effect on the EN data caused by the galvanic couple created when tank waste leaks in behind the electrode and contacts the stainless steel stud that holds the electrode to the probe. No laboratory data that captures a gasket failure has been recorded. It is assumed that potential noise data will shift if a gasket were to fail, but the magnitude and direction of the shift are unknown.

Another potential problem related to the corrosion probe gaskets is crevice corrosion. The area between the electrode sealing surface and the gasket creates a likely environment for crevice corrosion. Although no crevice corrosion problems were noted in the Hanford laboratory

development work, crevice corrosion could become a problem over time in the field if the gasket changes due to exposure to the high radiation levels in the tank. Crevice corrosion could potentially create an EN signal several orders of magnitude larger than the signal created by naturally occurring corrosion processes on the electrodes due to their exposure in the tank waste. In other words, an active crevice between the gasket and the electrode would effectively overwhelm any other EN signal being recorded by the corrosion monitoring equipment. It is not known how likely it is for a crevice to occur, where exactly the crevice would occur, how long it would take to propagate to the point of failing the gasket, how large the current or potential transients created by the crevice would be, and if the crevice would remain active once it became active.

Since very little is known about crevice formation in nuclear waste environments and no actual field or lab data exists on crevice formation on corrosion probe electrode/gasket surfaces, it was decided to modify the original probe design to improve the sealing surface and potentially reduce the potential for crevice corrosion. A new seating surface was incorporated on the 241-AN-105 corrosion probe. This seating surface still utilizes a glass-lined feed-through as in previous probes, but the feed-through is now countersunk into the probe such that the electrode now seats on a round cut EPDM O-ring. A detail of the new electrode seating surface is shown in Figure 9.

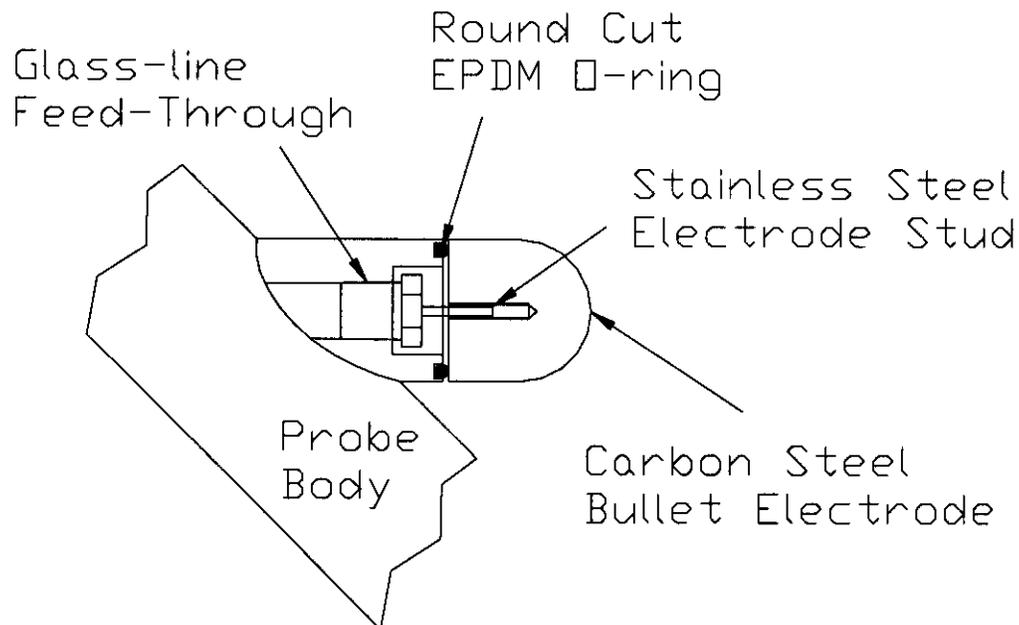


Figure 9: Round cut O-ring gasket design for sealing surface used on 241-AN-105 probe

Although the new gasket design is untested in the lab or field, the design appears to be superior to the square cut gasket system utilized on the first probes. Round cut O-rings seal better and create less of an area for crevice growth should crevice formation occur. If the 241-AN-105

corrosion monitoring system performs properly, future probes will also incorporate the round cut O-ring gasket design.

Impact on Tank Farm AB

As the Hanford site moves closer to utilizing corrosion monitoring systems in its day to day operations, it will be necessary to examine the administrative changes necessary for proceduralized use of these systems. Of primary concern are the two main documents that form the current tank farm AB: the Final Safety Analysis Report (FSAR) and the Technical Safety Requirements (TSRs) [28, 29].

