The Honorable Peter S. Winokur  
Chairman  
Defense Nuclear Facilities Safety Board  
625 Indiana Avenue, NW, Suite 700  
Washington, DC 20004-2901

Dear Mr. Chairman:

In your January 6, 2010, letter regarding inspection techniques for waste tanks the Defense Nuclear Facilities Safety Board recommended that the Department of Energy (DOE) pursue new technologies for tank inspection for reducing uncertainty associated with tank corrosion. You were provided a briefing on the waste tank structural integrity programs at the Hanford and Savannah River Site on January 26, 2010. The briefing included the DOE’s plans for technologies for tank inspection. The enclosed report documents the DOE’s activities with high speed inspection techniques (i.e. new technology for tank inspection).

If you have any questions, please contact me or Dr. Steven L. Krahn, Deputy Assistant Secretary for Safety and Security Program at (202) 586-5151.

Sincerely,

Inés R. Triay  
Assistant Secretary for  
Environmental Management

Enclosure
Savannah River Site and Hanford Double Shell Tank Structural Integrity Program

Karthik H. Subramanian, Matthew Maryak
Savannah River Remediation

Kayle Boomer
Washington River Protection Solutions

Bruce Wiersma
Savannah River National Laboratory

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1 Introduction

High level radioactive waste (HLW) incident to nuclear weapons production is stored in large underground storage tanks at the Savannah River Site (SRS) and Hanford Site. The typical double shell (DST) storage tank designs for SRS and Hanford are shown in Figures 1 and 2, respectively. The structural integrity of the tanks is critical to confinement of the waste throughout the operational life of DSTs within the DOE complex. The DSTs are nominally constructed of a primary tank structure with a secondary (sometimes partial) carbon steel tank within a concrete vault. The tanks are expected to be in-service beyond their initial intended design life and it is critical to ensure their structural and leak integrity (SI) during current storage, as well as waste processing operations.

Figure 1: SRS Double Shell Tank

Figure 2: Hanford Double Shell Tank
A complete technical basis for the demonstration of structural integrity of the high level waste tanks has multiple facets. The DOE Order/Guide 435.1 states that a HLW SI program includes the key elements as outlined by BNL-UC-406, “Guidelines for Development of Structural Integrity Programs for DOE High Level Waste Storage Tanks.” These key program elements are as follows:

1. Identification of Aging Mechanisms
2. Quantification of the Degree of Degradation
3. Evaluation of the Effect of Degradation on Tank Integrity
4. Verification of Leak Tightness (for non-leaking tanks)
5. Verification of Structural Adequacy

The objective of the program is to establish a complete technical basis to demonstrate each of these five key elements, and so meet the requirements of DOE Order 435.1. In addressing these key elements, the integrated double-shell tank (DST) structural integrity program focuses on: (1) corrosion mitigation; (2) in-service inspection; and (3) structural analyses. The SI program will evolve as operations dictate, as technologies progress, and as guided by DOE-EM workshops on Tank Integrity and expert panels from academia and industry and stakeholders. There are multiple applied research and development programs at Savannah River Site and Hanford that continue to improve on these facets of the structural integrity program. In addition, the SI program is integrated into the DOE-EM 30 Technology Development program as an enabler to the waste processing mission. The following sections provide an overview and status of the three areas of focus of the SI program, and identify the relevant applied R&D activities that are currently being pursued.

The experimental focus over the last decade has been on optimizing chemistry controls to support the waste disposition mission as well as addressing the uncertainties such as vapor space and liquid/air interfacial corrosion. The current corrosion control programs are constructed to prevent SCC and/or pitting depending upon the expected operations. The experiments in support of chemistry control optimization have provided the technical basis to develop specific controls for each corrosion mechanism, fill gaps, and resolve inconsistencies with the program. The experiments have also focused on simulating specific corrosion mechanisms such as vapor space and liquid-air interface corrosion (VSC/LAIC). The focus on chemistry control optimization and oversight by academia and industry expert panels has led to a robust corrosion control program that has evolved as the operations have dictated.

The inspection program over the last decade has focused on completion of the DST inspections as well as improvements to the volumetric (currently ultrasonic) inspection technique. First-cycle volumetric inspection using ultrasonic (UT) inspection of all the new-style tanks at SR and all DSTs at Hanford are complete. The next cycle of inspections will be based upon the results of the first cycle as well as improvement initiatives. The improvement initiatives include testing to minimize the uncertainties in the UT inspection technique. In addition, statistical methods
have been developed to support the area of inspection needed and these methods continue to mature. The most recent focus, through the EM Technology Development portfolio and contract baseline research and development, has been in the development of high speed volumetric inspection techniques. This program continues to mature with the insight of each of the stakeholders including the DNFSB.

1.1 Defense Nuclear Facilities Safety Board (DNFSB) Review

The Defense Nuclear Facility Safety Board provides an independent safety assessment of our program and recently reviewed several key aspects that have helped guide improvements to the Tank Structural Integrity program at both sites. Staff Issue Reports transmitted via DNFSB letters dated 9/4/2008 and 1/6/2010 were considered as guidance to the DOE tank integrity programs.

1.1.1 Excerpt from Staff Issue Report from DNFSB letter dated 9/4/2008

This Staff Issue Report documented a review of the Savannah River Site SI program and focused on three issues.

- **The Inspection Plan** is based on the assumptions that pits in the HLW tank steel liners are preexisting flaws and are not growing. These assumptions are not supported by sufficient and convincing data. As a result, the Inspection Plan should require reexamination of pits to evaluate pit growth rates in all five tanks known to have pits.

- **The Inspection Plan** is also based on an assumption that pitting varies only in the vertical direction along the tank walls and not in the circumferential direction. This assumption is not supported by sufficient data. The staff believes conducting inspections in all accessible risers, spaced around the full circumference of at least one Type IIIA tank, would help validate assumptions in and strengthen the basis for the Inspection Plan.

- **The Inspection Plan** does not adequately address the potential for liquid-air interface pitting at tank heights corresponding to stagnant waste levels. **UT** inspection of such an area is included in the Inspection Plan for only one tank. The staff suggests conducting a review of HLW tanks having a history of relatively constant waste levels. This review could identify areas that have a high potential for pitting, which then could be included in the Inspection Plan.

The SRS ISI Plan is designed to address each of these observations. The pitting that has been identified in the tanks is specifically called out to be revisited in the next round of inspections. This will allow for a growth evaluation that has spanned a period of 7-8 years and will provide valuable information with regard to the corrosion control programs effectiveness at mitigating pit growth along with general corrosion. The initial SRS ISI plan also utilized stagnancy to identify tanks to be inspected.
1.1.2 Excerpt from Staff Issue Report from DNFSB letter dated 1/6/2010

The Board's staff believes DOE should pursue additional research and development of new techniques for inspecting HLW tanks. Current techniques are costly and slow and may not provide full assurance of tank integrity, particularly in light of the uncertainties associated with tank corrosion. The present tank wall inspections only examine a vertical strip that covers 0.25-3.0 percent of the tank's circumference—although the extensive inspection of Tank 29 at SRS revealed no significant problems, there were some non-uniformities in pitting that may or may not be explained by pre-service conditions. Generally, much uncertainty remains regarding tank corrosion:

- Some corrosion mechanisms are not easily predictable or well understood, particularly for pitting and crevice corrosion and at the liquid-air interface.

- Some corrosion mechanisms observed in the laboratory cannot be reproduced in the high-level waste tanks and vice versa—for example, investigators have been unable to duplicate in the laboratory crevice corrosion that is observed on in-tank corrosion coupons.

- It is unclear that the same chemistry controls that address stress corrosion cracking also address pitting.

- The tanks are beyond their design lives and are continuing to age—improved and expanded data collection and analysis supports extension of the service lives of the high-level waste tanks.

The DOE continues to mature a robust corrosion control program and gain fundamental understanding of the corrosion mechanisms and their control in the tanks. In parallel, DOE continues to pursue development of higher speed inspection techniques that confirm the efficacy of the control programs.

2 Corrosion Mitigation Program

Current corrosion control programs at both Hanford and SRS utilize a chemistry/temperature envelope to prevent general and localized corrosion mechanisms. Historically, these control programs have evolved as corrosion mechanisms have arisen, as well as to address specific processing activities within the tanks. DOE sponsored laboratories, industry, and academia have been investigating corrosion mechanisms that occur in the high level waste tanks for more than fifty years. As a result, practical and effective corrosion controls have been identified to prevent stress corrosion cracking during waste storage and removal, pitting at the liquid air interface in dilute waste processing solutions, and pitting and stress corrosion cracking in the vapor space. However, several specific programs are currently ongoing as part of the corrosion mitigation efforts.

Understanding the environment and consequent corrosion mechanisms are critical to developing and implementing meaningful corrosion mitigation. The environment is a complex combination of operational parameters and chemistries as shown, for example, in Figure 3. There are three
regions where corrosion has been observed: the liquid, liquid-air interface and the vapor space.[1]
A summary of the SRS corrosion control program is shown in Figure 4.

![Diagram showing corrosion control program]

**Figure 4: Summary of Corrosion Control Program**

The corrosion control program at Hanford and SRS are based upon the same initial empirical data, but have evolved over decades based upon specific needs at each site. A comparison of the corrosion control programs is shown in Table 1.
The amounts of inhibitors added are based upon a library of empirical data developed over decades of corrosion-related research and operational knowledge. However, there are several initiatives to optimize these chemistry controls to better address tank conditions resulting from waste processing operations such as salt dissolution/preparation and evaporator operations. These initiatives involve experimental programs to establish the technical bases for revised chemistry controls and are broadly aimed at balancing inhibitor additions with waste minimization. There is also an initiative to improve the use of in-tank corrosion probes to reduce reliance on tank waste sampling to predict corrosion potential. In addition, there is an initiative to develop a probabilistic approach to tank corrosion in order to address inefficient discontinuities in the current chemistry control limits. Finally, there is an initiative to revise the corrosion control program in concentrated solutions to support salt dissolution. The current baseline for salt dissolution and removal will challenge the current requirements of the corrosion control program which were initially developed during the 1960’s and 1970’s for the “long-term” storage mission of the tanks. However, recent experimental evidence suggests that addition of inhibitors in these concentrated solutions can be reduced while maintaining the same level of protection for shorter-term salt dissolution goals. All of these initiatives involve experimental programs that will demonstrate the technical bases for revising the chemistry control program.

These multiple initiatives are broadly aimed at developing the technical bases for effective corrosion protection while minimizing the addition of corrosion inhibitors. Minimizing the addition of corrosion inhibitors will reduce operational costs, but perhaps more importantly, it will reduce the volume of waste and shorten the life-cycle associated with treating and disposing