Installation, operation, and maintenance of corrosion monitoring systems do not alter the design, function, or method of performing the function of systems, structures, and components described in the FSAR. Corrosion monitoring instrumentation is not described in any place within the FSAR. Procedures for corrosion probe installation, operation, or maintenance are not described in the FSAR. Existing pump systems and other equipment described in the FSAR are not impacted by the installation or operation of corrosion monitoring systems.

Installation and operation of corrosion monitoring systems will have no impact on the TSRs. Installation and operation of corrosion monitoring systems will have no impact on tank waste temperature or tank ventilation. Corrosion monitoring systems will add nothing to the waste. The in-tank portion of the corrosion monitoring system is constructed of low carbon dual-rated stainless steel to withstand the corrosive effects of the waste tank environment. Once installed the corrosion monitoring system will not disturb the waste or affect tank ventilation.

The installation activities associated with corrosion probe installation in a tank riser may slightly affect tank vapor space pressure and/or active tank ventilation. However, these effects would be temporary and would exist only during the installation process. Installation of tank riser-mounted equipment is a routine practice for which there are governing procedures for equipment lifting and containment. Brief openings of any but the larger tank risers have historically had insignificant effects on tank vapor space pressure or tank ventilation. Therefore, there is no impact to Safety Limit 2.1.1 (waste temperature), Limiting Condition for Operation (LCO) 3.3.2 (waste temperature controls for AWF tanks and double shell tanks) or LCO 3.2.1 (ventilation controls AWF tanks and double shell tanks). There are no other applicable LCOs for the proposed activities.

The applicable Administrative Controls (AC) from the TSRs are AC 5.9 (flammability controls), AC 5.10 (ignition controls), AC 5.11 (flammable gas monitoring controls), AC 5.16 (dome loading controls), and AC 5.17 (excavation controls). The required elements of these AC programs are implemented by HNF-IP-1266, Rev. 1, "Tank Farms Operations Administrative Controls" [37]. Many of the program elements are work controls that are incorporated into work packages and procedures.

Installation activities, operation, and maintenance activities associated with the corrosion monitoring system potentially involve Ex-Tank Intrusive, Dome Intrusive, and Waste Intrusive regions as defined in Section 1.1 of the TSRs. In addition, the corrosion monitoring/high level

detection system could be operated during Global Waste Disturbing operations, also defined in Section 1.1 of the TSRs. Based on this information and Table 5.10-1 of AC 5.10, Ignition Source Control Set #1 is generally applicable to the corrosion monitoring equipment and all associated installation, testing, operation, and maintenance activities. The subject corrosion monitoring equipment has been evaluated and is bounded by Flammable Gas Equipment Advisory Board (FGEAB) report FGEAB-97-040, Rev. 2 [38]. The FGEAB determined that all Dome Intrusive and Waste Intrusive components meet Ignition Source Control Set #1 requirements.

In summary, the corrosion probe installation, operation/maintenance activities have no impact on the FSAR, the TSRs, or any other approved Authorization Basis documents, including DOE-issued documents and approved letters shown in the Unreviewed Safety Questions procedure in HNF-IP-0842, Vol. IV, Section 5.4, Rev. 11B provided that the appropriate flammability (AC 5.9), ignition (AC 5.10), flammable gas monitoring (AC 5.11), dome loading (AC 5.16), and excavation controls (AC 5.17) are applied to installation and maintenance activities per HNF-IP-1266, Rev. 1 [37, 39].

Impact on Tank Farm OSDs

Installation, operation, and maintenance of corrosion monitoring systems do not alter the design, function, or method of performing the function of systems, structures, and components described in the Hanford's OSDs. Corrosion monitoring instrumentation is not described in any place within the OSDs. Procedures for corrosion probe installation, operation, or maintenance are not described in the OSDs. Existing pump systems and other equipment are not impacted by the installation or operation of the corrosion monitoring system.

The application of EN based corrosion monitoring to Hanford DSTs is still in the development process. After the major technical issues with probe operation are resolved, one possible method to move corrosion monitoring into the Hanford Site's operating procedures is to merge corrosion probe use with the existing corrosion chemistry control specification contained in the OSDs. In tanks containing functional corrosion monitoring systems, the results of any corrosion chemistry sampling and analysis could be compared with corrosion monitoring data collected at the same time. If the results of this comparison are consistent, specific tank operating specifications could be changed to incorporate the use of EN based corrosion monitoring systems instead of the existing waste chemistry control specification.