### Table 1: Comparison of Corrosion Control Programs

<table>
<thead>
<tr>
<th>Applicability</th>
<th>Parameter</th>
<th>SRS [Minimum Inhibitor M]</th>
<th>Hanford [M]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5 = [NO₂⁻] = 8.5</td>
<td>[OH⁻]</td>
<td>0.6</td>
<td>Not Allowed</td>
</tr>
<tr>
<td></td>
<td>[OH⁻] + [NO₂⁻]</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>2.75 (3.0 Hanford)</td>
<td>[OH⁻]</td>
<td>0.3</td>
<td>0.3 but not &gt; 10 for Waste Temp &lt; 100°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3 but not &gt; 4 for Waste Temp &gt; 100°C</td>
</tr>
<tr>
<td>1.0 = [NO₂⁻] = 2.75 (3.0 Hanford)</td>
<td>[OH⁻]</td>
<td>0.1*[NO₂⁻]</td>
<td>0.1*[NO₂⁻] but not &gt; 10 for Waste Temp &lt; 100°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1*[NO₂⁻] but not &gt; 4 for Waste Temp &gt; 100°C</td>
</tr>
<tr>
<td></td>
<td>[OH⁻] + [NO₂⁻]</td>
<td>0.4*[NO₂⁻]</td>
<td>&gt; 0.4*[NO₂⁻]</td>
</tr>
<tr>
<td>[NO₂⁻] &lt; 1.0 (Hanford)</td>
<td>[OH⁻]</td>
<td>1.0M</td>
<td>pH &gt; 10.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>pH &gt; 12 but not &gt; 8M for Waste Temp &lt; 75°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>pH &gt; 12 but not &gt; 6M for Waste Temp &lt; 100°C</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>pH &gt; 12 but not &gt; 4M for Waste Temp &gt; 100°C</td>
</tr>
<tr>
<td></td>
<td>[NO₂⁻]</td>
<td>n/a</td>
<td>1.66* [NO₂⁻] for Temp = 40 °C plus limits based on chloride and sulfate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.01 but not &gt; 5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[NO₂⁻] &lt; 2.5 *[OH⁻] + [NO₂⁻]</td>
</tr>
<tr>
<td>[NO₂⁻] &lt; 0.02</td>
<td>[OH⁻]</td>
<td>1.0M</td>
<td>pH &gt; 10.3</td>
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<tr>
<td></td>
<td>[NO₂⁻]</td>
<td>n/a</td>
<td>0.033 Temp = 40 °C plus limits based on chloride and sulfate</td>
</tr>
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</table>
of tank waste at Hanford and SRS. Corrosion mitigation initiatives specific to each site are outlined in Sections 2.1 and 2.2. Both sites are focused on addressing the issues of vapor space and liquid/air interfacial corrosion during the evolution of the program and these initiatives are discussed in Section 2.3.

2.1 Hanford

The Hanford site is currently focused on (1) optimizing corrosion controls to minimize the addition of NaOH and utilize nitrite based controls to support waste processing mission; and (2) optimization of the electrochemical corrosion probe for use in tanks that are difficult to sample and have suspect chemistry information through their history.

2.1.1 Corrosion control Optimization

During FY 2004, an Expert Panel was assembled to provide an assessment of three proposed initiatives to optimize the Hanford Site DST corrosion controls. The initiatives reviewed were to:

1. Define an acceptable time period during which DSTs can be safely operated outside the established corrosion control limits without risking the integrity or mission life of the primary tank.
2. Identify an approach for reducing or eliminating the number of sludge core samples needed from the DSTs without risking the integrity or mission life of the primary tank.
3. Revise the conservative corrosion control limits based on currently available information with respect to general and localized corrosion and confirm the effectiveness of these revised limits through an accelerated SCC experimental program.

In their report, the Expert Panel recommended accelerated testing using electrochemical techniques as part of a supernatant simulant testing program to establish the corrosion control limits for the DSTs [3]. The activities for Initiatives one and three above were rolled into a single program. Initiative two was implemented based on the panel’s report.

The Hanford site has tested numerous conditions over the past five years to develop new optimized corrosion controls for the DSTs. This testing has also dealt with five out-of-specification tanks, which under the conservative corrosion control program would have required the addition of caustic and the installation of mixing pumps. These operations would have caused delays and expense to the ongoing retrieval activities, which would have put mission critical tasks at risk along with increasing the cost of waste treatment. Results from these experiments supported changes in the corrosion control limits that provided corrosion protection while avoiding unnecessary impacts to the waste treatment mission.

In making these changes, the DST Integrity Project has been working with a group of reviewers from the Chemistry Optimization Expert Panel who have been providing oversight to the testing program. This Expert Panel Oversight Committee (EPOC) deemed sufficient work had been
accomplished to identify parameters important for corrosion control that a Statistical Test Matrix (STM) should be developed as a final step in establishing new controls for waste chemistry. The work on the STM was begun during FY 2009 and completed in FY 2010. With the completion of this matrix, Hanford will adopt a nitrite based control system.

2.1.2 Corrosion Probe

The corrosion probes installed at the Hanford tanks are an example of direct in-tank chemistry monitoring techniques that have evolved with concurrent laboratory experiments. The designs of corrosion monitoring systems at Hanford have invoked lessons learned from previous systems. The Electrochemical Noise (EN) technique was initially selected for further study based on numerous reports that showed this technique to be effective for monitoring and identifying the onset of localized corrosion.[44] Increasingly advanced systems of similar design were installed between 1996 and 2005. [5,6,7,8,9]

Though the data from the EN probes provided real-time data about localized corrosion in the DST, work initiated as part of the chemistry optimization work led to a rethinking of the corrosion monitoring in the tanks. In 2005, the functions and requirements for a new “Integrated Multi-Function Corrosion Probe” (IMCP) were developed at Hanford.[10] The first IMCP system was designed and installed in DST 241 AN-107 in September 2006. The IMCP actively monitors EN, linear polarization resistance (LPR), ER, and field-hardy silver/silver chloride reference electrodes (the “active” system) with traditional weight loss coupons (the “passive” system) to create a multifunction system capable of collecting a comprehensive set of tank environment corrosion data [11].

A more recent design, shown in Figure 5, focuses primarily on corrosion potential measurements. This probe can measure tank potentials with respect to the various primary and metal secondary electrodes located in the solid and supernate layers in the tank. It served as a test bed for the corrosion monitoring of the DSTs in support of the chemistry optimization work discussed in Section 2.1.1.
The design of the corrosion probes has evolved from the use of multiple reference and secondary reference electrodes to the use of a silver—silver chloride reference electrode, a copper secondary reference electrode, and an Electrical Resistance (ER) probe. The two reference electrodes provide a comparison of the tank environment to the chemical optimization testing. The surprising longevity of the Ag/AgCl electrode has provided data about the long-term potential of the tank chemistry versus the laboratory testing. The ER probe provides information about the general corrosion rate in the tanks, which to date have shown rates less than one mil per year.

The goal is to install seven in-tank probes which are representative of the various waste types at Hanford. With the testing program and data from these tanks, the Double Shell Tank Integrity Program (DSTIP) will be able to show the margin between the free corrosion potential in the tanks and over potentials that could lead to corrosion in the tanks. To date none of the testing has shown corrosion occurring at the free corrosion potential, thus by identifying this difference DOE can gain valuable insight into the long-term integrity of the HLW tanks.

2.2 Savannah River Site

The Savannah River Site is focused on the development of specific controls to support the progressing waste processing mission: (1) conditions resulting from salt dissolution/preparation; (2) conditions resulting from evaporator operations; and (3) probability/statistical corrosion controls similar to corrosion control optimization for the Hanford site. These specific initiatives are each geared towards specific waste chemistry/temperatures that are encountered during the waste processing mission.
2.2.1 Salt Dissolution/Preparation

Dissolution of salt from DSTs waste tanks at the Savannah River Site (SRS) may create solutions with inhibitor concentrations below those required currently for high nitrate salt solutions [12,13,14,15]. At these high nitrate solutions (>5.5 M NaNO₃), nitrate stress corrosion cracking (SCC) is the primary concern and inhibitor requirements are in place to preclude SCC. An experimental program was established to evaluate operating conditions for the new-style stress-relieved waste tanks at inhibitor concentrations below those currently used, which were established for old-style non-stress relieved waste tanks. [16,17,18]

The experimental program involved corrosion testing to evaluate the pitting and SCC susceptibility of the new-style waste tank materials. [19] Additionally the testing evaluated corrosion at the liquid-air interface and in the vapor space. [20] The experimental program concluded new style waste tanks exposed to high nitrate (> 5.5M) solutions at inhibitor levels below the current specifications (0.6M OH- and 1.1M OH- + NO₂⁻) are potentially susceptible to localized corrosion in the form of pitting and stress corrosion cracking during long-term storage (i.e., greater than 100 days) of dissolved salt solutions not meeting the current inhibitor specifications for high nitrate salt chemistries. However, short term storage (e.g., less than 100 days) at low temperatures (e.g., 50 °C) in these tanks was deemed permissible for waste removal purposes. The stress relief process greatly reduces the risk of SCC in the new-style waste tanks. On the other hand, the current inhibitor specifications should be strictly followed for the old-style tanks to prevent initiation of localized corrosion mechanisms, because of their lack of stress-relief.

Additionally electrochemical testing indicated that at lower temperatures (25 °C) carbon steel was not susceptible to localized attack at inhibitor concentrations as low as 0.1 M hydroxide and 0.1 M nitrite. At this time it is unknown as to what temperature between 25 and 50 °C the solutions would become more aggressive at this inhibitor concentration. These revised criteria do not apply for the old-style tanks because of their lack of stress-relief and the current inhibitor specifications should be strictly followed for the old-style tanks to prevent initiation of localized corrosion mechanisms.

An important finding of this work is the initiation of cracks in the vapor space. Cracks have been observed in the vapor space of non-stress relieved waste tanks. [21] However, previous experimental efforts were unsuccessful in reproducing this phenomenon in the laboratory. [22] Perhaps the most critical difference between these tests and the tests that were performed previously is the test time (approximately 3 months versus 18 months for the current tests). The initiation of vapor space cracks therefore may take extended periods of time at conditions below the current inhibitor requirements. The length of these cracks has not been measured at this time. The re-exposure of these samples would be useful to determine if arrested cracks that experience some degree of general corrosion can re-initiate crack growth, like the growth of cracks observed in Tank 15. [21] Additional testing may also include the effect of inhibitor concentration change (inside requirements to outside requirements) on this initiation. These activities will be pursued in conjunction with the vapor space and liquid-air interface corrosion testing discussed in 2.3.
The collective corrosion test results will be utilized to implement controls during salt dissolution operations. The controls will address low temperature (25 °C) and high temperature (50 °C) inhibitor requirements for tanks that handle dissolved salt solution. A revision to the corrosion control program is being prepared during FY10.

2.2.2 Evaporator Operations (Caustic Stress Corrosion Cracking Testing)

The corrosion control program specifies hydroxide and nitrite concentrations and temperature limits necessary to prevent nitrate-induced and caustic stress corrosion cracking (CSCC). However, highly efficient evaporator operations in conjunction with limited cooling capacity of specific tanks in the SRS system potentially challenge the current specifications identified by the corrosion control program. The tanks associated with the evaporator system were found to be in a chemistry/temperature regime where carbon steel is possibly susceptible to CSCC, which is known to occur at high concentrations of hydroxide and at high temperatures. An initial corrosion assessment concluded that the risk of CSCC was low due to the stress relief operation performed on the Type III tanks.[23,24,25] A suite of experiments are being performed supporting amendment to the current corrosion controls.

The experiments consisted of electrochemical testing and immersion tests in order to broaden the corrosion control envelope. The electrochemical testing consisted of cyclic potentiodynamic polarization (CPP) scans to determine electrochemical potentials where carbon steel may be susceptible to CSCC.[26] The immersion tests consisted of either welded U-bend samples or large welded plates exposed to high temperature (125°C), high caustic concentration (12 M) solutions for up to 3 months [27]. The results of these tests were compared with previous testing done on low-carbon steel in high hydroxide solutions, i.e. 8M NaOH.[28,29,30,31,32] CPP results showed no indications of localized corrosion, such as pitting, and all samples showed the formation of a stable passive layer as evidenced by the positive hysteresis during the scan. No cracks were observed on the welded plates or U-bends after two months of exposure to the hot, caustic waste.[27] Based on comparison with previous results, the presence of nitrite in the current test solutions appeared to reduce susceptibility to localized corrosion.

The combination of previous testing results with the results from current testing indicated that maintaining the R-value, or the ratio of the hydroxide concentration to the total inhibitor (nitrate and nitrite) concentrations, below 10 is important to prevent stress corrosion cracking in wastes with high hydroxide concentrations. In addition, the nitrite concentration should be maintained above 0.3 M and the temperature should be maintained below 115°C. Tests with high R-values, low nitrite concentrations, and high temperature showed active-passive transitions indicative of localized corrosion susceptibility. These recommendations will be implemented into a revision to the corrosion control program during FY10 allowing more efficient operation of the SRS tank farms without reducing tank integrity.