Summary and Conclusions

Some Hanford DSTs have historically been operated for long periods of time despite being outside the bounds of proper corrosion control chemistry specification. Currently, DSTs 241-AY-101, 241-AN-102 and 241-AN-107 are being operated, and have been operated for a number of years, despite being out of corrosion control specification. The impact of these out-of-specification conditions on the integrity of the tank walls is unknown other than there is no evidence that the tanks have failed. As the Hanford DSTs continue to age, corrosion control at Hanford will become more important. Corrosion-related failure of single-shell waste tank walls could lead to the leakage of radioactive contaminants to the soil and groundwater. Corrosion of

the walls of double-shell tanks could lead to leakage of waste into the annulus between shells and the resulting expensive and time consuming process of transferring waste from the failed tank to an intact tank.

Corrosion monitoring is currently provided at the Hanford Site through a waste chemistry sampling and analysis program. In this process, tank waste is sampled, analyzed and compared to corrosion control specifications derived from laboratory exposure of coupons in simulated waste. Tank wall corrosion is inferred by matching measured tank chemistries to the results of the laboratory simulant testing. This method is expensive, irregularly scheduled, time consuming, and does not yield real-time data. The existence of three out of specification tanks is a testament to the shortcomings of the management of the current corrosion control program at Hanford.

Over the last 20 years, a new corrosion monitoring technique has shown promise in detecting localized corrosion (pitting and SCC) and measuring uniform corrosion rates in process industries outside of Hanford. Pitting and SCC have been identified as the most likely modes of corrosion failure for Hanford DSTs. This new system measures electrochemical noise (EN) created by corrosion.

In an effort to improve the Hanford Site's corrosion monitoring program, a project to develop and integrate EN based corrosion monitoring into the existing corrosion control program was started in 1995. Four systems have been installed at Hanford to date. The first three systems met with limited success. The fourth system is working properly and returning high-quality data. A fifth system based on the fourth system design is scheduled for installation in early FY 2001. Interpretation of EN based corrosion monitoring data is currently the responsibility of the Equipment Engineering Organization within LMHC.

Several technical challenges remain before proceduralized use of corrosion monitoring is possible at the Hanford site. A prerequisite for using EN based corrosion monitoring systems as a means of corrosion monitoring at Hanford is to build a sufficiently large high-quality tank corrosion database to facilitate interpretation of new data as the number of monitored tanks is increased. The present database collected to date from EN monitoring of Hanford tanks is insufficient for this purpose. Systems installed to date during the development effort have been hampered by system configuration and hardware issues in collecting high quality data.

A new system was deployed into 241-AN-105 in FY 2000. The new system design corrected data collection problems experienced with previous systems installed in 241-AN-107 and 241-AN-102. Plans are being made to reconfigure the 241-AN-102 and 241-AN-107 systems to match the 241-AN-105 system. Since C-rings on the 241-AN-102 and 241-AN-107 systems could have cracked during system down time, these systems can no longer be used for SCC detection. However, provided that the electrodes and gaskets are intact, it should be possible to monitor for other forms of corrosion (pitting and uniform corrosion). System data will be evaluated closely at startup in an effort to determine the condition of the in-tank probe. If in-tank probes have failed (as identified by the production of unknown signals or lack of corrosion signals), in-tank probes will be replaced.

Data collection has never been terminated on the 241-AN-105 system. Although data have been periodically corrupted by signal interference, it has been determined that the probe can still be used to monitor for SCC since the initiation or growth of a crack in an electrode produces a signal many times greater than the interference signal levels. Even though the signal was corrupted for several months by the cable crosstalk, SCC would have produced a measurable change in signal visible despite the interference caused by crosstalk.

A fourth system is being designed and built for installation in FY 2001. Once all four systems are functioning properly, the EN database will grow rapidly. A large, high quality waste tank EN database is a necessity before proceduralized use of these systems is possible.

Additional laboratory testing needs to be performed to optimize electrode surface area and minimize the potential for crevice corrosion between gaskets and electrodes on the in-tank probes. Further testing should be performed to collect high quality EN data on carbon steel electrodes cracking in a high pH, off-normal, sodium nitrate based waste chemistry that is more reflective of typical Hanford tank waste chemistry. A record of this type of data would facilitate much more accurate interpretation of in-tank field data to be collected in the future, particularly if that field data were thought to contain SCC transients.

Installation and operation of corrosion monitoring systems will have no impact on the FSAR, the TSRs, or the site OSDs as they are currently written. One possible way to start the process of proceduralizing corrosion monitoring system use at Hanford is to incorporate corrosion data into the existing chemistry control OSD. In tanks containing functional corrosion monitoring systems, the results of chemistry sampling and analysis could be compared with corrosion monitoring data collected at the same time. If the results of this comparison are consistent, specific tank operating specifications could be changed to incorporate the use of EN based corrosion monitoring systems instead of the existing waste chemistry control specification. This process could be continued until all DSTs are instrumented.