2.2.3 Probability/Statistical Based Corrosion controls

This initiative addresses discontinuities in the corrosion control program that have evolved as tank farm operations have changed. These discontinuities result in inefficient or overly
conservative corrosion control limits under some conditions. The goals of the initiative are to eliminate or reduce discontinuities by developing a probabilistic approach to predict and mitigate localized pitting corrosion mechanisms typical of dilute solutions and concurrently integrate with the program facets designed to mitigate stress corrosion cracking typical of more concentrated solutions. The technical bases are being developed to regauge the necessary sodium nitrite additions which are currently hinged on dilute solutions but result in excessively large additions of inhibitors at higher concentrations of nitrate.

The technical approach to develop a probability based corrosion control program was based upon gathering sufficient data to develop a predictive tool for corrosion vulnerability.[33,34] Electrochemical testing and coupon exposure testing is being performed within the framework of the statistical test matrix to build the database which will be used for predictive purposes. The electrochemical testing was done to determine the electrochemical regimes in which low carbon steel is susceptible to pitting, while the coupon exposure testing was confirmatory.

Based on previous electrochemical testing, a statistical test matrix was developed to refine and solidify the application of the statistical mixture/amount model to corrosion of carbon steel. A mixture/amount model was identified based on statistical analysis of recent and historically collected electrochemical data.[35] This model provides a more complex relationship between the nitrate and nitrite concentrations and the probability of pitting than is represented by the model underlying the current corrosion control program, and it may provide a technical basis for the utilization of less nitrite to inhibit pitting at concentrations below 1 molar nitrate. The test results from FY09 fit within the mixture/amount model, and further refine the nitrate regime in which the model is applicable. The results indicated a potential for significant inhibitor reductions at nitrate concentrations near 1.0 M without a significant increase in corrosion risk.

The complete data sets from FY08 and FY09 testing have determined the statistical basis to confidently inhibit against pitting using nitrite inhibition with the current pH controls. Future testing in FY10 will complete the spectrum of nitrate concentrations around 1 molar. In FY11 it is anticipated that testing in more dilute solutions will increase the confidence in the model for solutions with low nitrate concentrations (i.e., less than 0.2 M). These results will be combined to provide a complete spectrum for corrosion controls with a risk based component. This will assist in applying different levels of risk based upon life cycle phase of the tank (i.e. operation or closure).

2.3 Vapor Space and Liquid/Air Interfacial Corrosion (VSC/LAIC) Program

Although solution corrosion controls are in place, experience has shown that steel not in contact with the bulk waste solution or slurry, but exposed to the “vapor space” above the bulk waste, may be vulnerable to the initiation and propagation of corrosion, including pitting and stress corrosion cracking. Previous research has also determined that degradation is possible at the liquid-vapor interface due to hydroxide depletion. Multiple integrated programs focusing on VSC/LAIC were completed and are ongoing at SRS and Hanford. The programs are complementary and provide the technical bases for both sites similar to the development of the liquid phase corrosion controls.
2.3.1 Savannah River Site

The scrutiny on vapor space corrosion in the high level waste tanks led to multiple workshops and expert panel reviews. The first workshop, held in March 2002 was a direct action result of discussion at the DOE Structural Integrity Workshop held in 2001 and focused on the development of a fundamental understanding of the important corrosion parameters in context of vapor space and liquid/air interface corrosion (VSC/LAIC).[36,37] The expert panel and participants offered feedback on the potential for such mechanisms within the context of the chemistry and operational conditions presented.[38] The Expert Panel provided feedback on vapor space corrosion and provided recommendations for improvement.[39] The Panel recommended that the program include efforts to:

1. Establish the surface chemistry on steels exposed in the vapor space
2. Define tank conditions (ventilation and temperature) that promote condensation,
3. Understand how the evolution of surface chemistry leads to pitting, wall thinning and/or other corrosion process, and
4. Develop surface corrosion controls by altering waste tank chemistries and/or tank operating conditions to mitigate vapor space corrosion.

Additionally, the Panel "cautioned against simple fixes" without understanding the chemistry on the material surface exposed to the vapor space.

A detailed experimental program was developed and performed in response to the panel recommendations. The objective of the vapor space and liquid/air interfacial corrosion program was to develop sufficient understanding to mitigate and accurately evaluate corrosion vulnerability in the waste tanks for the VS/LAI (similar to those made for liquid space) regions during tank farm operations. [40] The results of the program confirmed that corrosion in the vapor space has not been an unusually aggressive phenomenon in the tanks and the current corrosion control program has been sufficient to prevent consequential VSC/LAIC in the SRS DSTs.[41,42,43,44,45] Based upon these results, changes were recommended to the SRS corrosion control program. These changes were then used to guide the experimental program at Hanford in support of the chemistry optimization program.

SRS continues to perform fundamental studies to further understand the phenomenon of VSC and LAI corrosion. During FY09, initial experiments explored the hypothesis that vapor space corrosion may be accelerated by the formation of a corrosive electrolyte on the tank wall by a process of evaporation of relatively warmer waste and condensation of the vapor on the relatively cooler tank wall.[46] Results from initial testing do not support the hypothesis of electrolyte transport by evaporation and condensation. The analysis of the condensate collected by a steel specimen suspended over a 40 °C simulated waste solution showed no measurable concentrations of the constituents of the simulated solution and a decrease in pH from 14 in the simulant to 5.3 in the condensate. For FY10, the studies suggested by the observation of vapor space cracking on the welded U-bends above dissolved salt solutions will be performed.
During FY09, liquid/air interface corrosion was studied as a galvanic corrosion system, where steel at the interface undergoes accelerated corrosion while steel in contact with bulk waste is protected. The zero-resistance-ammeter (ZRA) technique was used to measure the current flow between steel specimens immersed in solutions simulating (1) the high-pH bulk liquid waste and (2) the expected low-pH meniscus liquid at the liquid/air interface. Open-circuit potential measurements of the steel specimens were not significantly different in the two solutions, with the result that (1) no consistent galvanic current flow occurred and (2) both the meniscus specimen and bulk specimen were subject to pitting corrosion. For FY10, improvements to the ZRA cell are being made to see if the mechanism can be elucidated.

2.3.2 Hanford

As work progressed for the chemical optimization, issues arose with respect to LAI and VSC. To investigate the concerns, investigations of these phenomena were included in the matrix of tests proposed. Consequently, Hanford expanded a rigorous laboratory testing program to include the VS and LAI regions of the tanks—areas that may be more susceptible to corrosion versus simple immersion conditions. A subsequent workshop regarding the assessment of DST VSC/LAIC was conducted in July 2006 to support the chemistry program. The results of the vapor space workshop were used to guide the most recent ongoing experimental program.

This program was initiated in FY09 at the Pacific Northwest National Laboratory to determine the chemistry of the condensates that form in the vapor space. Thermodynamic models were developed that predict the composition of a condensate layer in the vapor space and then validated with laboratory testing. During FY10, electrochemical testing is being performed in simulated condensates to determine the susceptibility of carbon steel to the vapor space environment. The results of these tests, and tests in simple salt solutions, will be evaluated to determine species or conditions that may accelerate or inhibit vapor space corrosion.

3 In-Service Inspection (ISI) Program

In-service inspection of the waste tanks is performed at Hanford and SRS to detect the early onset of degradation and/or verify the effectiveness of the corrosion control program. These inspections are performed by non-destructive evaluation (NDE) techniques; specifically ultrasonic testing for the steel walls of the tank and visual inspections for both the steel walls and accessible areas of the concrete vaults of the tanks.

The in-service inspection philosophies employed at Hanford and SRS are based on guidelines established by the Tank Structural Integrity Panel, as endorsed by DOE Order 435.1.[47] The UT inspection program was designed to detect generic degradation due to pitting, wall thinning, or stress corrosion cracking. Leak detection and visual inspection are used to detect random leaks due to stochastic localized corrosion processes. The panel interpreted that the role of in-service inspections is to detect conditions such as potentially unstable cracks in the steel shells or generic evidence of degradation (pitting, thinning, cracking) that might lead to leakage in the future. This employs a sampling philosophy that targets critical structural regions as well as regions most susceptible to corrosion.
An independent expert panel review/workshop was held in August 2009 to evaluate recent developments in (NDE) equipment and how they might be applied to the unique conditions of high level waste tanks. The review/workshop provided a forum for experts from academia and industry to provide recommendations and for vendors to present recent improvements to equipment. The workshop also provided a platform for discussion of the underlying philosophy of the use of NDE in an in-service inspection program. The use of statistical methods to evaluate the accuracy and disposition the results was also discussed. At the workshop, both SRS and Hanford made presentation of their ongoing activities.

Based upon the Independent Panel’s feedback at this meeting and the underlying philosophy of an ISI program, several key actions are actively being pursued by both sites. ISI improvement R&D is focused on improving the technical basis for sampling of the surface area to be inspected through 1) use of high-speed inspection techniques and (2) use of statistical methods to disposition the results. SRS is currently revising the ISI Plan for waste tanks to be responsive to the recommendations of the review panel. Hanford is leading an integrated effort to develop and mature EMAT technologies for the ISI program.

3.1 High Speed Inspection Techniques

At present, both Hanford and SRS sites employ conventional ultrasonic testing equipment to assess the condition of the tank walls.[48,49] While widely accepted, data collection using this NDE technique is extremely time intensive due to the extremely slow speed of the single transducer. This slow speed is necessary to both locate and size any detected flaws. The slow speed, however, limits the surface area inspected (~1-2% of the tank surface) and consequently limits the number of tanks that can be scanned. The sites are exploring numerous options in a complementary manner.

Hanford is exploring the use of an Electromagnetic Acoustic Transducer (EMAT) as a rapid scanning technique. EMAT technology provides an alternate method of generation of the acoustic waves for examination of the tank wall that removes the need for a physical couplant between the transducer and tank wall. Data can be collected by EMAT nominally 100 times faster than conventional UT. However, the scan rate needs optimization to maintain the necessary measurement sensitivity.[50] In 2003, Ames Laboratory, the Center for Non Destructive Evaluation (CNDE) and Sonic Sensors, Inc. demonstrated EMAT during a blind test on a corroded steel plate at the Hanford site.[51] The initial results were positive, however, no system optimization was performed.
SRS is in the process of taking initial steps to develop a rapid scanning technique.[52,53] To accomplish a four fold increase in speed with existing equipment an additional transducer was added to the system along with changing the pixel size for data collection from 50 mils to 100 mils.

### 3.2 Use of Statistical Methods to Evaluate and Disposition NDE data

Statistical methods have been employed at both Hanford and SRS for two purposes: 1) to disposition the UT data collected and (2) to evaluate the accuracy of the ultrasonic data.[54,55]

#### 3.2.1 Disposition of UT Data Collected

Vertical strip inspections of the exterior of the primary tank have been performed at both Hanford and SRS. The inspections involved thickness mapping for the detection of general wall thinning, pitting and interface attack, as well as vertically oriented cracks. These strips are typically 8.5 to 15 inches wide and extend over the accessible height of the primary tank wall, and include areas on the top and bottom knuckles. These scans are intended to inspect for interface attack (e.g., liquid-air or liquid-solid) at a historical stagnant level, and to detect any regions of accelerated attack due to a vertical concentration gradient that may occur because of stratification of the wastes. These inspections cover approximately 1-2% of the accessible surface area of the tank.
The technical basis for utilizing only vertical strips was that service induced corrosion would most likely occur in a circumferentially uniform pattern on the primary wall. For example, if a stagnant liquid-air interface exists in a tank, and the waste is not in compliance with the corrosion control program, pitting at the liquid level around the circumference of the tank may occur.\cite{56,57} Multiple reviews at SRS determined that a more rigorous technical basis must be developed to defend the assumptions in the SRS ISI program revision, i.e., circumferential uniformity and the presence of pre-service vs. service-induced incipient pitting.\cite{58}