Recommendations for Future Work

Several technical issues demanding future work have been detailed in this report. These issues include electrostatic noise pickup in the field, the need for additional laboratory testing on optimal electrode size, SCC signal generation in more stereotypical off-normal waste chemistries, the degradation rate of EPDM in radiation fields representative of those that could be encountered in Hanford waste tanks, and the potential for crevice corrosion with any chosen electrode/gasket interface. As work continues to progress in these areas, a critical area for future work is the need for a thorough peer review of the Hanford corrosion monitoring program. Although the program has made great strides forward over the last several years, it has never been subjected to a review by a panel of *corrosion monitoring* experts. A review by a group of people skilled in the area of electrochemistry, probe design, data reduction, and plant monitoring is essential before EN based corrosion monitoring systems can be seriously considered as the primary corrosion monitoring mechanism at the Hanford Site. Once the technical issues highlighted in this report and any additional concerns uncovered during a program review are resolved, real-time EN based corrosion monitoring should become an integral part of Hanford's

tank integrity program as it would help to ensure safe, efficient, long term waste storage until retrieval and final disposal can be accomplished.

References

- [1] R.K. Shukla, A.J. Perkins, P.M. Bourgeois, R.J. Jaramins, W.G. Secen, and, D.J. Stroud, Corrosion Monitoring of High Level Waste Storage Tank 8-D2 at the West Valley Demonstration Project, CORROSION/94, paper no. 121, (Houston, TX: NACE International, 1994).
- [2] D.C. Lini, Compilation of Hanford Corrosion Studies, Atlantic Richfield Hanford Company Report, ARH-ST-111, UC-70, July, 1975.
- [3] G. L. Edgemon and R. P. Anantamula, Hanford Waste Tank System Degradation Mechanisms Report, Westinghouse Hanford Company Report, WHC-SD-WM-ER-414, Rev. 1, October, 1996.
- [4] T. Haygard and J. R. Williams, Trans. Farad. Soc. 57, (1961): p. 2288.
- [5] P. Bindra, et al., Discussions of Faraday Soc. 56, (1974): p. 189.
- [6] M. Fleischmann, et al., Surface Science 100-101, (1980): p. 583.
- [7] G.J. Bignold and M. Fleischmann, Electrochemical Acta 19, (1974): p. 363.
- [8] E. Budevski, et al., Electrochemical Acta 28, (1983): p. 925.
- [9] G. Blanc, et al., Electrochemical Acta 23, (1978): p. 337.
- [10] K. Hladky and J. L. Dawson, Corrosion Science 22, (1982): p. 231.
- [11] U. Bertocci, Electrochemical Noise Analysis and Its Application to Corrosion, CORROSION/89, paper no. 24, (Houston, TX: NACE International, 1989).
- [12] J.L. Dawson, D.M. Farrell, P.J. Aylott, and K. Hladky, Corrosion Monitoring Using Electrochemical Noise Measurements, CORROSION/89, paper no. 31, (Houston, TX: NACE International, 1989).
- [13] D.A. Eden, A. N. Rothwell, and J.L. Dawson, "Electrochemical Noise for Detection of Susceptibility to Stress Corrosion Cracking, CORROSION/91, paper no. 444, (Houston, TX: NACE International, 1991).
- [14] D.M. Farrell, Industrial Corrosion 9, (1991): p. 7.