Based upon these concerns a comprehensive inspection of tank 29 at SRS was conducted in 2009 to provide this basis.\cite{59} Statistical protocols were developed to disposition the 2009 ultrasonic measurements taken from Tank 29. The protocols consisted of: (1) investigate riser to riser variability, (2) estimate the deepest pit on the tank surface, and (3) provide data to infer the origin of the pitting, i.e. pre-service or service induced. The results of these 2009 ultrasonic inspection indicated that no systemic corrosion has occurred in Tank 29 during the 38 year service history of the tank. This finding verifies the efficacy of the corrosion control program in mitigating general and pitting corrosion. Additionally, a comparison between ultrasonic results from 2009 and 2006 identified no discernable differences in pit depth or wall thickness (i.e., pitting or thinning) circumferentially around the tank. Thus, there has been no active corrosion occurring in this tank during this time and corrosion has been uniformly mitigated throughout the tank. Finally, service life estimation calculations, based on these results, indicate that the tank is expected to be viable for its intended service life.

However, the stochastic nature of the pitting corrosion mechanism, and the possibility of accelerated attack, requires monitoring a segment of the tank wall on a periodic basis. The analysis of the results from the 2006 and 2009 inspections provide the bases for trending a set of pits within a single vertical strip on a 10 year frequency, as well as looking for the development of new pits.

The following observations and conclusions were made from the analysis of the ultrasonic data from Tank 29:

- No reportable pits were identified.
- No cracking was identified.
- No reportable thinning was identified.
- Ultrasonic data was collected on virtually all of the plates in Tank 29. The vertical strips were uniformly spaced around the circumference of the tank so that data could be collected from critical areas such as the liquid-air interface and the high stress regions.
- 100% of the inspected plates have average thicknesses greater than the specified minimum mill tolerance requirement (i.e., nominal – 0.01 inches) after 38 years of service.
- The expected uncertainty with the multiple echo technique in field conditions for a single measurement is ± 0.00553 inches. The actual tolerance obtained was determined to be within ±/− 0.002 inches for the difference between matched pairs of multiple echo measurements. The uncertainty for the difference between two multiple echo measurements is at least ± 0.00553 inches and is conservatively bounded by ± 0.008
inches. Therefore, use of the multiple echo technique to analyze the ultrasonic data produces reliable and repeatable measurements.

- There is no evidence that active, systemic corrosion has occurred in Tank 29 during its 38 year service history. This finding verifies the efficacy of the corrosion control program in mitigating general, pitting corrosion, and stress corrosion cracking.
- The depth of the pits that were observed is consistent with fabrication related or pre-service corrosion. These pits do not currently impact the structural or leak integrity of the tanks. All identified pits are far less than the reportable depth of 25% of the nominal wall thickness.
- Riser to riser or plate to plate variability for pit depths was likely due to the fabrication history and pre-service environment that an individual plate experienced.
- Plate to plate variability for wall thickness was also observed. However, the average wall thickness was always within the tolerances specified by ASTM A20. There also was minimal wall thickness variability within a plate.
- A log-normal distribution was utilized to fit the pit distribution for the entire tank. A conservative upper tolerance limit with 95% confidence for pit depth is 0.070 inches for 99% of the distribution. The “distribution” referred to is that of the entire tank; strips that were inspected as well as areas that were not inspected since the inspected strips were uniformly distributed around the circumference of the tank wall.
- The mean difference in pit depths between 2006 and 2009 is less than 0.001 inches. This means that the pits have not been actively growing for the past 3 years.
- Mean thinning from 2006 to 2009 is circumferentially imperceptible (less than 0.001 inches). The mean difference in wall thickness measurements between years 2006 and 2009 were within ± 0.002 inches. The mean difference is less than 0.001 inches. Both vertical and horizontal wall thickness measurements show that thinning is virtually identical throughout the tank. Wall thickness variability within the sheets horizontal around the tank is minor in comparison to the differences between sheets.
- General corrosion rates were estimated based on Tank 29 wall thickness measurements from 2009 and 1974. It was confirmed that the general corrosion rate is less than 0.001 inches/yr.
- Life estimation calculations approximate that the tank wall will not reach the reportable criterion of 10% of the nominal thickness until 2059. The current system plan calls for closure of this tank by the 2030’s. Thus, from a general corrosion perspective the tank should be viable for its intended service life.
- Based on data from the last three years, pitting corrosion does not appear to be active. However, due to the random nature of pit initiation and the potentially accelerated growth of a pit, periodic monitoring for pit growth is prudent.
- The analysis of the Tank 29 ultrasonic measurements provides the basis for monitoring/trending of a set of pits in a single vertical strip, as well as looking for the development of new pits.

The Hanford site has also used statistics to investigate the issue of riser-to-riser variability. Two risers were inspected per tank in 2007 based on a 2001 study of Tank 241-AY-101. Riser-to-riser variability was indicated, so rather than incorporating an extra uncertainty margin when
inspecting only a single riser, it was decided to inspect two risers. However, since then, a more extensive set of tanks now have had complete inspections with multiple risers. Based on an analysis utilizing extreme value statistics, no riser-to-riser variability is indicated.

### 3.2.2 Accuracy of UT Data

Hanford is conducting a statistically-based study to determine the effects of several variables on UT measurements due to concerns over the uncertainty in the measurements.[61] These variables include:

- Effects of ultrasonic equipment/system on measurement.
- Effects of personnel (collection / analysis)
- Effects of mechanical configuration of scanning apparatus.
- Effects of surface condition.
- Effects of temperature variations.

During FY04, SRS conducted a statistical analysis of the uncertainty of the ultrasonic measurements.[62] The uncertainty of the P-scan measurement process was determined using National Institute of Standards and Testing (NIST) traceable standards that were measured in a manner consistent with field use. The approach utilized the statistical tool of analysis of variance to estimate the long-term bias associated with the P-scan measurements, as well as the precision error (or a measure of the repeatability of the P-scan process). Both “contact” and “multiple-echo” ultrasonic techniques were assessed by this approach. The 95% uncertainty for the contact method is approximately 0.008 inch, and the 95% uncertainty for the multiple echo method is 0.0055 inch. Data from this study can be correlated with the data from the FY09 task performed at Hanford.

The uncertainty associated with the measure of UT data at Hanford led to a series of in-tank and out-of-tank testing. This testing was conducted by PNNL using the NDE technicians from Hanford. The findings from that study showed considerable improvements could be made by tighter controls on the calibration block and couplant temperatures. Also many of the uncertainties would be reduced by adopting a multiple echo technique.

### 3.2.3 Revisions to SRS ISI Program

The SRS ISI program is currently under revision between inspection cycles as opposed to Hanford, which is currently performing a second cycle of inspections. The revision to the SRS ISI program addresses the key points raised by the Non-Destructive Examination Independent Review with respect to scope of inference and corrosion rate for thinning and pitting throughout the 27 type III/IIIA tanks within the program [63]. The review also recommended a statistical sampling of the tanks to improve the confidence of the single strip inspection program. The sampling plan provides the bases for intended scope of inference and spatial application of the current results. The current revision of the ISI program is an interim program to allow development of technologies capable of faster volumetric data collection while maintaining the necessary resolution to make accurate assessments. The revision of the ISI Program will provide
the statistical evidence to support the assertion that corrosion has been circumferentially mitigated. The supplemental information collected will support the primary goal of maintaining the tank integrity throughout the waste removal and tank closure mission.

The revised program will:

1) Continue to inspect a single baseline vertical strip in all the Type III/IIIA tanks for purposes of trending corrosion rates and developing credible serviceable life projections. Selected vertical and horizontal welds for each tank as well as high stress regions of selected tanks will also continue to be inspected.

2) Provide for a new set of up to 4 randomly selected locations in each tank scheduled for inspection. These random vertical strip inspections will be stratified by quadrant and tank. The results from the new random inspection will be utilized to develop a statistical confidence level in the corrosion control programs ability to mitigate pitting and thinning of the waste tanks.

3) Prioritize tanks that have had corrosion control program excursion(s) for greater than 3 months. A random detailed single vertical strip will be completed in any tank that meets this criterion.

In addition to the UT program, a comprehensive visual inspection (VT) program, which has been in effect since the 1970's, will continue as currently scoped in WSRC-TR-95-0076. [64]

The results from the new random inspection will be utilized to develop a statistical confidence level in the corrosion control programs ability to mitigate pitting and thinning of the waste tanks. The baseline strips will be used to define the thinning and pitting rates within the tank so that serviceable life projections can be made with confidence.

4 Structural Analysis Program

4.1 Hanford

As part of the integrity assessment of the DSTs, Hanford conducted a modern finite element analysis of the DSTs. The analysis was conducted by developing a tank model that bounded all 28 DSTs for combined static and dynamic loads,[65] In addition, a model was developed for the 241-AP tank farm in support of raising the fill height for those tanks from 422 inches to 460 inches. [66] The model assumed the bounding tank had aged through sixty years (2028) and had experienced five thermal cycles up to the maximum allowable tank temperature of 350 °F. These analyses showed the DSTs would maintain structural integrity under all load cases analyzed.

Analyses were also conducted with respect to allowable dome loading, vacuum, and total thinning of the primary tank. The dome load analysis showed that concentrated load well in excess of the current allowable would be required before the tanks would be damaged. The vacuum loading analysis re-affirmed acceptable vacuum loads in five of the six tank farms and the level in the sixth (241-AP) has been reduced base on the analysis. Finally, the wall thinning
analysis showed the allowable minimum wall thickness was well within the current guidelines used in the integrity program.

4.2 SRS

As part of the integrity assessment of the DSTs, SRS conducted a modern finite element analysis of the type III/IIIA DSTs in accordance with BNL 52361.[67,68] The analysis was conducted by developing a tank model that bounded all 27 type III/IIIA DSTs for combined static and dynamic loads. These analyses showed the DSTs would maintain structural integrity under all load cases analyzed.

Type I and II waste tanks without flaws (i.e., cracks) were evaluated per ASME Section VIII, Div. 2 criteria.[69,70] The results showed that the seismic condition loads are the controlling loads and the controlling primary membrane stress occurs in the tank shell wall. Allowable fill limits for these tanks were calculated from these analyses.

Due to the presence of cracks in several of the Type I and II waste tanks, fill limits for these tanks were established based on a fracture evaluation of the tanks.[71] The analysis utilized the Failure Assessment Diagram (FAD) to determine the allowable fill levels as a function of failure probability. The controlling criteria for the flawed tank were based on a failure probability of $10^4$ for the PC-3 seismic conditions.

Analyses have also been performed to evaluate all SRS tanks for various operational loading and are listed in calculation T-CLC-G-00147.[72] In addition to the design basis structural analysis a predictive degradation review was performed to determine the onset of structural integrity issues with the waste tanks. That evaluation is documented in WSRC-TR-2005-00196.[73] The earliest date that structural integrity issues would impact tank operations would be 2054. This does not represent the end of service life but a point where operational restrictions would be implemented to ensure structural integrity, such as the restriction of fluid levels within the tank.

In addition to the above load analysis, several facility administrative control programs are in place to protect the structural integrity of the DSTs. Those programs are as follows:

- Critical Lift program
- Structural Integrity Program
- Corrosion Control Program
- Traffic Control Program
- Tank Top/Secondary Containment Loading Program
5 Conclusions

The objective of the SI program is to demonstrate structural and leak integrity of waste tanks as we move forward. Through the Hanford and SRS SI programs, tools have been developed to meet the requirements of DOE Order 435.1 and to validate each of the key elements outlined in DOE Guide 435.1.
REFERENCES