- [15] A.N. Rothwell, T.G. Walsh, and W.M. Cox, On Line Corrosion Investigation and Surveillance - Chemical Plant Case Studies, CORROSION/91, paper no. 170, (Houston, TX: NACE International, 1991).
- [16] J.L. Dawson, et al., On-line Monitoring of Continuous Process Plants, ed. D. Butcher, (Ellis Horwood, NY, 1983).
- [17] D.M. Farrell, W.M. Cox, and D. Gearey, Multi-System Corrosion Monitoring in a Cyclic Reheat Test Facility; Phase 1, Electric Power Research Institute Report, CS-5776, 1988.
- [18] D.M. Farrell, W.M. Cox and D. Gearey, Multi-System Corrosion Monitoring in FGD Systems; Phase 2, Electric Power Research Institute Report, CS-5734, 1988.
- [19] B.C. Syrett and W.M. Cox, in: Proc. First Int. Symposium on Electrochemical Noise Measurements for Corrosion Applications, ASTM STP 1277, eds. J.R. Kearns, J.R. Scully, P.R. Roberge, D.L. Reichert, and J.L. Dawson, (American Society for Testing and Materials, Philadelphia, PA, 1996) p. 173.
- [20] C.A. Lotto and R.A. Cottis, Corrosion 45, (1989): p. 136.
- [21] G.L. Edgemon and G.E.C. Bell, Technical Basis for Electrochemical Noise Based Corrosion Monitoring of Underground Nuclear Waste Storage Tanks, Westinghouse Hanford Company Report, WHC-SD-WM-TI-772, November, 1996.
- [22] G.L. Edgemon, J.L. Nelson, P.C. Ohl, and G.E.C. Bell, Hanford Prototype Corrosion Probe Operational Experience, CORROSION/97, paper no. 97124, (Houston, TX: NACE International, 1997).
- [23] G.L. Edgemon, J.L. Nelson, and G.E.C. Bell, Design of an Electrochemical Noise Based Corrosion Monitoring Probe for High Level Nuclear Waste Storage Tanks, CORROSION/98, paper no. 98175, (Houston, TX: NACE International, 1998).
- [24] G.L. Edgemon and J. L. Nelson, Design of Second-Generation Corrosion Monitoring Probe, Lockheed Martin Hanford Company Report, HNF-2517, Rev. 0, April, 1998.
- [25] G.L. Edgemon and J. L. Nelson, Design of Multi-Function Hanford Tank Corrosion Monitoring System, Lockheed Martin Hanford Company Report, HNF-4285, Rev. 0, April, 1999.
- [26] N. W. Kirch, Technical Basis for Waste Tank Corrosion Specifications, Rockwell Hanford Company Report, SD-WM-TI-150, Rev. 0, August, 1984.
- [27] L. Ross, *Unclassified Operating Specifications for the 241-AN, AP, AW, AY, AZ, & SY Tank Farms*, Tank Farms Operating Specification Document, OSD-T-151-00007, Rev. H-21, September, 1998.

- [28] HNF-SD-WM-SAR-067, Rev 1, "RPP Final Safety Analysis Report", Fluor Daniel Hanford Corporation, Richland, Washington, October 1999.
- [29] HNF-SD-WM-TSR-006, Rev 0-S, "Tank Waste Remediation System Technical Safety Requirements", Fluor Daniel Hanford Corporation, Richland, Washington, March 1999.
- [30] M. J. Danielson, L. R. Bunnell, Sludge Washing Materials Study: The Behavior of Carbon Steel in a Dilute Waste Environment, Westinghouse Hanford Company Report, TWRS-PP-94-025, Rev. 0, August, 1995.
- [31] H. P. Shrivastava, Structural Evaluation of Second Generation Double Shell Tank Corrosion Probe Tree, Lockheed Martin Hanford Company Report, HNF-SD-WM-CN-090, Rev. 0, June, 1997.
- [32] H. S. Ziada, Analysis of the Effects of Corrosion Probe on Riser 241-AN-102-WST-16 During Seismic Event, Numatec Hanford Company Report, HNF-3162, Rev. 0, November, 1998.
- [33] G. L. Edgemon, J. L. Nelson, P. C. Ohl, Prototype Corrosion Probe Four Month Status Report, Lockheed Martin Hanford Company Report, WHC-SD-WM-TI-796, Rev. 0, December, 1996.
- [34] G.L. Edgemon, Tank 241-AZ-101 Prototype Corrosion Probe Two-Year Status Report, Lockheed Martin Hanford Company Report, HNF-3416, Rev. 0, September, 1998.
- [35] G.L. Edgemon, Corrosion Data From Hanford High-Level Waste Tank 241-AN-107, Lockheed Martin Hanford Company Report, HNF-3414, Rev. 0, September, 1998.
- [36] G.L. Edgemon, Data Analysis and Reduction in Hanford's Corrosion Monitoring Systems, Lockheed Martin Hanford Company Report, HNF-4653, Rev. 0, July, 1999.
- [37] HNF-IP-1266, Rev. 1, "Tank Farms Operations Administrative Controls", Lockheed Martin Hanford Corporation, Richland, Washington, December 1997.
- [38] FGEAB-97-040 Rev. 2, Flammable Gas Equipment Advisory Board Interpretation/Recommendation Report - Corrosion Monitoring System, Lockheed Martin Hanford Corporation, May 1998.
- [39] HNF-IP-0842, Vol. IV, Section 5.4, Rev. 11B, "RPP Administration", Lockheed Martin Hanford Corporation, Richland, Washington, February 1999.